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DEVELOPMENT OF A HEAT-STERILIZABLE 40-Ah SEALED SILVER-ZINC CELL

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16. Abstract

A heat-sterilizable sealed, nonmagnetic, silver-zinc cell of 40-Ah actual capacity was designed, developed, extensively tested, and fully engineered for fabrication as a unit element to be used in a battery assembly. Originally intended for possible use in a Viking spacecraft mission, it still retains the capability, with or without heat-sterilization, of having at least two years wet life (data beyond two years are still incomplete) and several hundred cycles of various periods (one to three cycles a day) and various depths of discharges (10 to 35 percent of actual capacity). Charged wet stand is greater than one year, with or without trickle charge, in the range of 10^{o} to 42^{o} C. The cell is capable of withstanding all environmental test requirements for launch and soft landing.

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FOREWORD

The research described in this report was conducted by the McDonnell Douglas Astronautics Company under NASA contract NAS 3-10928. Mr. William J. Nagle of the NASA Lewis Research Center Direct Energy Conversion Division was the NASA Project Manager. The report was originally issued as McDonnell Douglas Astronautics Company report DAC-60989-F.

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DEVELOPMENT OF A HEAT-STERILIZABLE 40-Ah SEALED SILVER-ZINC CELL

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SUMMARY

The present program objective is to design, develop, test and evaluate a heat-sterilizable, sealed, nonmagnetic, silver-zinc cell of 40-Ah actual capacity capable of long wet stand and long cycle life, suited originally for a planetary mission but fitting any other mission requiring a long-life and high-energy-density power source.

The mechanical development entailed search of a suitable heat-resistant plastic material found in glass fiber-filled polyphenylene oxide, proper case-to-cover sealing methods found in reliable ultrasonic welding, and a leakproof terminal assembly evolved from a triple seal design using "O" rings and epoxy with specially designed hardware.

The electrochemical development made use of an inorganic separator capable of heat sterilization. Several cell designs were attempted to devise proper assembly. The separator is used as a thin coating on an absorbent mat made as a bag enclosing an electrode.

The selected design for extensive testing was one having all electrodes bagged (HS-40-7).

Tests are in progress at the time of this writing. Acquired data to date show that the cell has at least a wet life of 26 months, a charged stand capability of 16 months, a cycling capability ranging from 400 cycles on a regime of one cycle a day at 13-percent depth to 1,000 cycles on a regime of three cycles a day at 40-percent depth (based on rated capacity).

Data of greater interest to the planetary mission originally planned are on a special regime of two cycles a day, one cycle at 10-percent and the other at 20-percent depth. The cells have reached 432 cycles and are still cycling.

At the close of this program period, many cells have been delivered to NASA for other testing.

INTRODUCTION

The program was intended to investigate and solve the problems of fabricating a large, heat-sterilizable, sealed, nonmagnetic, silver-zinc cell capable of a long wet stand capability.

Originally oriented toward a 40-Ah, high-rate cell, the program evolved in the first year toward a 40-Ah secondary cell capable of long cycle life. When mission requirements were narrowed down, the long testing required imposed an early design freeze to accumulate a substantial amount of data. A backup cell was introduced later, presumably capable of even longer wet stand. Forty such cells were delivered to, and will be tested by NASA. At the time of this writing, all earlier cells on stand are still on test after 17 months wet life.

The design leaned heavily on the use of an inorganic separator capable of withstanding the corrosive attack of a hot strong caustic medium (45-percent KOH at 135°C) for 200 hours as well as the oxidative attack of strong oxidants (silver oxides) for over two years. The 3420-25 Douglas inorganic material looked promising in this respect.

By proper design, the cell was made to eventually fulfill the requirements. Great care in manufacture and high quality control added to the reliability achieved.

WORK PERFORMED

The body of this section is developed according to the tasks of the main Work Statement redirected in part by Technical Direction No. 3.

After presenting the general requirements and the objectives of the program, the technical discussion revolves around the design concepts, resulting in the mechanical and preliminary electrochemical development. The various electrochemical designs evolved during the course of the program are then presented with all cell data.

The additional work directed by Technical Direction No. 3 follows in the next section.

General Requirements

The program is directed toward investigating and solving the problems of fabricating large heat-sterilizable, sealed, nonmagnetic, silver-zinc cells capable of long wet stand followed by cycling.

Task I consists of developing preliminary designs for primary and secondary cells. "Primary" is defined by the work statement as a high-rate, rechargeable cell capable of limited cycling, 25 deep cycles at the C rate. The secondary must be capable of long continuous cycling at medium depths of discharge.

The cell was to be approximately 13.3 by 8.9 by 3.17 cm (5.25 by 3.5 by 1.25 in.) with a capacity of 40 Ah for the primary and 50 Ah for the secondary. The original main objective was to place heavy emphasis on the primary cell and design the secondary with minor modifications of the design components of the primary (electrode weight and thickness, number of electrodes, separator thickness). Originally, only five secondary cells would have been tested. During the course of the program, emphasis shifted completely toward the secondary as a requirement of longer wet stand (from 10 to 21 months) was imposed; at the same time, the discharge rate requirement was modified from the high rate (40 A) to a low rate (10 A).

The mechanical requirements are that the cell be nonmagnetic, fully sealed, and heat sterilizable at 135°C for a total of 180 hours (three thermal cycles of 60 hours each) and capable of withstanding the environmental tests specified in Appendix B.

Design and Development

Design and development proceeded along two concurrent plans during the program—mechanical and electrochemical.

The mechanical development includes the case, cover, terminal and associated investigation concerning the case-to-cover seal and the terminal seal.

The electrochemical development includes the preliminary phase dealt with in this section relative to establishing the electrical and electrochemical design parameters—electrode characteristics, separator combination, cell pack, and electrical characterization. The evolution of several electrochemical designs is discussed. These designs varied only in degree (total separator thickness) as the need arose.

The basic separator selected for this project is a proprietary inorganic material coded 3420-25. It is heat sterilizable (no degradation in concentrated KOH at 135°C for prolonged periods) and does not gas when in contact with silver or zinc in a caustic medium. The separator is a 0.125-mm(5 mil) coating deposited on a 0.25-mm (10 mil), specially treated, inorganic absorbent mat. This integral assembly is then 0.375 mm (15 mils) thick. Used this way, it offers an ionic resistivity of 24 ohm-cm in 45-percent KOH, equivalent to 0.9 ohm-cm^2 (140 mΩ-$in.^2$). This material, having its built-in absorbent material, is used without the need of an extra absorbent material wrap around the negative or positive electrode as conventionally done with cellulosic or other films in silver cells.

The wrap design consists of a bag enclosing the desired electrode. The bag is made by cementing and heat sealing two pieces of the treated absorbent mats on three edges, then coating it with the thin layer of 3420-25 inorganic material.

Mechanical Development

This section deals with all the developmental work done during the program on the design and testing of the mechanical components of the cell (case, cover, hardware).

Case. —The case was originally designed to be 13.3 cm high by 8.9 cm wide by 3.17 cm thick (5.5 by 3.5 by 1.25 in.) in external dimensions with a wall thickness of 0.31 cm (0.125 in.) to minimize weight and volume. Later in the program the wall thickness was increased to 0.43 cm (0.175 in.), keeping all internal dimensions constant.

Cover. —The cover was designed with particular emphasis on case sealing.

The cover is provided with features for ultrasonic welding, based on experience drawn from the NASA contract NAS 3-10924 (ref. 1).

The secondary seal with epoxy has been improved by providing a groove between the cover edges and case walls, where the epoxy can flow and form a bead (Figure 1).

The center hole used for electrolyte filling is provided with threads so that a threaded, molded, plastic plug made of parent material can be used for sealing the cell so as to avoid possible stresses introduced by different heat dilatations of dissimilar materials (plastic and metal) (Figure 2).

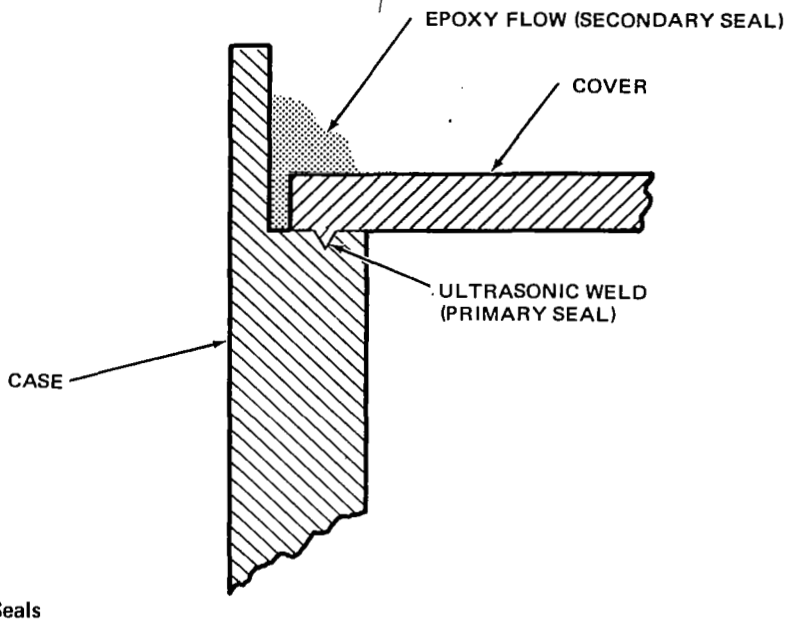


Figure 1. Case-to-Cover Seals

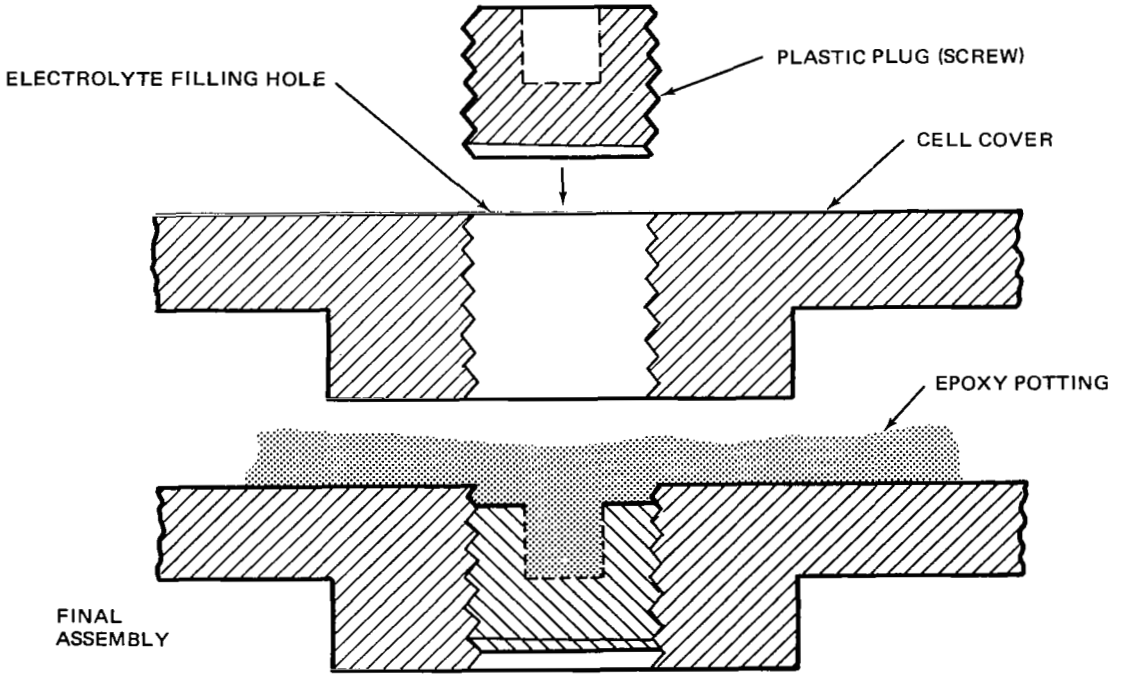


Figure 2. Center Hole Sealing

Terminal. —The terminal holes and terminal hardware were designed with triple "O" ring seals and epoxy seal at the base of the terminal (Figure 3).

Case and Cover Investigation. —A titanium welding horn for ultrasonically welding the cover to the case was designed. It was tried on several polysulfone cases and covers fabricated in our machine shop. The first attempts were very encouraging. Table I shows that pressure tests were limited by the fact that the first cases used were made with cemented polysulfone parts. The welded seams held up to at least the bursting pressure noted.

Work on cases and covers followed two lines—finalization of ultrasonic welding parameters for different heat-sterilizable plastic materials, and heat sterilization with KOH and under pressure to determine the final choice.

First, molded polysulfone and polyphenylene oxide cases and covers underwent a series of tests to determine the final choice of material for reliable ultrasonic welding and heat-sterilization capability under sealed, KOH-filled, and pressurized conditions.

After several trials, the ultrasonic welding parameters were tentatively set as follows for PPO and polysulfone (PS):

Material	Horn Pressure	Hold Time	Weld Time
PPO	40 psig	2.5 sec	3 sec
PS	45 psig	2.5 sec	3 sec

One empty PPO case was sealed and held 80 psig for 1 hr without leaking.

Primary cell packs were then used in eight cases to be welded and pressure-tested (four for each material). They all held 80 psig for 1 hr at 25°C.

The second step consisted of filling the cases with 20 cc of 30-percent KOH, sealing the center hole with the plastic plug, and potting the entire top recess with epoxy. The cases were then submitted to the heat-sterilization procedure (135°C for 200 hr) to determine various characteristics (possibility of crazing, leaking through seals, weight loss due to water vapor diffusion, etc.).

Three cases of each material; properly welded, filled, and sealed; were placed in sterilization vessels that were sealed (by means of a valve) only after the sterilization temperature was reached, so that at time zero of the test all pressure gauges of each vessel containing a case were reading zero pressure.

All cases were carefully weighed before the test. After the test was discontinued, they were weighed again to determine the nature of their weight

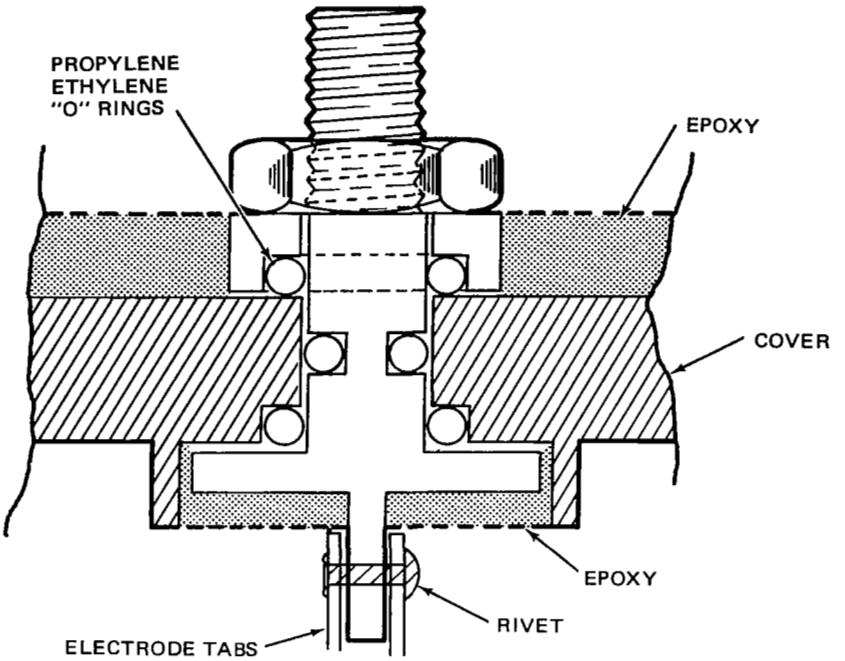


Figure 3. Terminal Seal Assembly

TABLE I

ULTRASONIC WELDING

Case	Settings	Pressure Test
No. 1	40 psig horn pressure 1.5 sec weld time 1.5 sec hold time	Case leaked at 15 psig
No. 2	40 psig horn pressure 2.5 sec weld time 2.5 sec hold time	20 psig for 5 min: No leak 30 psig for 5 min: No leak 40 psig for 5 min: No leak 45 psig for 5 min: Case cracked along cemented seams
No. 3	Same	30 psig for 1 hr: No leak
No. 4*	Same	30 psig for 2-1/2 hr: No leak

*Cell fully assembled with components of a primary cell design.

loss by the loss rate (leak versus diffusion through plastic). Table II gives a variation of the pressure with time for each case and a summary of the findings.

Two polysulfone cases were found cracked (the test was discontinued after 25 hr when the pressure rise of the sterilization vessel was thought to be too rapid for vapor diffusion). The third case showed a pressure reading of only 7 psig after 114 hr at 135°C. No sign of KOH leakage was found and no crazing occurred. The weight loss rate (0.8 g over 114 hr) confirmed also that it was solely due to water vapor diffusion through the plastic (the maximum to be lost based on the pressure readings was computed to be 0.89 g).

Out of the three PPO cases, two cases showed relatively high pressures after 25 hr and were discontinued. The cases were slightly crazed, but no sign of KOH was detected. One case continued its test for 114 hr and developed a slow pressure rise identical to the third polysulfone case. No sign of KOH leakage was found, no crazing occurred and the weight loss was 0.8 g after 114 hr.

TABLE II

CASE SEAL TEST AT 135°C IN SEALED VESSELS CONTAINING SEALED CASES

Case Material	PS			PPO		
Time / Case No.	1	2	3	4	5	6
0 Hr	0 psig	0 psig	0 psig	0 psig	0 psig	0 psig
17	20	10	2	2	19	5
21	21	11	3	3	20	6
25	22	12	3	3	21	7
114	-	-	7	7	-	-
Original weight	222.9 g	222.0 g	224.4 g	200.8 g	205.4 g	203.0 g
Final weight	209.0	220.6	223.6	200.0	203.2	202.1
Weight loss, g	13.0	1.4	0.8	0.8	2.2	0.9
KOH detected outside case*	Yes	Yes	No	No	No	No
Case	Cracked	Cracked			Crazed	Crazed

*No KOH detected along cover weld and around terminals.

In all six cases (polysulfone and PPO), no KOH was detected along the welded cover-to-case seam or around the terminals. These poor results were traced to the fact that the molded cases of the first shipment had excessive and irregular stresses. It was shown more dramatically by immersing the cases in an organic fluid known to promote crazing when stresses are present. Polysulfone cases were immersed in ethyl acetate for 3 sec. Severe crazing and cracking occurred in all cases and covers. After an attempt at annealing in a glycerine bath at 165°C for 4 min, the same immersion test reduced the crazing considerably. Two covers did not develop any crazing; the cases showed a small crack. The PPO cases and covers cracked excessively in the immersion test, using Skydrol for 10 min.

A third material, Arylon T-3198 (polyaryl ether) was considered and some molded cases and covers were obtained. No cracking or crazing occurred in the same immersion test used for the PPO cases. The material is known to be KOH resistant at high temperatures.

Investigation on case material was then actively pursued on the three candidate materials: polysulfone (PS), polyphenylene oxide (PPO), and polyaryl ether (Arylon T-3198).

Cases and covers molded from the three materials were investigated:

With Arylon, moldability was good; no sign of crack or craze was noticed on the cases, which were inspected upon receipt. Immersion in craze-promoting solvents did not produce any crazing. The ultrasonic welding was satisfactory, but the cases were distorted during the sealed-case heat exposure at 135°C for 200 hr. This temperature is probably too close to the temperature of heat deflection as defined by plastics manufacturers. According to the manufacturers' literature, it occurs at 145°C for Arylon, compared with 175°C for polysulfone and 172°C for PPO. No more work on Arylon was considered necessary at this point.

Polysulfone cases and covers appeared good upon receipt. However, the immersion test (in ethyl acetate for 3 sec) produced extremely severe cracking and crazing. Annealing to reduce the stresses was first attempted by dipping parts in glycerine at 165°C for 4 min. The covers passed the immersion test without cracking or crazing; some cases developed a very small craze. During heat sterilization, KOH-filled and sealed cases developed cracks or crazes somewhat erratically. A variant of polysulfone, made with glass fiber-filled polysulfone (Sulfil G-1500/20), was considered because of its supposed high resistance to crazing. Cases made out of Sulfil were also obtained. Four cases containing 40 cc of 40-percent KOH were welded and epoxy-sealed. They were restrained between steel plates and placed in sterilization chambers for heat sterilization at 135°C. After 24 hr, two cells were removed and examined. Pressures were in the range of 11 to 15 psig. The weight loss was about 0.1 g. The cases exhibited a very small crack at the top of one side. The other cases were removed after 48 hr. Pressures were in the range of 14 to 18 psig. Weight losses were in the range of 0.5 to 0.6 g. The same type of cracks were found at the top of the cases. Interest on polysulfone was discontinued at this point as work done concurrently on PPO showed more promising results.

Work was concentrated on PPO as preliminary tests showed that this material may be relatively satisfactory for immediate use in cells needed at that time for the long wet stand and preliminary electrical tests.

Upon receipt, the cases were inspected for cracks. The apparently good cases were then annealed in glycerine at 150°C for 1 hr. Some cases developed some cracks. The remaining good cases amounted to only 32 percent of the original cases received (Table III).

A second order of PPO cases was placed with the provision that PPO pellets be dried before the cases were molded. Repeating the same selection and procedure as above, only 13 percent of the cases survived.

The annealed cases passed the immersion test without crazing (Skydrol for 10 min) whereas the unannealed cases cracked in less than 2 min.

The ultrasonic weld was satisfactory; all sealed cases passed the pressure test of 50 psig for 10 min without the help of epoxy edge filling and cover encapsulation.

Six sealed cases containing KOH were heat sterilized for 66 hours at 135°C. Only three cases were satisfactory. The other three exhibited minute crazes, but no KOH leakage could be detected when the cases were left on stand for several days at room temperature. This condition appears to be traceable to the reintroduction of stresses in the case and cover during the ultrasonic welding. Annealed cases, ultrasonically welded, could not pass the immersion test. Before welding, they passed the Skydrol immersion test for 10 min. After welding, they developed a crack after only 7 min.

Several corrective actions were undertaken almost concurrently: One was to replace the rigid enclosure holding the case during cover-to-case ultrasonic welding with an elastic nest capable of absorbing the excess ultrasonic energy. Four cases so welded were submitted to the Skydrol immersion test. Three passed the 10-min period without crazing; one crazed after 9 min.

TABLE III

PPO CASES

Shipment	As Received			After Annealing		Percentage Recovered
	Inspected	Cracked	Left	Crazed	Left	
1	44	8	36	22	14	32
2	95	13	82	70	12	13
3	Case: 48	1	47	0	47	98
	Cover: 48	1	47	4	43	90

Also, a third order of PPO cases was placed with the requirement that they be annealed and capable of passing the Skydrol immersion test for 10 min without crazing. In this way, a first selection was made prior to delivery. Inspection of a certain sample number showed a definite improvement over the previous shipments (Table III). Four cases containing 40 cc of 40-percent KOH were welded and epoxy-sealed. They were restrained between steel plates and placed in sterilization chambers for heat sterilization at 135°C. After 24 hr, two cells were removed and examined. Pressures were in the range of 11 to 15 psig. The weight loss was in the range of 0.3 to 0.8 g. The cases exhibited a very small crack at the top of one side. The other cases were removed after 48 hr. Pressures were in the range of 14 to 18 psig. Weight losses were in the range of 0.8 to 1.1 g. The same type of cracks were found at the top of the cases.

Another possibility was to increase the case wall thickness by about 50 mils and to remove all sharp corners by substituting a radius of about 60 mils. This change could be made in the existing mold without incurring a change in the internal case volume so as to leave all electrode pack designs unaffected. Technically, the increased wall thickness will result in an increase of about 50 g in cell weight.

Work on heat sterilization of sealed PPO cases was continued on some minor variations of sealing methods to determine the cause of case crazing or cracking:

(1) The top lip of the case holding the cover epoxy potting is very thin and may have been unable to support the expansion of epoxy, thus resulting in a crack toward the top of the case. It was therefore cut off on some cases that were sealed by ultrasonic weld only. These cases were submitted to the same test as before (KOH-filled, sealed, and submitted to 135°C). They failed after approximately 20 hr.

(2) Three cases were ultrasonic welded only; there was no epoxy potting to avoid any possible stress caused by the expansion of epoxy. These cases were submitted to the same test. These cases also failed after approximately 20 hr.

(3) One case was fully encapsulated in 1/4-in. epoxy after the usual seals. The case cracked after 64 hr on the same test.

A summary of the results obtained to date is presented in Table IV.

It appeared at this point that increasing the wall thickness and introducing smoother corner radii were necessary to reinforce the cell case under the heat-sterilization conditions.

TABLE IV

HEAT STERILIZATION OF SEALED, KOH-FILLED PPO CASES

Case No.	Seals		Variation	Hours to Failure	Weight Loss, g	Failure Type	
	Weld	Epoxy				Crack	Seal
1	x	x		48	2.9	top lip	
2	x	x		48	0.8	top lip	
3	x	x		24	0.8	top lip	
4	x	x		24	1.1	top lip	
5	x	x		24	10.9	sidewall	
7	x			24	4.1	sidewall	
12	x			22	2.0		bad weld
13	x			21	2.0	sidewall	
6	x		lip around top cut off	24	9.9	sidewall	
9	x			17	1.0	sidewall	
10	x			41	4.0		bad weld
11	x			17	2.0		bad weld
8	x	x	encapsulated in 1/4 in. epoxy	64	8.0	sidewall	

While waiting for the case mold change and delivery of the new molded cases, work continued on a variant of PPO [glass fiber-filled PPO, (GF-PPO) coded GF(30)-PPO, meaning PPO filled with 30 percent glass fibers]. Molded cases and covers made of this material were investigated.

(1) Two cases tested for stresses passed the Skydrol immersion test for 10 min without crazing. They were not annealed prior to the test, which showed a definite improvement in the integrity of the molded parts.

(2) Two other cases filled with 40 cc of 40-percent KOH and sealed with pressure gauges connected and were submitted to 135°C ambient.

The pressures stabilized at around 23 psig. After 70 hr in the oven, they were removed and examined. Their weight loss was about 2 g, they were not cracked or crazed and their internal pressure was -10 in. Hg, at room temperature. The cells were weighed with the restraining steel plates, but without the pressure gauge hardware set-up; even so, the total weight was 2,140 g. The weight loss was therefore about 0.1 percent—too close for the accuracy of the scale. Some water vapor may also have condensed in the pressure gauge tubings. Because of these reasons, the test was repeated differently (item 3 below). The cases were then pressure-tested again for 15 min; they held 50 psig without leaking. They were put back in the oven at 135°C for 108 hr. Their pressure stabilized around 19 psig.

(3) Two GF-PPO cases were filled with 40 cc of 40-percent KOH and sealed without pressure gauges connected. They were restrained with steel plates and placed in sealed vessels. After 84 hr at 135°C, they were removed, stripped of their steel plates and weighed again. They were not cracked and their weight loss was 0.6 g and 0.8 g respectively (out of 300 g total). Two glass fiber-filled PPO material cases containing KOH and fully sealed were submitted to 135°C for 425 hr without exhibiting cracks or crazes. No KOH or air leakage could be detected.

(4) Two cases filled with 45-percent KOH were submitted to 135°C for weeks to determine the extent of KOH attack. Periodically the liquid was removed and analyzed for silica. Data were as follows:

After 33 days at 135°C:	0.2 g of silica (0.1 percent of the KOH amount). No detectable weight loss on the cases.
After 48 days at 135°C:	0.3 g of silica (0.18 percent of the KOH amount). No detectable weight loss on the cases.

Other cases filled with electrolyte were also left standing at room temperature for silica analysis of KOH after a long storage. Of all tests, the maximum that could be extracted was 0.4 g of silica or 0.004 g/cc of KOH after 35 days at 135°C. Figure 4 shows the amount of silica extracted as a function of time spent at 135°C. No weight loss of the cases could be detected. It is known that the case material absorbs a very small amount of water (0.06 percent in 24 hours at room temperature, according to the manufacturer's data sheet). This is about the same amount as the extracted silica.

Two questions may be raised on the presence of silica: "What is the capability of the case to hold for at least the duration of the mission?" and, "What is the effect of silica impurity on the life or electrical performance of the cell?

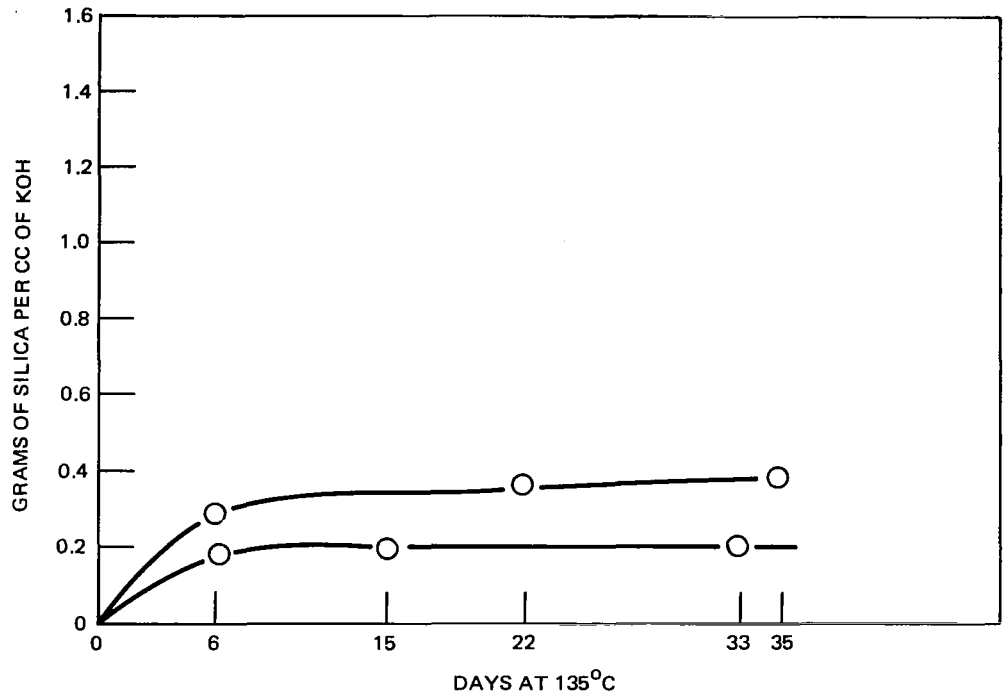


Figure 4. Silica Extracted from GF-PPO Cases by KOK Attack

In answer to the first question, it can be said that the above data hold true for an equivalent period of at least 24 months at room temperature, even on very conservative terms. If the approximate exponential law of reaction rate doubling for every 10°C is applied here, it would yield an equivalent period of over 15 years at room temperature.

In answer to the second question, the inorganic separator support (absorbent) material is known to consist of various silicates, among other things. It is therefore of interest to determine the amount of silica extracted from it when submitted to heat sterilization. To determine this effect (and to compare it to the amount of silica extracted from cases), the following test was performed:

Eleven separator bags (as used in the cell design) were placed in a plain PPO case filled with 45-percent KOH. The same amount of KOH was placed in a GF-PPO case, without separator bags. Both cases were submitted to heat sterilization, then the KOH was analyzed for silica content. Results in grams of silica per cc of KOH are:

PPO case with separator bags and KOH: 0.004 g/cc

GF-PPO case with KOH only: 0.002 g/cc

(Even after 35 days exposure at 135°C, the range was only 0.002 to 0.004 g/cc for the GF-PPO case.)

These results stress the fact that all cell data obtained are based on cells containing a larger amount of silica than could be extracted from GF-PPO cases over a period of 24 months at room temperature, without any apparent ill effect on the performance of the cells. The conclusion is obvious. At this time, considering all the advantages of GF-PPO, increased reliability dictates its choice over plain PPO material.

The new cases with thicker walls obtained from the modified case mold were submitted to various mechanical tests. Two materials were used—PPO (grade 534-801) and GF-PPO (glass-filled PPO of the same grade). Without annealing, PPO crazed in Skydrol within 10 min. GF-PPO did not and passed the 10-min test. After annealing, PPO passed the 10-min test.

Cases of both materials were ultrasonically weldable and passed the pressure test of 100 psig for 10 min without leaking. Ultrasonic welding was the primary seal (without epoxy potting on the cover top).

Cases partially filled with 45-percent KOH and fully sealed were submitted to heat sterilization at 135°C and watched periodically for KOH leakage by wiping phenolphthalein solution on all external surfaces and all seals.

(1) Two PPO cases out of three exhibited a reaction at a pinpoint on one of the narrow sides. Very careful examination revealed a minute craze. However, upon return to room temperature, no leakage could be detected even after a few days. The average weight loss from each of the three cases was 2.8 g after 200 hours at 135°C, which is in the range of the expected loss due to water vapor diffusion through the plastic. The case that did not leak lost 2.5 g.*

(2) The same test applied to three GF-PPO cases did not cause any leakage (or visual crazes), even after 200 hours. The average weight loss was 2.4 g after 200 hours at 135°C.

In review, the cases, when received, are generally subjected to three consecutive tests to determine their resistance to crazing:

(Test A) Immersion in Skydrol for 10 min.

(Test B) Heat sterilization on sealed case. The case is filled with KOH, sealed, and submitted to 135°C for 180 hr.

(Test C) Heat sterilization on sealed cell. The cell is assembled, formed, sealed, and submitted to 135°C for 180 hr.

*Figure 5 is a plot of weight loss as a function of time spent at 135°C. The Viking heat-sterilization requirement being 140 hours, the weight loss after 140 hours is 2.0 g and 1.7 g for PPO and GF-PPO respectively. It is in the range of 1 to 1.5 cc of electrolyte, which could be added prior to sealing the cell, if necessary.

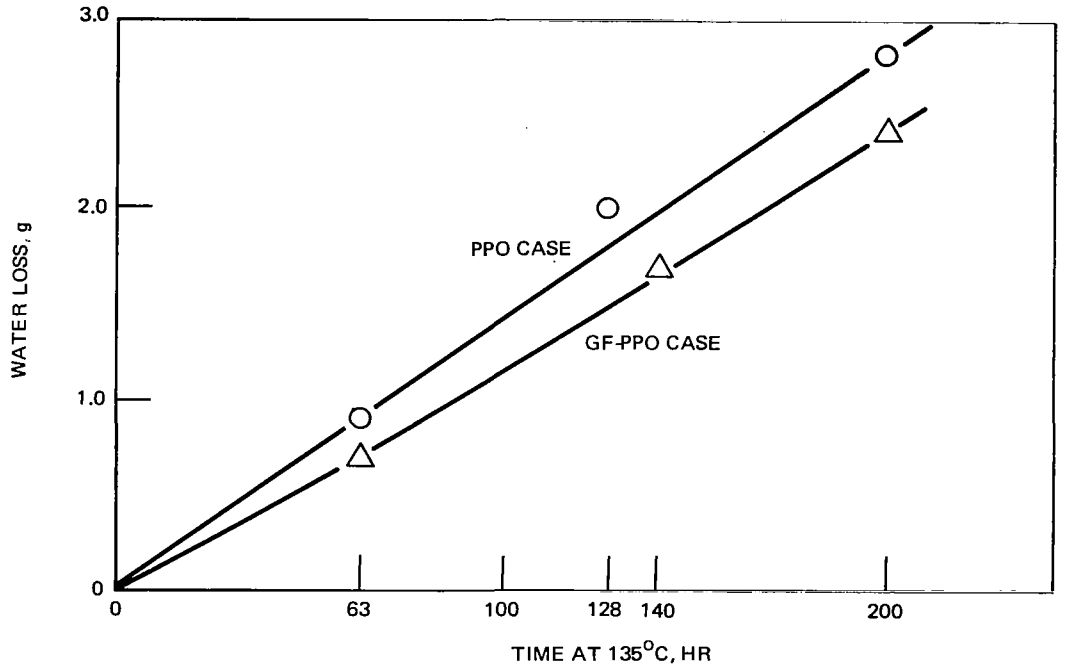


Figure 5. Weight Loss (Water Vapor) From Heat Sterilization

The first case mold provided thin-wall cases. All shipments of such PPO cases passed Test A 100 percent, Test B 80 percent, and Test C 0 percent (slight crazing).

It was then decided to modify the case mold to provide thicker walls and rounded corners for the new case. Also a variant of PPO, 30-percent glass fiber-filled PPO material, coded (GF(30)-PPO was considered for its resistance to crazing as reported above.

Various lots were ordered in the course of our investigation:

(Lot 0-1) Thin-wall GF(30)-PPO cases

(Lot 0-2) Thick-wall PPO cases

(Lot No. 1) Thick-wall GF(30)-PPO

(Lot No. ?) Thick-wall GF(30)-PPO

All lots passed Test A and Test B 100 percent of the time. However, to pass Test B, welding parameters of the cover-to-case had to be modified

from lot to lot. On Test C the results showed a large improvement, even without the benefit of long heat-treatment prior to sealing.

(Lot 0-1) Ten cells tested; nine cells out of ten did not leak; loss was 4 to 5 g per cell for all cells; they had thin wall cases.

(Lot 0-2) Two cells tested; slight craze; loss of 2.5 to 6 g.

(Lot No. 1) Three cells tested; leaked very slightly; loss of 2 to 5 g.

(Lot No. 2) Two cells tested; one cell leaked very slightly, one cell did not leak; loss of 3 g for each cell.

At any rate, all cells that leaked showed insignificant traces of leakage. After the test, the cells were cleaned and left standing on their leaky side. None showed any further sign of leakage, even after 450 days to date.

In order to obtain reproducible results, it was decided in accord with the NASA Project Monitor to order a single batch of 2,000 lb of PPO molding pellets of very specific characteristics to avoid variations in the ultrasonic welding parameters and minimize, if not eliminate, the small unreliability still left in the case-to-cover seal. Three lots of cell cases were molded, all using the same batch of PPO as a base material (from the large single shipment ordered from the General Electric Company).

(Lot No. 3) PPO alone (control)

(Lot No. 4) Glass fiber 20 percent in PPO, coded GF(20)-PPO*

(Lot No. 5) Glass beads 20 percent in PPO, coded GB(20)-PPO*

Cases of the three lots successfully passed Test A. They also passed Test B. Two cases of each lot were partially filled with KOH and sealed. After exposure at 135°C for 205 hr, their weight loss was about 3 g. In addition, one case of each lot was pressurized at 50 psig and maintained at 135°C for 235 hr without developing a leak. At the end of the test, the cases tested at 100 psig for 10 min did not leak.

Test C was conducted with full heat-treatment prior to sealing. Three cells, each one in a case of different material, were fabricated from leftover parts in order to test the seal integrity under heat-sterilization conditions.

*The 20-percent glass-fill content was used to reduce the weight of the case because the glass increases the PPO case weight by almost 20 percent. The glass beads replacing the glass fibers give supposedly better craze resistance to the material, according to the manufacturer.

After one charge (input 41 Ah) and a discharge (output 38.5 Ah), the cells were heat treated at 100°C to completely discharge the zinc electrodes since there was a deficit of approximately 2.5 Ah between input and output.

The cells were connected to a gas collection setup and were left at 100°C until gas evolution stopped or dropped to a very low rate. Each cell generated approximately 930 cc of gas after 142 hr at 100°C. Using the theoretical value of zinc utilization, this gas amount corresponds to a deficit of 2.2 Ah (comparing closely to the value of 2.5 Ah reported above).

The cells were then sealed and heat sterilized for 205 hours at 135°C. Their weight loss ranged from 2 to 2.9 g after 205 hr, which is in line with the weight loss registered with sealed cases filled only with KOH and subjected to the same heat-sterilization conditions (Figure 6).

One cell (plain PPO) had a slight leak at one terminal. The other two cells (glass filled PPO) held without leakage.

It was finally established the GF (30)-PPO cases on hand could also be used without reservation by properly modifying the ultrasonic welding parameters when a cell is fully assembled (loaded weight compared with an empty case) and by properly heat treating the cell prior to sealing. (The ultrasonic welding parameters of a cell fully loaded are 55 psig applied horn pressure, 4 sec hold time, 4 sec weld time.) More evidence was obtained on cells fabricated and tested in the last part of the program.

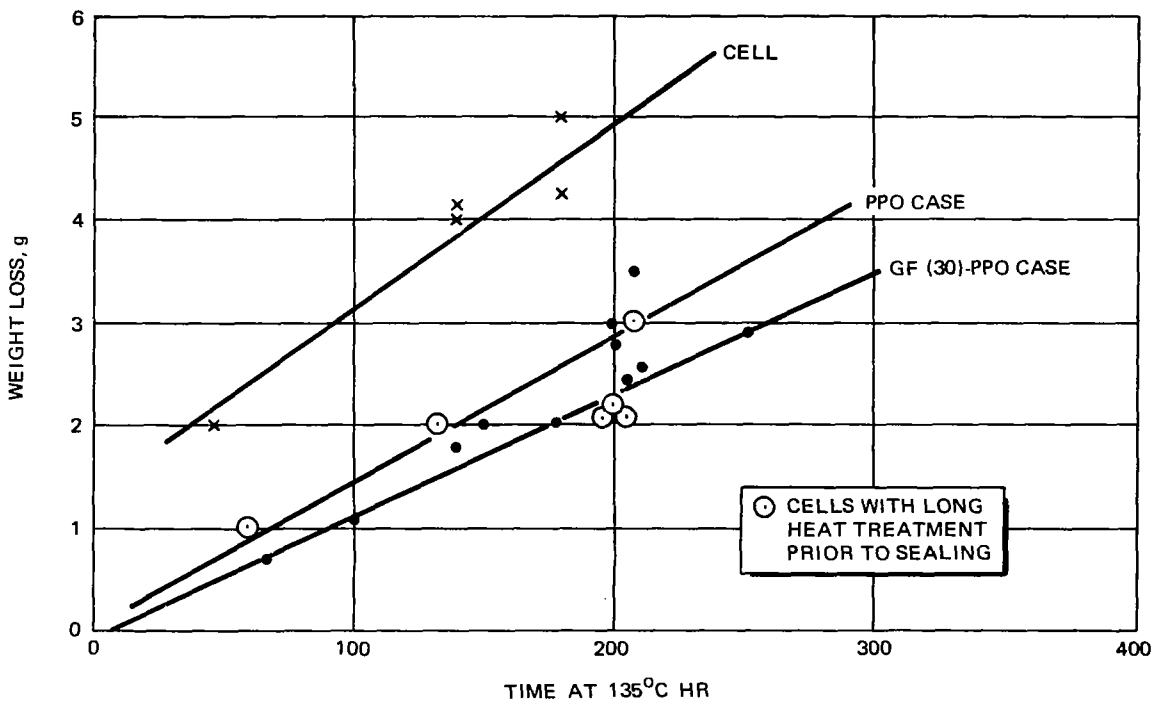


Figure 6. Weight Loss of KOH-Filled and Sealed Cases and Cells at 135°C

A graph of weight loss with time during heat-sterilization (Figure 6) depicts the accumulated evidence in the various cases.

In summary, thick- or thin-wall cases made with glass-filled PPO material, whether 20 percent or 30 percent fibers or beads, can hold their seals during heat sterilization. There is a good chance that this material would also be acceptable for long wet storage without detrimental effect from KOH at room temperature.

Terminal Investigation. —The terminal and associated hardware were tested for seal capability under heat-sterilization conditions. An assembly was made in a terminal hole and seat arrangement fabricated in a polysulfone flat piece the size of a 5-Ah cell cover. This mock-up cover was welded to a 5-Ah cell case and the top epoxy-potted as usually done in the 5-Ah cell assembly. A volume of 10 cc of 40-percent KOH was first introduced in the case before sealing.

Three such case-and-cover assemblies were placed in an oven at 135°C to be watched for leakage over 200 hr (cases HS-3-1 through HS-3-3). Only one case (HS-3-3) passed the no-leakage requirement successfully after 200 hr. The other two leaked after 48 hr and 144 hr, respectively, at the cover-to-case weld, not around the terminal assembly.

After dimensional adjustment, the test was repeated on three new cases with careful weight control. After 200 hr, no leakage was noticed; no trace of alkali could be detected at the weld seams or around the terminals.

The following is a tabulation of the weight measurements:

Case	Initial Weight	Final Weight After 200 Hr at 135°C	Water Weight Loss
HS-3-4	92.72 g	90.81 g	1.91 g
HS-3-5	91.34 g	89.22 g	2.12 g
HS-3-6	92.38 g	90.60 g	1.78 g
Average			1.94 g

As required by the work statement, the metal hardware must be nonmagnetic. Brass being also excluded by the work statement, our investigation covered the silver alloys as primary choice for minimal chemical and electrochemical corrosion, good electrical conductivity, and good mechanical properties with respect to strength and machinability. Our choice converged on the following alloys:

(1) 92.5 percent Ag/7.5 percent Cu (Sterling silver)

(2) 90.0 percent Ag/10 percent Cu (Coin silver or Consil 901)

(3) 72.0 percent Ag/28 percent Cu (Consil 7228)

All have good electrical and mechanical characteristics, with Consil alloys mechanically better. The choice depends on the chemical and electrochemical corrosion resistance in alkali. Two series of tests were undertaken:

(1) Chemical—Samples of identical surface area (1 in. long wire of 0.062 in. diameter) of each alloy were placed in a 45-percent KOH solution at 135°C for 200 hr. Weights were measured before and after exposure. Data presented in Table V show no loss in weight or diameter for the Sterling and Consil 901 alloys.

(2) Electrochemical—The same size wire samples of each alloy were placed in a 40-percent KOH solution and oxidized under a current of 10 mA for 77.5 hr against nickel counterelectrodes. Measurements of weights and wire diameters were made before and after the test. Data presented in Table VI show again the definite advantage of Sterling and Consil 901.

In summary, the choice, narrowed down to Sterling and Consil 901, was made in favor of Consil 901 because of its better mechanical strength.

The soldering of leads to the terminal was considered to be unsatisfactory from a reliability viewpoint in a sealed cell destined for heat sterilization and long life operation. The electrodes will have tabs instead of wire leads. The tabs (0.25 by 0.006 in.) will be riveted (with a Consil 901 rivet) to the base of the terminal. Preliminary electrical tests show that this assembly presents a voltage drop of less than 20 mV at 50 A. The good conductivity of the silver alloy terminal certainly helps keep it low, compared with the usual steel solder-filled terminal.

Instead of machining the terminals one by one, which is an expensive operation, it was found more economical to cast the terminal bodies slightly oversize and machine them to the proper finished dimensions.

Some of the first shipment cast silver alloy terminals were found deficient; they broke when the nuts were tightened during the assembly. It appeared that during the centrifugal casting, the body of some terminals was porous. X-ray photographs showed clearly the deficiencies. X-ray was then adopted for quality control and receiving inspection. After discussion with the vendor and correction, terminals of the second shipment were satisfactory; photographs of all terminals showed a rejection rate of only five parts out of 213 (about 2.5 percent).

During the course of cell testing, it was noticed that the positive terminal base was lightly blackened by electrochemical oxidation, which in some instances was conducive to KOH leakage around this terminal. For more safety, a thin layer of gold was electroplated onto the terminal hardware to avoid any corrosion at the base and tarnishing at the top during very long storage tests.

TABLE V

TEST A – EXPOSURE OF SILVER ALLOYS TO 45-PERCENT KOH AT 135°C FOR 200 HOURS

Percent Silver/ Copper	Description	Before Exposure		After Exposure				Remarks
		Weight, g	Diameter, in.	Weight, g	Weight Percent Loss	Diameter, in.	Diameter, Percent Loss	
92.5/7.5	Sterling Ag	0.5471	0.064	0.5471	0	0.064	0	
90/10	Consil 901	0.5041	0.062	0.5041	0	0.062	0	
72/28	Consil 7228	0.4907	0.062	0.4700	4.2	0.062	0	KOH turned bright blue

TABLE VI

TEST B – ELECTROCHEMICAL OXIDATION OF SILVER ALLOYS IN 40-PERCENT KOH AGAINST NICKEL FOR 77.5 HOURS AT 10 mA

Percent Silver/Copper	Description	Before Exposure		After Exposure & Rinse			
		Weight, g	Diameter, in.	Weight, gm	Weight, Percent Loss	Diameter, in.	Diameter, Percent Loss
92.5/7.5	Sterling Ag	1.0833	0.064	1.0688	1.3	0.064	0
90/10	Consil 901	1.0195	0.062	1.0070	1.2	0.0615	0.8
72/28	Consil 7228	0.9946	0.062	0.9729	2.2	0.061	1.6

The very nature of the triple "O" ring seals dictates a strict control of the terminal assembly. An engineering assembly procedure covers the details: Assurance that the "O" rings are compressed to the proper and desired thickness is obtained through the measurement and control of the height of the assembled terminal over the cover and the torque value sufficient to tighten the top nut. The importance of such a control is dramatically shown on two cut-away terminal pictures (Figure 7) showing a leaky terminal assembled in the cover. The bottom "O" ring was not properly tightened. Figure 8 shows shows a terminal where the "O" rings are properly squeezed; it does not leak.

Early in the program, some cells assembled with pressure gauge and metal adapters screwed in their center hole were found to develop cracks in the cover radiating toward one or two terminals during heat sterilization, thus causing leakage around the terminals.

Discounting these cells in our statistical computation, a study of terminal leakage was made on all cells available at a particular time during the program in various testing conditions. Table VII gives a general idea of the capability of the seal in actual cells on 1 January 1970 (average 8-month period). Cells were clustered within a range of temperature to simplify the overall presentation, although it is recognized that temperature may have an effect on the leakage possibility.

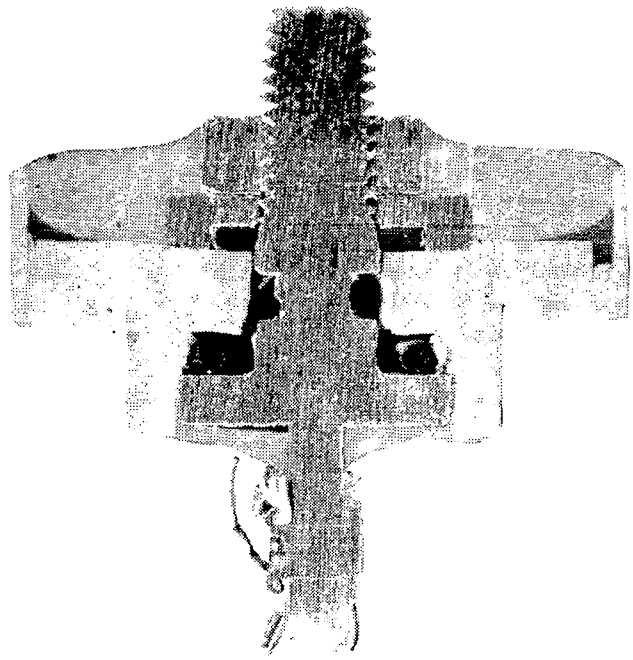


Figure 7. Leaky Terminal

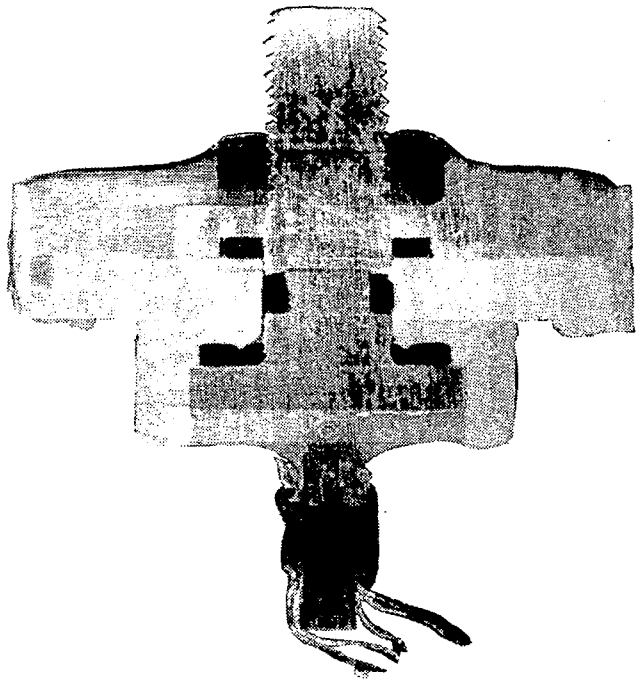


Figure 8. Good Terminal

Table VIII gives a more detailed view of cells on test as of 9 November 1970 (average 15-month period). Essentially after 8 months or 15 months, the percentage of terminals that don't leak is about the same, with negative terminals leaking more often than the positive ones. The effect of stand condition (charged or discharged) and of cycling is apparent also from the tables. Discharged stand leads to no leak. Cycling contributes to the maximum number of leaks. The overall view should take into account the fact that some terminals showing a very slight dry carbonation after a long period of test may be considered acceptable. Under these conditions, the percentage of acceptable terminals is 100 percent for positives and 94 percent for negatives over a 15-month testing period.

Two types of tests were conducted on the standard terminal assembly:

(1) The terminal was fitted into the cover of a small test vessel duplicating the cover terminal assembly so that the terminal head stood outside; the vessel was filled with 45-percent KOH and subjected to 135°C for 180 hr and to pressures ranging from 50 psig to 137 psig. The highest pressure was maintained for 40 hr. No leak was detected around the terminal.

TABLE VII

TERMINAL SEAL LEAKAGE

(Status on 1 January 1970)

Test Type	Number of Cells, n	Temperature Range, °C	Average Wet Life, t	Percent Terminals			
				OK		Acceptable	
				P	N	P	N
Charged Wet Stand	42	10 to 62	7 months	96	81	96	93
Float Wet Stand	37	10 to 32	9 months	100	65	100	95
Discharged[a] Wet Stand	14	25	6 months	100	100	100	100
Cycling Only	67	10 to 32	8 months	98	79	100	98
Stand Followed by Cycling	16	25	11 months	93	63	100	93
Overall Average on Total	152	10 to 32	$t = \frac{\Sigma n_i t_i}{\Sigma n_i}$ 8 months	$\leftarrow p\% = \frac{\Sigma n_i p_i}{\Sigma n_i} \rightarrow$ 98	76	99.5	96

Legend:

P = positive terminal

N = negative terminal

OK = no leak

Acceptable = include the terminals that did not leak and those with very slight dry carbonation

(a) Includes some charged stand and some cycling.

TABLE VIII

TERMINAL SEAL LEAKAGE

(STATUS ON 9 NOV 1970)

Test Type	Number of Cells, n	Temperature Range, °C	Average Wet Life, t	Percent Terminals			
				OK		Acceptable	
				P	N	P	N
Charged Wet Stand	17	10 to 32	16 Months	94	70	100	100
Float Wet Stand	15	10 to 32	16 Months	100	80	100	93
Discharged(a) Wet Stand	13	25	14 Months	100	100	100	100
Cycling Only	32	10 to 32	14 Months	97	50	100	88
Stand Followed by Cycling	8	25	18 Months	100	75	100	100
Overall Average on Total	85	10 to 32	$\left(t = \frac{\Sigma n_i t_i}{\Sigma n_i}\right)$ 15 Months	$\leftarrow \left(P\% = \frac{\Sigma n_i t_i}{\Sigma n_i}\right) \rightarrow$ 98		100	94

Legend:

P = positive terminal

N = negative terminal

OK = no leak

Acceptable = include terminals that did not leak and those with very slight dry carbonation

(a) Includes some charged stand and some cycling.

(2) A NASA-suggested test for checking the hermeticity of the seal against KOH was conducted on the standard terminal as presently used. Two terminals were assembled in a cover welded to a case containing 40 cc of KOH, maintained inverted while heated at 135°C for 72 hr and then cooled to 32°C. A voltage of 1.20 V was then impressed across the terminals. No leak was detected visually or with phenolphthalein after 430 days to date.

As directed by Technical Direction No. 3, more case assemblies were prepared. For each variation, six cases are assembled, three to be tested upside down and three upright (in these cells, tabs are attached to the terminal base and they dip in electrolyte), as the test (2) above.

(1) The first group consists of six cases using the standard terminal seal with current assembly methods. They have been on test for 140 days to date.

(2) The second group consists of six cases using the standard terminal seal with all hardware vapor-degreased by trichlorethylene for 40 min. They have been on test for 140 days to date.

(3) A third group consists of six cases using the standard terminal seal with epoxy applied to the bottom well after tightening all "O" rings. They have reached 85 days to date.

(4) Two terminal seal designs with hardware were supplied by NASA for assembly of two groups of six cases (dA) and (dB). They have reached 85 days to date.

All terminals are checked weekly for leakage. None has shown any trace of leakage or carbonation to date.

Electrochemical Development (Preliminary)

The electrochemical cell design covers the electrode size and weight, the selection of a proper separator system, separator overall dimensions and edge sealing, and a choice among possible cell-pack assemblies. In order to establish electrical and electrochemical design parameters for the full cell, a few cell elements (three-plate configuration) of various designs were investigated.

Cell Elements. — The cell elements consist of three electrodes (one positive and two negative or vice-versa), assembled with the selected separator system in large polysulfone cases supplied by NASA while waiting for our molded cases. These cell elements are part of the full cell design considered for the primary cell and the secondary cell designs. Extrapolation of the electrical performance to the full cells would then be more realistic.

The basic design characteristic is the flexible separator bag, which will contain either the zinc electrode or the positive electrode. However, variants

can be introduced if a thicker separator system is required for long wet stand, such as double bagging (both electrodes are contained in bags) or an extra separator layer on the electrode that is not bagged.

All of these variations are succinctly referred to as designs A, B, C, and D, for each design primary (P) or secondary (S). Details are given in Table IX. Two cells per variation were built, using large polysulfone substitute cases, polysulfone shims, and machined covers.

The cells were submitted to one full cycle, charge and discharge at a low rate (about C/5), then heat treated at 100°C to complete residual zinc metal discharge to avoid or minimize hydrogen evolution during subsequent heat sterilization. The cells were then heat sterilized in sealed vessels at 135°C for 200 hr. A few regular cycles followed at the C rate as required. Table X gives the cycling history of all cell elements built. After completing their tests of heat sterilization and four deep discharge cycles, they were recharged and left on stand to get additional information about their capacity and OCV retention capability.

Table XI gives the status of OCV versus stand days for various designs up to 8 months. The separator bag b encloses either the negative electrode (design A) or the positive electrode (design B) or both (design C). (In design D, the positive electrode is wrapped in a "U" of inorganic separator instead of being bagged.) The purpose at this point was to test the separator system design. The distinction between primary and secondary was therefore discontinued as the only difference was in electrode silver content and thickness in order to design the full cell with more or fewer plates. (As a

TABLE IX

MAIN DESIGN CHARACTERISTICS
OF CELL ELEMENTS

Code	Configuration Electrode-Separator	Silver Weight per Positive Electrode	
		Primary	Secondary
A	$1^{+}/2^{-}b$	20 g	30 g
B	$2^{+}b/1^{-}$	20 g	30 g
C	$1^{+}b/2^{-}b$	20 g	30 g
D	$1^{+}L/2^{-}b$	20 g	30 g

Legend: b = Separator bag + = Positive eletrode

L = Separator layer - = Negative electrode

TABLE X

OUTPUTS OF CELL ELEMENTS

(3-Plate Cells)

Configuration	Cell No.	Presterilization	Poststerilization		
Primary	P-	Cycle 1 at 1.5 A	Cycle 2 at 7 A	Cycle 3 at 7 A	Cycle 4 at 7 A
A	1-1	6.5 Ah	6.4 Ah	6.4 Ah	7.0 Ah
	1-2	6.7	6.3	6.1	6.7
B	2-1	7.2 Ah	9.5 Ah[a]	7.7 Ah	7.7 Ah
	2-2	7.2	9.4 [a]	7.7	8.1
C	3-1	6.5 Ah	6.1 Ah	5.6 Ah	5.3 Ah
	3-2	6.5	5.8	5.7	5.3
D	4-1	6.5 Ah	7.0 Ah	6.7 Ah	6.0 Ah
	4-2	6.5	7.1	6.4	6.0
Secondary	S-	at 1.5 A	at 10 A	at 10 A	at 10 A
A	1-1	10.7 Ah	8.4 Ah[b]	9.0 Ah	9.0 Ah
	1-2	10.7	7.6 [b]	8.3	8.5
B	2-1	12.0 Ah	10.6 Ah	11.2 Ah	9.5 Ah
	2-2	11.5	9.8	10.3	10.8
C	3-1	9.5 Ah	9.4 Ah	7.6 Ah	8.4 Ah
	3-2	9.7	8.4	7.6	8.4
D	4-1	9.7 Ah	10.0 Ah	8.4 Ah	9.5 Ah
	4-2	9.7	8.8	7.8	9.5

NOTE: In design B, capacity is negative limited.

[a] Cells were overcharged

[b] Cells were undercharged

TABLE XI

CHARGED STAND DATA FOR VARIOUS ELECTRODE PACK DESIGN CONFIGURATIONS AFTER FOUR DEEP CYCLES

(Days Versus OCV)

Design—	A ($1^+/2b^-$)				B ($2b^+/1^-$)				C ($1b^+/2b^-$)				D ($1L^+/2b^+$)			
OCV over or Equal to	HS-13 1-1	HS-13 1-2	HS-14 1-1	HS-14 1-2	HS-13 2-1	HS-13 2-2	HS-14 2-1	HS-14 2-2	HS-15 1-1	HS-15 1-2	HS-16 1-1	HS-16 1-2	HS-15 2-1	HS-15 2-2	HS-16 2-1	HS-16 2-2
1.85 V	185	111	151	130	56	97	95	88	241	241	239	239	165	241	239	239
1.84 V		140		151			102	95					183			
1.83 V							123									
1.82 V		204						102								
1.80 V	204	223	165	183	62								234			
1.75 V		244	183				130									
1.65 V	237			209		104										
1.60 V	244			220		153	138	109								
1.55 V			241	241	70	212	183	138					240			

Note: Days since activation (total wet life) may be calculated as follows:

For HS-13: Days since activation = days open circuit stand + 29 days

HS-14: Days since activation = days open circuit stand + 31 days

HS-15: Days since activation = days open circuit stand + 26 days

HS-16: Days since activation = days open circuit stand + 29 days.

reminder, the primary required on this program is defined as a rechargeable high-rate cell of limited cycle life, 25 deep cycles at the C rate. Its design therefore required a larger number of plates than the low-rate secondary.)

At the end of the 8-month charged stand, the cell elements were discharged.

The best group (HS-16 cells) had two cells with an average residual capacity 65 percent of the previous capacity prior to stand. After recharge, their output averaged 95 percent (capacity prior to stand practically recovered).

Another group (HS-15 cells), of different plate design but of the same double-bag construction, did not perform as well, although the OCV after 8 months was still 1.85 V, the residual capacity was only 36 percent average and after recharge the output was only 54 percent average. All the cell elements assembled at the origin of the program were not sealed adequately nor uniformly and this may have accounted for a heavier carbonation of the electrolyte in some cells.

The last group of HS-16 cells that had a good OCV had a design L^+/b^- (layer and a bag) equivalent in separator thickness to the double-bag construction, but open on two sides. It may be considered for information only and its data are added to the others in Table XII, which is a summary of the cell element data. It is interesting to note that their data are in the same range as the other group HS-16.

After the two capacity-check cycles, the cells were put on automatic cycling on a regime prorated down from the 40-Ah cell regime. They are being cycled at the rate of one cycle per day, discharge at 0.7 A for 2 hr and recharge in 22 hr, voltage limited to 2.02 V/cell. The cells have completed 464 cycles to date, which brings to 26 months their total wet life since activation.

At cycle 224, the cycling was temporarily stopped and an OCV check was run. After 21 hr on open circuit, the four cells (b^+/b^-) had a reading of 1.86 V and the two cells (L^+/b^-), 1.84 V (see Table IV for cell reference number). This was after 17 months total wet life out of which 8 months are charged stand followed by 8 months of cycling time (or 224 cycles).

It is worth noting that the two cells L^+/b^- by their OCV show a slight short leakage.

At cycle 457, the cells were again stopped and left on OCV. The first four cells (b^+/b^-) again had a reading of 1.86 V after 72 hours. The last two cells (L^+/b^-), after 2 hr, read 1.85 V and after 72 hr 1.72 V and 1.56 V respectively. This design has not been used anywhere else in the program. Only the design b^+/b^- has been extensively used.

TABLE XII

POST-WET STAND DATA OF CELL ELEMENTS

(9 Months Total Wet Life Including Four Deep Cycles Followed By 8-month Charged Stand)

Separator Design	Cell Number	Input Prior to Stand, Q_i	Calculated Output Prior to Stand, $0.9Q_i$	OCV after 8-Month-Charged Stand	Residual Capacity Q_r	Recharge (Q_i')	Output (Q_o')	Residual, Percent	Actual Recovered, Percent
b^+/b^-	HS-15-1-1	5.3 Ah	4.8 Ah	1.85 V	1.8 Ah	2.4 Ah	2.8 Ah	37	58
	HS-15-1-2	5.3	4.8	1.85	1.7	2.2	2.4	35	50
	Average							36	54
	HS-16-1-1	9.7 Ah	8.7 Ah	1.85 V	6.0 Ah	7.1 Ah	8.5 Ah	69	98
	HS-16-1-2	9.7	8.7	1.85	5.3	7.1	8.0	61	92
	Average							65	96
L^+/b^-	HS-16-2-1	9.8 Ah	8.8 Ah	1.85 V	4.9 Ah	7.1 Ah	8.2 Ah	56	93
	HS-16-2-2	9.5	8.5	1.85	5.5	7.1	6.1	65	72
	Average							60	82

NOTE: Last output Q_o' is higher than previous input Q_i', which means that all capacity, although available, was not usable on prior discharge (Q_r), just after wet stand, probably because of bad wetting or carbonation.

Full Cells. — The first series of full cells consisted of five primary cells and five secondary cells. Since the choice between polysulfone and PPO cases was not yet determined, PPO cases were used in the construction of this series as a candidate more likely to stand heat sterilization. (During heat sterilization of the cell elements, the substitute polysulfone cases supplied by NASA crazed and the cell pack had to be transferred into new cases to continue the cycling tests.)

Selecting first the configuration where positive electrodes are enclosed in a separator bag, the primary and secondary cells were designed to deliver 40 Ah and 50 Ah respectively.

The cells underwent the complete series of the electrical acceptance testing required by the work statement:

(1) Formation (charge and discharge), then recharge

(2) Open circuit stand for 72 hr

(3) High rate discharge

Table XIII summarizes the data of this test sequence, for the five 40-Ah and the five 50-Ah cells respectively. Figures 9 and 10 show their typical formation discharge and Figures 11 and 12 their typical high rate discharge. All results are within close limits.

Polarization tests were run on two cells. Figure 13 shows the voltage versus current curve of the test run on the 40-Ah cell. Such a test must be qualified: after removing 25 percent of the capacity of the cell at a relatively low rate (10 A for 1 hr) to reach the argenteous oxide plateau voltage, the cell was submitted to a series of short discharges of 1 min duration (for plateau voltage stabilization), separated by a no-load period sufficiently long to let the open circuit voltage recover and avoid residual electrode polarization effects after a high current discharge.

With current raised up to 200 A, the cell voltage was still above 1.0 V (range 1.05 to 1.08 V). The same test run on the 50 Ah cell gave approximately the same results within 20 mV.

A variant was introduced in the design of two cells of each group. They used a special honeycomb silver grid called Distex in the negative electrode instead of the regular Exmet grid. The cells are noted D after their cell number in Tables I and II. Their data are not different from those of the rest of the group.

This feature was retained in cells fabricated subsequently throughout the program, as it was speculated that zinc shape retention would be improved.

TABLE XIII

PRELIMINARY CELL DATA

Type and Design	Cell No.	Cycle 1 (Ah)		Cycle 2 (Ah)			
		Input	Output at 7 A and drain	Input	Output at 40 A to 1.0 V	Drain at 4 A to 1.0 V	Total Output
40 Ah $6b^+/7^-$	HS-24-1	44.9	42.9	40.8	38.7	2.4	41.1
	HS-24-2	44.9	42.4	40.8	38.0	2.6	40.6
	HS-24-3	44.6	42.9	40.9	38.7	2.0	40.7
	HS-24-4D	44.5	43.1	41.6	38.6	2.5	41.1
	HS-24-5D	44.6	42.7	40.8	39.3	2.0	41.3
	Average	44.7	42.8	41.0	38.7	2.3	41.0
50 Ah $5b^+/6^-$	HS-25-1	52.5	50.6	50.8	48.0	3.0	51.0
	HS-25-2	52.0	50.0	50.0	47.3	2.8	50.1
	HS-25-3	52.0	48.5	49.5	46.7	3.2	49.9
	HS-25-4D	53.5	49.0	50.0	46.7	2.9	49.6
	HS-25-5D	53.7	51.4	50.2	48.0	2.4	50.4
	Average	52.7	49.9	50.1	47.3	2.8	50.1

Notes:

1. Input at 2.5 A to 2.05 V

2. Cells noted D use a special grid called Distex in the negative electrode.

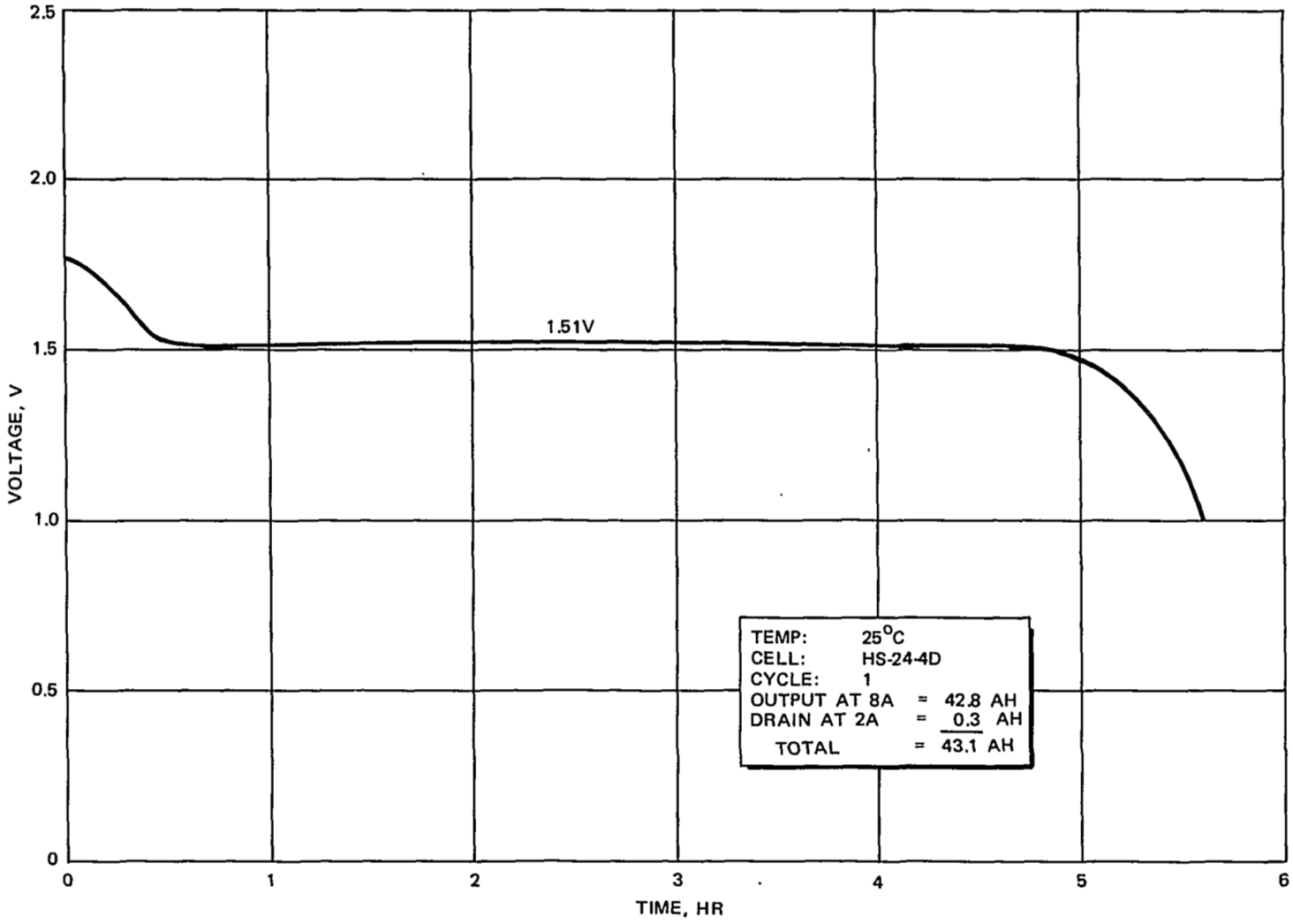


Figure 9. Typical Formation Discharge of 40-Ah Cell

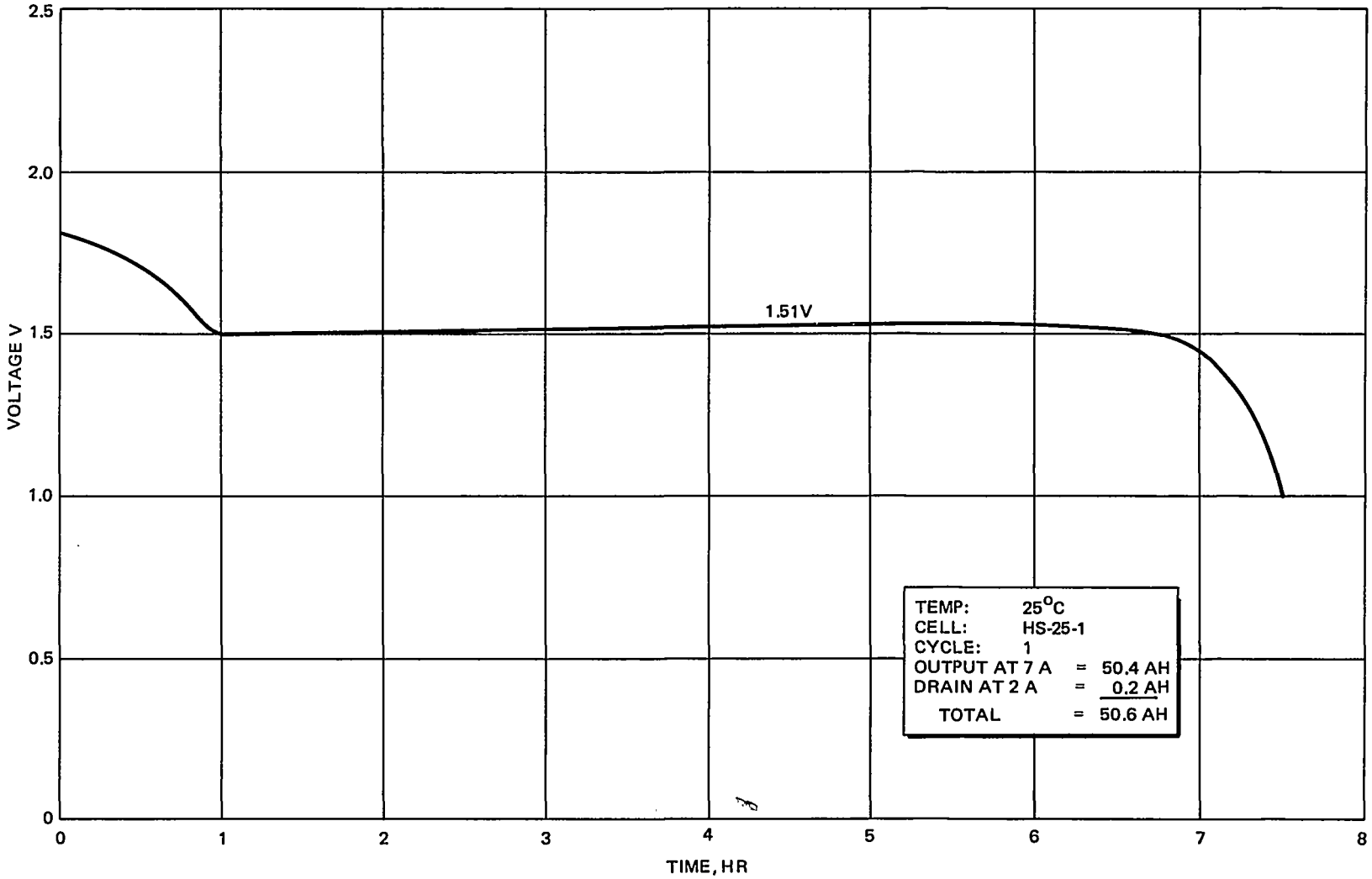


Figure 10. Typical Formation Discharge of 50-Ah Cell

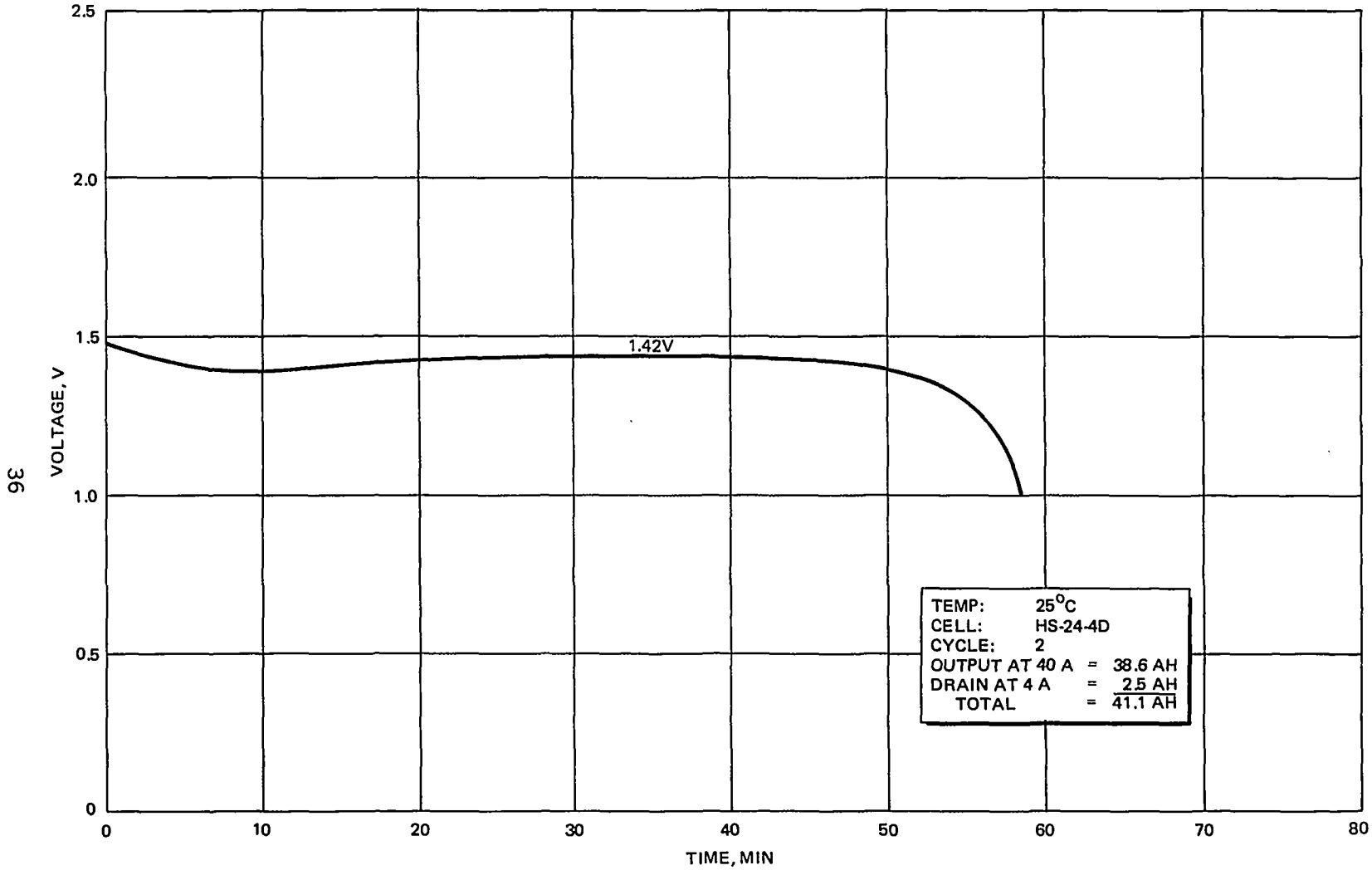


Figure 11. High-Rate Discharge of 40-Ah Cell

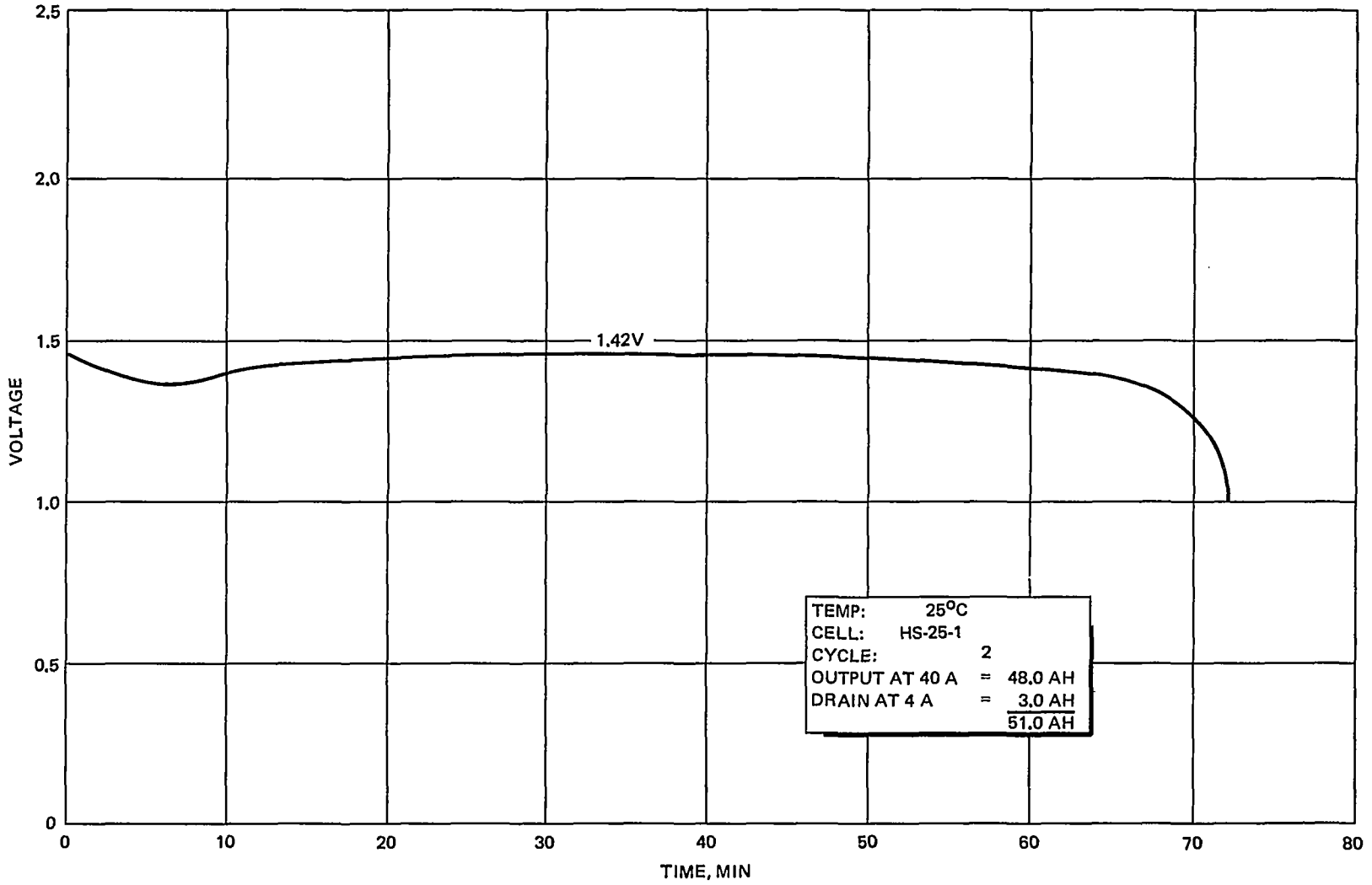


Figure 12. High-Rate Discharge of 50-Ah Cell

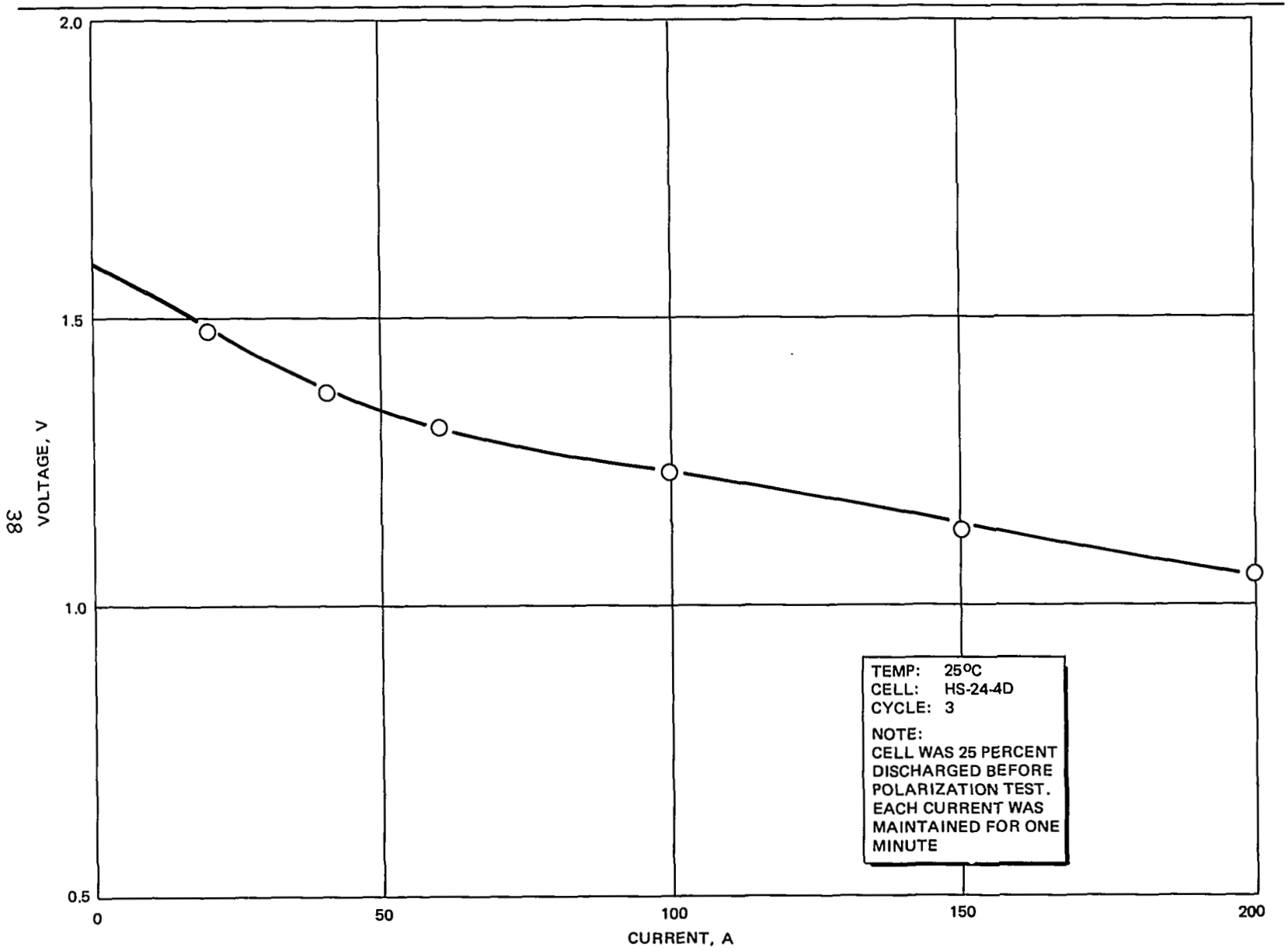


Figure 13. Polarization Curve Rim on 40-Ah Cell Discharge by 25 Percent

Various Designs

This section emphasizes the various electrochemical designs evolved during the program. They are in chronological and logical order although fabrication, testing, and data evolution were done sometimes concurrently. Data are presented up to the date of issuance of this report.

Except in a few instances where noted, all cells followed a standard test procedure prior to any specific test, such as wet stand on cycling. Each cell underwent a charge and discharge (formation cycle) at a relatively low rate not exceeding C/5, then a heat-sterilization at 135°C for 200 hr (in some cases 180 hr) then a check cycle.

In the early part of the program, while case-to-cover seal was being investigated, the cells were heat sterilized in sealed vessels. They were then removed and their center hole was fully sealed prior to the check cycle. Later, the sealing was done prior to the heat sterilization, which was therefore conducted without the help of a sealed vessel.

The sealed vessels were designed to hold one full cell restrained by two 1/4-in. steel plates on its two large faces. A pressure gauge setup helped monitor the pressure developed by the cell during heat sterilization.

Design 1

In accordance with the work statement, a series of 28 primary cells, 40-Ah capacity, were fabricated, selecting the same design used for the five cells submitted to the electrical acceptance test above. It is a $6b^+/7^-$ pack configuration (six bagged positives and five negatives not bagged). The tests are summarized as follows:

(1) Charged wet stand with continuous float at 1.86 to 1.88 volts per cell—total of 18 cells divided in four groups of various subtests as follows:

   (a) Five cells on float with periodic capacity checks after 3, 6, and 10 months at 25°C

   (b) Five cells on float for 10 months

   (c) Five cells on float with capacity checks every month for 3 months at 65°C

   (d) Three cells on float for 10 months with pressure and gassing measurements

(2) Electrical characterization (five unsterilized cells and five sterilized cells)

Table XIV gives the formation capacities and heat sterilization pressures. Table XV gives the high rate capacities of the 18 cells intended for wet stand. The three cells intended for gas analysis were heavily potted in epoxy as

TABLE XIV

DESIGN 1 ($6b^+/7^-$) FORMATION AND HEAT STERILIZATION DATA OF FIRST SERIES OF 28 CELLS

Cell Number	Output, Cycle 1, Ah (7 A to 1.0 V + 2 A to 1.0 V)	Maximum Pressure, psig
HS-34-1	36.4	36
HS-34-2	40.9	36
HS-34-3	38.2	33
HS-34-4	39.9	31
HS-34-5	36.2	25
HS-34-6	38.5	35
HS-34-7	39.9	40
HS-34-8	40.3	34
HS-34-9	36.5	41
HS-34-10	38.2	23
HS-34-11	38.2	29
HS-34-12	39.6	29
HS-34-13	41.7	30
HS-34-14	41.0	28
HS-34-15	38.2	31
HS-35-1	38.5	30
HS-35-2	41.3	38
HS-35-3	37.1	26
HS-36-1	38.5	Not sterilized
HS-36-2	41.3	Not sterilized
HS-36-3	39.6	Not sterilized
HS-36-4	36.8	Not sterilized
HS-36-5	39.6	Not sterilized
HS-36-6	41.7	32
HS-36-7	40.3	26
HS-36-8	39.8	30
HS-36-9	39.6	30
HS-36-10	39.9	35
Average	39.2	31

Note:
Cells were heat-treated first at 100°C for 24 hours, then heat-sterilized at 135°C for 60 hours, cooled to room temperature, then sterilized again at 135°C for 120 hours.

TABLE XV

DESIGN 1 ($6b^{+}/7^{-}$) CYCLE 2 OUTPUT DATA ON FIRST SERIES OF 28 CELLS SCHEDULED FOR CHARGED STAND

Cell Number	Output, Cycle 2, Ah (40 A to 1.0 V +4 A to 1.0 V)
HS-34-1	38.3
HS-34-2	37.4
HS-34-3	38.1
HS-34-4	34.2
HS-34-5	39.8
HS-34-6	38.0
HS-34-7	39.1
HS-34-8	38.5
HS-34-9	41.3
HS-34-10	34.9
HS-34-11	36.9
HS-34-12	38.0
HS-34-13	38.3
HS-34-14	35.3
HS-34-15	38.4
HS-35-1	40.1
HS-35-2	42.5
HS-35-3	40.1
Average	40.0

required by the work statement and put on stand and floated at 1.85 to 1.88 volts per cell. Table XVI gives their data. The ten cells submitted to electrical characterization have their data listed in Table XVII and Table XVIII (four current-level and three temperature-level combinations). Table XIX is a summarized presentation of such data for reference and comparison purposes. Figures 14 and 15 present the results graphically for outputs and plateau voltages at the indicated temperature for sterilized and unsterilized cells. Out of the 15 cells scheduled for wet stand, seven cells showed signs of failure after a few days and were eliminated. In order to pursue the tests, they were tentatively replaced by cells used for electrical characterization after completion of their tests (Table XX).

Some cells continued to fail on the wet stand test at 25°C by showing a voltage below the 1.86-V lower limit maintained on float charge. When removed and left on plain stand without the benefit of the float charge, their OCV's dropped to low values (1.55 V to 1.72 V). The remaining cells were discontinued since this design did not meet the desired objectives.

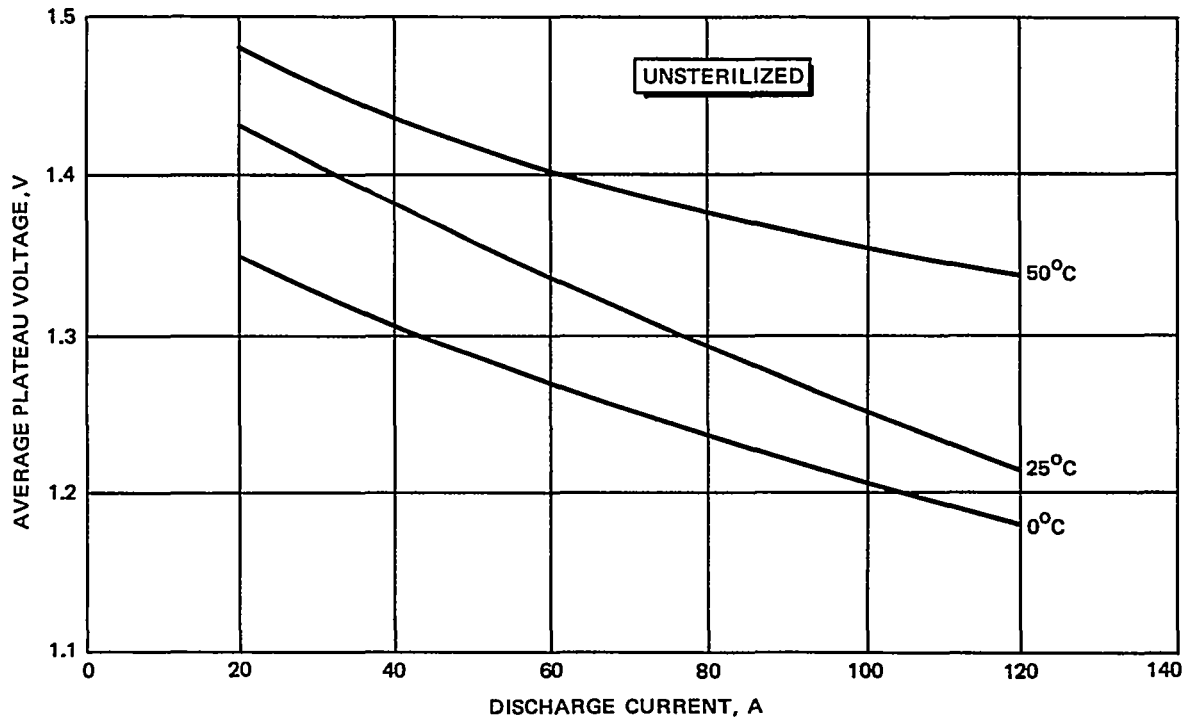
TABLE XVI

DESIGN 1 ($6b^+/7^-$) CHARGED STAND
WITH FLOAT CHARGE

Conditions: 1.86 to 1.88 Volts per Cell and
20-mA Current Limit

Pressure on Float				
	Pressure			
Cell No.	Beginning of Float	11 Days on Float	40 Days on Float	63 Days on Float
HS-35-1	15 psig	15 psig	5 psig	2 psig
HS-35-2	7 psig	20 psig	10 psig	2 psig
HS-35-3	3 psig	0 psig	0 psig	0 psig

Gas Analysis on Float									
	Volume Percent After								
	11 Days on Float			40 Days on Float			63 Days on Float		
Cell No.	H_2	O_2	N_2	H_2	O_2	N_2	H_2	O_2	N_2
HS-35-1	48	2	50	23	4	73	17	3	80
HS-35-2	56	2	42	48	trace	52	45	1	54
HS-35-3	3	17	80	3	20	77	3	17	80



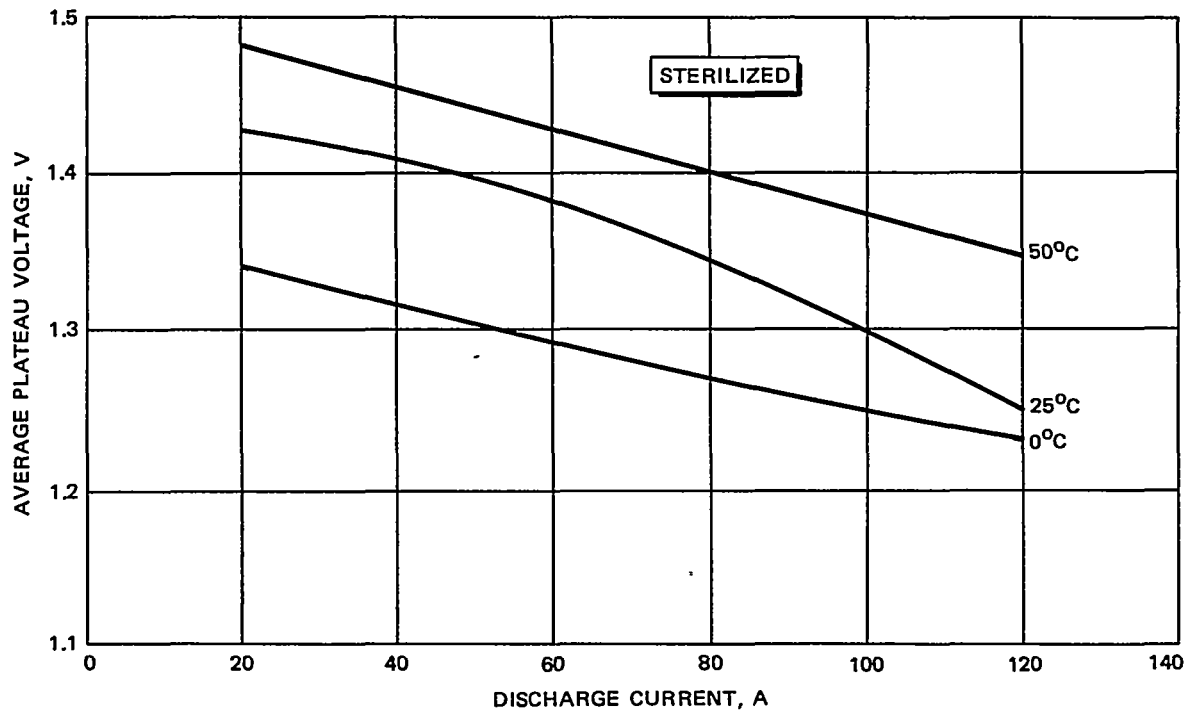
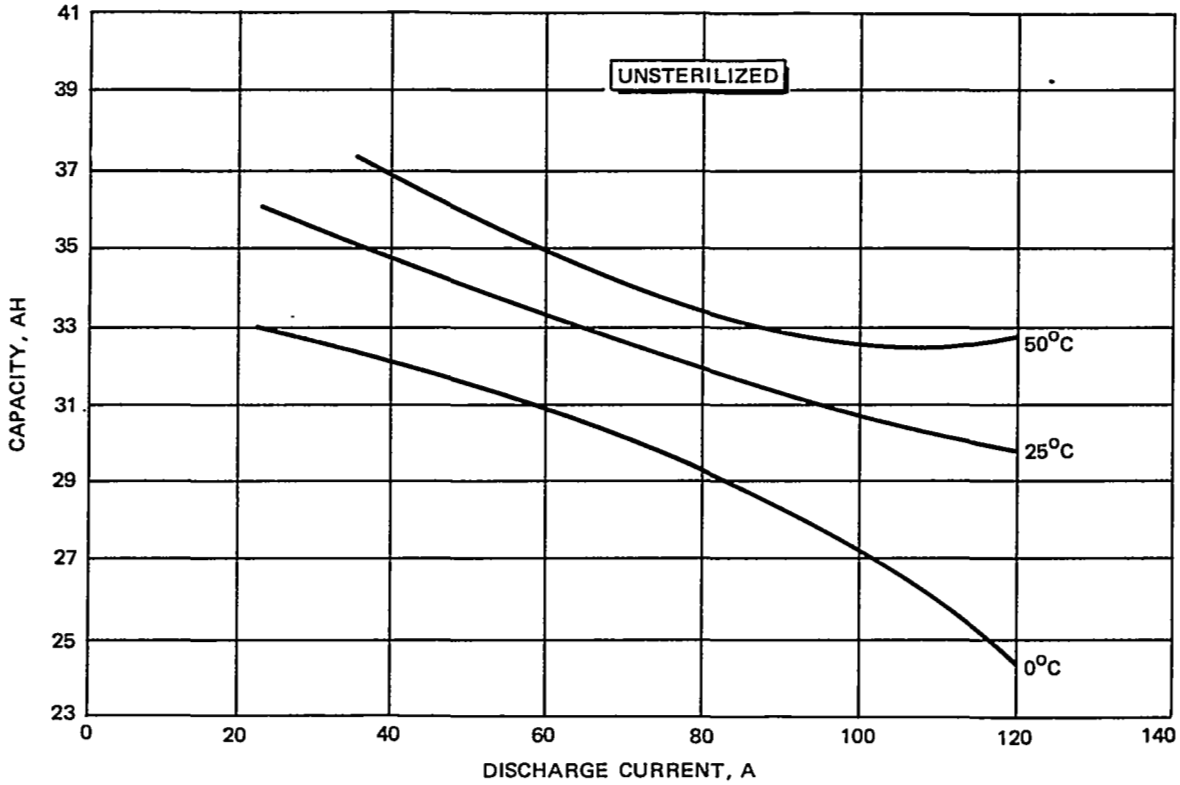


Figure 14. Plateau Voltage at Various Temperatures Versus Discharge Currents—Design $6b^{+}/7^{-}$



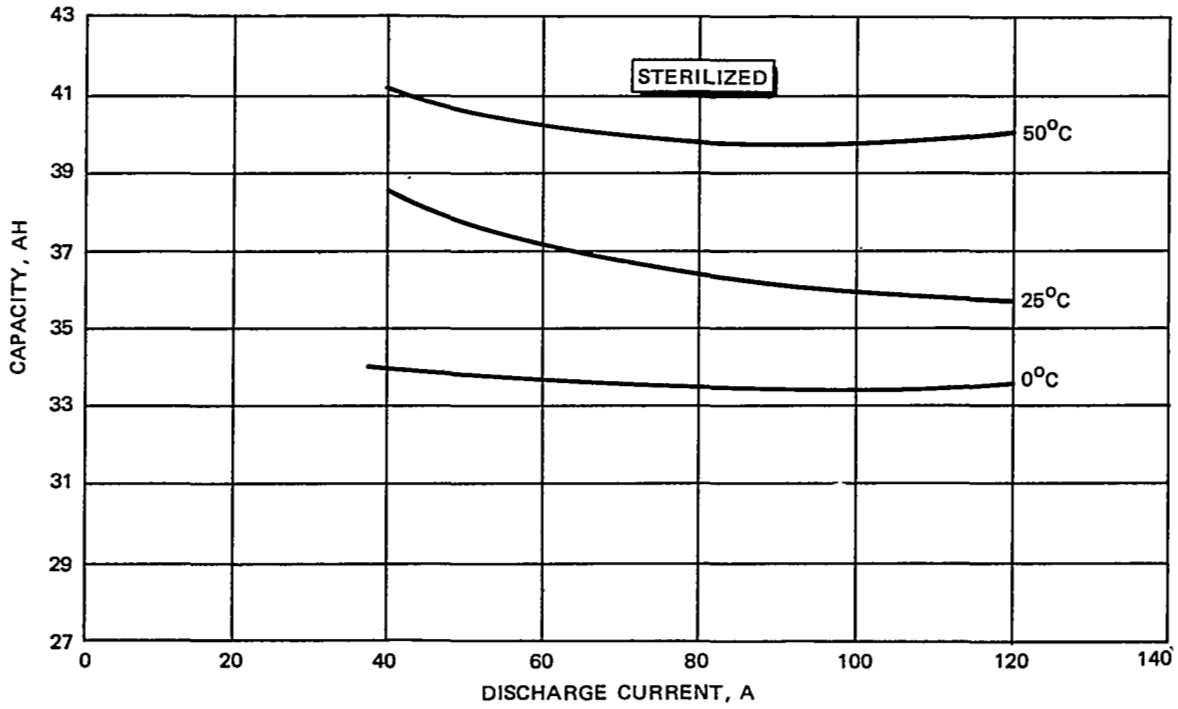


Figure 15. Output at Various Temperatures Versus Discharge Currents—Design $6b^{+}/7^{-}$

TABLE XVII

DESIGN 1 ($6b^+/7^-$) CAPACITIES AT VARIOUS TEMPERATURES AND DISCHARGE CURRENTS

(Cells Not Sterilized)

Cell No.	(a) Cycle No.	(b) Temp, °C	Discharge Current, A	Plateau Voltage, V	Output at Temperature, Ah	(c) Drain, Ah	(d) Output, Ah
HS-36-1	1	0	20	1.35	33.0	5.4	38.4
	2	0	120	1.18	24.0	5.8	29.8
	3	50	120	1.33	32.4	4.1	36.5
HS-36-2	1	0	40	1.30	32.0	5.4	37.4
	2	0	80	1.26	29.6	5.1	34.7
HS-36-3	1	25	20	1.43	36.4	3.5	39.9
	2	25	120	1.24	30.0	4.0	34.0
HS-36-4	1	25	40	1.38	33.6	3.1	36.7
	2	25	80	1.29	32.0	3.0	35.0
HS-36-5	1	50	40	1.42	36.8	1.5	38.3
	2	50	20	1.48	34.4	1.0	35.4
	3	50	80	1.38	33.6	2.1	35.7
	4	50	120	1.34	33.6	2.2	35.8

(a) Formation cycle not included. See Table XIV.

(b) Cells were stabilized at temperature for a minimum of one hour prior to being discharged.

(c) Cells were drained at room temperature (4 A to 1.0 V).

(d) Total output = output at temperature + drain at room temperature.

TABLE XVIII

DESIGN 1 ($6b^+/7^-$) CAPACITIES AT VARIOUS TEMPERATURES AND DISCHARGE CURRENTS

(Heat Sterilized Cells)[a]

Cell No.	(a) Cycle No.	(b) Temp, °C	Discharge Current, A	Plateau Voltage, V	Output at Temperature, Ah	(c) Drain, Ah	(d) Output, Ah
HS-36-1	1	0	20	1.34	32.0	3.0	35.0
	2	0	120	1.23	33.6	3.3	36.9
	3	50	120	1.36	38.4	1.5	39.9
HS-36-7	1	0	40	1.32	34.0	3.7	37.7
	2	0	80	1.31	33.6	4.1	37.7
HS-36-8	1	25	20	1.43	34.0	1.4	35.4
	2	25	120	1.25	36.0	2.5	38.5
HS-36-9	1	25	40	1.42	38.8	2.0	40.8
	2	25	80	1.33	36.0	2.2	38.2
HS-36-10	1	50	40	1.43	41.2	0.4	41.6
	2	50	20	1.50	38.4	0.5	38.9
	3	50	80	1.40	40.0	1.5	41.5
	4	50	120	1.36	42.0	2.6	44.6

[a] 135 C for 60 hr, cooled; 135°C for 120 hr.

[b] Formation cycle not included. See Table XIV.

[c] Cells were stabilized at temperature for a minimum of one hour prior to being discharged.

[d] Cells were drained at room temperature (4 A to 1.0 V).

[e] Total output = output at temperature + drain at room temperature.

TABLE XIX

DESIGN 1 ($6b^+/7^-$) ELECTRICAL PERFORMANCE AT VARIOUS TEMPERATURES AND DISCHARGE CURRENTS

Temperature	Discharge Current, A	Unsterilized Cells		Sterilized Cells	
		Average or Plateau Voltage, V	Capacity, Ah	Average or Plateau Voltage, V	Capacity, Ah
0°C	20	1.35	33.0	1.35	32.0
	40	1.30	32.0	1.32	34.0
	80	1.26	29.6	1.31	33.6
	120	1.18	24.0	1.23	33.6
25°C	20	1.43	36.4	1.43	34.0
	40	1.38	33.6	1.42	38.8
	80	1.29	32.0	1.33	36.0
	120	124	30.0	1.25	36.0
50°C	20	1.48	34.4	1.50	38.4
	40	1.42	36.8	1.43	41.2
	80	1.38	33.6	1.40	40.0
	120	1.34[a]	33.0[a]	1.35[a]	40.2[a]

Notes:

[a] Averages of data for two cells.

Data are taken from Tables XVII and XVIII.

TABLE XX

DESIGN 1 ($6b^{+}/7^{-}$) CHARGED STAND DATA
ON SERIES 1 CELLS AT 25°C

Conditions: All Cells on Float Charge At 1.86 V to 1.88 V with 20-mA Current Limit

Cell No.	Days at 1.86 V or greater
HS-34-5	62
HS-34-6	62
HS-34-7	62
HS-34-9	62
HS-35-1(a)	63
HS-35-2(a)	63
HS-35-3(a)	55 F
HS-36-1	48 F
HS-36-3	54 F
HS-36-5	37 F
HS-36-6	56
HS-36-9	60 F
HS-36-10	56

(a) Pressure and gassing data in Table XVI.

F = Cell OCV dropped below 1.86 V on float charge after number of days indicated.

Design 2

As one cell element of Design 1 type dropped in OCV (1.57 V) after a relatively short stand (70 days), a backup design for the 40-Ah cell was started almost concurrently with the previous series of 28 cells.

One peculiarity of the Design 1 is the reduction of space between electrodes. No KT paper (absorbent) is used on the positives since the separator bag is made of an absorbent mat supporting an inorganic film. The mat facing the positive electrode served as an interseparator in lieu of KT. This construction was tried because of the cell space needed to insert a pack of six positive electrodes and seven negative electrodes in order to obtain a high voltage at the 1-hour rate (1.40 to 1.45 V) as required by the work statement. However, a five-positive, six-negative pack design showed no significantly lower voltage at this rate when a backup design (Design 2) using separator bags on the negative electrodes was introduced.

Only six cells were first built to acquire electrical performance data. They were formed (discharged at 8 A), then all cells except for one used as a control, were heat-sterilized at 135°C for 200 hr, and then given a high rate (40 A) cycle. Their preliminary data are given in Table XXI. The cells were then divided in groups placed on various tests while a new series of 28 cells were being fabricated to replace the Design 1 series.

The first three cells left on plain charged wet stand degraded in OCV (1.60 V to 1.86 V) after a period ranging from 125 to 156 days, which is in line with the 4- to 5-month capability of the cell elements of similar design.

TABLE XXI

DESIGN 2 ($5^+/6b^-$) PRELIMINARY CELLS--FORMATION AND POSTSTERILIZATION DATA

Cell No.	Cycle 1 Output at 8 A + Drain, Ah	Heat Sterilization (135°C, 200 hr) Maximum Pressure, psig	Cycle 2 Output at 40 A + Drain, Ah
HS-38-1(a)	41.7	Not sterilized(a)	39.8
HS-38-2	41.0	20	41.7
HS-38-3	42.6	21	43.1
HS-38-4	40.9	30	39.7
HS-38-5	40.6	37	40.7
HS-38-6	40.7	36	41.6
Averages	41.3	29	41.1

(a) Used as control

The next two cells were cycled manually on deep discharge (8 A to 1.0 V, recharge at 2.5 A to 2.0 V). Table XXII gives their output and pressure cycle by cycle. They failed at around 50 cycles. The primary type design is therefore capable of meeting the 25-cycle minimum requirement of the work statement.

The last cell was placed on an automatic cycling regime, at 40-percent depth-of-discharge (based on actual capacity), on a 3-hr cycle (1/2-hr discharge at 32 A, 2.5-hr charge at 7 A). The cells failed after 90 such cycles. Figure 16 showed some cycling curves.

Based on early results of these six cells, the second series of 28 cells of identical design (Design 2) were fabricated. Formation and sterilization data are presented in Table XXIII.

After formation cycle, sterilization and another cycle, the cells were grouped for their respective tests.

Electrical Characterization. —Five unsterilized cells and five sterilized cells were submitted to a temperature-discharge current matrix extending from 0°C to 50°C and 20 A to 120 A. Data are presented in Table XXIV and Table XXV respectively. A summary of all data is presented in Table XXVI for reference and comparison purposes as well as in Figure 17. The data are not too different for sterilized and unsterilized cells. If anything, the sterilized cells show a little better performance in some instances, probably because of a better and more uniform wetting of the cell pack.

Wet Stand. —Eighteen cells were left on charged and float stand at 1.86 V to 1.88 V as follows:

Five cells placed at 65°C dropped in OCV after approximately 30 days (data in Table XXVII). Examination of the disassembled cells pointed to the fact that a single separator bag was insufficient to stop the silver migration at this relatively high temperature (65°C). Thirteen cells placed at 25°C were tested in groups as follows:

(1) A group of five cells was discharged every 3 months, recharged and put back on stand until 7 months elapsed. Data are in Table XXVIII with the next group.

(2) A group of eight cells was left continuously on stand for seven months, after which they were discharged. Data are in Table XXVIII with the previous group.

For these two groups, capacity retentions are computed in Table XXIX. All cells were disassembled and appeared capable of longer wet stand. Although silver migration was noticeable to some extent, no short was apparent. Before opening the last three cells, a capacity recovery check was run. The cells were fully recharged and discharged. They showed a remarkable 100-percent capacity recovery of original capacity prior to stand (see Table XXX).

TABLE XXII

DESIGN NO. 2 ($5^{+}/6b^{-}$) DEEP DISCHARGE CYCLING

(8 A to 1.0 V)

Cycle No.	Output		Pressure	
	Cell HS-38-4, Ah	Cell HS-38-5, Ah	Cell HS-38-4, psig	Cell HS-38-5, psig
1	40.9	40.6	Not sealed	Not sealed
2	39.7	40.7	Not sealed	Not sealed
3	36.2	34.2	0	21
4	35.8	35.8	1	21
5	35.6	35.4	3	22
6	34.4	35.0	5	22
7	33.4	34.8	8	23
8	32.5	33.6	5	18
9	36.0	35.4	11	21
10	34.6	34.8	12	22
11	32.2	32.6	7	16
12	35.4	35.4	9	17
13	34.4	34.8	10	18
14	34.8	34.8	11	19
15	37.8	38.8	14	27
16	33.6	36.2	13	19
17	33.4	34.6	13	14
18	33.4	34.6	13	13
19	32.6	38.6	14	12
20	35.2	38.6	19	15
21	32.6	32.8	17	12
22	32.6	32.8	17	11
23	32.0	33.2	17	12
24	31.0	31.4	16	11
25	34.4	35.4	20	16
26	30.2	30.8	19	14
27	30.4	32.0	19	20
28	29.4	30.6	18	14
29	30.6	31.8	18	16
30	32.3	33.8	20	22
31	28.6	29.8	21	21
32	29.0	30.0	20	20
33	32.3	34.2	21	21
34	27.4	29.2	20	20
35	27.8	28.2	20	19
36	27.4	29.0	35	19
37	27.1	26.8	21	18
38	26.6	27.4	19	18
39	25.6	27.4	17	17
40	24.8	26.8	17	17
41	27.2	30.0	17	16
42	23.6	21.4	13	16
43	24.0	27.0	12	14
44	23.4	24.4	11	13
45	25.7	27.0	15	15
46	22.4	24.0	15	14
47	21.6	23.2	14	14
48	24.8	24.8	20	15
49	25.4	29.8	15	10
50		27.2		8
51		24.0		13
52		20.6		10
53		24.4		13
54		22.0		13

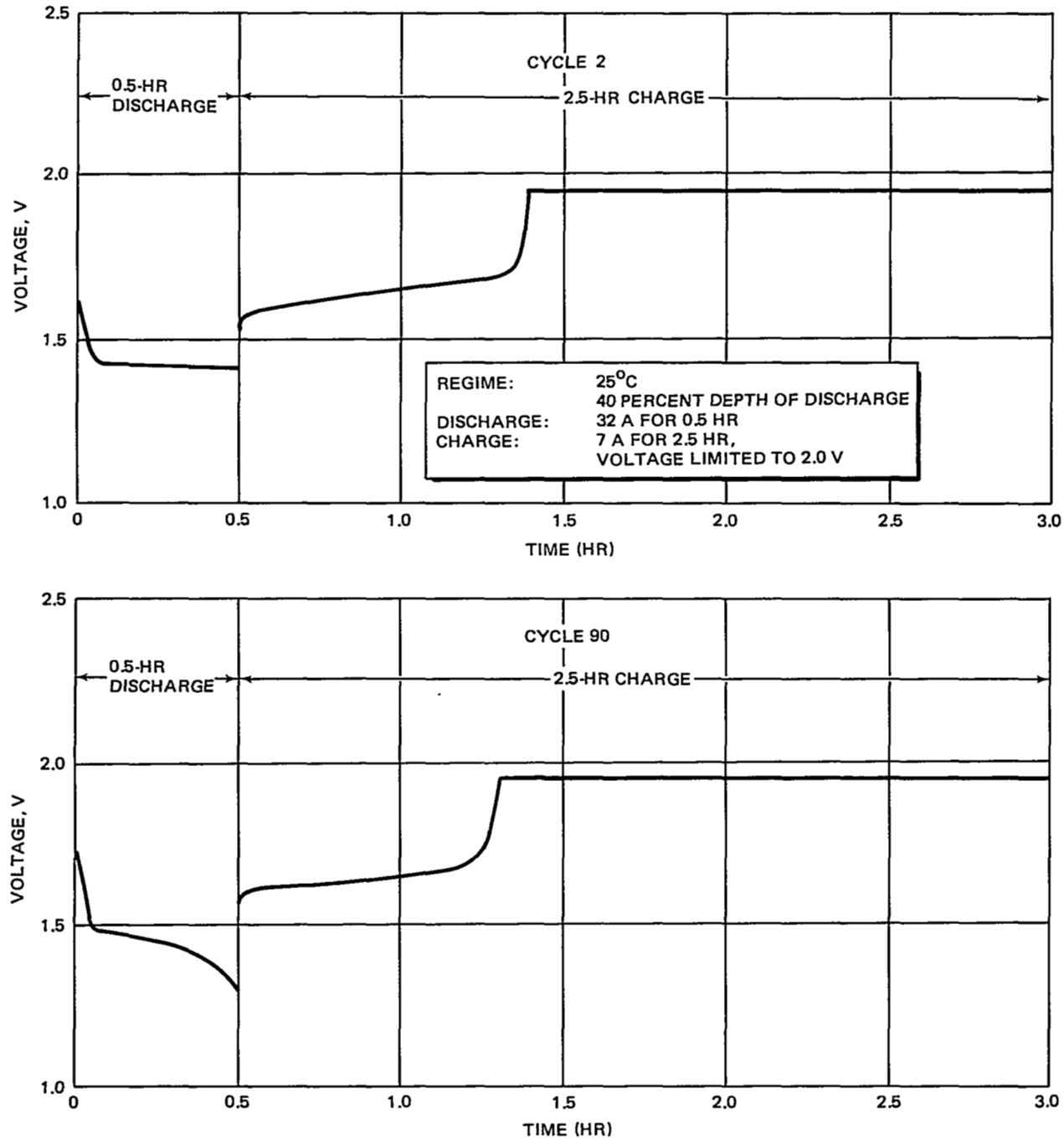


Figure 16. Autocycling 50-Ah Cell HS-38-6—Design 2 ($5^{+}/6^{+}$)

TABLE XXIII

DESIGN 2 ($5^{+}/6b^{-}$) FORMATION AND HEAT STERILIZATION DATA OF SECOND 28-CELL SERIES

Cell Number	Output, Cycle 1 (7A to 1.0 V + 2A to 1.0 V), Ah	Maximum Pressure, psig	Output, Cycle 2 (40 A to 1.0 V + drain), Ah
HS-45-1	40.8	40	38.4
HS-45-2	41.2	35	36.0
HS-45-3	40.6	41	35.3
HS-45-4	39.6	42	35.1
HS-45-5	40.7	32	39.4
HS-45-6	42.2	41	37.5
HS-45-7	41.9	33	38.8
HS-45-8	40.3	37	39.0
HS-45-9	40.3	34	39.0
HS-45-10	41.1	38	39.0
HS-45-11	40.3	42	36.2
HS-45-12	41.0	50	36.3
HS-45-13	40.4	35	37.4
HS-45-14	41.4	43	38.9
HS-45-15	41.6	37	38.9
HS-46-1	42.3	38	39.1
HS-46-2	42.4	33	39.4
HS-46-3	41.5	37	38.6
HS-47-1	42.8	Not treated or sterilized	High Rate Discharges Reported in Next Tables
HS-47-2	42.7	Not treated or sterilized	
HS-47-3	43.0	Not treated or sterilized	
HS-47-4	41.8	Not treated or sterilized	
HS-47-5	41.2	Not treated or sterilized	
HS-47-6	41.8	36	
HS-47-7	42.1	36	
HS-47-8	40.6	41	
HS-47-9	42.4	41	
HS-47-10	42.3	38	
Average	41.4	38	37.9

Note:
Cells were heat treated first at 100°C for 24 hr, then heat sterilized at 135°C for 60 hr, cooled to room temperature, then sterilized again at 135°C for 120 hr.

TABLE XXIV

DESIGN 2 ($5^+/6b^-$) CAPACITIES AT VARIOUS TEMPERATURES AND DISCHARGE CURRENTS

(Cells Not Sterilized)

Cell No.	(a) Cycle No.	(b) Temp, °C	Discharge Current, A	Plateau Voltage, V	Output at Temperature, Ah	(c) Drain, Ah	(d) Output, Ah
HS-47-1	1	0	20	1.34	31.0	7.1	38.1
	2	0	120	1.10	27.6	9.1	36.7
	3	50	120	1.26	30.0	5.7	35.7
HS-47-2	1	0	40	1.26	30.8	5.3	36.1
	2	0	80	1.14	26.4	7.2	33.6
HS-47-3	1	25	20	1.42	36.4	1.5	37.9
	2	25	120	1.17	26.4	7.1	32.5
HS-47-4	1	25	40	1.36	36.0	2.8	38.8
	2	25	80	1.25	26.4	5.0	31.4
HS-47-5	1	50	40	1.42	34.8	1.2	36.0
	2	50	20	1.47	37.0	0.5	37.5
	3	50	80	1.35	34.4	2.4	36.8
	4	50	120	1.28	32.4	4.9	37.3

(a) Formation cycle not included. See Table XXIII.

(b) Cells were stabilized at temperature for a minimum of 1 hr prior to being discharged.

(c) Cells were drained at room temperature (4 A to 1.0 V).

(d) Total output = output at temperature + drain at room temperature.

TABLE XXV

DESIGN 2 ($5^+/6b^-$) CAPACITIES AT VARIOUS TEMPERATURES AND DISCHARGE CURRENTS

(Heat Sterilized Cells)[a]

Cell No.	(b) Cycle No.	(c) Temp, °C	Discharge Current, A	Plateau Voltage, V	Output at Temperature, Ah	(d) Drain, Ah	(e) Output, Ah
HS-47-6	1	0	20	1.37	29.0	10.3	39.3
	2	0	120	1.12	21.6	14.3	35.9
	3	50	120	1.29	33.6	4.7	38.3
HS-47-7	1	0	40	1.32	28.0	9.1	37.1
	2	0	80	1.22	30.4	10.2	40.6
HS-47-8	1	25	20	1.45	35.0	2.0	37.0
	2	25	120	1.24	30.0	5.3	35.3
HS-47-9	1	25	40	1.39	35.2	2.1	37.3
	1	25	80	1.31	29.6	4.6	34.2
HS-47-10	1	50	40	1.45	32.8	1.4	34.2
	2	50	20	1.50	35.6	0.5	36.1
	3	50	80	1.37	33.6	1.8	35.4
	4	50	120	1.29	33.6	4.9	38.5

[a] 135°C for 60 hours, cooled; 135°C for 120 hr.

[b] Formation cycle not included. See Table XXIII.

[c] Cells were stabilized at temperature for a minimum of 1 hr prior to being discharged.

[d] Cells were drained at room temperature (4 A to 1.0 V).

[e] Total output = output at temperature + drain at room temperature.

TABLE XXVI

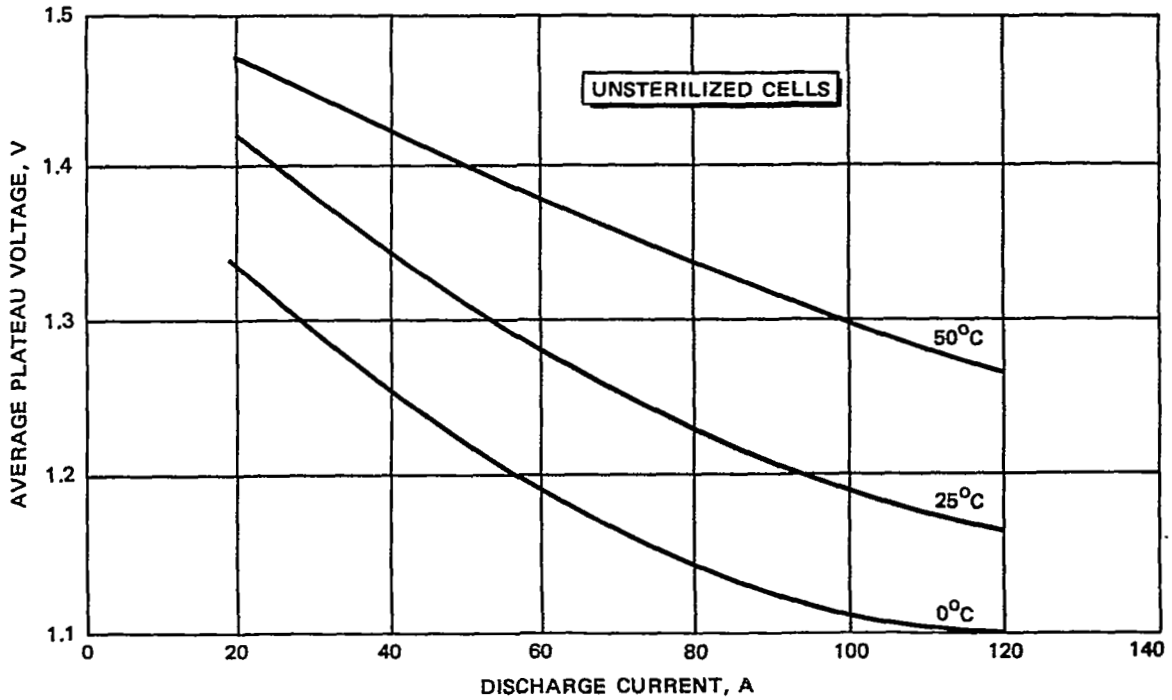
DESIGN 2 ($5^{+}/6b^{-}$) ELECTRICAL PERFORMANCE AT VARIOUS TEMPERATURES AND DISCHARGE CURRENTS

Temperature	Discharge Current, A	Unsterilized Cells		Sterilized Cells	
		Average or Plateau Voltage, V	Capacity, Ah	Average or Plateau Voltage, V	Capacity, Ah
0°C	20	1.34	31.0	1.37	29.0
	40	1.26	30.8	1.32	28.0
	80	1.14	26.4	1.22	30.4
	120	1.10	27.6	1.12	21.6
25°C	20	1.42	36.4	1.45	35.0
	40	1.36	36.0	1.39	35.2
	80	1.25	26.4	1.31	29.6
	120	1.17	26.4	1.24	30.0
50°C	20	1.47	37.0	1.50	35.6
	40	1.42	34.8	1.45	32.8
	80	1.35	34.4	1.37	33.6
	120	1.27[a]	31.2[a]	1.29	33.6

Notes:

[a] Average of data for two cells.

Data are taken from Tables XXIV and XXV.



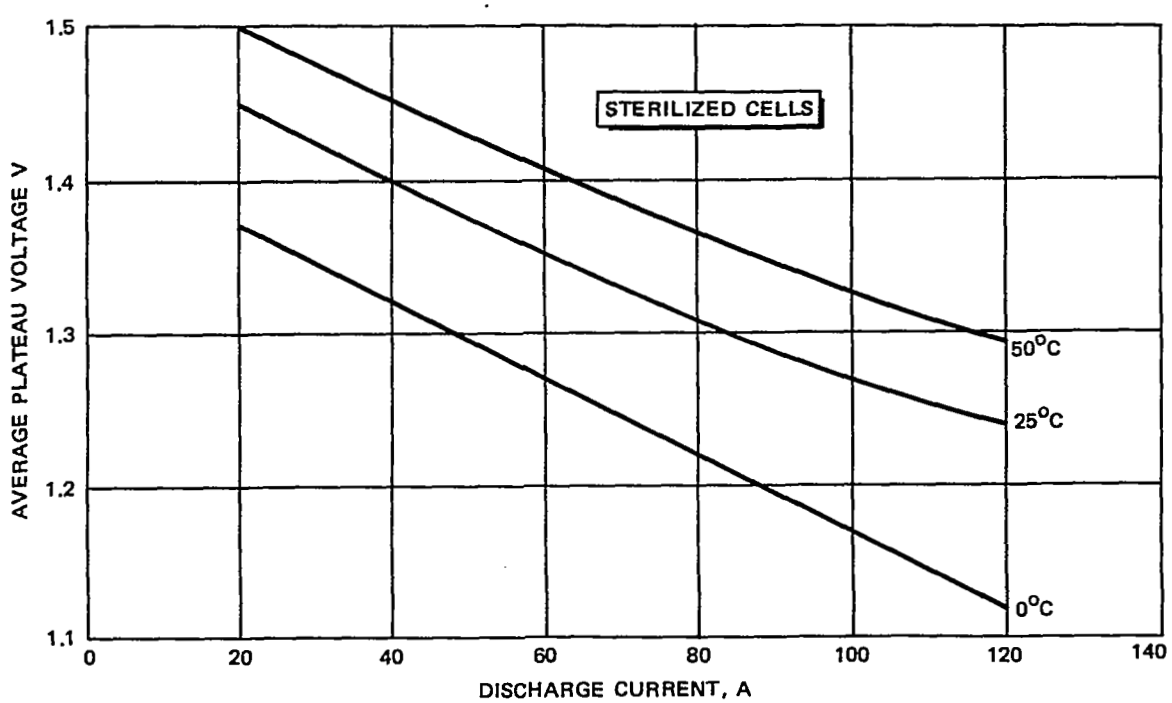


Figure 17. Plateau Voltage at Various Temperatures Versus Discharge Currents–$5^{+}/6b^{-}$

TABLE XXVII

DESIGN 2 ($5^+/6b^-$) CHARGED
STAND AT 65°C

Conditions: All Cells on Float Charge At 1.86 V to 1.88 V, 20-mA Current Limit

Cell No.	Days (a)
HS-45-11	39
HS-45-12	34
HS-45-13	25
HS-45-14	28
HS-45-15	28

(a) Days after which OCV could not be maintained at or over 1.86 V.

Analyses of the data show that Design 2, using one single separator bag (on the negative plate), presents a capacity loss of 4 percent in the first 3 months and 11 percent over 7 months, i.e., approximately 1.5 percent per month, with full recovery (100 percent or better) upon recharge.

Gassing and Pressure Measurements. —Three cells of the previous group were heavily potted in epoxy, equipped with pressure gauges and had provisions for gas analysis, which was done periodically over this 7-month stand. They are HS-46-1 through -3. Their electrical data are reported in the previous subsection. Their pressure and gassing characteristics are reported in Table XXXI.

One cell HS-46-2 (out of a total of 13 of the same category) exhibited an abnormal behavior as evidenced by high pressure, gassing and associated excessive capacity loss, whereas the other cells had good average capacity retention. It may have been caused by an impurity accidentally introduced during fabrication or processing. This particular cell however, after recharge, recovered 100 percent of its original capacity (prior to stand) as well as the two companion cells of the same group (see previous Table XXX).

Sterilized Versus Unsterilized Cells. —The 10 cells left over from the previous test on electrical characterization were on discharged stand for 4 months after completion of their temperature-current matrix test, i.e., a total of four deep cycles.

TABLE XXVIII

DESIGN 2 ($5^+/6b^-$) RESIDUAL CAPACITY OF CELLS AFTER CHARGED STAND WITH FLOAT AT 25°C

(1.86 to 1.88 V/cell, 20-mA Current Limit)

Total Stand ⟶		3 Months	6 Months	7 Months
Cell No.	Capacity Prior to Stand, Ah	Residual Capacity After First 3 Months, Ah	Residual Capacity After Second 3 Months, Ah	Residual Capacity After Total 7 Months, Ah
HS-45-1	38.4	34.8	28.3	34.6
HS-45-2	36.0	34.2	28.7	36.2
HS-45-3	35.3	34.2	29.2	36.9
HS-45-4	35.1	33.9	29.8	36.4
HS-45-5	39.4	33.1	26.6	31.2
Average	36.8	34.0	28.5	35.1
HS-45-6	37.5	Continuous stand		32.0
HS-45-7	38.8			28.8
HS-45-8	39.0			23.5
HS-45-9	39.0			32.5
HS-45-10	39.0			33.9
HS-46-1	39.1			31.4
HS-46-2	39.4			16.3[a]
HS-46-3	38.6			29.2
Average	38.8	Continuous stand		30.1

[a] Not counted in average: Cell had abnormal behavior (pressure, gassing, capacity loss).

TABLE XXIX

DESIGN 2 ($5^{+}/6b^{-}$) CAPACITY RETENTION OF CELLS ON CHARGE FLOAT

Cell No.	Input Prior to Stand, Ah	Calculated Output (a) If Cell Immediately Discharged, Ah	After 3 Months	
			Residual Capacity, Ah	Percent Retention
HS-45-1	37.6		34.8	
HS-45-2	37.6		34.2	
HS-45-3	37.6		34.2	
HS-45-4	37.6		33.9	
HS-45-5	36.4		33.1	
Average	37.3	35.4	34.0	96
HS-45-6	38.4		32.0	
HS-45-7	36.5		28.8	
HS-45-8	30.5		23.5	
HS-45-9	36.4		32.5	
HS-45-10	37.6		33.9	
HS-46-1	37.8		31.4	
HS-46-2	36.8		16.3(b)	
HS-46-3	37.0		29.2	
Average	36.4	33.6	30.1	89

(a) Based on 95-percent coulombic efficiency found in previous cycles.

(b) Not counted in average: cell had abnormal behavior (pressure, gassing, capacity loss).

TABLE XXX

DESIGN 2 ($5^+/6b^-$) RECOVERED CAPACITY AFTER 217 DAYS ON CHARGED STAND WITH FLOAT

Cell No.	Capacity Prior to Stand, Ah	Recovered Capacity, Ah	Percent Recovery versus Original
HS-46-1	39.1	41.3	100
HS-46-2	39.4	39.2	100
HS-46-3	38.6	39.3	100
Average	39.0	39.9	100

As time permitted, some extra tests were run on these cells. They were recharged and put on charged wet stand for 7 months. They were then discharged at 7 A to 1.0 V. Their outputs averaged the following:

(1) Sterilized: 19.5 Ah

(2) Unsterilized: 20.8 Ah

Their OCV check gave the following:

	Good OCV	Failing OCV	Fully Shorted
(1) Sterilized:	two cells	one cell	two cells
(2) Unsterilized:	two cells	one cell	two cells

Average output of the good cells:

(1) Sterilized: 23.0 Ah

(2) Unsterilized: 25.9 Ah

After recharge of the three relatively good cells, the recovered capacity was as follows:

(1) Sterilized: 38.9 Ah

(2) Unsterilized: 41.3 Ah

TABLE XXXI

DESIGN 2 ($5^+/6b^-$) PRESSURE AND GAS ANALYSIS ON STAND AND FLOAT OVER 7 MONTHS

Time, Days	Pressure and Gas	Cell HS-46-1	Cell HS-46-2	Cell HS-46-3
1	P, psig	4	3	9
4	P, psig	0	5	9
	H_2, percent	49	28	46
	O_2, percent	7	3	2
	N_2, percent	44	69	52
33	P, psig	0	5	1
	H_2, percent	53	32	52
	O_2, percent	3	2	2
	N_2, percent	44	66	46
56	P, psig	0	4	0
	H_2, percent	46	27	39
	O_2, percent	3	3	5
	N_2, percent	51	70	56
85	P, psig	0	2	0
	H_2, percent	32	31	34
	O_2, percent	9	1	7
	N_2, percent	59	68	59
123	P, psig	0	0	0
	H_2, percent	28	35	32
	O_2, percent	10	2	7
	N_2, percent	62	63	61
152	P, psig	0	14	0
	H_2, percent	23	48	44
	O_2, percent	10	3	5
	N_2	67	49	51
180	P, psig	0	32	8
	H_2, percent	42	76	85
	O_2, percent	5	0	0
	N_2, percent	53	24	15
214	P, psig	0	52	10
	H_2, percent	58	81	88
	O_2, percent	3	1	1
	N_2, percent	39	18	11

The cells were then put on automatic cycling (coded VK-1) on a 24-hr period regime, one cycle a day, discharge at 2 A for 2 hr, charge at 0.32 A for 22 hr, voltage limited to 2.0 V/cell. This regime is the one given by NASA during the course of the program to simulate the Viking mission regime as proposed at one time.

After 77 cycles, two cells of each group failed. One cell of each group continued cycling and has reached 260 cycles to date.

The total wet life was then:

(1) 12 months for two cells of each group

(2) 14 months for two cells of each group

(3) 27 months for one cell of each group to date

This test showed that sterilization does not impair the performance of the cell very significantly. Cells of the same design and tested identically, whether sterilized or not, closely follow the same pattern of performance.

MDAC Cells. —Some cells of the same design were bought and tested on another program for proposal purposes, but because their data are relevant to the present program, they are reported here.

Five cells were formed, sealed, heat-sterilized and cycled on the following regime:

(1) Cycling: 8-hr period

(2) Discharge: 20 A for 1 hr

(3) Charge: 3 A for 7 hr, Voltage limited to 2.0 V/cell

(4) Frequency: Three cycles/day

The cells failed after 88 to 90 cycles. The depth-of-discharge can be computed with respect to actual capacity (DA) or rated capacity (DR). The actual capacity is approximately 40 Ah, the depth-of-discharge is then 50 percent DA. It was agreed to call the rated capacity 30 Ah; the depth is therefore 66 percent DR.

Two other cells were filled with electrolyte and left unformed on stand for six months, then formed, sealed, and heat sterilized. They were then cycled for the following regime:

(1) Cycling: 8-hr period

(2) Discharge: 10 A for 1 hr

(3) Charge: 1.5 A for 7 hr, voltage limited to 2.0 V/cell

(4) Frequency: Three cycles/day

(5) Depth-of-Discharge: 25-percent DA (of actual) or 33-percent DR (of rated)

The two cells failed at 107 and 219 cycles. Their total wet life was 12 ar 13 months, respectively.

Delivery. —Ten cells of this design were delivered to NASA-Langley Research Center according to NASA-Lewis direction for their own test and evaluation.

Designs 3 and 5 (Preliminary)

Two preliminary designs were tested partly prior to finalization of the electrode pack configuration.

Design 3. —Design 3 featured a double bag construction, one separator or each electrode of either polarity, coded $5b^+/6b^-$ and used 40-percent KOH electrolyte. However, this configuration restricted the amount of silver to 105 g, not sufficient for a reliable 40-Ah capacity. After some partial tests, the same configuration b^+/b^- was used on a redesign where the amount of silver was increased, which resulted in Design 7 ($6b^+/5b^-$), reported extensively later in this report.

Design 3 was tried on six cells only. Formation and poststerilization capacities were relatively low, although uniform. This was probably due to insufficient wetting prior to sealing. A second formation cycle may have been necessary. This is evidenced by the fact that the capacity, expected to be originally about 32 Ah, was, after the recharge following the 7-month stand, approximately 34 Ah on all cells.

After sterilization, the six cells were recharged and divided (four cells on stand, two on plain charged stand and two on float for 7 months, and two cells on automatic cycling).

The wet stand data are summarized in Table XXXII. As expected, the float charge helped the cells retain a higher capacity than the plain charged stand (92 percent versus 81 percent respectively). The recovered capacity was 34 Ah. After 7 months stand, the cells were placed on the same VK-1 regime (one cycle per day, discharge 2 A for 2 hr, charge at 0.32 A for 22 hr). The cells are still cycling. They have reached 311 cycles to date with a total wet life of 20 months.

The other two cells were cycled on the following regime:

(1) Cycling: 8-hr

(2) Frequency: Three cycles per day

(3) Discharge: 10 A for 1 hr

TABLE XXXII

DESIGN 3 ($5b^+/6b^-$) WET STAND DATA

Cell Number	HS-51-1	HS-51-2	HS-51-3	HS-51-4
Formation Output, Ah	30.5	29.9	29.9	29.8
Poststerilization Output, (Ah)	25.9	26.2	26.3	26.2
Input Prior to Stand, Ah	30.5	30.5	30.5	30.5
Stand Type	Plain Charged Stand for 7 Months		Float Charge for 7 Months	
OCV After Stand, V	1.85	1.85	1.86	1.86
Residual Capacity, Ah	21.1	21.3	24.1	24.3
Average Percent Residual Versus Capacity Prior to Stand[a]	77		88	
Recovered Capacity After Recharge, Ah	34.4	33.9	34.1	34.4
Percent Recovered[a]	100		100	
Cycled on VK-1 Regime, Cycles to Date	261		260	
Total Wet Life to Date	20 Months			

[a]Assuming 90-percent coulombic efficiency (output/input): Output prior to stand will be 90 percent of input prior to stand.

(4) Charge: 2 A for 7 hr, voltage limited to 2.0 V/cell

(5) Depth-of-discharge (based on 32 Ah actual capacity, or 25 Ah rated): 31-percent DA, 40-percent DR

The cells had a periodic capacity check approximately every 90 cycles (or once a month), by giving them a deep discharge at 6 A to 1.0 V. One cell failed at cycle 463, the other at cycle 1,093. It is remarkable that their capacity maintenance is 100 percent throughout their cycle life up to the time of failure (Table XXXIII).

Design 5. —The other design used an extra layer of supported inorganic separator between the bags enclosing the electrodes ($b^+/L/b^-$). The cell configuration was $4b^+/L/5b^-$. Again 40-percent KOH electrolyte was used. Only seven cells were fabricated to acquire partial data. One cell was made in a clear polysulfone case to visually determine the proper amount of electrolyte before sealing. This cell HS-54-7 was not heat sterilized because polysulfone was ruled out for heat sterilization. However, this cell was put on discharged stand with the cells on charged stand and float to compare their poststand cycling capability.

The cells were tested as follows:

(1) One cell on plain charged stand

(2) One cell on float charge

(3) One cell on discharged stand

After 7 months stand, the cells were put on the VK-1 regime previously used (one cycle per day, discharge 2 A for 2 hours, charge 0.32 A for 22 hours).

Data are presented in Table XXXIV. The cells have reached 259 cycles to date with a total wet life of 19 months.

Two cells were put on automatic cycling three cycles/day, 40-percent DR, based on rated capacity 25 Ah. They reached approximately 540 cycles, also with a good capacity maintenance when checked periodically. Data are presented in Table XXXV.

Two cells cycling at 100-percent depth (total discharge down to 1.0 V). Data are presented in Table XXXVI. A comparison of capacity decrease versus cycling between Design 1 and Design 5 is shown in Figure 18. Not only does Design 5 give more than twice the number of cycles (over 120 versus 50), but the capacity degrades at a much slower rate.

Design 7

Design 7 was intended to be the final design with a double bag configuration (b^+/b^-), one separator bag on each electrode of either polarity. After the preliminary Design 3 of same bag configuration, the purpose of Design 7

TABLE XXXIII

DESIGN 3 ($5b^+/6b^-$) CYCLING AT 40-PERCENT RATED CAPACITY

Discharge: 10 A for 1 hr
Charge: 2 A for 7 hr
Voltage limited to 2.02 V/cell

Cell No.		HS-51-5	HS-51-6
Formation Capacity, Ah		29.6	29.7
Poststerilization Capacity, Ah		26.0	25.9
Cycling		Periodic Capacity Checks, Ah	
Cycle Number:	93	28.2	30.2
	184	32.4	32.6
	249	37.5	38.4
	289	35.4	34.2
	372	34.3	33.6
	463	Failed	32.8
	615		32.9
	616		33.1
	1093		Failed
Total Wet Life to Date		9 Months	17 Months

was to increase the cell capacity to the required 40-Ah level. The electrode pack consisted then of six bagged positives and five bagged negatives.

NASA Technical Direction No. 2 slightly modified the testing conditions to conform to more hardware-oriented missions than proposed. The next series of cells consisted of cells intended for various wet-stand conditions (plain-charged versus float at temperatures from 10°C to 32°C) and of cells cycling at the same temperatures.

Cell No.	HS-54-1	HS-54-2	HS-54-7
Formation Output, Ah	25.3	24.7	25.1
Poststerilization Output, Ah	36.1	36.0	33.8[a]
Input Prior to Stand, Ah	34.0	34.0	--
Stand Test	Plain Charged Stand for 7 months	Float Charge Stand for 7 months	Discharged Stand for 9 months
OCV after 7 months, V	1.85	1.86	Not Applicable
Residual Capacity, Ah	26.8	33.1	Not Applicable
Percent Residual versus Capacity Prior to Stand[b]	88	100	Not Applicable
Recovered Capacity After Recharge, Ah	30.6	34.0	39.5
Percent Recovered	100	100	100
Cycled on VK-1 Regime, Cycles to Date	259	259	250
Total Wet Life to Date	19 Months		

[a] Not heat sterilized because in polysulfone case (not sealed).

[b] Assuming 90-percent coulombic efficiency (output/input): Output prior to stand will be 90-percent of input prior to stand.

TABLE XXXV

DESIGN 5 ($4b^+/L/5b^-$) CYCLING AT 40-PERCENT RATED CAPACITY

Discharge: 10 A for 1 hr
Charge: 2 A for 7 hr
Voltage limited to 2.02 V/cell

Cell No.	HS-54-3	HS-54-4
Formation Output, Ah	25.0	25.0
Poststerilization Output, Ah	35.5	36.0
Cycling	Periodic Capacity Checks, Ah	
Cycle Number: 90	35.5	35.3
200	35.0	35.2
283	33.9	33.1
374	31.8	31.4
515	18.8	33.2
541	Failed	
546		Failed
Total Wet Life	11 Months	11 Months

Because the wet-stand time was emphasized and the high discharge rates were no longer required, a shift of KOH concentration from 40 to 45 percent appeared to be in order. It is known that improvement of wet stand (delay in OCV degradation and higher residual capacity) will result with higher KOH concentration. The resulting higher cell resistance would not affect the discharge voltage as low discharge rates replaced the previous high rates (40 A and 150 A).

This was verified on actual cells. One cell was made in a polysulfone case to determine the proper amount of electrolyte (40-percent KOH) by watching the level variations during soak and formation. At the same time, another cell made in a PPO case was filled with 45-percent KOH to compare the effect of electrolyte change on capacity and voltage before and after sterilization, with respect to the 40-percent KOH cell. Data in Table XXXVII show

TABLE XXXVI

DESIGN 5 ($4b^+/L/5b^-$) DEEP DISCHARGE CYCLING

(Output at 6 A to 1.0 V + Drain 2 A to 1.0 V)

Cycle	HS-54-5, Ah	HS-54-6, Ah
1 (Formation)	25.2	25.9
2 (Poststerilization)	33.2	32.8
3	31.8	32.2
9	34.6	33.1
11	33.6	33.0
18	31.7	31.0
23	30.0	31.5
30	27.3	31.0
35	28.0	29.4
40	27.8	29.3
45	27.9	30.4
50	27.0	30.6
55	27.2	30.1
60	24.7	29.4
65	24.0	26.5
70	25.0	30.6
75	25.0	29.6
80	24.0	28.2
85	23.5	29.4
90	23.4	25.3
95	23.2	28.1
100	22.5	26.7
105	23.4	24.4
106	28.0	27.3
110	26.8	31.0
111	25.5	26.1
112	28.7	30.3
116	28.7	28.0
119	24.5	25.8
122	29.8	27.6
	Still cycling	

Notes:

(1) Total wet life to date—18 months.

(2) The high values noted for outputs include the drains. To speed up cycling, drain discharge was sometimes omitted.

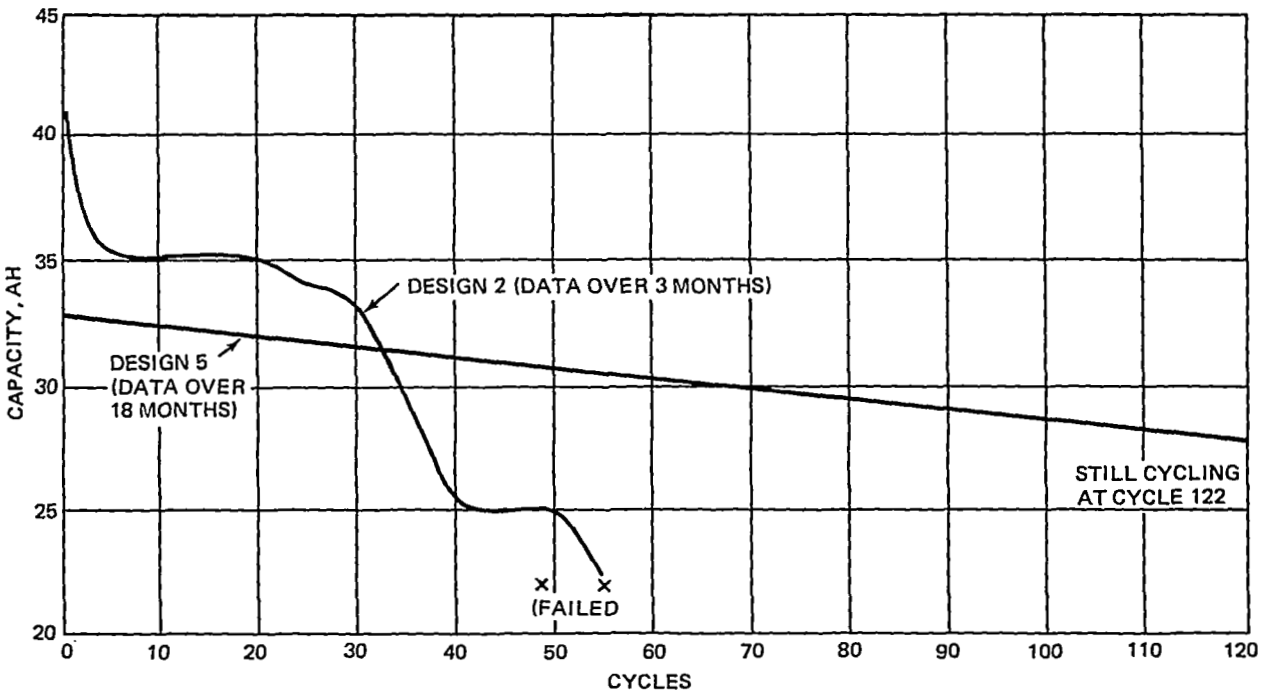


Figure 18. Deep Discharge Cycling to 1.0V cutoff (Average of Two Cells per Design)

no significant difference. Consequently all subsequent cells were filled with 45-percent KOH, formed, sealed, and heat sterilized at 135°C for 200 hr.

Two lots of cells were fabricated. Data on their formation and pore-sterilization capacity are presented in Tables XXXVIII and XXXIX respectively.

Wet Stand. —The test plan for charged wet stand is presented in a matrix form in Table XL. It compares plain charged stand versus charged stand with float at 1.88 V with 20 mA trickle current limit, at three temperature levels (10, 22, and 32°C). Each variation includes a group of five cells.

Although originally the charged wet stand duration was to be 7 months, new requirements developed during the last year of the program and the total wet stand time since activation was changed to 21 months (equivalent to 19 to 20 months charged condition). It was decided that no attempt be made to discharge the cells regardless of OCV decay, until the 21-month period elapsed.

Early data are as follows:

(1) Plain Charged Stand: At 12 months, the 10°C and 22°C groups are holding an OCV of 1.85 V. The 32°C group was holding an OCV of 1.85 V up to 11 months; afterwards, the OCV's started decaying. Table XLI gives a detailed degradation of the OCV versus time.

TABLE XXXVII

DESIGN 7 ($6b^+/5b^-$) EFFECT OF ELECTROLYTE CONCENTRATION

Cell No.	KOH Concentration, percent	Formation Discharge Capacity, Ah	Formation Discharge Plateau V	Post-Sterilization Discharge Capacity Ah	Post-Sterilization Discharge Plateau Voltage V
HS-59-29	40	40.7	1.50	Not applicable(a)	Not applicable(a)
HS-59-30	45	40.7	1.48	43.7	1.50

NOTE: All discharges at 6 A to 1.0 V.

(a) Because of polysulfone case.

(2) Charged Stand with Float: Groups at the three temperatures are still holding after 15 months.

Some extra tests were run with cells of the same design left over from mechanical tests. Besides the charged stand at 10, 22, and 32°C, a few cells were placed on the same charged stand test at higher temperatures in increments of 10°C (two cells at 42°C, two cells at 52°C, two cells at 62°C). The purpose of this test was to tentatively project the cell capability at room temperature by obtaining data in a shorter time and extrapolating on a time-temperature relationship scale.

It was decided to discharge these cells as soon as their OCV dropped to 1.60 to 1.65 V (argenteous oxide level) to determine their residual capacity.

Cells at 62°C dropped in approximately 76 days. Residual capacity was 50 percent of their capacity prior to stand. After full recharge, they recovered their original capacity (100-percent recovery).

Cells at 52°C dropped in an average of 165 days. Residual capacity was 48 percent. After recharge, they had also 100-percent full recovery.

Cells at 42°C (actual controlled temperature was only 40°C) have dropped only to 1.83 V after 377 days. Table XLII summarizes all their data to date.

From the present data, it appears that on a short term, the relationship of reaction doubling for every 10°C increment holds true (at 62°C, 76 days; at 52°C, 165 days; at 40°C, over 377 days). It would not be wise to project to room temperature (approximately 22°C) on this basis alone, as a secondary

TABLE XXXVIII

DESIGN 7 ($6b^+/5b^-$, 45-PERCENT KOH) FORMATION AND POSTSTERILIZATION CYCLES

Cell No.	Formation Output, Ah	Poststerilization Output, Ah
HS-59-1	43.0	43.6
-2	42.9	43.6
-3	42.7	43.6
-4	42.8	43.7
-5	42.8	43.6
-6	42.8	43.5
-7	42.7	43.3
-8	42.9	43.5
-9	42.5	42.4
-10	42.9	43.7
-11	42.8	43.7
-12	42.9	43.6
-13	42.7	43.6
-14	42.7	43.8
-15	42.4	43.8
-16	42.4	43.7
-17	42.4	43.7
-18	42.4	43.7
-19	42.5	43.9
-20	42.5	43.5
-21	42.5	43.9
-22	42.5	43.9
-23	42.8	43.6
-24	42.4	43.9
-25	41.8	43.6
-26	42.4	43.9
-27	42.3	43.8
-28	42.4	43.6
Average	42.6	43.7

TABLE XXXIX

DESIGN 7 ($6b^+/5b^-$, 45-PERCENT KOH) FORMATION AND POSTSTERILIZATION CYCLES

Cell No.	Formation Output, Ah	Poststerilization Output, Ah
HS-61-1	42.2	42.6
HS-61-2	42.2	42.9
HS-61-3	42.4	42.7
HS-61-4	42.5	42.6
HS-61-5	42.2	42.8
HS-61-6	42.3	42.7
HS-61-7	41.9	42.9
HS-61-8	41.9	43.0
HS-61-9	42.4	42.8
HS-61-10	42.4	42.8
HS-61-11	42.3	42.9
HS-61-12	42.4	42.9
HS-61-13	42.2	42.9
HS-61-14	42.2	42.6
Average	42.3	42.8

effect enters the reaction when stand time gets longer; whereas voltage drop and consequently capacity loss are only a function of argentic silver oxide degradation by temperature on a short term basis (less than 6 months), the negative electrode may also start losing capacity appreciably when stand time extends over one year. Data from stand at 22°C show a capability beyond 461 days to date. Expected stand time before reaching 1.60 V at this temperature would be in the range of 17 to 18 months. At 10°C, the expectation is over 2 years.

TABLE XL

DESIGN 7 TEST PLAN FOR CHARGED WET STAND TO BE FOLLOWED BY CYCLING

State / Temp	Plain Charged Stand	Charged Stand and Float
10°C	5 cells	5 cells
22°C (R. T.)	5 cells	5 cells
32°C	5 cells	5 cells

After completion of these tests, the cells were left on discharged stand, with other cells of the same design already on discharged stand after completion of their tests. All these cells constitute a group of cells, that will provide good information on cycling after completing a 21-month total wet life period, mostly on discharged stand at room temperature. The data could be compared with those of cells on plain charged stand and on charged stand with float.

Cycling. —Cells of same design were cycled on the following automatic cycling regime (VK-1) fitting the mission requirements of the moment, as supplied by NASA.

Cycling: 24 hr

Frequency: 1 cycle per day

Discharge: 2 A for 2 hr

Charge: 0.32 A for 22 hr, voltage limited to 2.02 V/cell average

One cycle prior to the above cycling regime, was run as follows:

Discharge: 2.2 A for 8 hr minus 40 sec

then pulse of 11.4 A for 40 sec

Charge: 0.32 A for 14 hr

This cycle amounts to approximately 60-percent DR (depth of rated capacity of 30 Ah) or 45-percent DA (depth of actual capacity).

TABLE XLI

PLAIN CHARGED STAND TIME
(Cells HS-59 except 61-13)
(Days at or over Indicated OCV)

Temperature	32°C					22°C					10°C				
Cell No.	11	12	13	14	61-13	10	9	8	7	6	5	4	3	2	1
Formation Output	42.2	42.7	42.7	42.9	42.8	42.9	42.5	42.9	42.7	42.8	43.0	42.9	42.7	42.8	42.8
Post-Sterilization Output	42.9	43.8	43.8	43.6	43.7	43.7	42.4	43.5	43.3	43.5	43.6	43.6	43.6	43.7	43.6
OCV, V															
1.86	54	54	54	54	32	222	118	222	112	118	187	271	187	271	118
1.85	224	187	236	173	312	388	420	335	222	420	461	461	461	461	461
1.84	263		273	187				376	461						
1.83	271	203	274	224			461			453					
1.82		216	291	270	417			388		461					
1.81	279							404							
1.80	298	277													
1.79		291													
1.78	327	319	298			461									
1.77			319	271	438										
1.76								453							
1.75															
1.74	335		335	291											
1.73			420					461							
1.72															
1.71	360														
1.70				319											
1.65			440												
1.57 (First)	376	327	453	327											
1.57	461	461	461	461											

Note: To continue to total wet life of 21 months

TABLE XLII

PLAIN CHARGED STAND TIME
(Cells AH-39-)
(Days at or over Indicated OCV)

Temperature	62°C			52°C			42°C		
Cell No.	-6	-5	Average	-4	-3	Average	-2	-1	Average
Formation Output, Ah	40.6	40.5	40.5	40.6	40.9	40.7	40.6	40.8	40.7
Post-sterilization Output, Ah	41.7	41.5	41.6	41.5	41.5	41.5	41.3	41.3	41.3
OCV, V									
1.86	5	5		12	34		47	47	
1.85	28	12		47	75		134	134	
1.84	47	34			124		369	369	
1.83		42		75	145		377	377	
1.82		47		82	169				
1.81	65				180				
1.80				89	187				
1.79				91	191				
1.78	75				195				
1.77	77				205				
1.76					208				
1.75									
1.74					214				
1.73		65							
1.72	79				217				
1.71				100	221				
1.70				104	223				
1.65	82	70	76	105	225	165			
Q_R, Ah	20.8	20.9	20.8	20.9	18.8	19.9	(a)	(a)	(a)
Percent Q_R Based on Last Output Prior to Stand	50	50	50	50.5	45.5	48			

(a) To be done when cells drop to 1.65 V.

The automatic cycling amounts approximately to 13 percent DR or 10 percent DA.

The following variations were done:

(1) Six cells at 10°C

(2) Six cells at 22°C (R.T.)

(3) Four cells at 32°C

Each group had four cells tested in series as a battery. The first two groups had two cells run individually. One cell of the 32°C group failed at cycle 310. Examination of the separator revealed a zinc short.

Data to date are as follows:

	Cycles	Total Wet Life
10°C	418	15 months
22°C	423	15 months
32°C	372	12 months

Curves at cycle 7 and at cycle 300 are shown in Figures 19 through 24 for each temperature respectively.

Another cycling regime (VK-2) was introduced by NASA later in the program.

Cycling: 24 hr

Frequency: Two different cycles per day

1st cycle

Discharge: 3 A for 1 hr

Charge: 0.45 for 7 hr

2nd cycle

Discharge: 3 A for 2 hr

Charge: 0.45 A for 14 hr

The first cycle corresponds to 10-percent DR and the second cycle to 20-percent DR. All charges are voltage-limited to 2.0 V/cell. The automatic cycling started after the cell had been cycled 3 times as follows:

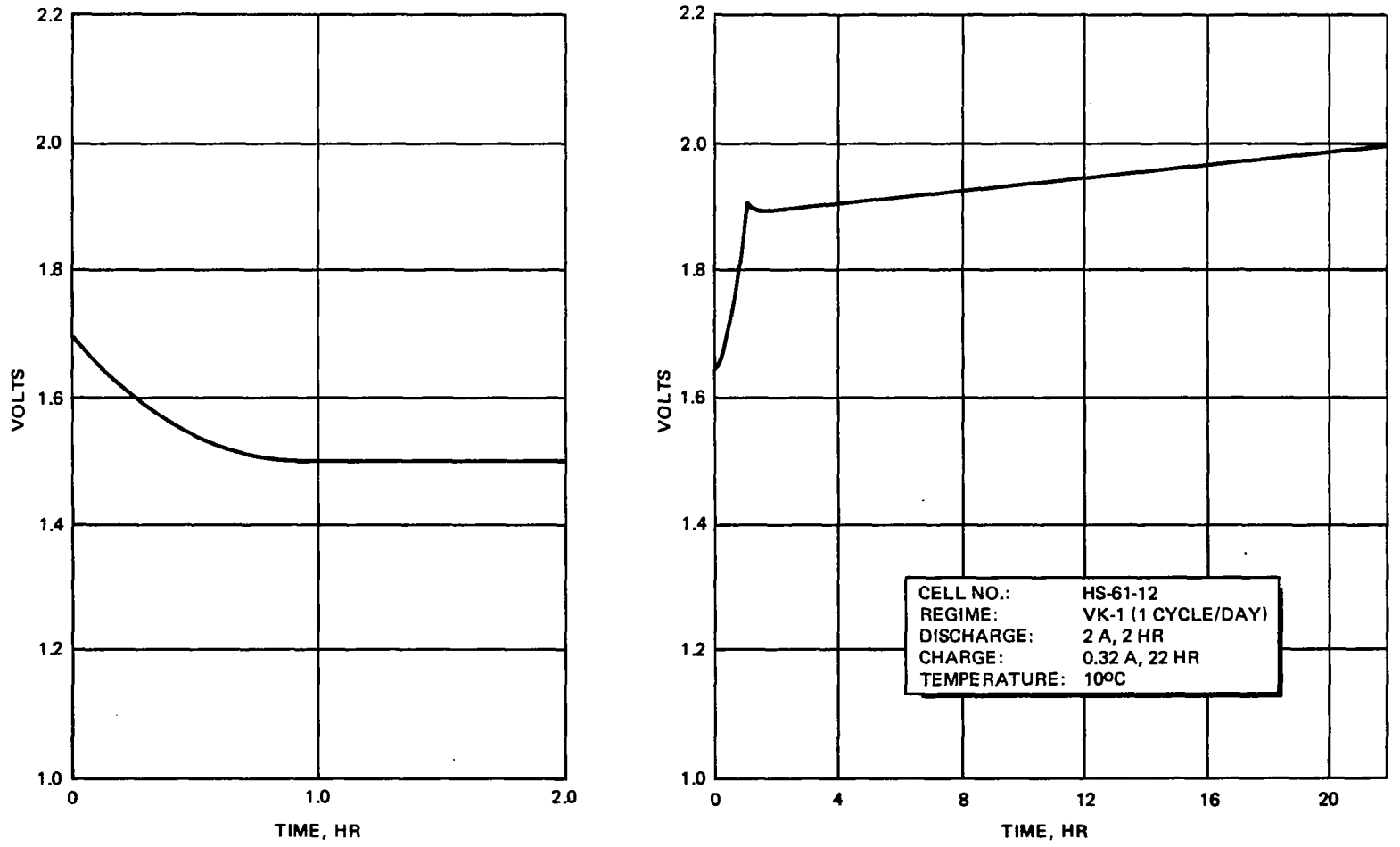


Figure 19. Cycling Curve, Design 7, Cycle 7, 10°C

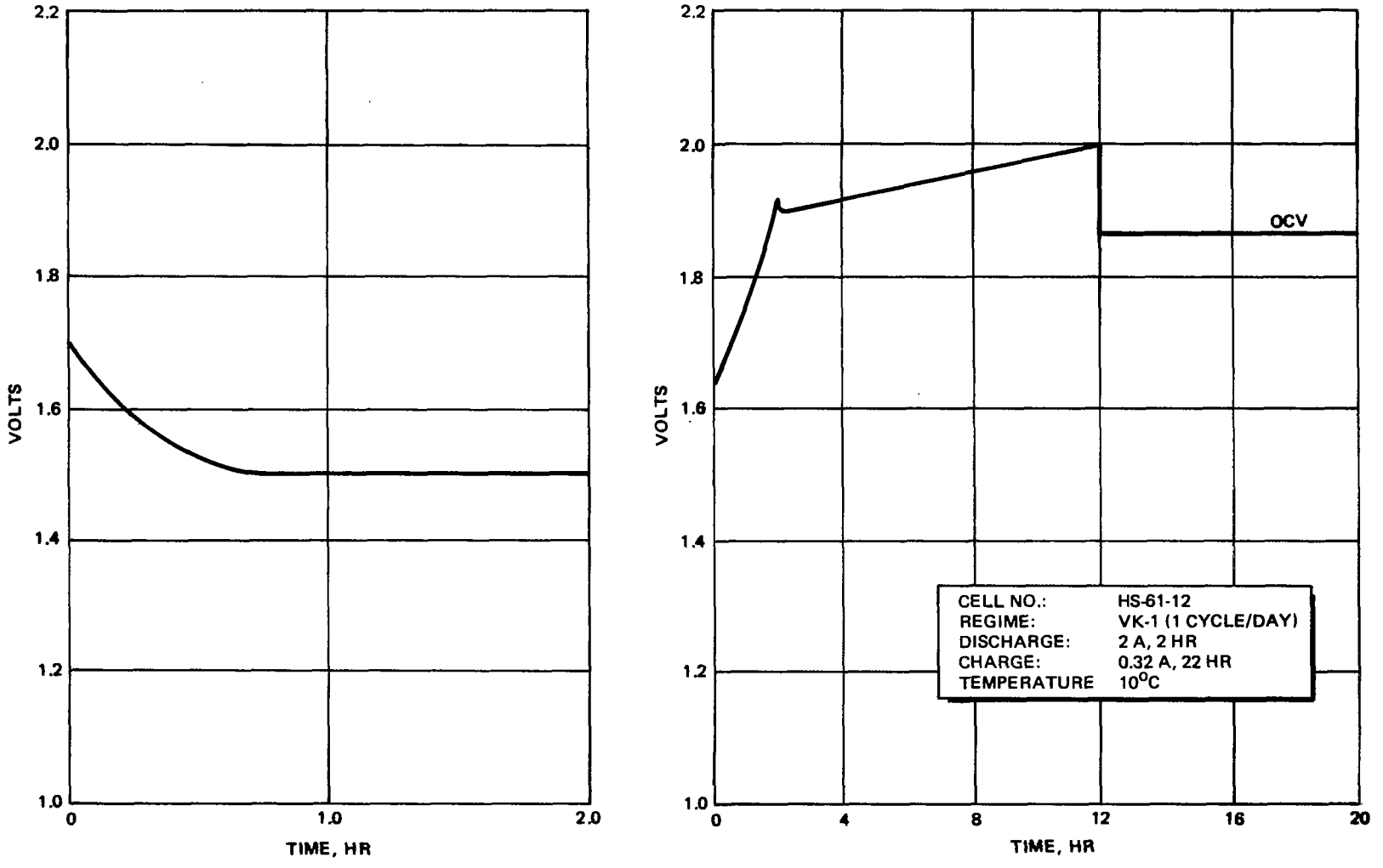


Figure 20. Cycling Curve, Design 7, Cycle 300, 10°C

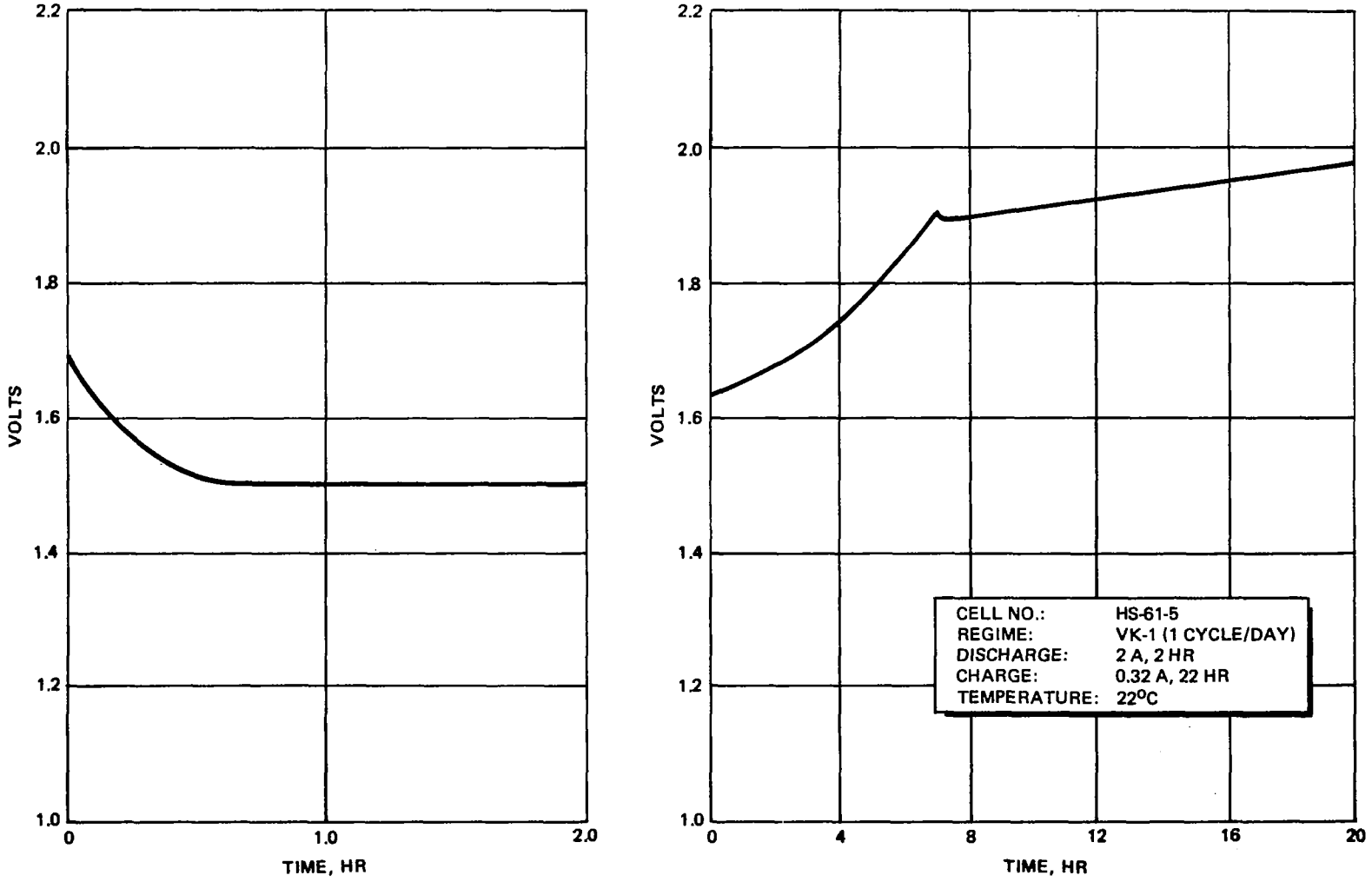


Figure 21. Cycling Curve, Design 7, Cycle 7, 22°C

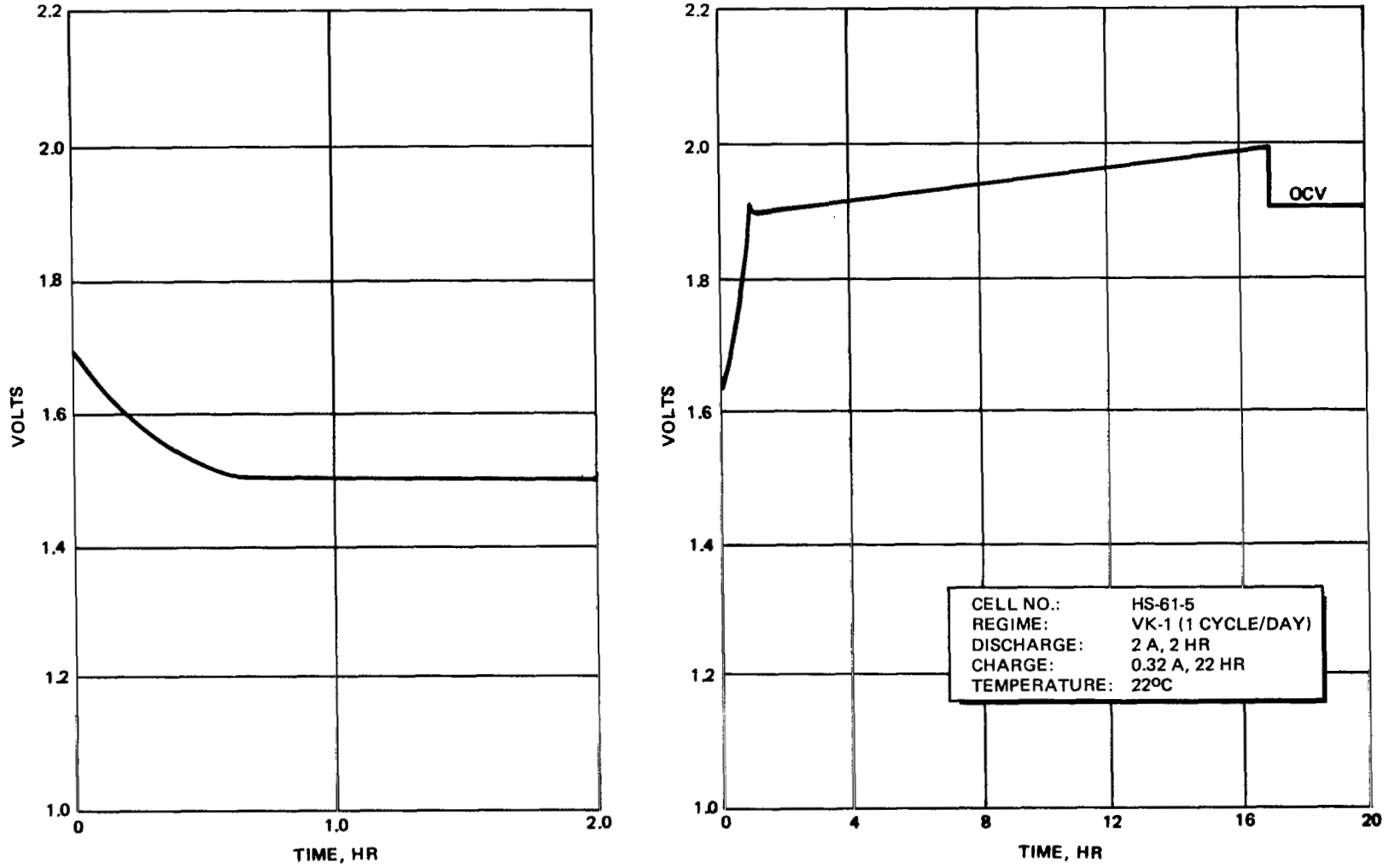


Figure 22. Cycling Curve, Design 7, Cycle 300, 22°C

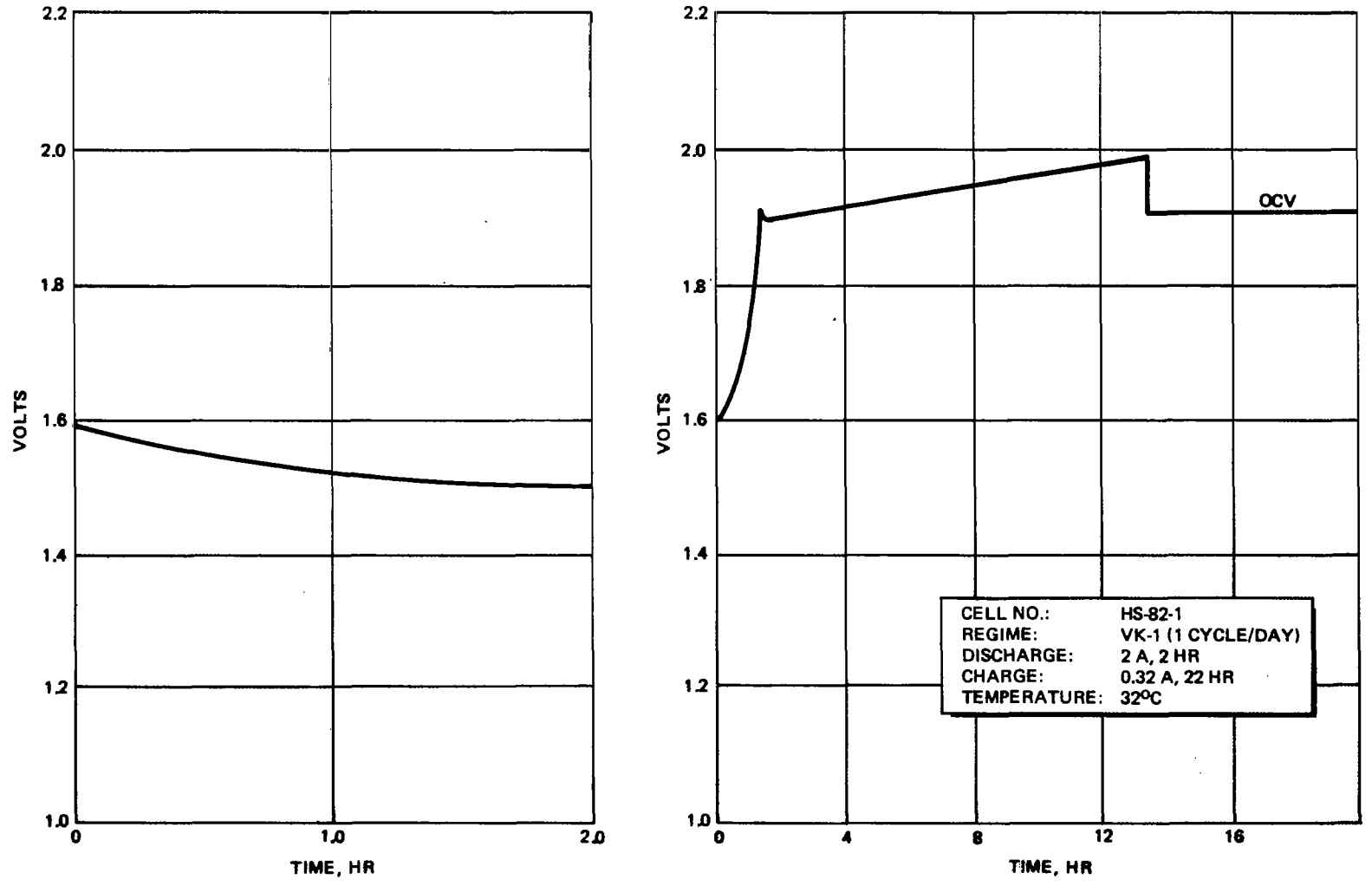


Figure 23. Cycling Curve, Design 7, Cycle 8, 32°C

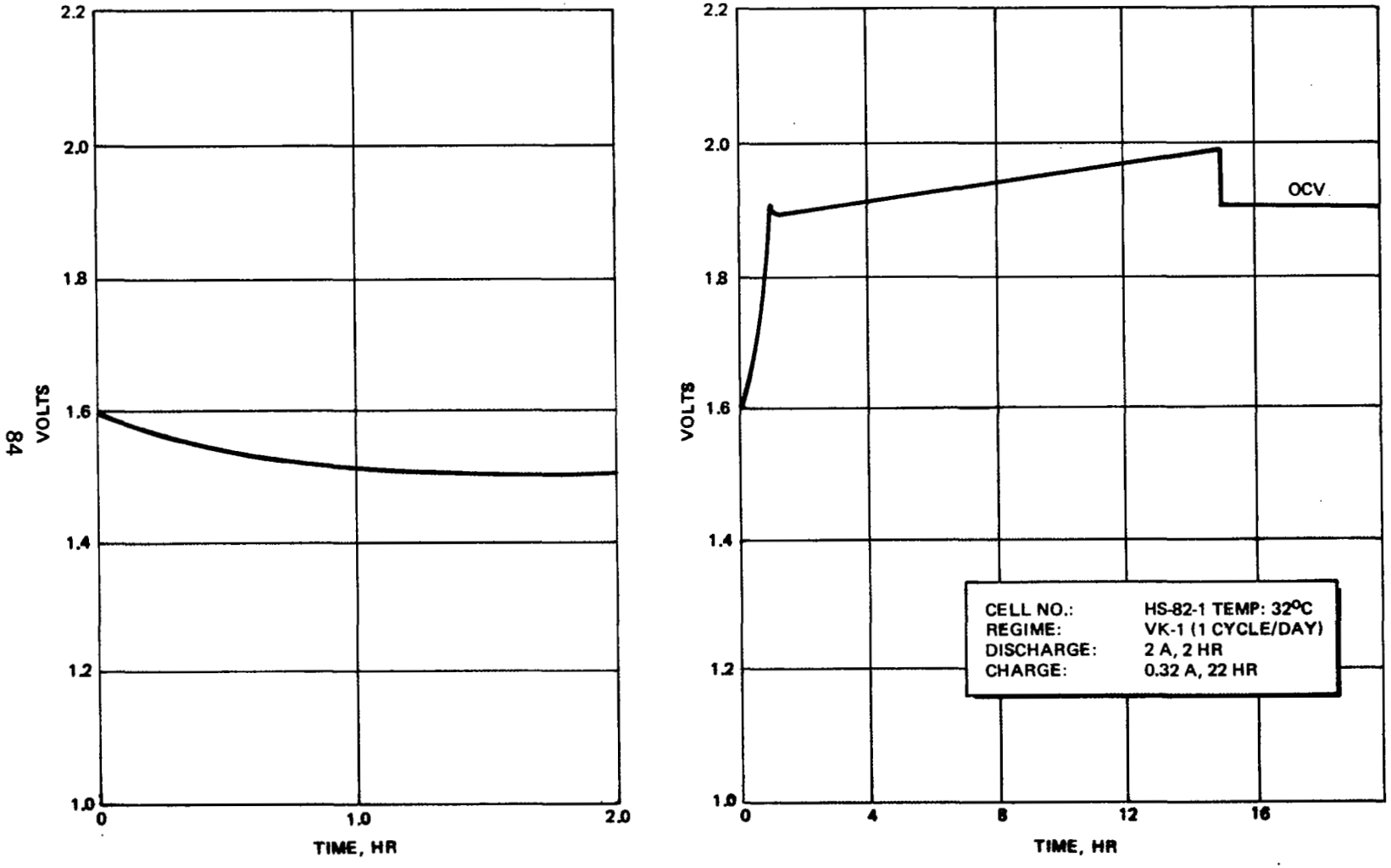


Figure 24. Cycling Curve, Design 7, Cycle 300, 32°C

Discharge: 7 A for 3 hr (70-percent DR)

Charge: 1.5 A to 2.0 V (One pulse 12 A for 40 sec at end of last discharge)

One characteristic of this overall regime is that the cell starts its automatic repetitive cycling in a partially discharged state (21 Ah deficient) and the subsequent charges are neither long enough nor high enough to bring the cell to a fully charged state. The increment of charge input over discharge output is only 0.45 Ah per day. It takes a certain number of days to reach full charge. The rise from argenteous oxide voltage plateau to argentic oxide voltage plateau took a few days of cycling.

Four cells of Design 7 were placed on this regime at room temperature. To date, three cells have reached 432 cycles and one cell has reached 386 cycles, over a total wet life of 8 months.

Curves for a full period are shown at beginning and at cycles 100, 200, 300, 400, on Figure 25 through Figure 29. It is worth noting the difference between charge curves at the beginning and afterwards.

Designs 6 and 8 (Backups)

Two new designs, using a third layer of inorganic separator between the two separator bags ($b^+/\ell/b^-$) were applied to two groups of five cells each and compared with a group of five cells of the previous design (b^+/b^-) considered standard design (Design HS-40-7). These designs were considered as backups. Their formation and poststerilization performances are shown in Table XLIII. At the discharge rate of 6 A, the plateau voltage differences are not significant. The capacity differences relate to the reduction in active material made necessary by the introduction of a third inorganic separator layer in the backup designs.

After sterilization, their average capacities were respectively 35 Ah for the HS-40-6 design and 40 Ah for the HS-40-8 design. The three groups of five cells each were discharged at various rates (20 A to 120 A) and temperatures (0°C to 50°C) (Temperature-Current Matrix T-I). Table XLIV presents the data for each design. The backup design HS-40-8 appears to be a prime candidate as it offers higher capacity and voltage than the other, although lower than the control design.

They were then placed on the battery duty cycle as described previously and referenced VK-1. They have completed 347 cycles to date over a total wet life of 15 months. The HS-40-8 design may be considered as a backup if longer or more reliable wet stand is required.

Cycling curves at cycle 8 and at cycle 300 are shown for Design 6 (Figures 30 and 31), for Design 7 (Figures 32 and 33) and for Design 8 (Figures 34 and 35).

CELL NO.:	HS-86-1
REGIME:	VK-2 (2 CYCLES/DAY)
CHARGE:	0.45 A, 7 HR
DISCHARGE:	3 A, 1 HR
CHARGE:	0.45 A, 7 HR
DISCHARGE:	3 A, 2 HR

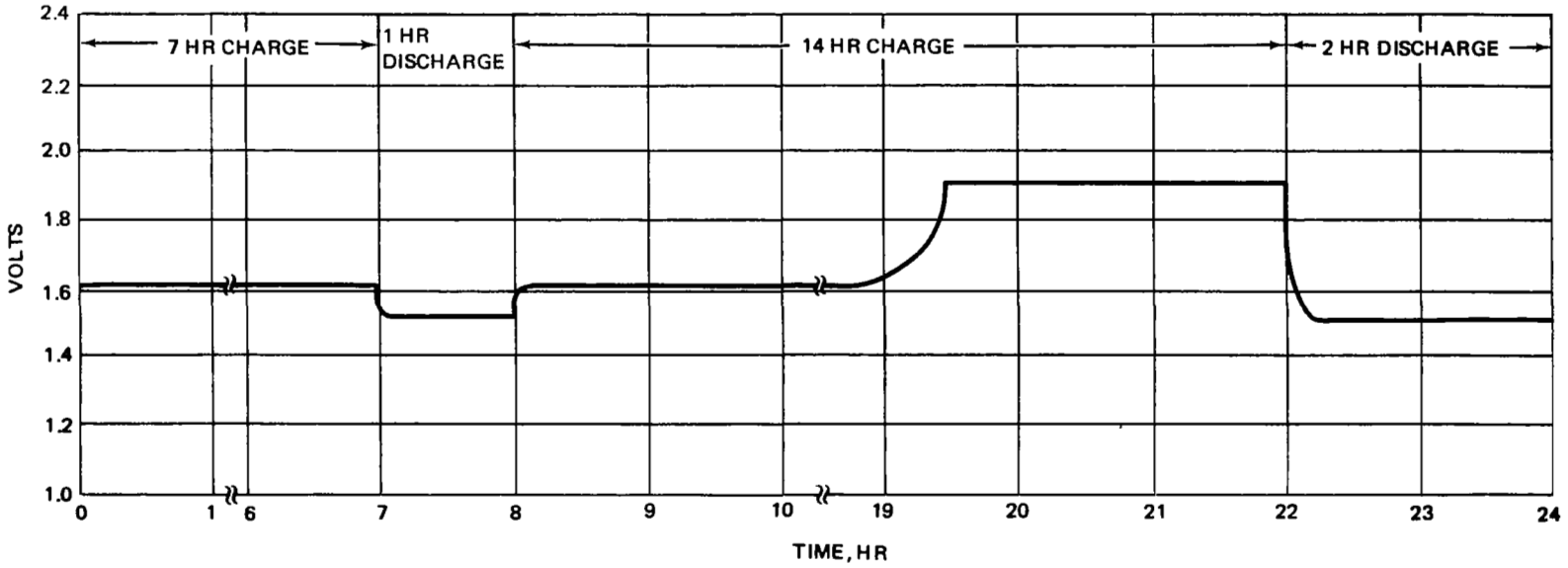


Figure 25. Cycling Curve, Design 7, Cycles 8 and 9

CELL NO.:	HS-86-1
REGIME:	VK-2 (2 CYCLES/DAY)
CHARGE:	0.45 A, 7 HR
DISCHARGE:	3 A, 1 HR
CHARGE:	0.45, 14 HR
DISCHARGE:	3 A, 2 HR

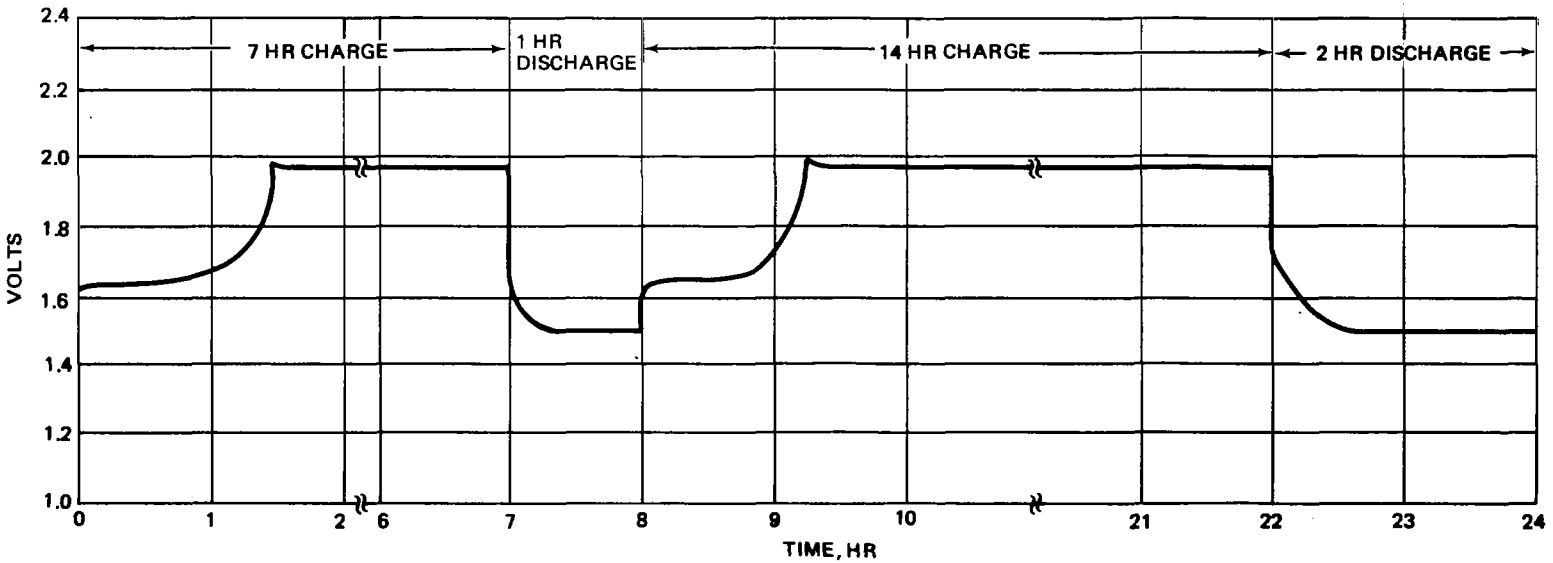


Figure 26. Cycling Curve, Design 7, Cycles 100 and 101

CALL NO.:	HS-86-1
REGIME:	VK-2 (2 CYCLES/DAY)
CHARGE:	0.45 A, 7 HR
DISCHARGE:	3 A, 1 HR
CHARGE:	0.45 A, 14 HR
DISCHARGE:	3A, 2 HR

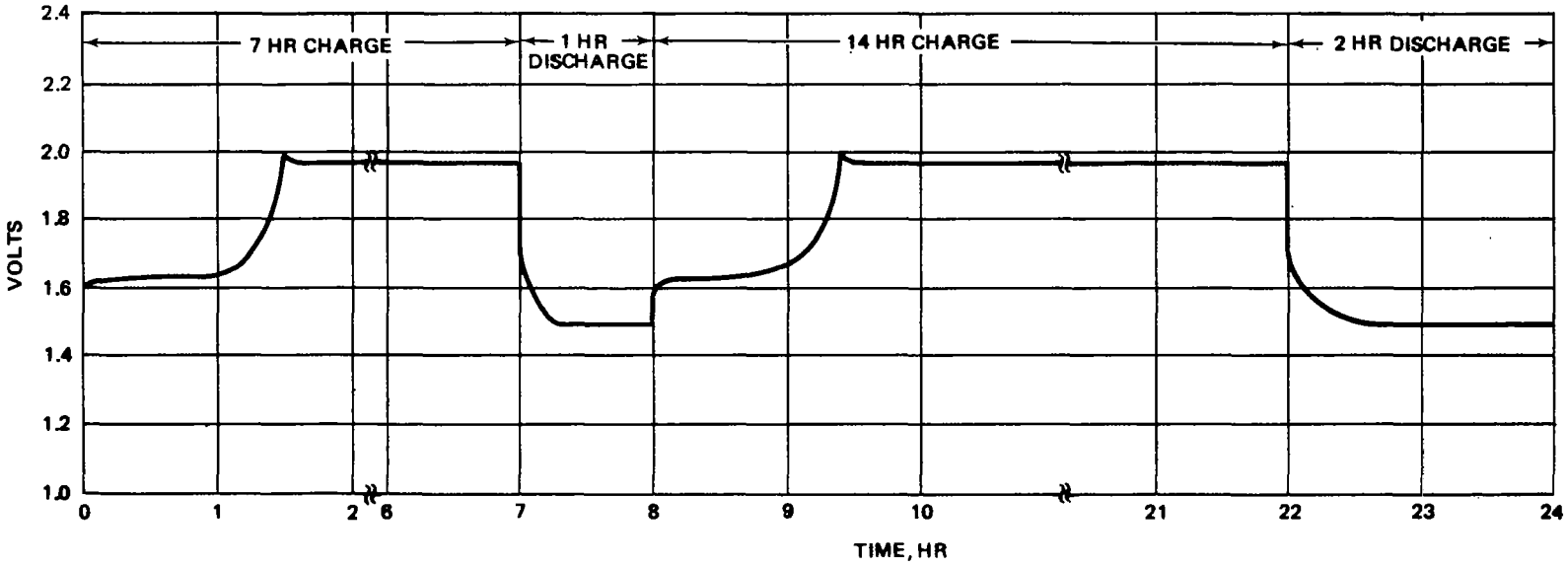


Figure 27. Cyclin g Curve, Design 7, Cycles 200 and 201

CELL NO.:	HS-86-1
REGIME:	VK-2 (2 CYCLES/DAY)
CHARGE:	0.45 A, 7 HR
DISCHARGE:	3 A, 1 HR
CHARGE:	0.45 A, 14 HR
DISCHARGE:	3 A, 2 HR

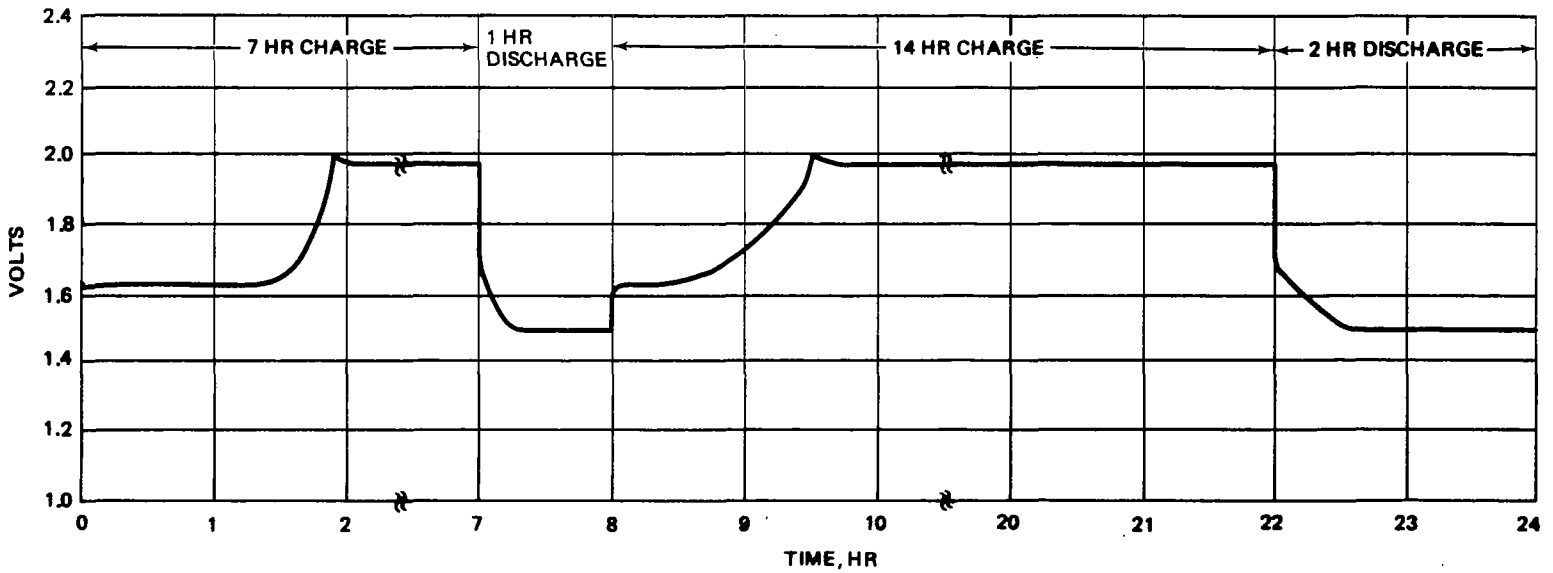


Figure 28. Cycling Curve, Design 7, Cycles 300 and 301

CELL NO.:	HS-86-1
REGIME:	VK-2 (2 CYCLES/DAY)
CHARGE:	0.45 A, 7 HR
DISCHARGE:	3 A, 1 HR
CHARGE:	0.45 A, 14 HR
DISCHARGE:	3 A, 2 HR

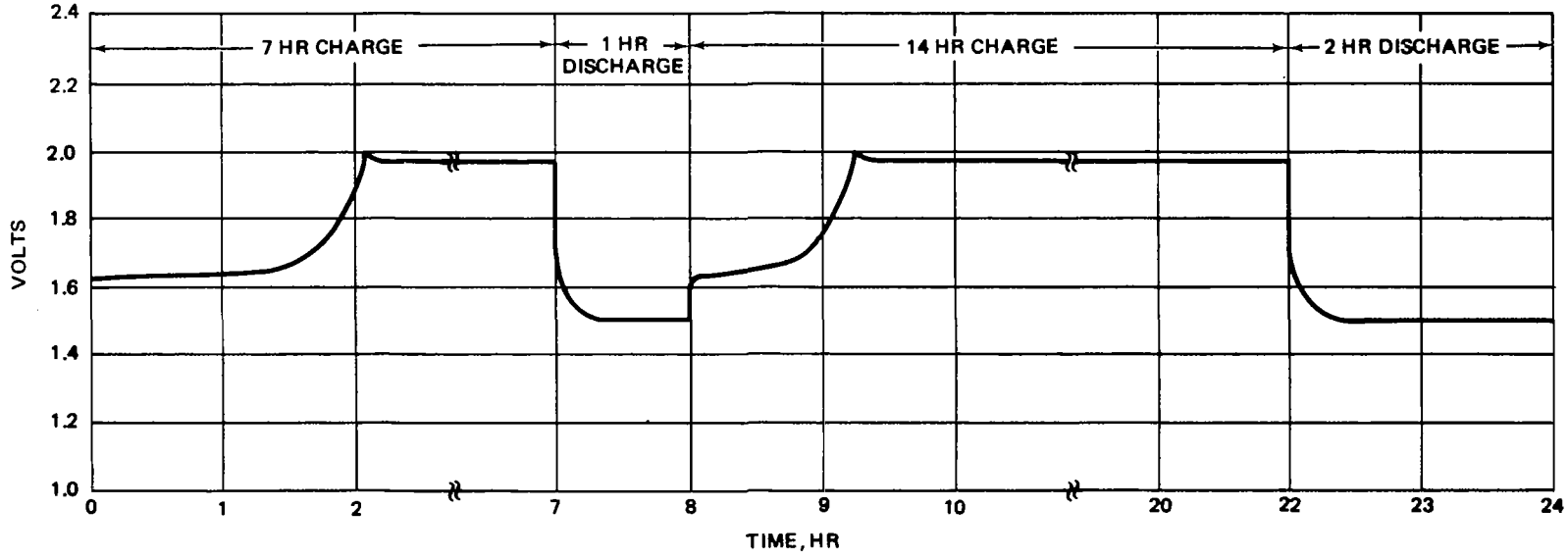


Figure 29. Cycling Curve, Design 7, Cycles 400 and 401

TABLE XLIII

ELECTRICAL PERFORMANCE OF STANDARD AND BACKUP DESIGNS

Design Code	Formation[a]	Poststerilization[b]	
	Capacity, Ah	Capacity, Ah	Plateau Voltage, V
HS-40-7 (Standard) ($6b^+/5b^-$)	42.8	44.0	1.49
	42.4	44.0	1.49
	41.8	44.1	1.49
	42.5	44.1	1.49
	42.4	44.1	1.49
Average:	42.4	44.0	1.49
HS-40-6 ($4b^+/\ell/5b^-$)	33.8	35.1	1.47
	33.9	35.1	1.47
	33.4	35.0	1.47
	33.4	35.1	1.46
	33.5	35.1	1.47
Average:	33.6	35.1	1.47
HS-40-8 ($6b^+/\ell/5b^-$)	39.9	40.6	1.48
	39.0	40.5	1.48
	38.5	40.5	1.48
	38.0	40.5	1.48
	38.1	40.7	1.48
Average:	38.5	40.6	1.48

[a]Discharge at 6 A to 1.0 V and drain at 2 A to 1.0 V.

[b]Charge at 2.5 A to 2.05 V on formation and 1.5 A to 2.0 V on the second cycle.

TABLE XLIV

CAPACITY AND PLATEAU VOLTAGE OF VARIOUS CELL DESIGNS

Design	Temp	Current							
		20 A		40 A		80 A		120 A	
		Ah	V	Ah	V	Ah	V	Ah	V
HS-40-7 (standard) ($6b^+/5b^-$)	0°C	33.3	1.27	28.6	1.15	30.4	1.14	26.4	1.22
	25°C	40.0	1.38	38.0	1.31	37.6	1.20	32.4	1.11
	50°C	41.3	1.47	38.6	1.38	34.6	1.27	31.9	1.25
HS-40-6 ($4b^+/\ell/5b^-$)	0°C	25.0	1.21	24.6	1.03	24.0	0.99	24.0	0.96
	25°C	32.2	1.33	30.0	1.17	29.6	1.09	26.4	1.01
	50°C	34.3	1.38	31.3	1.30	32.0	1.07	25.9	1.13
HS-40-8 ($6b^+/\ell/5b^-$)	0°C	30.0	1.25	24.6	1.14	25.6	1.11	27.6	1.06
	25°C	39.0	1.37	32.0	1.25	29.6	1.14	30.0	1.08
	50°C	39.0	1.43	36.0	1.33	36.0	1.17	27.0	1.17

Notes: 1. Data obtained after formation and heat sterilization.

2. Cells were drained at 2 A to 1.0 V after each specific discharge (drain output not shown).

Design 10

In view of the Viking battery requirements, at one time of the program, a need arose to cut down the cell weight and select the best design based on all data then available to meet maximum reliability for a nominal 30-Ah capacity and 24-month wet life.

The concept of the Design 8 was used (two separator bags and a separator film in between) and applied to a cut down cell version to minimize weight. All engineering drawings were prepared, but a redirection in the program did not permit the hardware phase, fabrication, and testing. The engineering drawing package has been delivered to NASA.

By calculation, it was established that the HS-40-10 design cell would have delivered an actual capacity of 40 Ah with a maximum weight of 651 g compared with 886 g for the HS-40-7 cell and 868 g for the HS-40-8 cell. Its

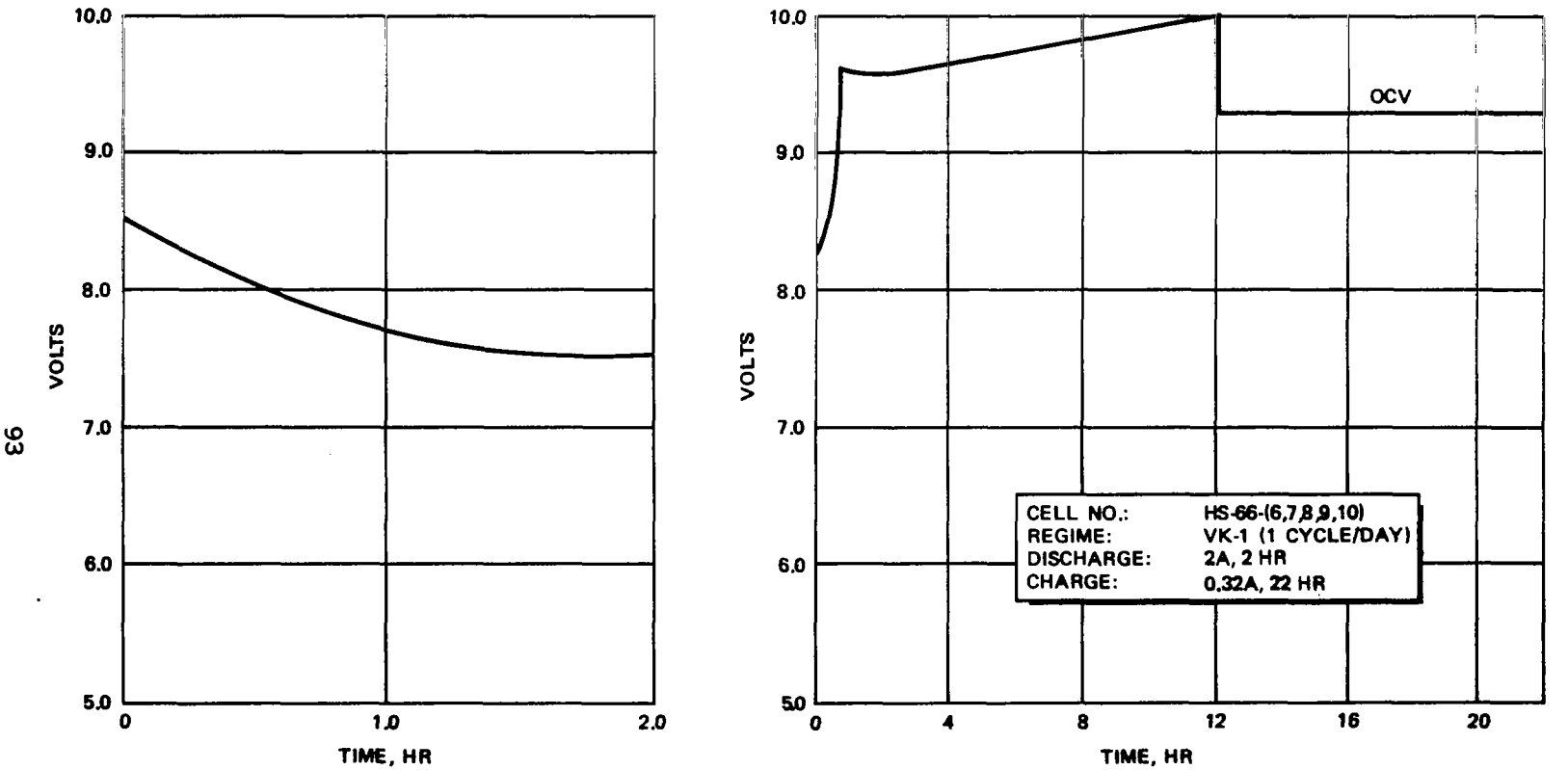


Figure 30. Cycling Curve, Design 6, Cycle 8

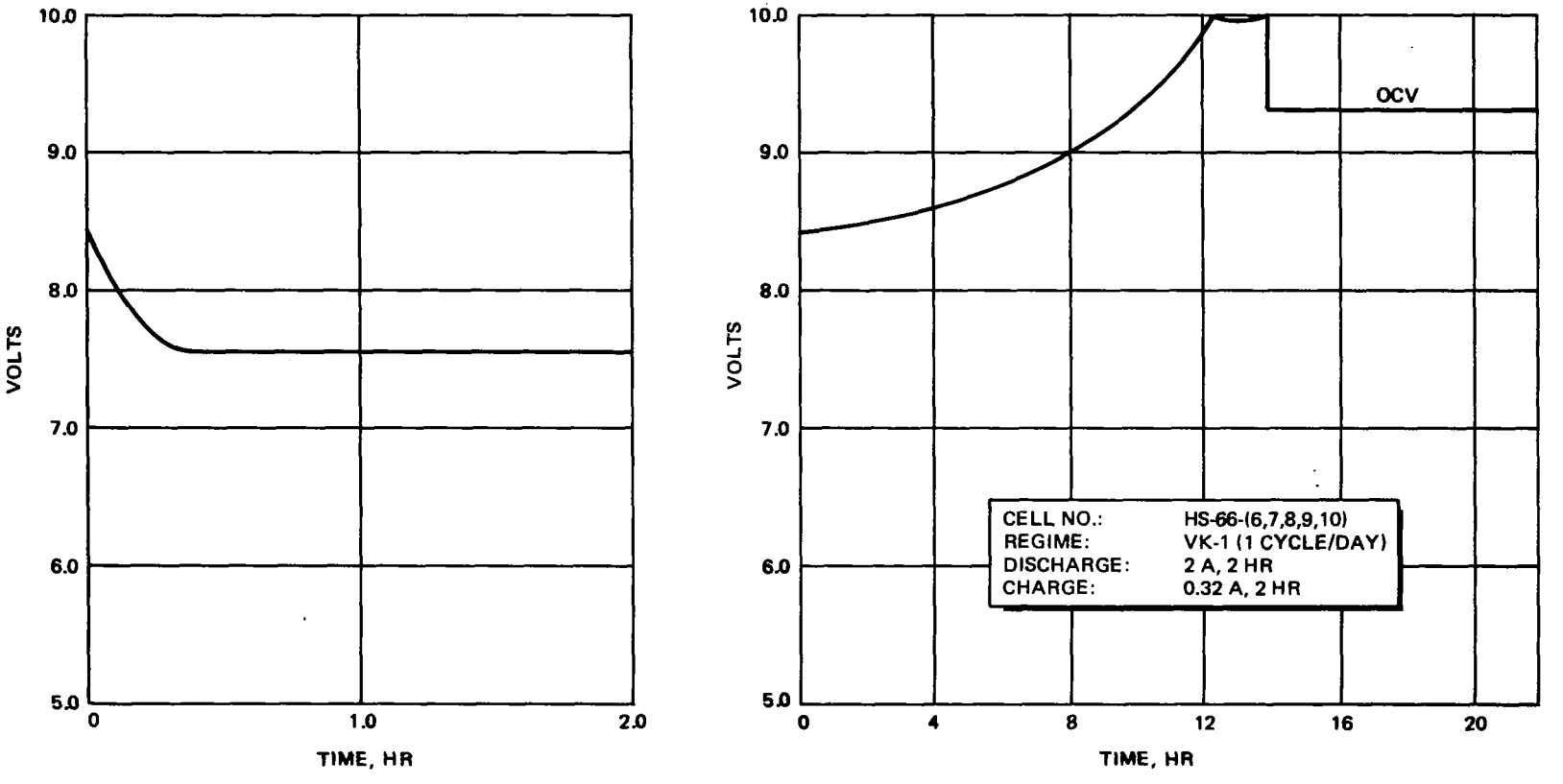


Figure 31. Cycling Curve, Design 6, Cycle 300

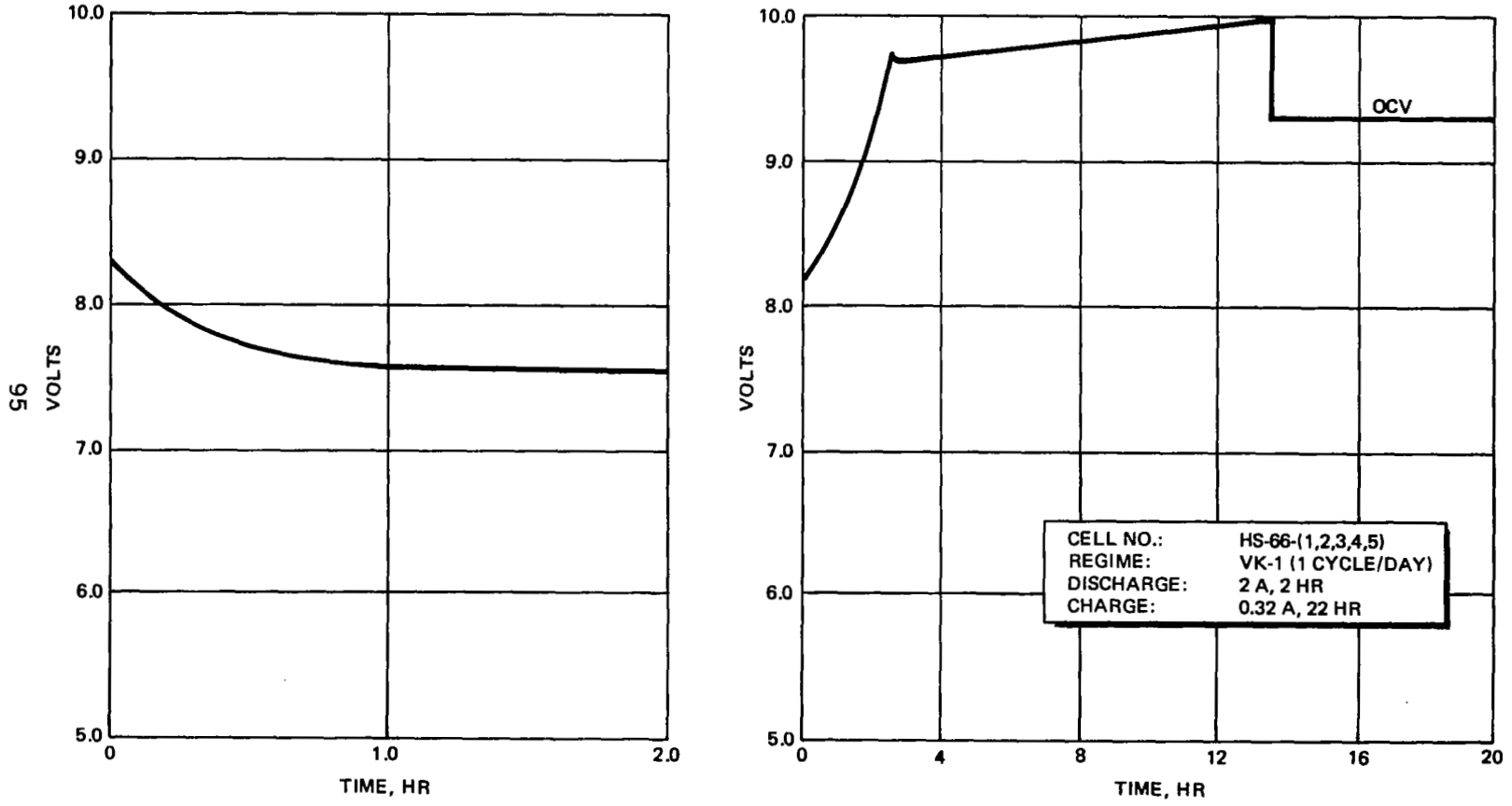


Figure 32. Cycling Curve, Design 7, Cycle 8

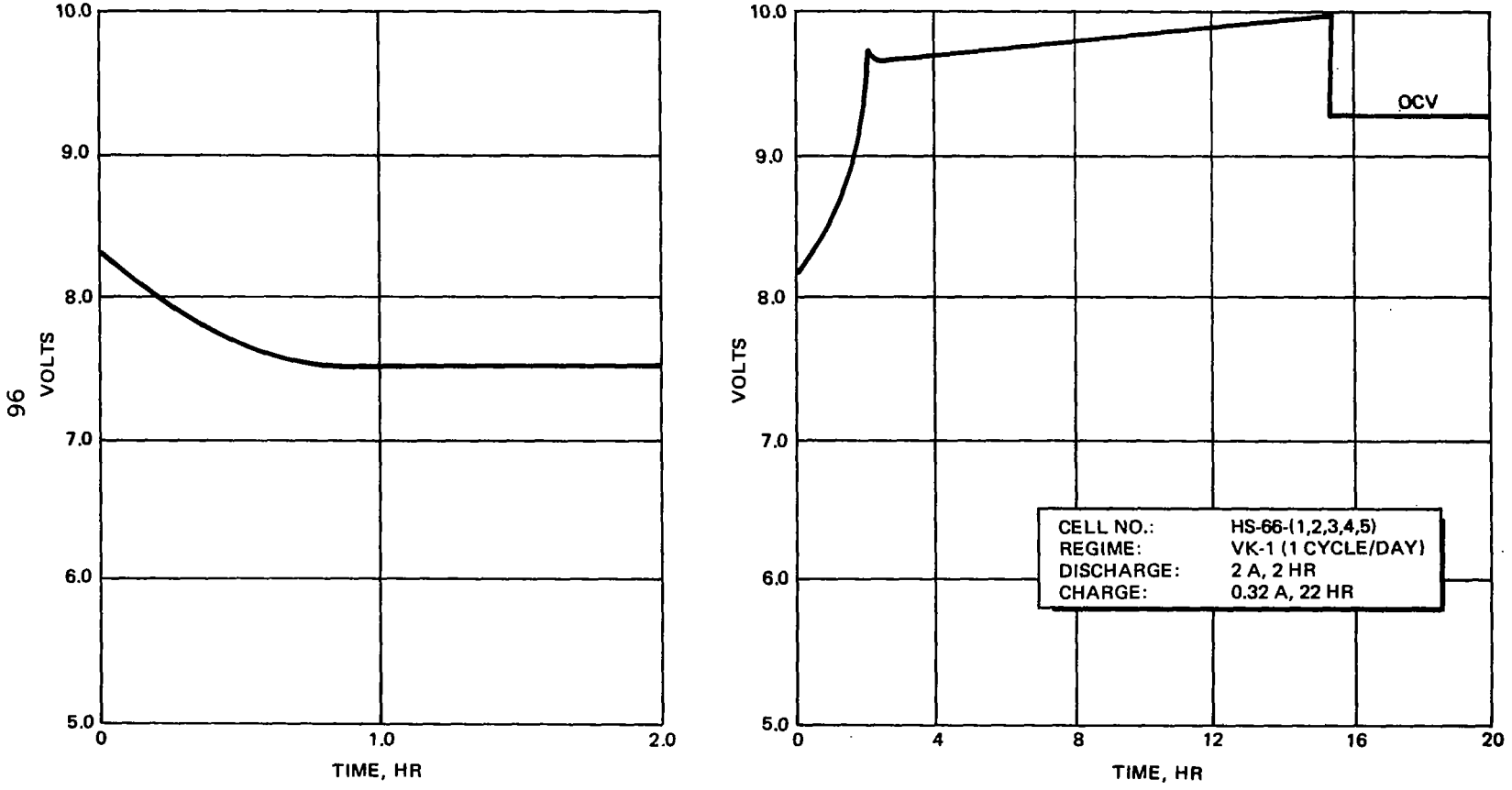


Figure 33. Cycling Curve, Design 7, Cycle 300

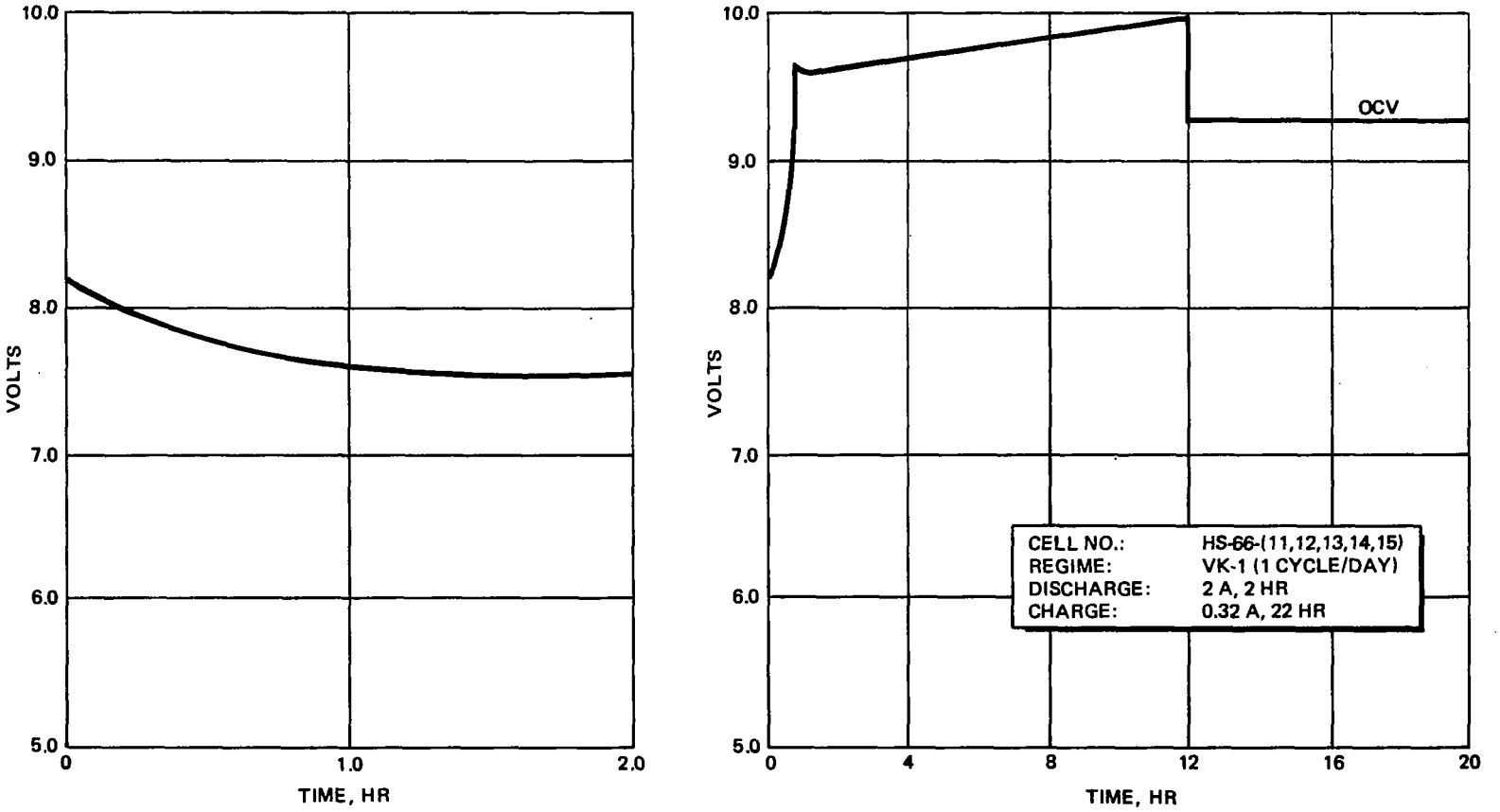


Figure 34. Cycling Curve, Design 8, Cycle 8

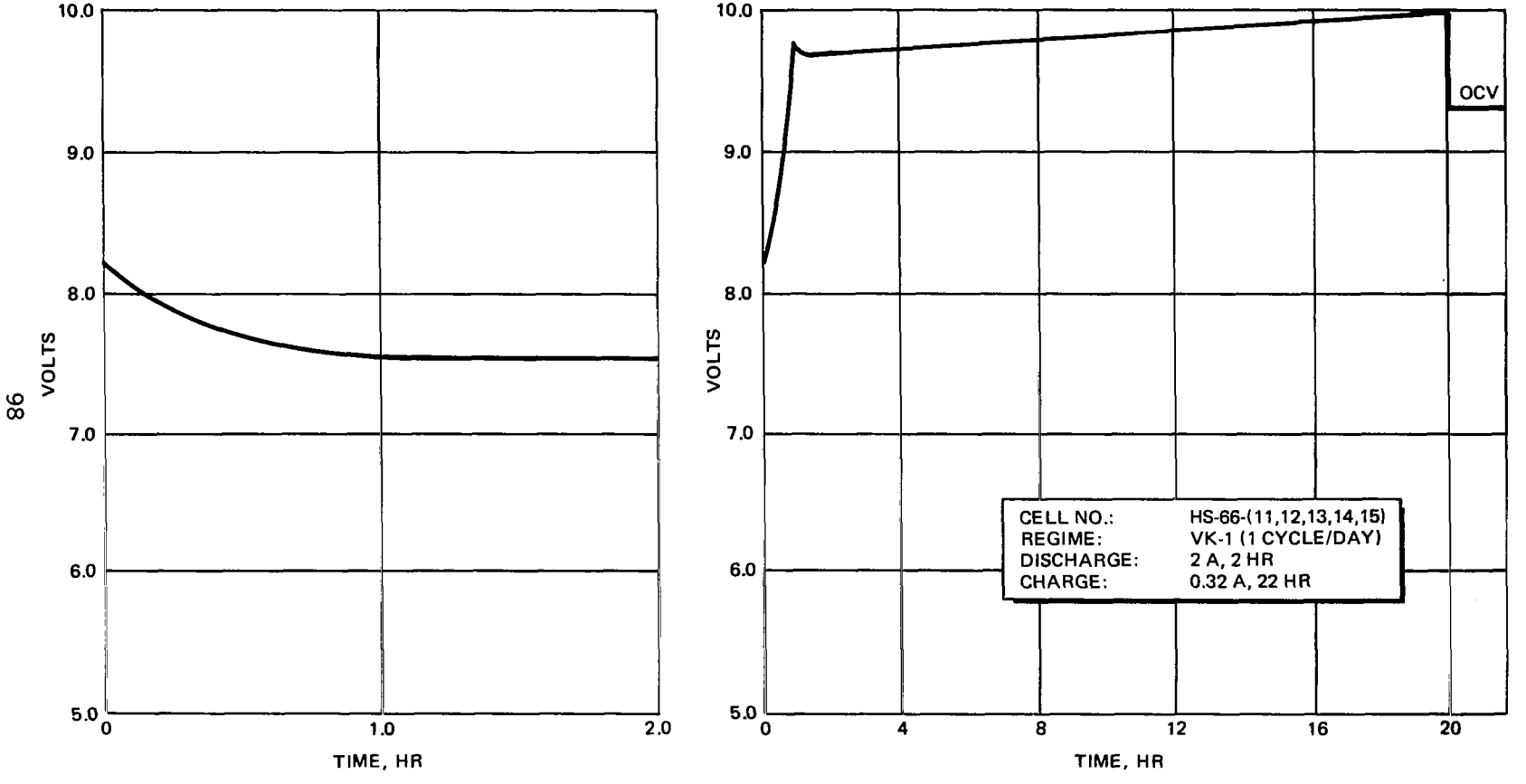


Figure 35. Cycling Curve, Design 8, Cycle 300

volume, excluding terminals, was 335 cm^3, compared with 442 cm^3 for both the HS-40-7 and HS-40-8.

The weight and volume savings were due to better design fitting the specific Viking mission, which was then accurately defined. The relatively low rate permitted redesign of smaller terminal hardware, smaller head space over the cell pack, smaller amounts of active materials. The high strength of glass fiber-filled PPO material helped in redesigning the new case and contributed to substantial weight saving.

Summary and Overall View

The design evolution described above has been logical and covered all alternatives in increasing order of complexity matching the mission requirement severity. As the electrical requirements increased wet life, charged wet stand, and cycle life; it was demonstrated that an optimum design for a low to medium rate discharge can be obtained with the Design 7 and more safely and reliably, with the Design 8 by extrapolation.

All data are presented in an overall view for each specific set of test conditions—stand (Table XLV), cycling only (Table XLVI), cycling following stand (Table XLVII).

Table XLVIII gives the status of cells still on test at the time of this writing, including cells mentioned in the next section.

Failure analysis was done by examining the cell pack, electrodes and separator, analyzing the separator for silver content, and when necessary, photographing the interesting component.

To date the failures encountered occurred on cells of the earlier design types and are therefore not fully representative of the preferred designs (HS-40-7 and HS-40-8) which are still on test. However, some clear signs indicate the value of increased separator thickness in dealing with penetration, whether by zinc or by silver.

Design 1 (one bag on positives only) suffered from early silver penetration, due to accumulation of soluble species within a tight space. Design 2 (one bag on negatives only) was an improvement in instances where test conditions were conducive mainly to silver penetration, such as charged stand. When cycling was added, some zinc penetration appeared when the cell was accidentally overcharged by imbalance in a series of cells. Other designs having at least one bag on positives and one bag on negatives showed an immediate improvement in all respects. An early model of this configuration (cell HS-51-6) failed on cycling after 517 days wet life and 1,093 cycles (three cycles/day, 40-percent depth). The amount of silver in the two layers of separator between plates of opposite polarity was 29.2 mg/cm^2 (188 mg/in^2). However the zinc plate retained a good shape (Figure 36), as already discovered in all dissected cells (other cell in Figure 37). It therefore appears that the present zinc plate design and assembly are favoring a good shape retention. This is also evidenced by the good capacity maintenance obtained during cycling of actual cells, whether on partial or total discharge.

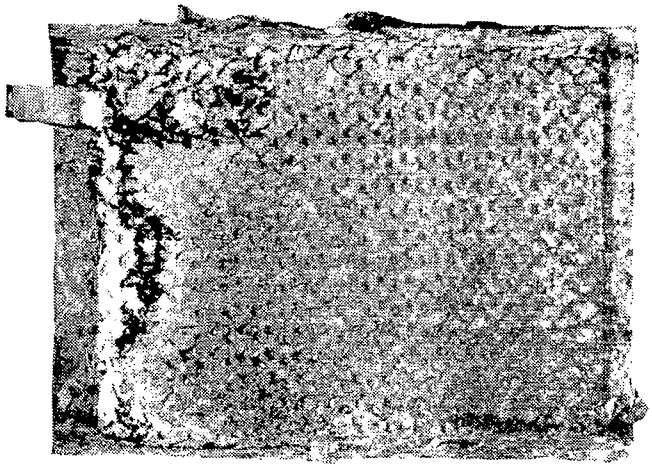


Figure 36. HS-51-6 Cell Typical Electrode — 517 Days Wet Life, 1,093 Cycles (Three Cycles Per Day, 40 Percent Depth)

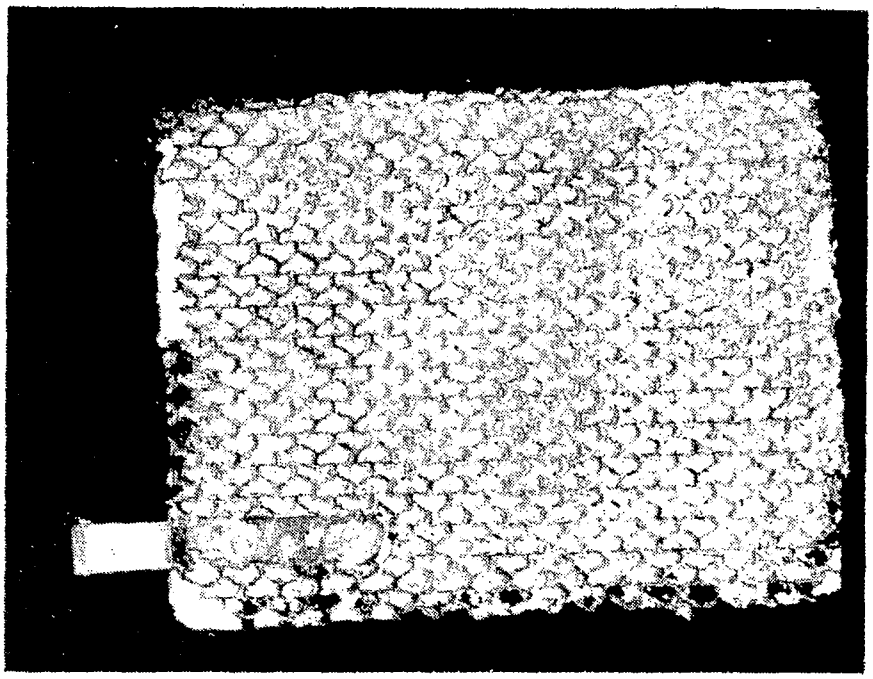


Figure 37. HS-54-4 Cell Typical Negative Electrode — 345 Days Life, 541 Cycles (Three Cycles Per Day, 40 Percent Depth)

TABLE XLV

STAND DATA

Design	KOH, percent	Cell Type	Charged			Float			Discharged	
			Temp	Cells	Months	Temp	Cells	Months	Cells	Months
1 (b^+/)	40	7 Ah	R.T.	4	3 (F)					
		40 Ah				65°C	5	1 (F)		
						R.T.	13	4 (F)		
2 (/b^-)	40	7 Ah	R.T.	4	5 (F)					
		40 Ah				65°C	5	1 (F)		
						R.T.	13	7 (OP)		
7 (b^+/b^-)	45	40 Ah	10°C	5	16	10°C	5	15	11 at R.T.	7 to 17
			R.T.	5	16	R.T.	5	15		
			32°C	5	16	32°C	5	15		
			42°C	2	13					
			52°C	2	6(a)					
			62°C	2	3(a)					
			R. T.	21	2				4 at R.T.	3

NOTE: All cells still on test except where indicated by F (failed) or OP (opened for examination).

(a) Cells completed their temperature-stand test and were placed on discharged stand at R. T.

TABLE XLVI

CYCLING ONLY

Design	KOH, percent	Cell Type	Cells	Regime	Cycles	Wet Life, Months
2 ($/b^-$)	40	40 Ah	2	100 percent DOD (total discharge)	50 (F)	3
			2	three cy/day, 66 percent	90 (F)	1
3 (b^+/b^-)	40	32 Ah	2	three cy/day, 40 percent	463(F);1093(F)	9;17
5 ($b^+/L/b^-$)	40	35 Ah	2	100 percent DOD (total discharge)	122	18
			2	three cy/day, 40 percent	543 (F)	11
6 ($b^+/\ell/b^-$)	45	35 Ah	5	one cy/day, 13 percent	347	15
8 ($b^+/\ell/b^-$)	45	40 Ah	5	one cy/day, 13 percent	347	15
7 (b^+/b^-)	45	40 Ah	5	one cy/day, 13 percent	347	15
			5	10°C, one cy/day, 13 percent	418	15
			5	22°C, one cy/day, 13 percent	423	15
			5	32°C, one cy/day, 13 percent	372	14
			4	two cy/day (10 percent, 20 percent)	432	8
			15	three cy/day, 47 percent	140 to 196	3

NOTE: All cells still on test except where indicated F (failed).

TABLE XLVII

CYCLING FOLLOWING STAND

Design	KOH, Percent	Cell Type	Cells	Stand Time, Months/Type	Regime	Cycles	Total Wet Life, Months
2 (/b⁻)	40	40 Ah	2	7/Charged	one cy/day, 13 percent	260	21
3 (b^+/b^-)	40	7 Ah	6	8/Charged	one cy/day, 13 percent	464	26
		32 Ah	2	7/Charged	one cy/day, 13 percent	311	16
			2	7/Float	one cy/day, 13 percent	311	16
			1	8/Discharged	one cy/day, 13 percent	257	16
5 ($b^+/L/b^-$)	40	35 Ah	1	7/Charged	one cy/day, 13 percent	259	18
			1	7/Float	one cy/day, 13 percent	259	18
			1	9/Discharged	one cy/day, 13 percent	259	18
7 (b^+/b^-)	45	40 Ah	None at this time: scheduled after 21 months wet life				

NOTE: All cells still on test.

TABLE XLVIII

STATUS OF CELLS STILL ON TEST

(Room Temperature Except Where Indicated Differently)

Design	Wet Stand						Cycling			
	Charged		Float		Discharged					
	Cells	Days (w)	Cells	Days (w)	Cells	w	Regime	Cells	Cycles	w
-2 (/b⁻)							VK-1 After Stand	2 HS-47	260	621
-3 (b^+/b^-)							VK-1 After Stand	6 Elements 4 HS-51 1 HS-51	464 311 257	766 579 579
-5 (b+/L/b⁻)							VK-1 After Stand	3 HS-54	259	553
							100 percent DOD	2 HS-54	122	553
-6 ($b^+/\ell/b^-$)					1 HS-66	476	VK-1	5 HS-66	347	449
-8 (b+/ℓ/b⁻)					1 HS-66	461	VK-1	5 HS-66	347	449
-7 (b+/b⁻)	10°C 5 HS-59	463(487)	10°C 5 HS-59	454(476)	2 HS-59 3 HS-81 2 HS-84 4 AH-39 1 HS-90 1 HS-91	503 417 458 413 217 200	VK-1	5 HS-66	347	449
	22°C 5 HS-59	463(487)	22°C 5 HS-59	454(476)			VK-1(10°C) VK-1(22°C) VK-1(32°C)	6 HS-61 6 HS-61 3 HS-82	418 423 372	462 462 410
	32°C 4 HS-59 1 HS-61	463(487) 440(462)	32°C 4 HS-59 1 HS-61	453(476) 440(462)			VK-2	3 HS-86 1 HS-86	432 386	253 253
	42°C 2 AH-39	379(413)					100 percent DOD	1 HS-123-GX	11	81
	1 NHS-114-0 5 NHS (A) 5 NHS (B) 5 NHS (C) 5 NHS (D)	83(137) 76(95) 60(104) 60(102) 60(102)			2 NHS-104 2 NHS-126	170 75	VK-3 VK-3 VK-3 VK-3 VK-3	1 NHS-119-GX 4 NHS (A) 3 NHS (B) 4 NHS (C) 4 NHS (D)	162 196 158 140 160	98 95 103 101 104

Notes:
All NHS cells are not heat sterilized.
w = total wet life
days since activation

On the other hand, the capacity retention on charged stand is a function of silver penetration, consequently a function of the number of separator layers. This is supported by the data obtained after 7-month charged stand on earlier designs using 1, 2, or 3 layers. Table IL shows the effect of each design. It is worth remembering that the data presented were obtained with cells using 40-percent KOH. The new designs 7 and 8 are using 45-percent KOH which should improve the capacity retention even further.

Failure analysis and test conditions for all dissected cells may be found in Appendix C.

TABLE IL

CAPACITY RETENTION AFTER 7-MONTH STAND AT R. T.
(40-PERCENT KOH)

Design No.	Number of Separator Layers	Capacity Retention	
		Plain Charged Stand	Charged Stand With Float
2	1	-	89 percent
3	2	77 percent	88 percent
5	3	88 percent	100 percent

Redirection of Program

Because of budgetary changes in the overall Viking mission project, the present battery program was redirected by NASA Technical Direction No. 3, dated 15 July 1970. The heat-sterilization requirement was removed on all new cells to be fabricated or tested. Other areas of investigation were introduced.

Environmental Testing

The effect of environmental testing on the present cell remained to be demonstrated. So far, the cell is designed to meet certain electrochemical and electrical performance requirements. A mechanical plate-lock may be needed to firmly hold the cell pack in place during the stresses imposed by launch and soft landing conditions.

At an earlier date, a sealed cell without the benefit of any plate-lock was tested by Martin-Marietta Corporation, Denver, Colorado (Prime Contractor for Viking spacecraft), on a special shock test, called pyrotechnic shock with a spectrum amplitude up to 2,000 Hz and 1,050 g's peak, for a duration ranging from 10 to 50 ms, in both directions of the three mutually perpendicular axes (three times in each direction). No physical damage resulted from this test. X-ray pictures were taken (Figure 38) showing electrode pack shifted toward the terminal bases. The cell was then checked electrically. It was given one cycle, yielding 40.8 Ah, recharged, then left on OCV for 15 days. It held 1.86 V constantly. It was then cut open; the electrode stack was still satisfactory (see Figure 39).

Since a cell without plate-lock did not show any catastrophic failure, the plate-lock method devised was kept as simple as possible. Using an epoxy, which was previously used extensively and found compatible with KOH and high temperature (Allbond), a small amount in each corner of the cell bottom before cell pack insertion was found sufficient to hold it in place after curing. This method is coded PL (for single platelock).

The entire cell pack is thus held, but it was speculated that bagged electrodes may still have the possibility of shifting out of their bags under vibration in the vertical direction. The separator bag tops were then also heat sealed, except for the tab area.

These mechanical additions to the cell design may affect the electrical behavior of the cell and therefore two cells were fabricated in this manner to be tested electrically. They did not show any difference in formation cycle behavior or electrical performance.

It was then decided to use this plate-lock method on all 30 cells required for environmental testing.

As directed by the work statement, four groups of 10 cells each of the HS-40-7 type were fabricated for comparative evaluation during and after environmental testing. These cells were not to be heat sterilized and are

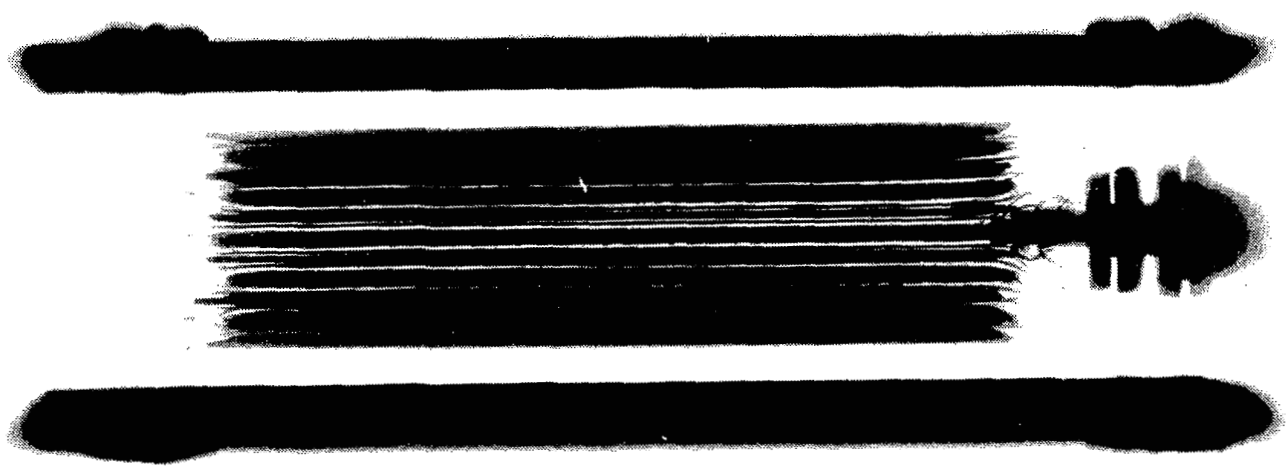


Figure 38. X-Ray 40-Ah Cell Submitted to Pyrotechnic Shock (1,050 G's)

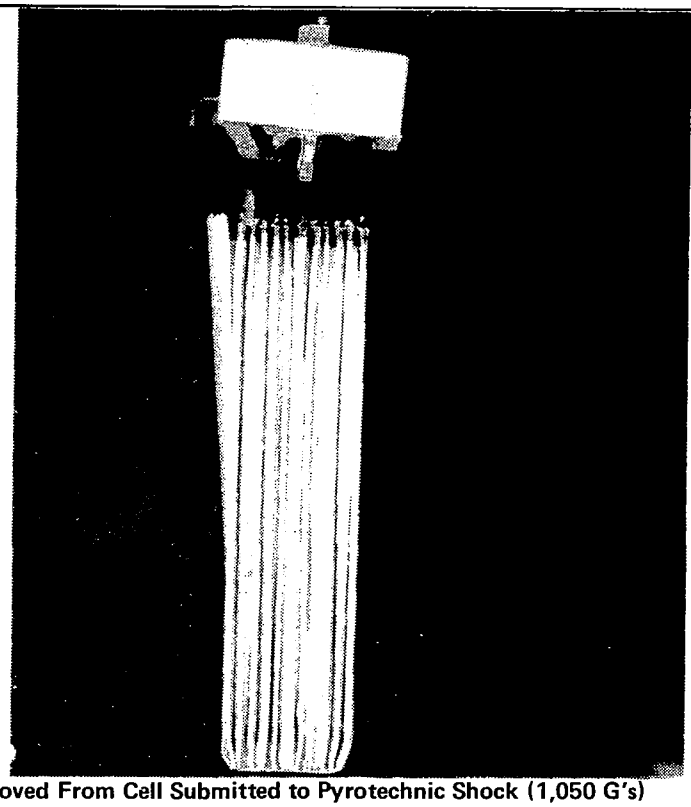


Figure 39. Cell Pack Removed From Cell Submitted to Pyrotechnic Shock (1,050 G's)

therefore denoted NHS in their identification to differentiate them from the heat-sterilized cells (HS). The variations between the four groups A, B, C, D are listed in Table L.

The cells were given a formation cycle (data on Table LI) and sealed. Thirty cells (B, C, D) were then assembled in blocks of five cells, each block weighing 4,300 g and submitted as a unit to the following environmental tests in succession. All applied in both directions in each of the three mutually perpendicular axes. (Details are given in Appendix B).

(1) Steady state acceleration: 35 g's, 5 min per direction

(2) Sinusoidal vibration: 5 to 34 Hz, 0.25-in. D.A.; 34 to 2,000 Hz ± 15 g's

(3) Random Vibration: Up to 2,000 Hz, overall acceleration 19.1 g's (rms), 5 min per axis

(4) Shock: Three times 45 g's, terminal peak sawtooth, 10 ms

After each test of the environmental series, the cells were examined. No physical damage was noticed on any cell. The OCV's monitored before and after each test were uniform and approximately 0.40 V as the cells were

TABLE L

PLATE-LOCK CELLS

Group	Plate-Lock	Epoxy Curing	Environmental Testing
A	Yes	Normal (24 hr at R.T. followed by 1/2 hr at 100°C	No
B	Yes	Normal	Yes
C	Yes	Extended (100°C for 24 hr)	Yes
D	No	---	Yes

fully discharged prior to testing. No resonance node was found during vibration at any level. However, some terminal leaks were evident. After acceleration, one cell out of 30 leaked. After vibration tests, four more cells showed leakage. After shock, there were no more leaks (Table LI).

Overall terminal leakage is summarized as follows:

(1) Plate-lock cells: three cells out of 20, i.e., 15 percent

(2) No plate-lock cells: two cells out of 10, i.e., 20 percent

X-rays were taken of all cells. All cells using plate-lock did not show any shifting of electrode packs whereas five cells without plate-lock showed shifting of their electrode packs from 3.8 to 11.3 mm up toward the cover base. The two leaking cells in the no-plate-lock group were both in the same subgroup of five cells tested together and showing the maximum pack shifting. Figures 40 and 41 show some of the X-rays.

The cells with shifted packs were given a few shocks on a table in the vertical direction in an attempt to lower their packs to their normal position. Another X-ray was taken; it did not show any appreciable change. The cells were then recharged fully to 2.0 V (Table LI) and accepted an input in the range of 52 to 53 Ah. Table LII gives the average of all groups of cells treated in the same manner. No real difference appears in their electrical behavior.

However, on recharge, all cells acted normally except one (cell No. 31) of the control group D (no plate-lock). The end-of-charge voltage was only

TABLE LI

DATA ON PLATE-LOCK CELLS (PL)

(NHS-114 Series)

Group	Sub-Group	Cell No.	Cycle 1 Output, Ah_o	Leakage After Environmental Testing	Cycle 2 Input, Ah_i
A (PL; No Env. Test)	A-1	1	39.6	--	53.0
		2	39.3	--	53.0
		3	39.6	--	53.0
		4	39.6	--	53.0
		5	39.0	--	53.0
	A-2	6	38.9	--	52.4
		7	39.0	--	52.4
		8	38.7	--	52.4
		9	39.0	--	52.4
		10	38.8	--	52.4
B (PL; Env. Test)	B-1	11	40.2	--	52.2
		12	39.9	--	52.2
		13	39.7	--	52.2
		14	39.7	--	52.2
		15	40.3	--	52.2
	B-2	16	40.0	--	53.8
		17	39.8	--	53.8
		18	39.8	--	53.8
		19	39.8	P, N	53.8
		20	40.5	--	53.8
C (PL; Env. Test)	C-1	21	40.2	P, N	51.5
		22	40.4	--	51.5
		23	40.6	--	51.5
		24	40.4	P	51.5
		25	40.2	--	51.5
	C-2	26	39.5	--	52.3
		27	39.7	--	52.3
		28	39.8	--	52.7
		29	39.9	--	52.3
		30	39.9	--	52.7
D (No PL; Env. Test)	D-1	31	40.5	--	52.8
		32	40.5	--	52.8
		33	40.5	--	52.8
		34	40.6	--	52.8
		35	39.8	--	52.8
	D-2	36	40.2	P, N	52.8
		37	40.0	--	53.8
		38	40.3	--	53.8
		39	40.3	P, N	53.8
		40	40.0	--	53.8

NOTES: Cycle 1 - Charge is fixed input of 45 Ah_i resulting in an end of charge voltage = 1.95 to 1.96 V

Cycle 2 - Charge to 2.0 to 2.02 V.

P = positive terminal

N = negative terminal

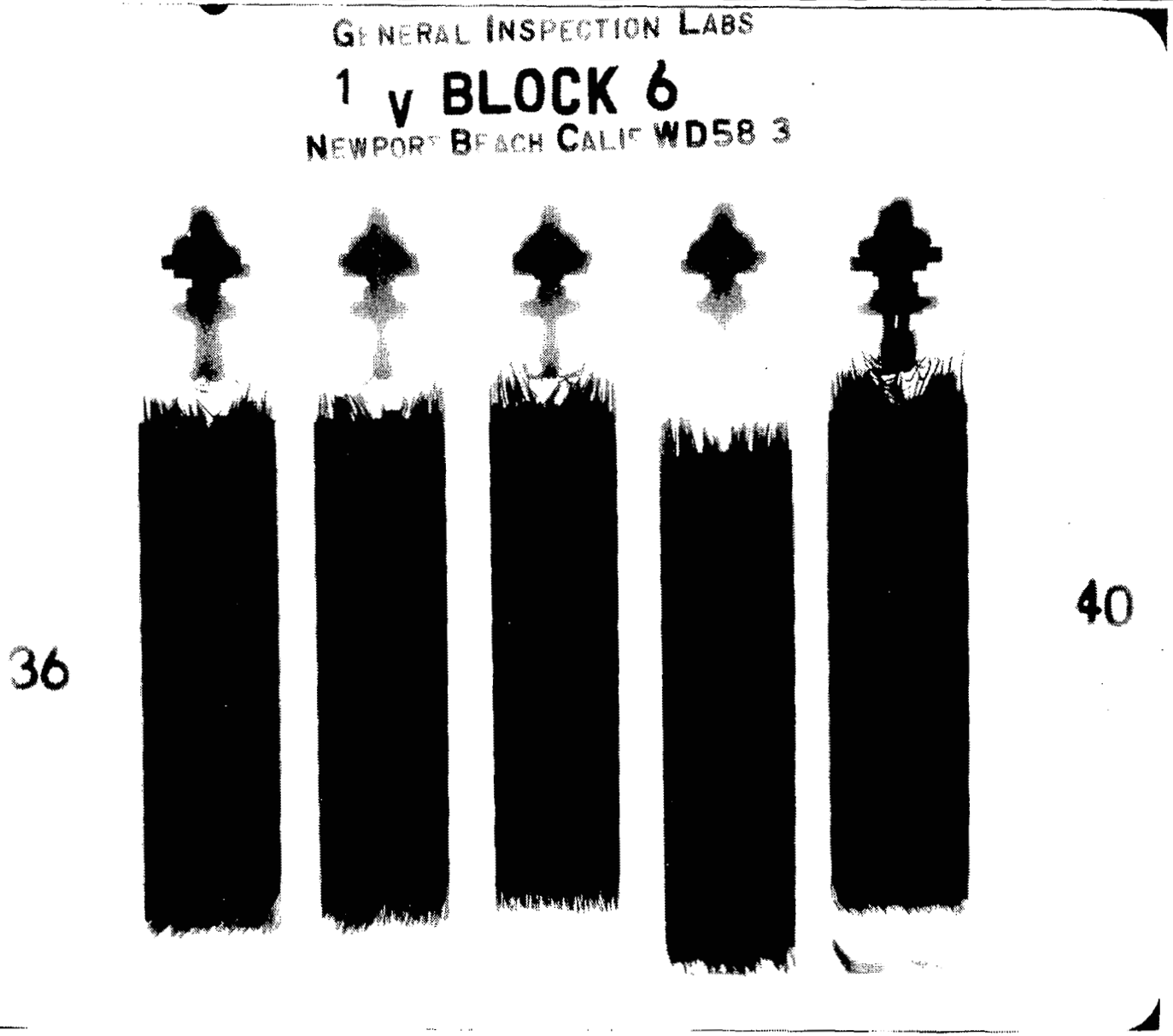


Figure 40. Cells Without Plate-Lock After Environmental Testing

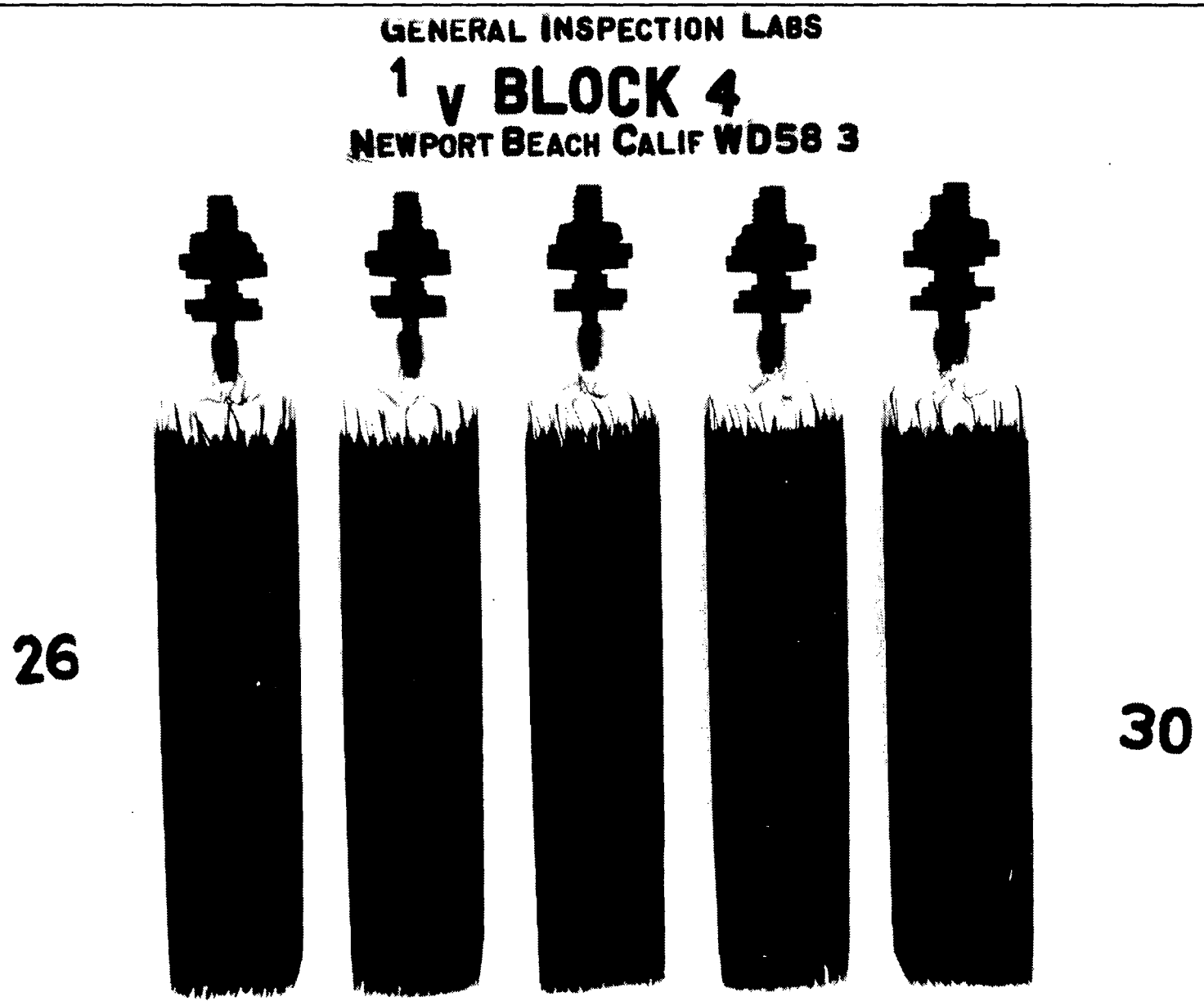


Figure 41. Plate-Lock Cells After Environmental Testing

TABLE LII

AVERAGE OF PLATE-LOCK CELL DATA
BEFORE AND AFTER ENVIRONMENTAL TESTING

Group	Characteristic	Cycle 1 Output, Ah_o	Group	Characteristic	Cycle 2 Input, Ah_i
A	Plate-lock	39.7	A	No Environmental Test	52.7
B			B	Environmental Test	52.5
C			C		
D	No Plate-lock	40.3	D	Environmental Test	53.2

1.91 V, even after the same input as the cells of the same group. This may be the sign of a slow short. It was decided to discharge the cell for a further check, along with cell No. 32 of normal behavior for a direct comparison.

Cell No. 31 delivered 43.0 Ah, while cell No. 32 delivered 51.4 Ah. The cells were recharged and put on charged stand with their sister cells intended for this test (subgroup D-1). The charged stand will show readily whether the suspicious cell is really damaged and to what extent.

All the cells were recharged and divided in two subgroups of five cells each. The first one was put on charged wet stand and the second one on a special cycling regime. Data are presented later in this section.

Although the first method of simple plate locking (PL) appeared satisfactory (no cell pack shifting during environmental testing), another method was tested on three cells. Besides the bottom plate locking as above on PL cells, a second epoxy locking was done around and in between the tabs, preventing motion of the tabs during vibration and resonance to avoid any possible damage to the connections. Also it was speculated that the tab vibration may have caused in some instances a motion of the terminals leading to a leakage; five PL cells had shown terminal leakage.

The three cells were formed, sealed, and submitted to the same environmental testing. No terminal leak appeared this time. The cells were X-rayed before and after environmental testing. The epoxy used had been previously loaded with barium oxide to make it appear on the X-ray to visualize its final location.

The cells were cycled once and behaved normally. One cell was cut open for examination and appeared normal. The other two cells were left on discharge stand until needed for further use.

Wet Stand. —Cells of the same subgroups were left on charged wet stand at room temperature to be discharged according to the NASA technical direction (10 A to 1.0 V followed by a drain at 2 A to 1.0 V at the end of 30 days). The cell No. 31 of the D Group, which was suspect of a slow short held its OCV but its output after the first 30-day period was 38.7 Ah compared with 48 Ah for the cells of the same subgroups. The cells were recharged and put back on stand for a second 30-day period. Its output was then in line with the others. Once cell with plate-lock (NHS-114-0) built in advance for checking purposes was left on straight charged stand without monthly discharge. It could provide useful information on prolonged stand. It has stood 83 days to date.

The data collected to date are presented in Table LIII showing inputs prior to each 30 day-period and outputs after the 30 day-period. The cells were again recharged and left on stand for another period.

Cycling. —The automatic cycling regime used is as follows (Code VK-3):

(1)	Cells in series:	Five
(2)	Frequency	Three cycles/day
(3)	Regime:	8-hr period
(4)	Discharge:	7 A for 2 hr
(5)	Charge:	2.5 A for 6 hr, voltage limited to 2.0 V/cell average (10.0 V total).

At cycle 11, 23, 27, 31, 33, Group B failed to meet the discharge requirements, dropping below the voltage specifications (five cells x 1.0 V = 5.0 V) about 1/2 hour prior to the end of the 2-hr scheduled discharge period. One cell at least must have reversed as evidenced by the low voltage (0.2 to 0.5 V total voltage for the five cells) at the end of the discharge period.

All these failures occurred during the night or over a weekend and the cells could not be stopped prior to the end of the discharge period.

TABLE LIII

CHARGE STAND OUTPUT AFTER 30-DAY PERIODS
PL CELLS ENVIRONMENTALLY TESTED

(NHS-114 Series)

Group	Cell No.	Input, [a] Ah	Output After First 30 Days, [c] Ah	Input, [b] Ah	Output After Second 30 Days, [c] Ah
A (PL, not environmentally tested)	1	53.0	49.5	41.0	40.8
	2	53.0	49.5	41.0	40.9
	3	53.0	49.5	41.0	40.7
	4	53.0	49.8	41.0	40.9
	5	53.0	49.0	41.0	40.6
	Average	53.0	49.4	41.0	40.8
B (PL, environmentally tested)	16	53.8	49.1	38.4	38.1
	17	53.8	48.9	38.6	38.5
	18	53.8	49.1	38.5	38.3
	19	53.8	49.5	40.5	40.3
	20	53.8	49.2	38.5	39.0
	Average	53.8	49.1	38.9	38.8
C (PL, environmentally tested)	26	52.3	48.0	38.4	38.3
	27	52.3	48.0	38.4	38.3
	28	52.7	48.5	39.6	39.4
	29	52.3	48.3	40.8	40.8
	30	52.7	48.7	38.8	38.8
	Average	52.5	48.3	39.2	39.1
D (No PL, environmentally tested)	31	52.8	38.9	38.9	38.9
	32	52.8	49.2	39.4	39.5
	33	52.8	48.2	40.3	40.2
	34	52.8	48.4	40.4	40.3
	35	52.8	47.5	39.8	39.7
	Average	52.8	46.4	39.8	39.7

[a] Charge 1.5 A to 2.02 V
[b] Charge 1.5 A to 2.0 V
[c] Discharge at 10 A to 1.0 V followed by 2 A to 1.0 V.

The cells recovered on charge and between the failed cycles mentioned above. However, these repeated reversals must have caused hydrogen generation and pressure buildup. At cycle 38, one cell No. 15 of this group blew out its top, tearing the tabs riveted to the terminal base, except one that was apparently disconnected from the rivet. This tab was from one end negative plate and could have been easily disconnected from its rivet, either during assembly or environmental testing if the assembly was poor. The bad contact made by this tab must have caused a capacity shortage of the cell with respect to the other cells of the group; this in turn explains the increasing imbalance of the cells during cycling and severe reversals of this particular cell.

Examination of the cell pack showed considerable sponge zinc deposited above the separator bags, which probably came out because of some overcharge during the imbalance of the cells. The OCV between all opposite polarity plates was still 1.86 V.

Pursuant to this incident, all cycling cells of this test (Groups A, B, C, D) were stopped and, after consultation with the NASA Project Monitor, a small hole was drilled into the cover of all cells to determine whether they had built up pressure. Only one cell of the same Group B (No. 14) released some pressure (as expected since Group B underwent several failures, which must have caused reversals of some cells).

All cells were discharged, averaging 46.4 Ah. One cell of each group was cut open for further examination. All their tabs were in order.

The cells were then recharged and put back on cycling on the same regime VK-3 mentioned above (three cycles per day). To date, the cells have reached the following number of cycles on this regime:

Group	Number of Cells	Cycles
A	4	196
B	3	158
C	4	130 to 150
D	4	160

Representative cycling curves at beginning and at cycle 150 are shown for each group in Figure 42 through Figure 49.

Cell Design With SWRI-GX Separator. —One new task was to fabricate cells of the HS-40-7 design, substituting to the McDonnell Douglas inorganic separator, the organic separator film developed for JPL by Southwest Research Institute (grafted, crosslinked and irradiated polyethylene film) coded GX.

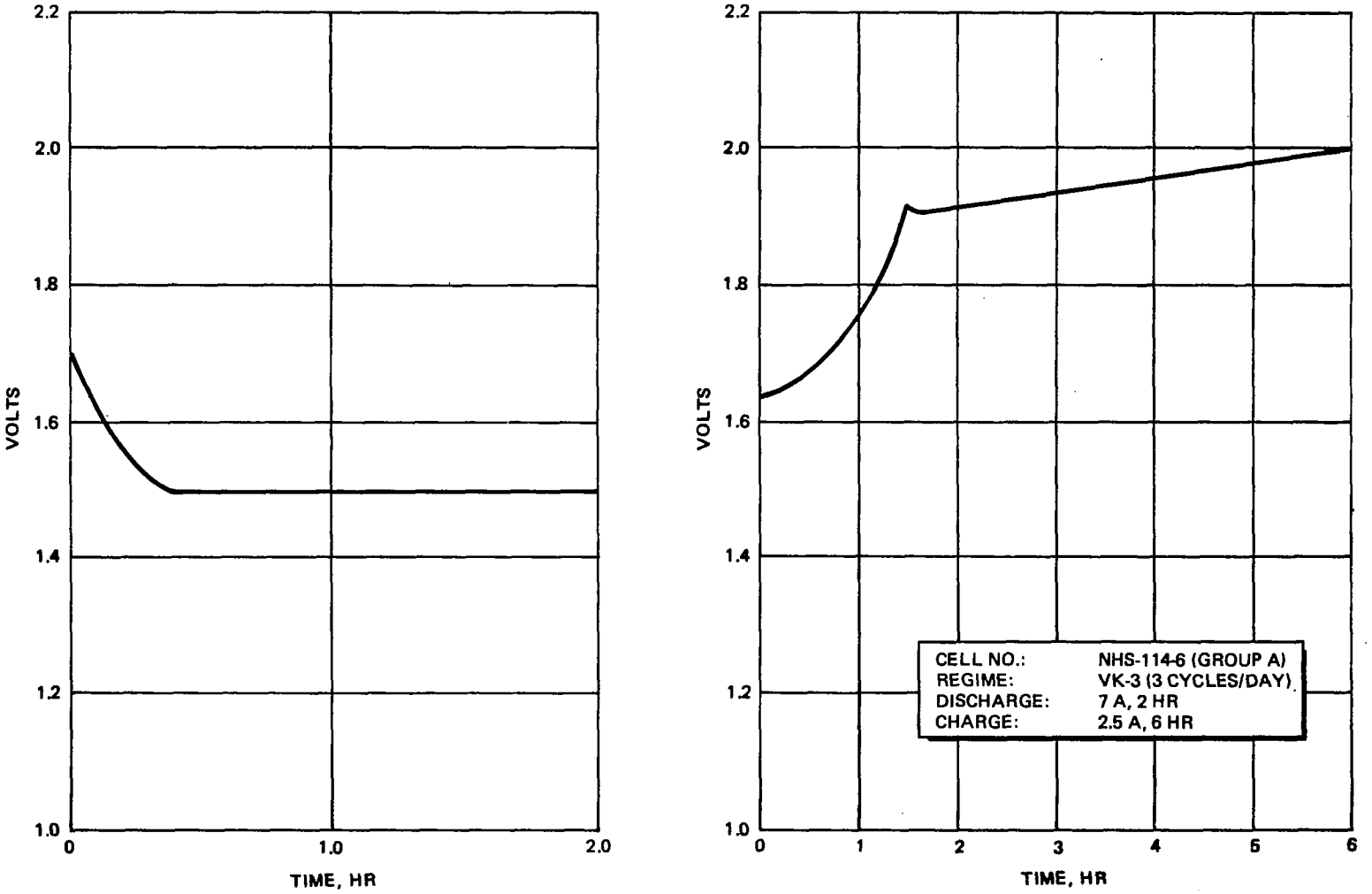


Figure 42. Cycling Curve, Design 7, Cycle 8

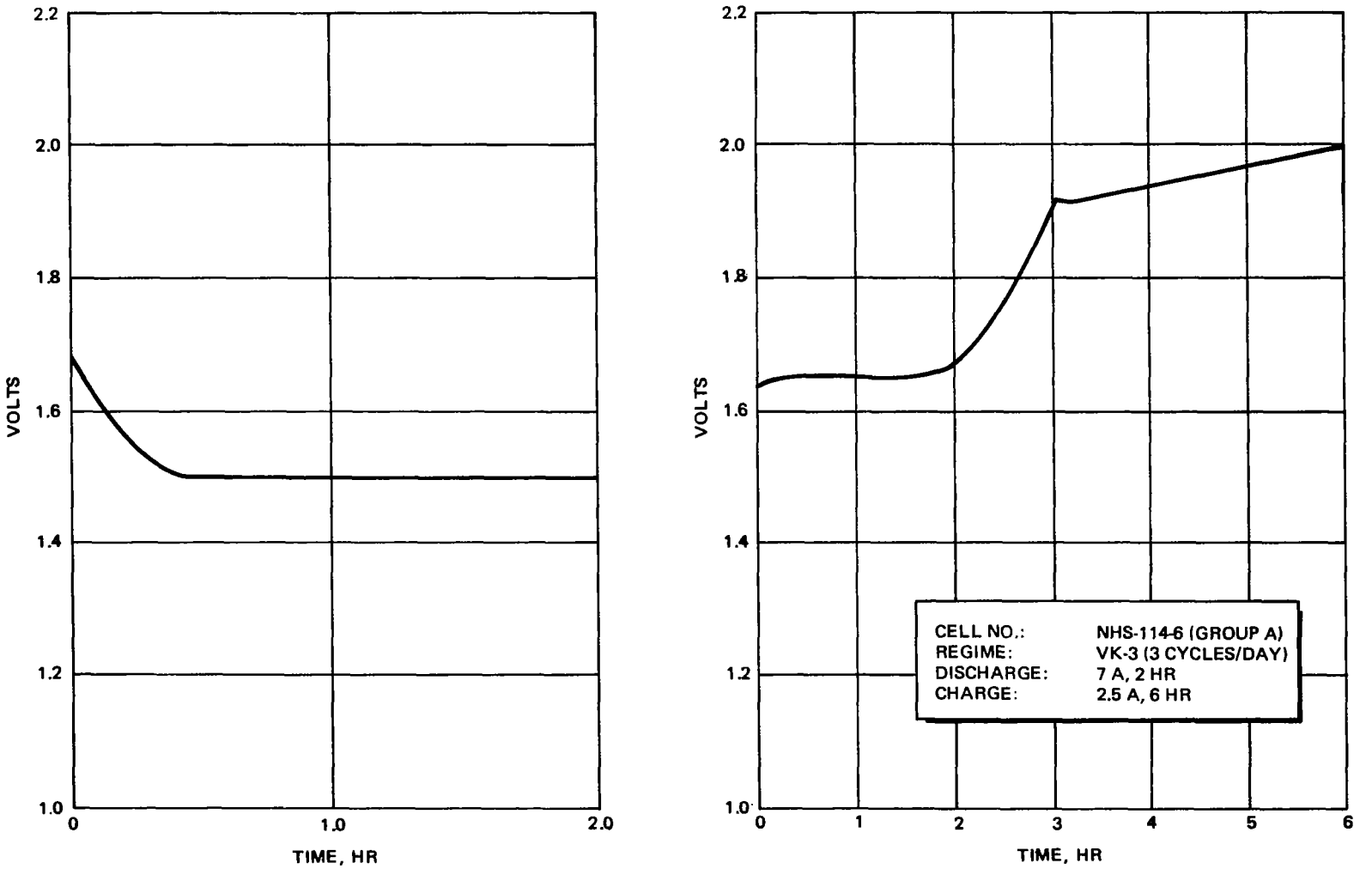
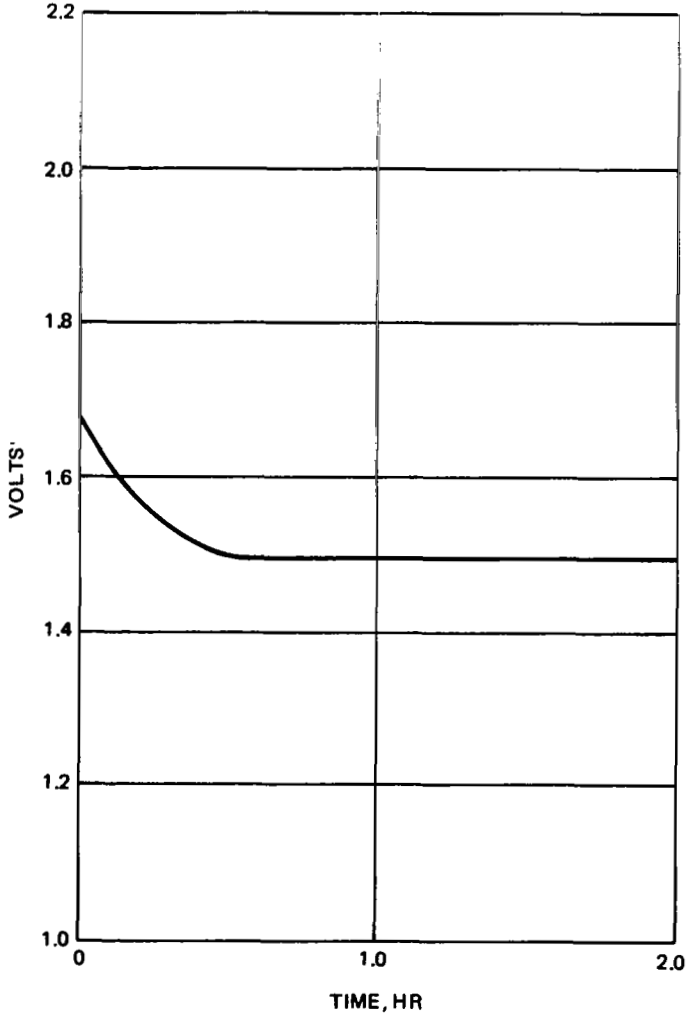


Figure 43. Cycling Curve, Design 7, Cycle 150



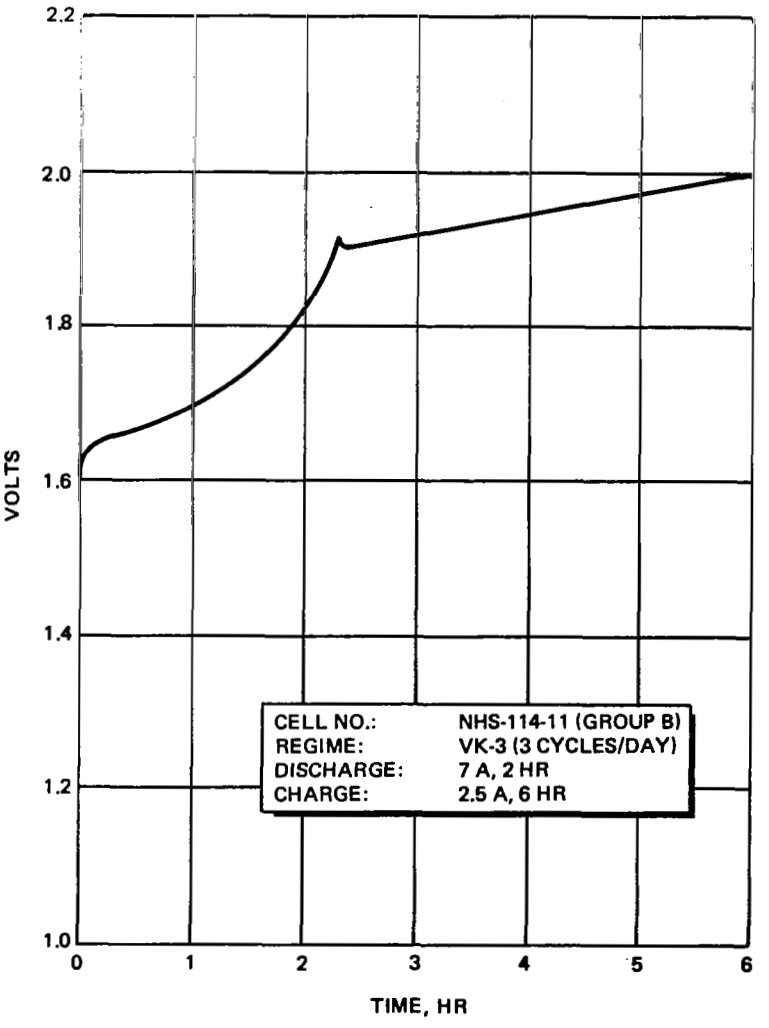


Figure 44. Cycling Curve, Design 7, Cycle 8

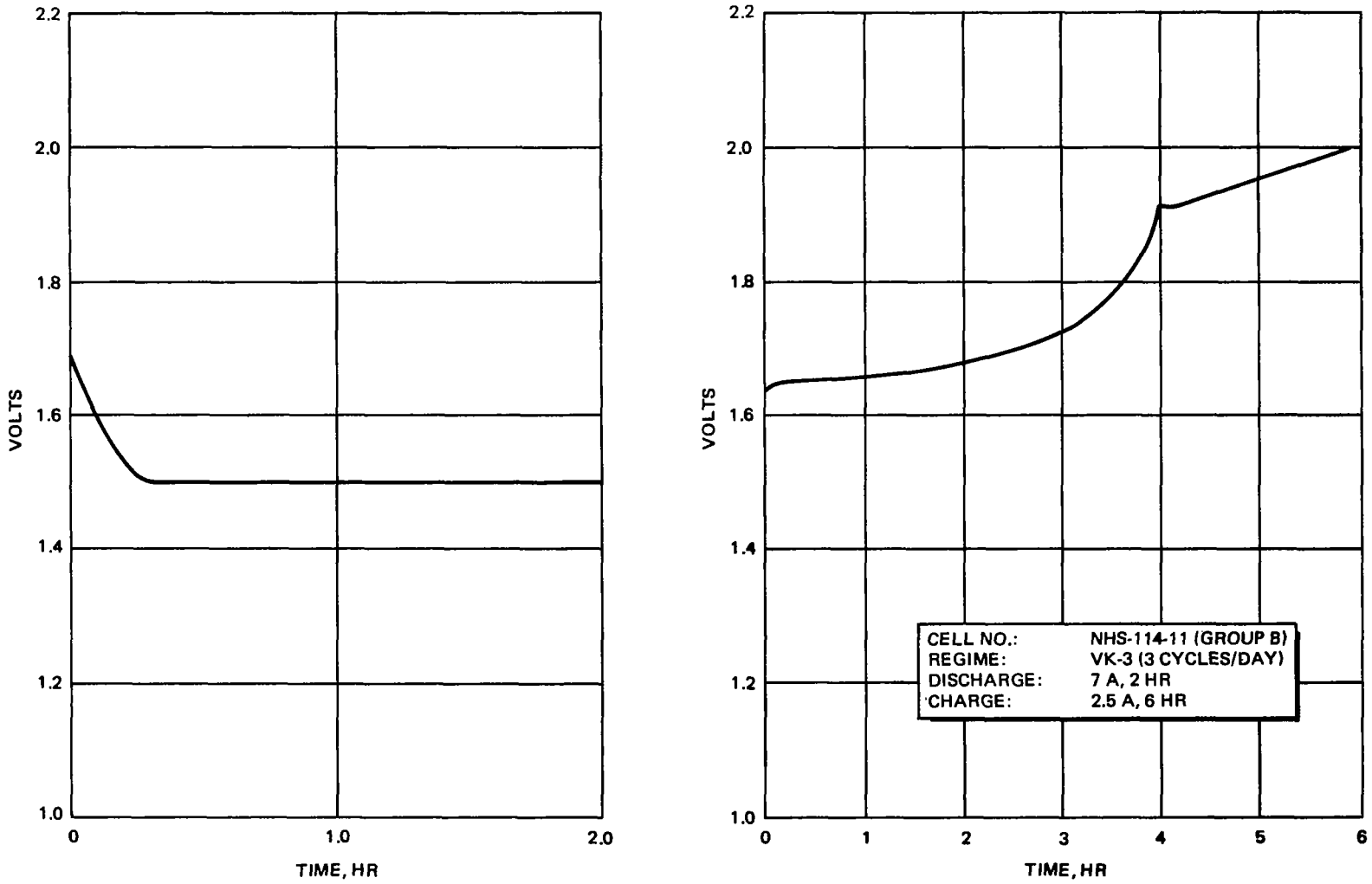


Figure 45. Cycling Curve, Design 7, Cycle 150

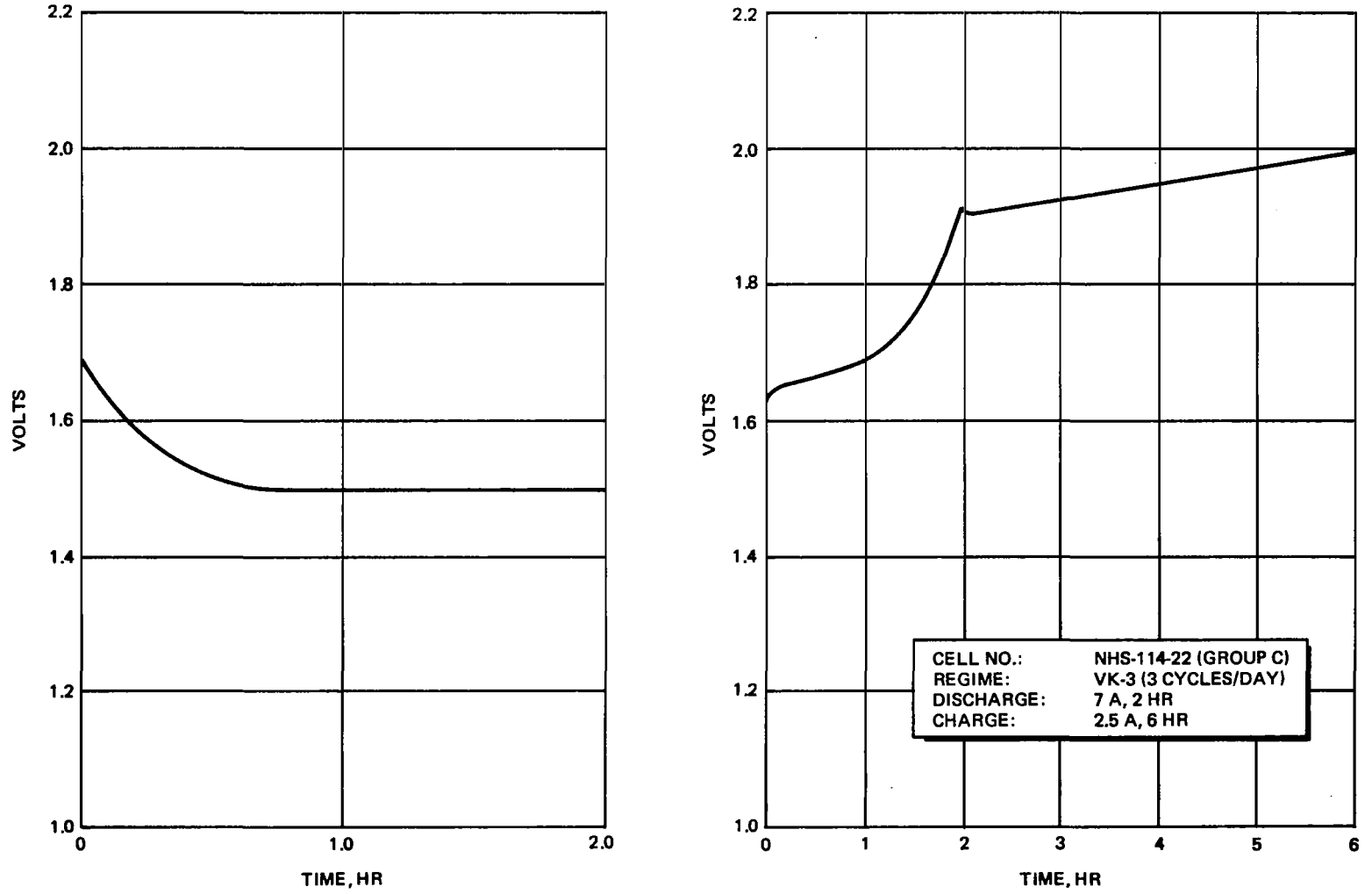


Figure 46. Cycling Curve, Design 7, Cycle 8

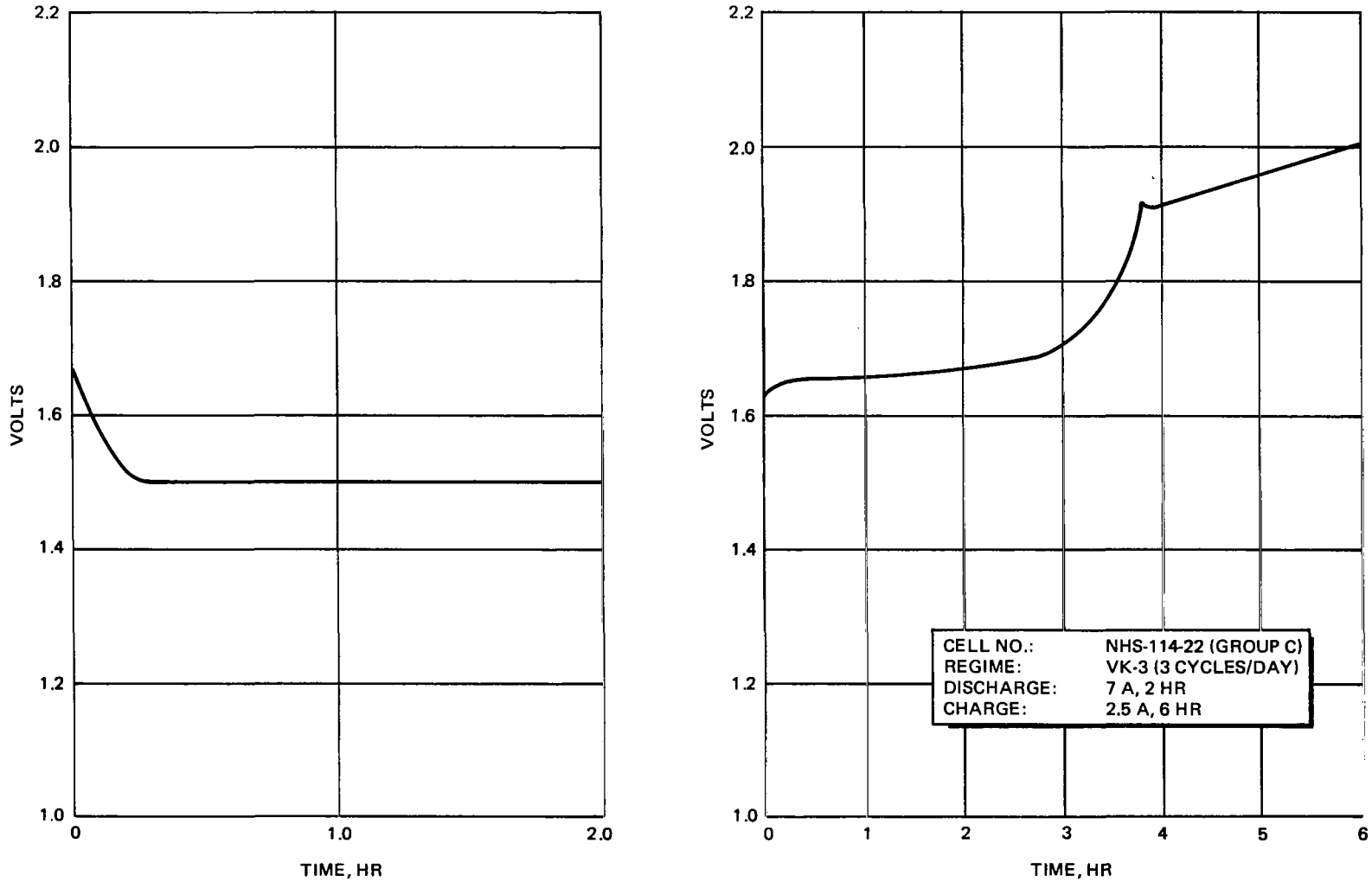


Figure 47. Cycling Curve, Design 7, Cycle 125

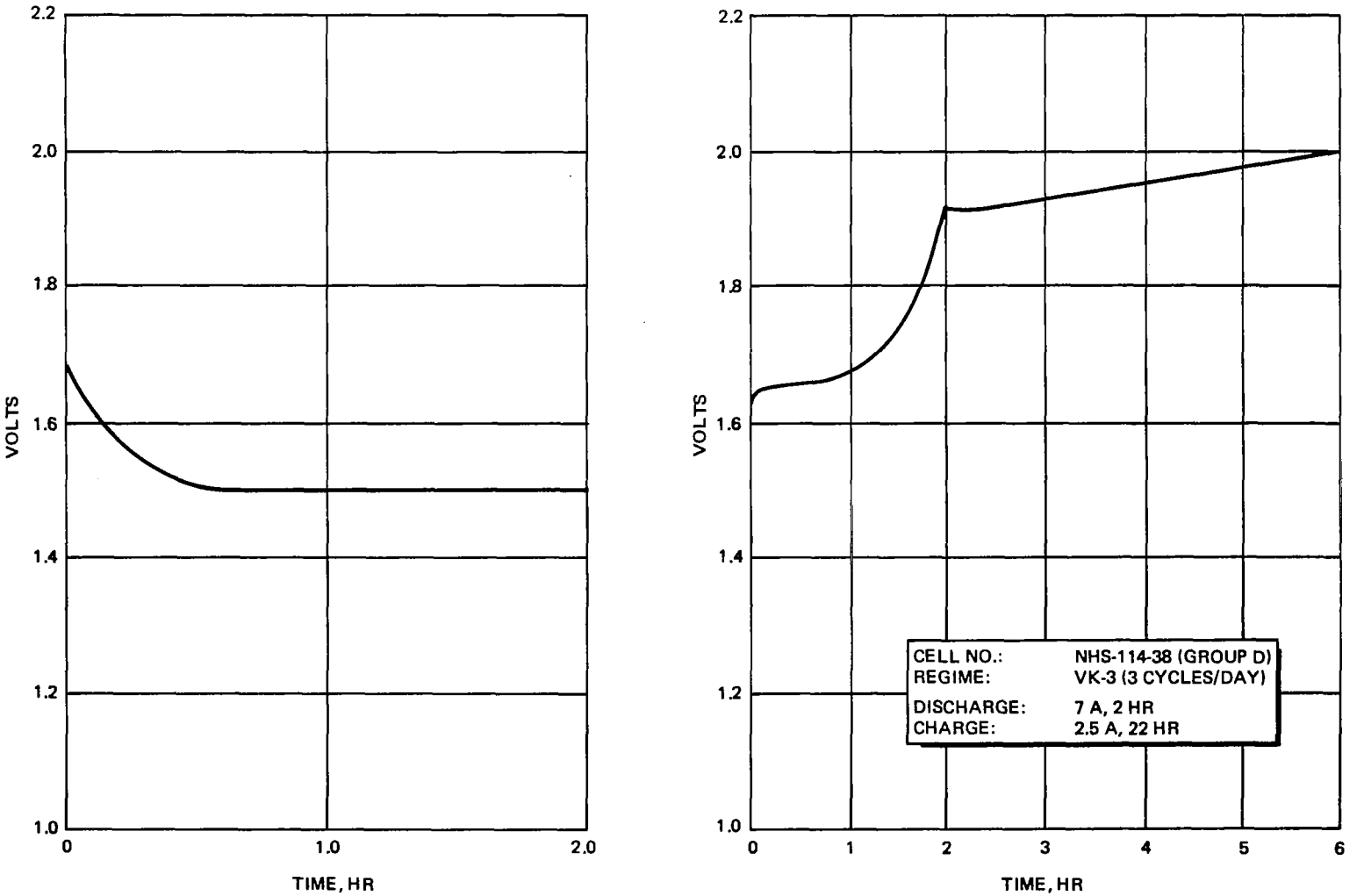


Figure 48. Cycling Curve, Design 7, Cycle 8

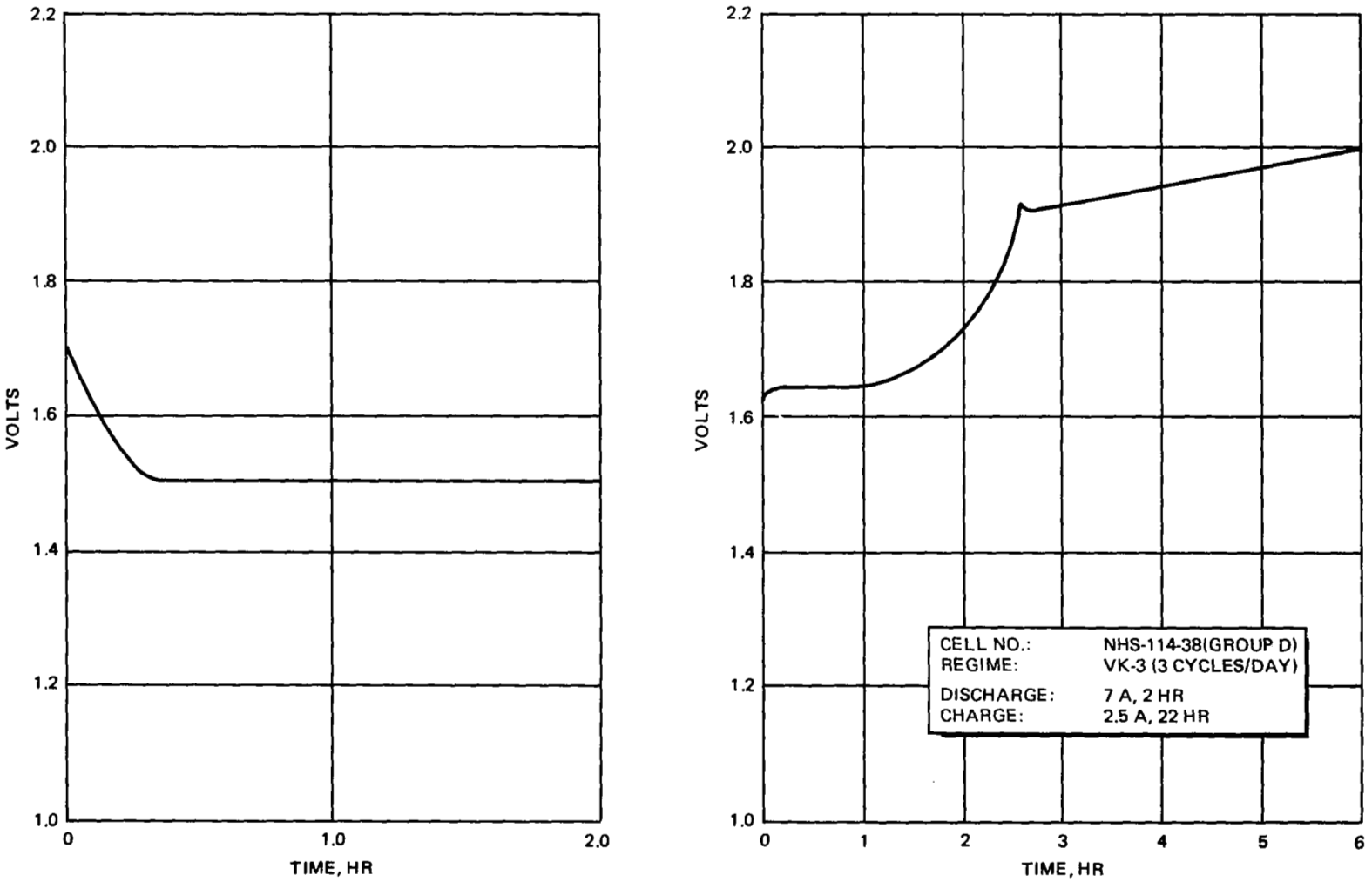


Figure 49. Cycling Curve, Design 7, Cycle 150

It was calculated that eight layers of GX could be accommodated in place of the thin inorganic coating used in the HS-40-7 cell. This hybrid design is coded HS-40-7GX. The SWRI-GX separator material was ordered and received in five rolls of approximately 100 ft^2 each. The resistance as indicated in their accompanying data sheet varies from 13 to 23 $m\Omega$ -$in.^2$ depending on the roll.

Selecting material from the roll of 13 to 15 $m\Omega$ -$in.^2$, one cell was fabricated to establish the assembly procedure of HS-40-7 type electrodes with eight layers of GX membrane. No mechanical difficulty was encountered when allowing 2 mil thickness for the GX membrane. The cell was fabricated in a polysulfone case to also determine the proper amount of electrolyte.

The cell was charged by the normal charge procedure of the regular HS-40-7, i.e., at 1.5 A to 2.05 V cutoff, or to an input of 45 Ah, whichever occurs first. The coulombic efficiency, on discharge, was 98 percent compared with 91 to 92 percent for the HS-40-7 cell, probably due to a better and more uniform wetting of the separator. On the second cycle, however, there is practically no difference.

To allow full charge input on the GX cell, the cutoff voltage on the second cycle was set at 2.05 V, made possible by the fact that the cell was vented. The output was then 53.9 Ah. The normal procedure of the HS-40-7, when sealed is to charge not higher than 2.0 V or 45 Ah_i input. The cell always reached 45 Ah_i input with an end voltage of 1.98 V. When allowing the cell to reach 2.0 V, the input and output are then comparable to those of the GX cell, as evidenced by the second cycle in Table LIV.

The total resistance offered by 8 GX layers is only 120 $m\Omega$-$in.^2$, when calculated from the accompanying data sheet. However, the polarization tests run on the GX cell showed that, although voltages at low rates (up to 6 A) are comparable to those obtained with the inorganic separator, the polarization curve is steeper at rates over 10 A, probably due to poor diffusion (Figure 50). The maximum current that could be drawn before the voltage dropped below 1.0 V was only 80 A, whereas the cell with inorganic separators can reach 120 A with a voltage dipping to 1.1 V. The difference with the regular HS-40-7 cell was as much as 230 millivolts at the C/1 rate (40 A).

To clear up this inconsistency, actual resistance measurements were made with our own resistivity test set-up. The test was carried out with 45-percent KOH on duplicate samples taken from each of the five rolls of GX material. Data are presented in Table LV. The mean value of all rolls is 43 $m\Omega$-$in.^2$, giving for a presumed thickness of 1 mil for the GX membrane a resistivity of 108 ohm-cm.

Our 3420-25 FM inorganic separator, measured under the same conditions, gives a mean value of 146 $m\Omega$-$in.^2$ or a resistivity of 24 ohm-cm (for a thickness of 15 mils).

TABLE LIV

COMPARATIVE PERFORMANCE
OF HS-40-7 AND HS-40-7 GX CELLS

Cycle	Sequence	GX Cell	-7 Cell	-7 Cell
1	Charge	-------- Normal Procedure --------		
	End Voltage, V	1.95	1.96	1.96
	Input, Ah_i	45	45	45
	Discharge			
	Plateau Voltage, V	1.49	1.49	1.49
	Output, Ah_0	44.2	41.4	42.3
	Coulombic Efficiency, Percent	98	91.5	92
2	STATE	Not Sealed	Sealed	Sealed
	Charge	--	Normal Procedure	--
	End Voltage, V	2.05	1.98	2.00
	Input, Ah_i	54.3	45.0	52.8
	Discharge			
	Plateau Voltage, V	1.49	1.49	1.49
	Output, Ah_0	53.9	44.7	51.4
	Coulombic Efficiency, Percent	99	99	97

Comparing the sum of resistances of all membrane layers between opposite polarity plates, the HS-40-7 cell has a total resistance of 292 $m\Omega$-in.^{2} whereas the HS-40-7 GX has 450 $m\Omega$-in.^{2}.

The GX was measured by SWRI in a 40-percent KOH solution. But the difference in KOH concentration in the resistance measurement does not account for all the discrepancy. KOH has a resistivity of approximately 2.5 ohm-cm at 45 percent and 2.0 at 40 percent, i.e., only 25-percent increase. The actual measurement in 45 percent gives a value more than double, after adjusting the SWRI value for KOH concentration change.

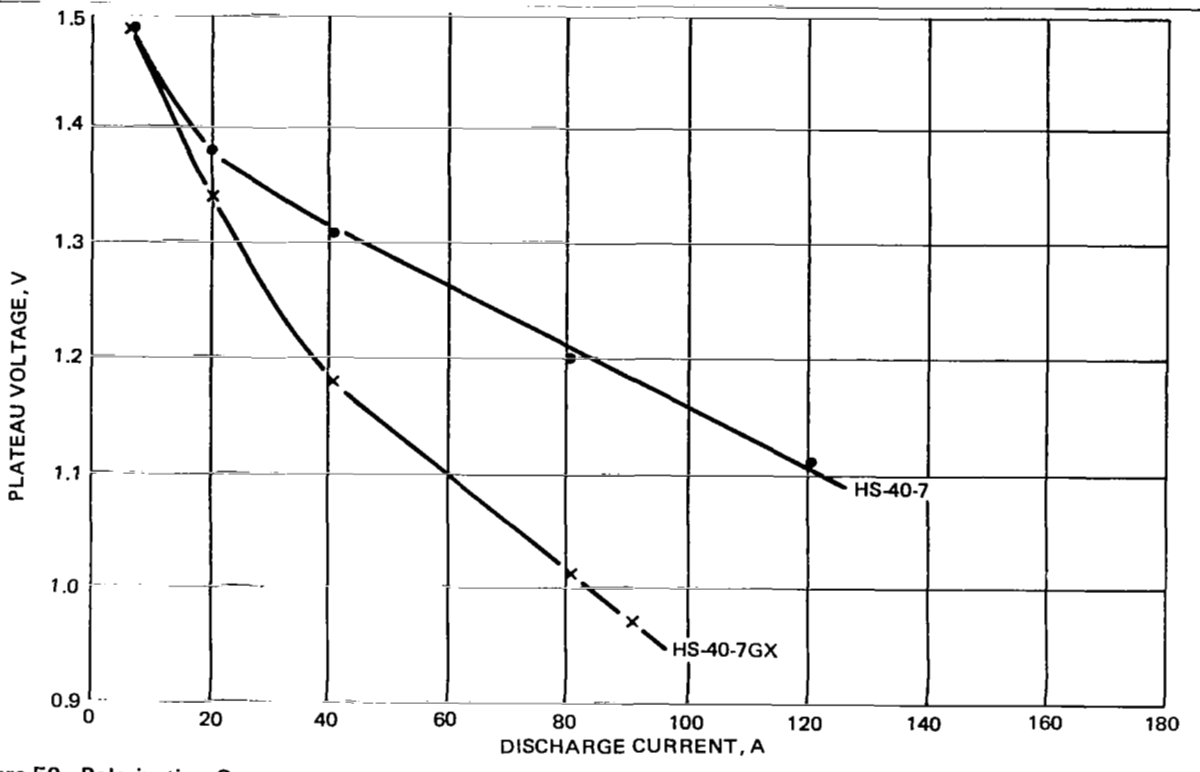


Figure 50. Polarization Curves

It may be possible to decrease the resistance of the GX cell design, if so desired or when necessary, by removing the negative bag, with the attendant problem of faster zinc-shape change. Cycling of the present cells fabricated according to the first design will tell to what extent a modification of this design is necessary

Cycling Data. —The cell in the polysulfone case (NHS-119-GX) was then used on the same automatic cycling regime used for the plate-lock cells for direct comparison. The regime 2, coded VK-3, is as follows:

(1) Frequency: Three cycles per day

(2) Regime: 8 hr

(3) Discharge: 7 A for 2 hr

(4) Charge: 2.5 A for 6 hr, voltage limited to 2.0 V/cell

TABLE LV

RESISTANCE OF SEPARATORS MEASURED BY OUR METHOD (IN 45-PERCENT KOH)

Type	Sample 1, $m\Omega$-in.^{2}	Sample 2, $m\Omega$-in.^{2}	Average, $m\Omega$-in.^{2}	Thickness, mils	Resistivity, Ω-cm
GX					
Roll No. 1	33	47			
No. 2	42	52			
No. 3	42	52			
No. 4	42	47			
No. 5	33	40			
Average	38.4	47.6	43	1	108
3420-25FM	137	155	146	15	24
Cellophane(a)	8.2	8.3	8.2	3	7

(a)Measured for reference, as value is known in the literature.

To date, the cell has reached 162 cycles. Capacity checks were made twice:

(1) Cycle 93: 49.3 Ah

(2) Cycle 162: 52.2 Ah

The cell was recharged and put back on cycling. Cycling curves are shown in Figures 51 and 52, for cycle 6 and cycle 150 respectively.

Another cell with GX was fabricated in a PPO case and handled identically to earlier HS-40-7 cells, viz. formed, fully sealed, and heat sterilized at 135°C for 200 hr. It was then cycled on a 100-percent depth, total discharge regime, to establish its full capability. To date, this cell, HS-123 GX, has reached 11 cycles. Data are presented in Table LVI. The capacity maintenance is still good so far, which shows a good zinc shape retention as a result of the overall design.

Based on these cycling results, the same design was adopted for the manufacture of the 41 cells as required by the work statement.

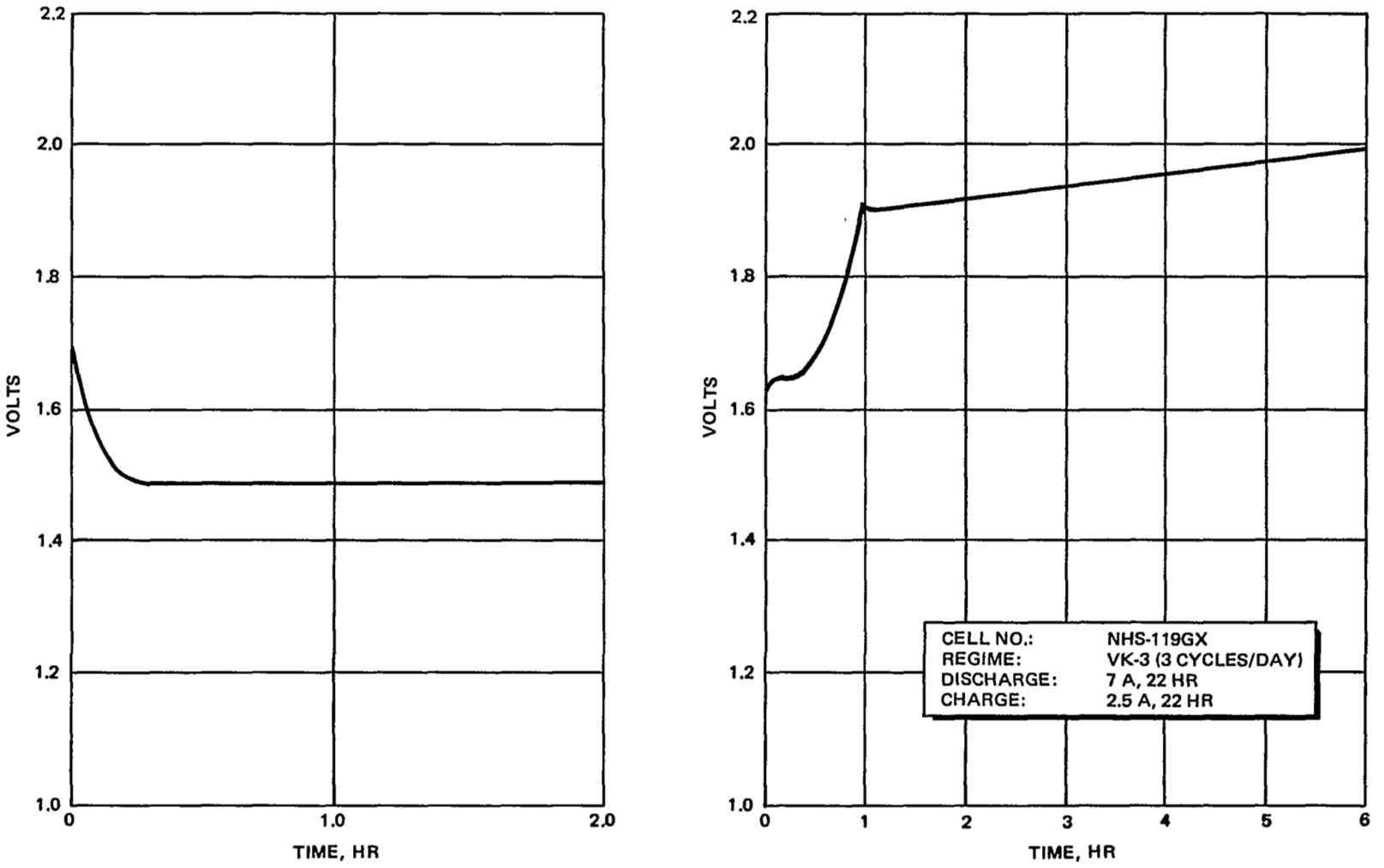
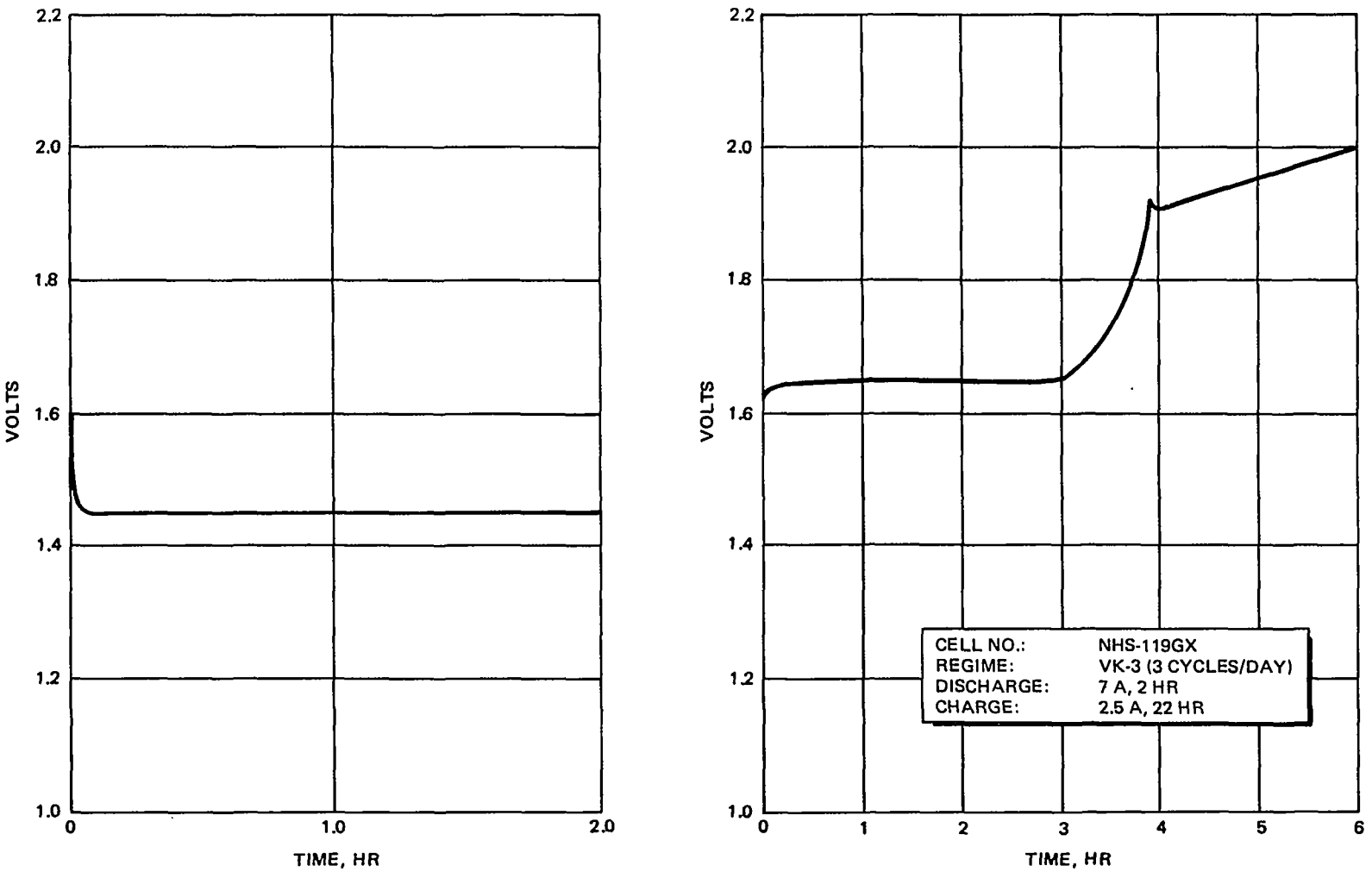


Figure 51. Cycling Curve, Design 7GX, Cycle 6



Fi[illegible]. Cycling Curve, Design 7GX, Cycle 150

TABLE LVI

CELL HS-123-GX CAPACITY OUTPUTS,
TOTAL DISCHARGE REGIME

Discharge: 6 A to 1.0 V

Charge: 1.5 A to 2.0 V or 45 Ah input, whichever occurs first.

Cycle	Input, Ah_i	End Voltage	Output, Ah_o
1	45.0	1.95 V	44.2
2	45.0	1.91	42.1
3	45.0	1.98	40.7
4	45.0	1.96	43.6
5	45.0	1.98	44.8
6	45.0	1.97	45.3
7	45.0	1.96	45.6
8	45.0	1.98	45.3
9	45.0	1.97	45.2
10	45.0	1.96	45.6
11(a)	52.0	1.99	51.4

(a) On cycle 11, cell was charged to voltage. not to fixed input.

Delivery

Cells

Cells left uncompleted from an ex-Viking project inventory were transferred to the present NASA program and were scheduled, according to Technical Direction No. 3, to be completed, cycled twice and delivered. The breakdown is as follows:

(1) 155 cells HS-40-7 design

(2) 40 cells HS-40-8 design

(3) 41 cells HS-40-7GX design

The cells were formed (charge and discharge cycle 1) in a vented state, sealed, then given another cycle (cycle 2) at a specified rate: 9 A for 3 hr, followed by a drain at 3 A to 1.0 V.

The first category of 155 cells of the HS-40-7 design is numbered M-1 through M-155. Data are given on Tables LVII through LXII. The cells were in small groups of 20 cells at a time on one single set-up. This accounts for some small differences between groups, although cells of each group have outputs clustered around their average. However the grand average of 155 cells is 41.0 Ah for the first cycle and 41.9 Ah for the second cycle. The average weight is 886.2 g per cell. Cell specifications are given in Appendix A in a short form. Cell engineering drawings, design information and fabrication procedures were delivered to NASA.

The second category of 40 cells of the HS-40-8 design is numbered 8-1 through 8-40. These cells required a second formation cycle, due to the increased separator system (three layers) to bring their capacities to the 40-Ah level. The average weight is 868.3 g per cell. Data are on Table LXI averages were then 41.7 Ah for the vented cycle and 39.9 Ah for the sealed cycle. Cell specifications are given in Appendix A in a short form. Cell engineering drawings, design information and fabrication procedures were delivered to NASA.

The third category of 41 cells of the HS-40-7GX design is numbered M-156 GX through M-196 GX. Data are presented in Table LXII. Averages are 42.7 Ah for cycle 1 (vented) and 44.6 Ah for cycle 2 (sealed). The average weight is 840.1 grams per cell (Cell Specifications, Appendix A).

Separator Bags

A certain number of separator bags for positive electrodes supplied by NASA for another project were fabricated and shipped. They were:

(1) 75 bags with inorganic separator 3420-25

(2) 75 bags with inorganic separator 3420-09

Data Package

The following were delivered to NASA:

(1) Engineering drawings, design information, and fabrication procedures for the HS-40-7 and HS-40-8 cells.

(2) Design drawings for the HS-40-10 cell.

(3) Environmental Test Report; tests run and report written by Wyle Testing Laboratories, Norco, Calif.

Materials

All unused inorganic separator materials, PPO material and unused hardware for the 40 Ah cell were delivered to NASA.

TABLE LVII

40 CELLS HS-40-7 OUTPUTS

(Series M-)

No.	Cycle 1, Ah_o	Cycle 2, Ah_o	No.	Cycle 1, Ah_o	Cycle 2, Ah_o
1	41.0	40.1	21	42.2	44.4
2	40.8	38.9	22	42.3	44.6
3	40.8	39.5	23	42.1	44.5
4	40.8	40.1	24	42.2	44.0
5	41.2	39.9	25	42.1	44.0
6	41.0	41.0	26	42.0	44.1
7	41.3	39.1	27	42.0	43.7
8	41.2	39.2	28	42.4	44.0
9	41.2	39.2	29	42.6	44.9
10	41.6	40.0	30	42.6	44.6
11	41.5	39.2	31	42.2	44.2
12	41.8	39.1	32	41.3	43.4
13	42.3	39.0	33	41.5	44.9
14	42.1	38.7	34	41.5	44.4
15	42.2	38.7	35	41.3	43.4
16	42.0	39.1	36	41.6	44.0
17	42.1	37.3	37	41.7	44.0
18	42.3	37.5	38	41.7	44.9
19	42.6	38.3	39	41.4	44.8
20	42.4	43.0	40	41.5	44.2
Subaverage	41.6	39.4	--	41.9	44.2
Average of 40 Cells	41.7	41.8			

Notes:
Cycle 1 (Vented) = 6 A to 1.0 V + 2 A to 1.0 V.
Cycle 2 (Sealed) = 9 A for 3 hr + 3 A to 1.0 V.

TABLE LVIII

40 CELLS HS-40-7 OUTPUTS
(Series M-)

No.	Cycle 1, Ah_o	Cycle 2, Ah_o	No.	Cycle 1, Ah_o	Cycle 2, Ah_o
41	42.0	45.6	61	40.8	45.0
42	42.0	45.4	62	41.0	45.5
43	41.8	44.0	63	41.3	46.0
44	41.9	44.4	64	41.3	45.4
45	41.9	44.7	65	40.9	46.2
46	41.7	44.7	66	40.8	43.9
47	42.1	45.6	67	40.9	44.4
48	41.8	44.0	68	40.7	45.2
49	41.8	45.3	69	40.5	46.1
50	41.7	45.6	70	40.4	45.2
51	41.7	44.6	71	40.9	44.7
52	41.6	43.3	72	40.4	44.7
53	42.4	45.2	73	40.4	45.2
54	42.2	45.6	74	41.1	46.2
55	42.2	45.3	75	40.7	44.2
56	42.3	44.7	76	40.7	45.1
57	42.0	45.1	77	40.9	44.2
58	41.4	45.5	78	41.1	46.0
59	41.8	45.7	79	41.3	45.8
60	42.0	45.7	80	40.8	44.7
Subaverage	41.9	45.0	--	40.9	45.2
Average of 40 Cells	41.4	45.1			
Average of Previous Cumulative Cells (80)	41.5	43.5			

Note:
Cycle 1 (Vented) = 6 A to 1.0 V + 2 A to 1.0 V.
Cycle 2 (Sealed) = 9 A for 3 hr + 3 A to 1.0 V.

TABLE LIX

40 CELLS HS-40-7 OUTPUTS

(Series M-)

No.	Cycle 1, Ah_o	Cycle 2, Ah_o	No.	Cycle 1, Ah_o	Cycle 2, Ah_o
81	41.5	40.0	101	40.2	40.3
82	41.3	40.4	102	40.4	40.0
83	41.2	40.7	103	40.5	39.7
84	41.2	39.8	104	40.6	39.8
85	41.5	39.1	105	40.8	39.4
86	41.9	40.9	106	40.7	38.9
87	41.6	38.2	107	40.7	37.4
88	41.7	39.1	108	41.0	40.9
89	41.8	40.0	109	40.9	40.7
90	41.7	40.6	110	40.9	40.8
91	41.3	38.5	111	41.0	41.5
92	40.9	37.0	112	40.9	39.8
93	41.0	40.7	113	41.5	40.7
94	41.2	39.7	114	41.2	41.0
95	40.9	39.7	115	41.1	39.5
96	41.2	38.9	116	41.1	38.3
97	41.3	41.5	117	41.3	40.7
98	40.1	40.3	118	40.7	41.2
99	40.0	40.2	119	40.7	41.5
100	40.2	40.9	120	41.0	42.9
Subaverage	41.1	39.8	--	40.9	40.2
Average of 40 Cells	41.0	40.0			
Average of Previous Cumulative Cells (120)	41.2	41.8			

Notes:
Cycle 1 (Vented) = 6 A to 1.0 V + 2 A to 1.0 V.
Cycle 2 (Sealed) = 9 A for 3 hr + 3 A to 1.0 V.

TABLE LX

35 CELLS HS-40-7 OUTPUTS

(Series M-)

No.	Cycle 1, Ah_o	Cycle 2, Ah_o	No.	Cycle 1, Ah_o	Cycle 2, Ah_o
121	41.0	43.2	141	40.6	42.6
122	40.8	43.4	142	40.5	44.0
123	40.9	42.5	143	40.5	42.4
124	40.7	41.5	144	40.2	42.2
125	40.6	42.4	145	40.2	42.5
126	40.6	41.7	146	40.2	43.1
127	40.7	42.8	147	40.2	42.2
128	40.6	41.8	148	40.1	41.6
129	40.6	42.9	149	40.0	43.3
130	40.8	43.3	150	40.2	42.1
131	40.6	42.8	151	39.9	43.2
132	40.4	42.8	152	39.8	42.4
133	41.3	44.0	153	39.7	41.3
134	41.2	43.1	154	40.1	41.6
135	41.5	42.5	155	40.2	41.8
136	41.2	41.5			
137	41.4	42.7			
138	41.6	42.0			
139	41.5	43.1			
140	41.5	43.8			
Subaverage	41.0	42.7	--	40.1	42.4
Average of 35 Cells	40.6	42.5			
Average of Previous Cumulative Cells (155)	41.0	41.9			

Notes:
Cycle 1 (Vented) = 6 A to 1.0 V + 2 A to 1.0 V.
Cycle 2 (Sealed) = 9 A for 3 hr + 3 A to 1.0 V.

TABLE LXI

40 CELLS HS-40-8 OUTPUTS

(Series 8-)

No.	Cycle 1A, Ah_o [a]	Cycle 2, Ah_o [b]	No.	Cycle 1A, Ah_o [a]	Cycle 2, Ah_o [b]
1	40.3	38.5	21	42.3	41.0
2	39.5	39.3	22	42.3	41.5
3	39.3	39.1	23	42.2	41.0
4	39.4	39.1	24	42.3	41.5
5	38.9	39.4	25	42.2	41.3
6	39.7	39.7	26	42.1	40.5
7	42.3	37.7	27	42.2	40.1
8	41.5	37.7	28	42.3	42.1
9	42.4	37.6	29	42.2	40.1
10	42.3	39.2	30	42.2	38.8
11	42.6	40.2	31	42.0	40.7
12	42.5	39.2	32	42.1	42.1
13	41.9	38.5	33	42.0	41.1
14	41.4	37.7	34	42.0	42.2
15	41.7	37.7	35	42.1	41.9
16	41.5	38.2	36	42.0	41.8
17	41.9	37.8	37	42.0	42.0
18	42.0	38.2	38	42.0	42.0
19	42.2	38.5	39	42.0	41.0
20	42.2	39.2	40	42.0	39.0
Subaverage	41.3	38.6	--	42.1	41.1
Average of 40 Cells	41.7	39.9			

Notes:

[a] Cycle 1 (Vented) = Average output was 36.3 Ah.

[a] Cycle 1A (Vented) = Repeat of cycle 1 = 6 A to 1.0 V + 2 A to 1.0 V.

[b] Cycle 2 (Sealed) = Charge to 2.0 V
Discharge 9 A for 3 hr + 3 A to 1.0 V.

TABLE LXII

41 CELLS HS-40-7GX OUTPUTS

(Series M-)

No.	Cycle 1, Ah_o [a]	Cycle 2, Ah_o [b]	No.	Cycle 1, Ah_o [a]	Cycle 2, Ah_o [b]
156	42.6	44.6	176	42.2	44.6
157	43.4	44.6	177	43.4	44.6
158	42.7	44.6	178	43.5	44.6
159	42.8	44.6	179	43.6	44.6
160	42.9	44.6	180	43.5	44.6
161	43.1	44.6	181	43.6	44.6
162	43.1	44.6	182	43.6	44.6
163	43.0	44.6	183	43.5	44.6
164	42.9	44.6	184	43.6	44.6
165	43.0	44.6	185	43.4	44.6
166	42.9	44.6	186	43.4	44.7
167	41.5	44.6	187	44.1	44.6
168	41.6	44.6	188	44.0	44.8
169	41.8	44.6	189	42.1	44.6
170	41.9	44.6	190	42.1	44.6
171	42.9	44.6	191	42.2	44.6
172	41.9	44.6	192	42.1	44.6
173	42.1	44.6	193	42.1	44.6
174	42.3	44.8	194	42.0	44.6
175	42.3	44.7	195	41.9	44.6
			196	41.8	44.6
Subaverage	42.5	44.6		42.9	44.6
Average of 41 Cells	42.7	44.6			

(All Inputs = 45 Ah)

Notes:

[a] Cycle 1 (vented) = 6 A to 1.0 V + 2 A to 1.0 V

[b] Cycle 2 (sealed) = 9 A for 3 hr + 3 A to 1.0 V

CONCLUSIONS AND RECOMMENDATIONS

From the data presented so far, it can be inferred that the present program achieved more than its original objectives. As the requirements were increased during the course of the program, the time element due to the new long stand (21 months) did not permit reaching the ultimate objective through the actual cells. But enough data on earlier models have been accumulated to draw the conclusion that 24-month wet life will be achieved.

The Design HS-40-7, which is being extensively tested, has a good chance of attaining this target in about 6 months. However Design 8, having an extra separator layer, will certainly meet the requirements more easily. Design 8 cells only are cycling at this time. More cells were delivered to NASA and should be put through the stand test, if extrapolation is not considered to be sufficient.

The outcome of this work is essentially that an inorganic separator has been found suitable for a sealed silver-zinc cell (heat sterilizable or not). The separator is compatible with strong alkali, strong oxidants and is absolutely nongassing with the cell active materials (silver, zinc, mercury). Its use is also perfectly suited for any size cell as it is formed as semi-flexible bag enclosing each electrode.

Its shortcomings so far appear to be in its economics. Although the raw materials are inexpensive, the hand labor cost presently involved in making the bags is high. No effort was made at this time to engineer the processes and fabrication, which undoubtedly could be done if need be.

Electrochemically, it is worth noting that a more zinc-penetration resistant separator would be desirable for batteries requiring frequent cycling, as a string of cells may get imbalanced and one cell may have to withstand an occasional overcharge without premature zinc penetration. It is known that zinc penetration is promoted by overcharge.

This will help in designing a proper nickel-zinc cell where overcharge is often the dominant mode. As it is, the separator bag could be successful to a large extent in the development of a nickel-zinc. It is recommended that such a cell be fabricated with the same zinc electrodes, bags, and hardware as for the 40-Ah cell. Fast acquisition of data would be helpful in setting up proper direction of new programs.

Obviously this separator system is of immediate interest in a silver-cadmium cell where the zinc problem is eliminated. It would also be helpful to establish the effect on the cadmium electrode, which suffers from utilization fading in conventional cells, probably because of formation of cadmium carbonate caused by decomposition products of cellophane; cadmium carbonate is known to be relatively difficult to electrochemically reconvert to cadmium. With the inorganic separator, there is no possibility of introducing carbon dioxide in the electrolyte. This may shed a new light on the silver-cadmium problem.

APPENDIX A

CELL SPECIFICATIONS

TYPE: HS-40-7

MODEL: $6b^{+}/5b^{-}$

POSITIVES	
Number of electrodes	6^{+}
Dimensions	3.625 in. high by 2.8 in. wide
Thickness	28 mils
Ag Powder	23.0 grams
Electrode-Bag assembly Weight	35.3 grams
Thickness	60 mils
NEGATIVES	
Number of electrodes	5^{-}
Dimensions	3.625 in. high by 2.8 in. wide
Thickness (including KT)	88 mils
Mix A2 powder	30 grams
Electrode-Bag assembly Weight	48.35 grams
Thickness	119 mils
SEPARATOR	
(1) Bag of Z-3420-25-FM(A) inorganic separator as per BFDO No. 2036	One on positives, one on negatives
ELECTROLYTE	
45-percent KOH	110 cc
OTHER	
Teflon film wrapper (5 mil thick)	9.25 by 3.15 in.

CELL SPECIFICATIONS

TYPE: HS-40-8

MODEL: $6b^{+}/\ell/5b^{-}$

POSITIVES

Number of electrodes	6^{+}
Dimensions	3.625 in. high by 2.8 in. wide
Thickness	26 mils
Ag powder	21 grams
Electrode-Bag assembly Weight	33.5 grams
Thickness	59 mils

NEGATIVES

Number of electrodes	5^{-}
Dimensions	3.625 in. high by 2.8 in. wide
Thickness (including KT)	82 mils
Mix A2 powder	25 grams
Electrode-Bag assembly Weight	43.35 grams
Thickness	113 mils

SEPARATOR

(1) Bag of Z-3420-25-FM(A) inorganic separator as per BFDO No. 2036	One on positives, one on negatives
(2) Layer of 3420-25 film (3 mil thick) one on each side of negative bag	4.1 in. high by 3.15 in. wide

ELECTROLYTE

45-percent KOH	110 cc

OTHER

Teflon film wrapper (5 mil thick)	9.25 by 3.15 in.

CELL SPECIFICATIONS

TYPE: HS-40-7 GX

POSITIVES	
Number of electrodes	6^+
Dimensions	3.625 in. high by 2.8 in. wide
Thickness	28 mils
Ag powder	23.0 grams
Interseparator	Pellon 2506K (6 mils) "U" wrap
NEGATIVES	
Number of electrodes	5^-
Dimensions	3.625 in. high by 2.8 in. wide
Thickness (including KT)	88 mils
Mix A2 powder	30 grams
Inseparator	10-mil asbestos bag
SEPARATOR	
SWRI-GX	Eight layers normal wrap around positives
ELECTROLYTE	
45-percent KOH	112 cc
OTHER	
Teflon film wrapper (5 mil thick)	9.25 by 3.15 in.

APPENDIX B

ENVIRONMENTAL TESTS

a. Vibration

1. Sinusoidal Vibration

Levels. - The applied vibration shall be swept at a logarithmic rate between the frequency limits and at the vibratory acceleration levels specified below in each of three mutually perpendicular axes.

Frequency	Level	Sweep Rate
5-34 Hz	.25" D.A.	2 oct/min
34-2000 Hz	± 15 g	2 oct/min

2. Random Vibration

Levels. - Gaussian random vibration shall be applied in three mutually perpendicular axes with instantaneous acceleration peaks limited to three times the rms acceleration levels as specified below. The filter roll-off characteristics above 2000 Hz shall be at a rate of 40 db/oct or greater. Acceleration density levels shall be held to within ± 3 db of the specified levels.

Frequency	PSD Level or slope	Overall Acceleration Level	Duration
20-90 Hz	+ 3 db/oct		
90-1000 Hz	.25 g^2/cps	19.1 g (rms)	5 min/axis
1000-2000 Hz	-6 db/oct		

b. Shock

Levels. - The shock level shall be applied three times in each direction of three mutually perpendicular axes at the levels specified below.

Acceleration Level	Wave Shape	Duration
45 g	terminal peak sawtooth	10 ± 1 ms

c. Steady State Acceleration

Levels. - The steady state acceleration shall be applied in both directions in each of three mutually perpendicular axes to the levels and duration specified below.

Acceleration Level	Duration
35 g	5 min/direction

APPENDIX C

FAILURE ANALYSIS AND TEST CONDITIONS OF DISSECTED CELLS

Cell No.	Design Configuration	Wet Life, Days	Stand, Days	Cycling Regime	Cycles	Separator Silver Content ($mg/in.^2$)
HS-45-1	/b^-	274	Float 210	100 percent DOD	5	41.0
-2	/b^-	315	Float 210	100 percent DOD	6	52.0
-3	/b^-	315	Float 210	100 percent DOD	6	41.0
-4	/b^-	315	Float 210	100 percent DOD	6	54.0
-5	/b^-	273	Float 210	100 percent DOD	5	42.2
-6	/b^-	315	Float 210	100 percent DOD	4	49.0
-7	/b^-	315	Float 210	100 percent DOD	4	46.5
-8	/b^-	315	Float 210	100 percent DOD	4	46.5
-9	/b^-	315	Float 210	100 percent DOD	4	38.6
-10	/b^-	274	Float 210	100 percent DOD		0.0
HS-46-1	/b^-	315	Float 217	100 percent DOD	4	36.6
-2	/b^-	314	Float 217	100 percent DOD	4	51.0
-3	/b^-	326	Float 217	100 percent DOD	4	52.0
HS-47-1	/b^-	356	Charged 209	100 percent DOD	6	28.7
-3	/b^-	362	Charged 209	100 percent DOD	5	31.0
-4	/b^-	440	Charged 210	One cy/day, 13 percent DOD	77	34.0
-5	/b^-	440	Charged 210	One cy/day, 13 percent DOD	76	30.6
-6	/b^-	309	Charged 181	100 percent DOD	6	27.8
-7	/b^-	410	Charged 209	One cy/day, 13 percent DOD	48	51.4
-9	/b^-	437	Charged 210	One cy/day, 13 percent DOD	77	41.7
-10	/b^-	354	Charged 209	100 percent DOD	7	40.7
HS-51-5	b^+/b^-	273	None	Three cy/day, 40 percent DOD	463	30.0[a][c]
-6	b^+/b^-	518	None	Three cy/day, 40 percent DOD	1,093	188.0[a][c]
HS-54-3	b^+/L/b^-	345	None	Three cy/day, 40 percent DOD	541	74.7[b][c]
-4	b^+/L/b^-	345	None	Three cy/day, 40 percent DOD	547	85.4[b][c]
HS-82-3	b^+/b^-	347	None	One cy/day, 13 percent DOD	310	31.2[a][c]

(a) Amount for two layers between electrodes

(b) Amount for three layers between electrodes

(c) Cells marked (c) shorted by a zinc nodule. All cells failed by diffuse silver penetration.

REFERENCES

1. Himy, A: Development and Testing of a 5 Ah silver-zinc cell. NASA CR-72551, May 1969, McDonnell Douglas Corporation, Newport Beach, Calif.

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