NX

JANUARY 1967
REPORT SM-49109-Q2

# DEVELOPMENT OF ONE AMPERE-HOUR HEAT STERILIZABLE SILVER-ZINC CELL

PROGRESS REPORT FOR PERIOD
1 OCTOBER TO 31 DECEMBER 1966
UNDER CONTRACT NAS 2-3819




ASTROPOWER LABORATORY
2121 CAMPUS DRIVE • NEWPORT BEACH, CALIFORNIA

MISSILE & SPACE SYSTEMS DIVISION
DOUGLAS AIRCRAFT COMPANY, INC.
SANTA MONICA/CALIFORNIA

Report SM-49109-Q2

# DEVELOPMENT OF ONE AMPERE-HOUR HEAT STERILIZABLE SILVER-ZINC CELL

Progress Report for Period
1 October to 31 December 1966

Contract NAS 2-3819


By:

Albert Himy

A. Himy
Senior Research Scientist

Approved by:

Carl Berger

C. Berger, Ph.D.
Head, Electrochemistry Department



MISSILE & SPACE SYSTEMS DIVISION
ASTROPOWER LABORATORY
Douglas Aircraft Company, Inc.
Newport Beach, California

## TABLE OF CONTENTS

## LIST OF ILLUSTRATIONS

## 1.0 INTRODUCTION AND SUMMARY

The salient achievement of this period was the demonstration of the capability of a silver-zinc cell using inorganic separators to be sterilized, whether in the unformed state, or in a discharged state after formation, and to run successfully on its duty cycle. To establish the extent of their reliability, the cells were automatically cycled on a simulated low-orbital flight of 60-minute period and yielded up to 274 cycles.

As expected, the cells, which were sterilized in sealed vessels, exhibited different pressures depending on their presterilization state of formation. The preformed cell ran 27 psig higher than the unformed cell and developed a very high hydrogen content. However, higher amalgamation of the zinc in preformed cells will help reduce hydrogen generation and probably the pressure margin.

Different approaches were considered for establishing a seal. The rectilinear case, made of polysulfone, cannot be reliably sealed with solvent or epoxy cements. Ultrasonic welding has been tried, showed encouraging results, and will be pursued as well as hot-gas welding.

As a back-up to the rectilinear case, a cylindrical configuration is following a parallel course. Preliminary seal testing showed the feasibility of achieving a hermetic seal capable of withstanding the sterilization procedure of 145$^{\circ}$C for 108 hours. A cylindrical separator cup made of inorganic material was developed for the electrochemical cell design intended for this type of configuration.

## 2.0 MECHANICAL TESTING

### 2.1 Terminal Seal

As shown in Figure 1, a new design terminal seal (Design #3) to be used as a back-up was tested under sterilization conditions in the special test fixture described in the first quarterly report.(1) The design consists of a teflon circular wedge pressed into a countersink by the terminal base when the terminal top is tightened with a nut. Extra sealing was provided with epoxy resin, filling all void space around the terminal body as well as the top and bottom.

The terminal assembly held a pressure of 48 to 53 psig at 145°C for 119 hours, after which the test was discontinued. The terminal top did not show any traces of alkali.

With teflon etching, it is expected that the bonding will be better and will improve the reliability of the seal over a long period.

### 2.2 Cover-to-Case Seal

More work was done on the cover-to-case sealing. Figure 2 depicts another type of sealing. The cell case is held in an inverted position, fitting into the cover where a fresh layer of epoxy resin 1/8 inch thick has been poured. The epoxy is also spread between the junction surfaces of the case and cover until it is squeezed out. Fiberglas tape (3M Scotch 361) impregnated with fresh epoxy is wrapped around the case at the junction line.

Before assembling the case, the holes for terminals were plugged and a polyethylene tube was temporarily fitted into the filling hole to leave the opening free for adapting the pressure devices.

After curing the epoxy at 120°C for two to three hours, the assembly was subjected to 145°C. After 10 hours, it developed a leak around the pressure fitting in the center hole at about 16 psig.

The test was repeated more carefully. The case was partly filled with 45% KOH, fitted with a pressure gauge and placed in an oven at 145°C. After holding a constant pressure of 14 psig for 20 hours, it developed a minute leak and the pressure gradually dropped to 0 over the next 20 hours. A minute crack was found on the junction line.

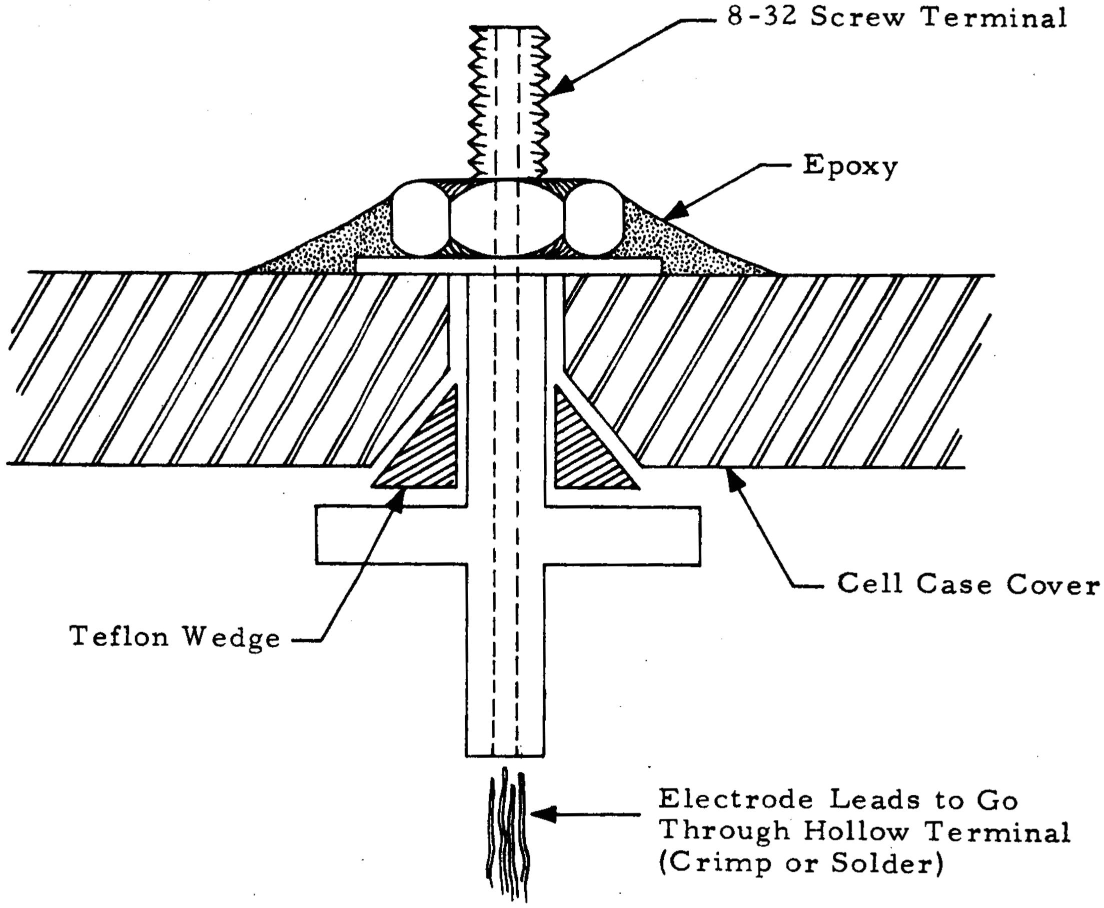



Figure 1. Terminal-to-Cover Seal Design #3

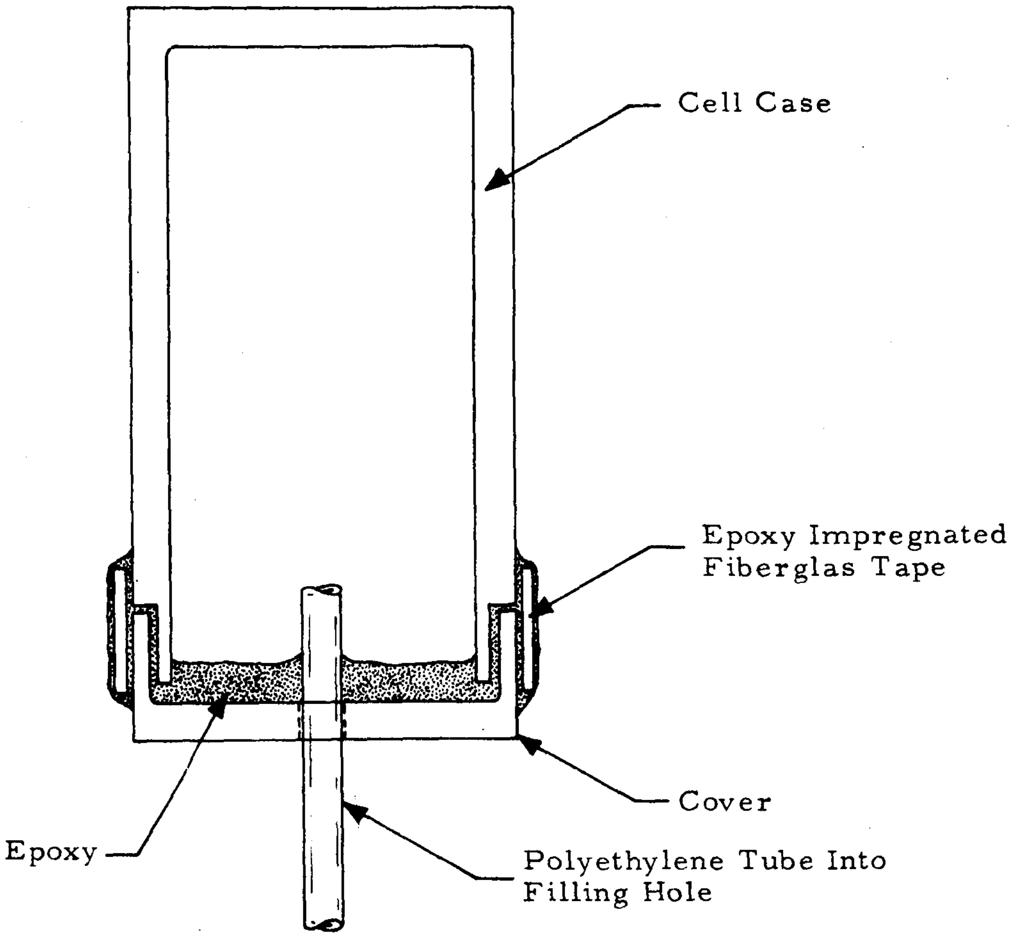



Figure 2. Cover-to-Case Sealing

This type of seal does not appear to be reliable for several reasons: The case and cover presently tested are machined out of polysulfone sheet. This operation introduces stresses in the material and the sterilization temperature certainly enhances its aptitude to crazing. On the other hand, the epoxy sealant does not provide a good surface bond to polysulfone, mainly at high temperature and in an alkaline medium. The pressures encountered during sterilization are not so high as to promote a catastrophic mechanical failure of the seal. The failure is more related to a wear-out or fatigue of the bonded and bonding materials, due to prolonged exposure to high temperature and alkaline medium.

Rather than trying to improve this approach on this limited program, it was decided to scan rapidly other alternatives.

In order to eliminate the effect of machining on polysulfone, tests will be carried out on molded five ampere-hour cases and covers presently available from another NASA program.[2]

Only Polysulfone P-1700 is readily available. All PPO grades under consideration are still in process, but may not be available for test for some time.

Other sealing methods to be investigated are ultrasonic welding and hot-gas welding.

A horn for ultrasonic welding was fabricated to fit the molded five ampere-hour case and cover. Several polysulfone cases were welded at various settings (three cases per setting):

| Identification | Weld Time (sec) | Hold Time (sec) | Horn Pressure (lbs) |
|---|---|---|---|
| #1 | 1.25 | 0.50 | 60 |
| #3 | 1.00 | 0.50 | 60 |
| #5 | 0.80 | 0.50 | 69 |

The cases were pressure-tested in succession as follows: (Any subsequent test was done only on cases having passed the previous test.)

1. Pressure tested at 10 psig for 5 minutes at $25^{\circ}C$
2. Pressure tested at 50 psig for 5 minutes at $25^{\circ}C$
3. Submitted to $145^{\circ}C$ ambient for 16 hours, then pressure tested at 50 psig for 5 minutes at $25^{\circ}C$.

At this point all cases were potted with epoxy (Allbond) along all the welded seams to plug leakage paths. The epoxy would be used as a sealant rather than an adhesive since the ultrasonic weld seemed to offer a strong joint, but possibly an incomplete seal.

The cases were put back on test as follows:

4. Pressure tested at 50 psig for 5 minutes at $25^{\circ}C$
5. Submitted to $145^{\circ}C$ ambient for 16 hours, then pressure tested at 50 psig for 5 minutes at $145^{\circ}C$.

Results

| Weld Identification | Case Identification | Test Identification | | | | |
|---|---|---|---|---|---|---|
| | | Without Epoxy | | | With Epoxy | |
| | | 1 | 2 | 3 | 4 | 5 |
| #1 | 11 | + | | | o | + |
| | 12 | o | + | | o | + |
| | 13 | o | o | | o | o |
| #2 | 21 | o | + | | o | + |
| | 22 | + | | | + | |
| | 23 | + | | | o | o |
| #3 | 31 | + | | | + | |
| | 32 | + | | | + | |
| | 33 | + | | | + | |

\+ leaked

o passed

Blank = not done

## 2.3 Other Concepts – Cylindrical Cell

In light of the difficulties regarding availability of material and lack of molded cases and covers of the proper size and design, and in anticipation of the problems involved in sealing a rectilinear configuration, a parallel course was set for a cylindrical case.

The crucial part of the assembly is a separator cup made of inorganic material having the same composition, wall thickness and porosity as the flat inorganic separator.

The case is made of metal or Teflon while the covers are made of Teflon, or Teflon and metal, or metal. Cases and covers are described in the next paragraph.

### 2.3.1 Case and Cover Design

Several designs of case and cover are shown in Figures 3, 4, 5, 6, 7, and 8. They vary only in the cover seal configuration.

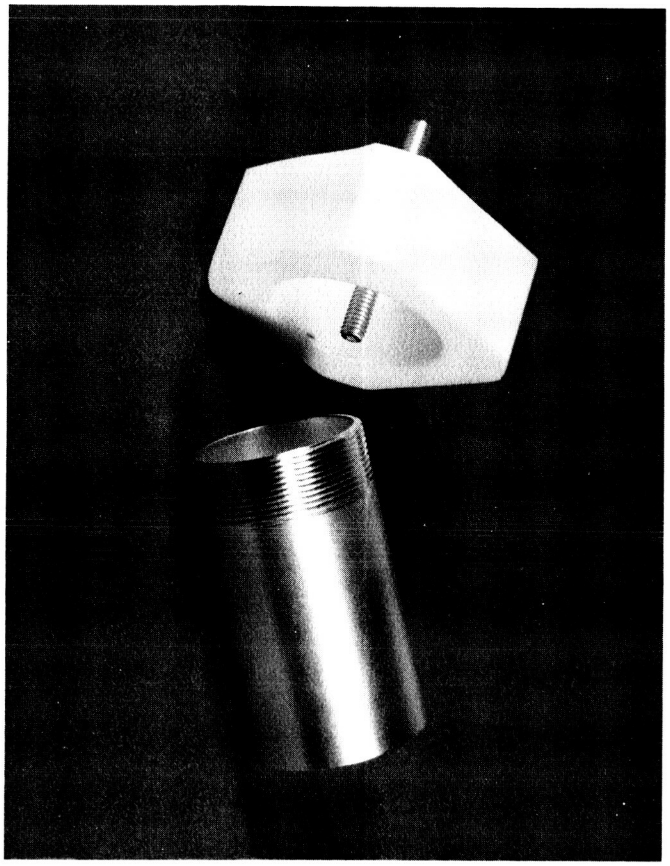
The first five models feature a closed bottom cylindrical case, made of silver plated soft brass, which has the negative polarity and serves as a current collector.

Designs #1 and #4 (Figures 3 and 6) have a Teflon cover screwed on the metal case. Here a terminal seal (positive polarity) is also needed.

Designs #2 and #3 (Figures 4 and 5) do not present a terminal seal problem since the positive leads can be soldered to the metal cover. A threaded Teflon insulator screwed on case and cover seals both the case and cover threads.

Design #5 (Figure 7) features a welded metal cover which has a ceramic seal around a center terminal.

The design #6 (Figure 8) is an open-end Teflon cylinder which presents on the walls of both ends a circular groove provided for an "O" ring seal. A metal cap is screwed on each end, thus tightening the "O" ring. As an improvement, a silver collector is welded to the bottom cap which is the negative polarity. The silver collector is circular and fits in the Teflon cylinder snugly, thus providing a large area for the current collection.

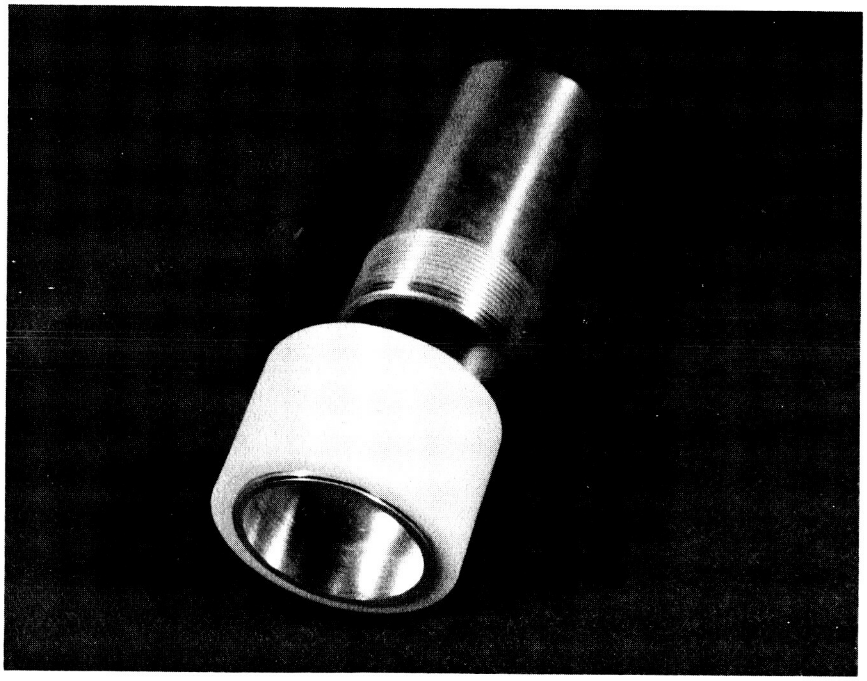


c2602

Figure 3. Cylindrical Cell, Design #1

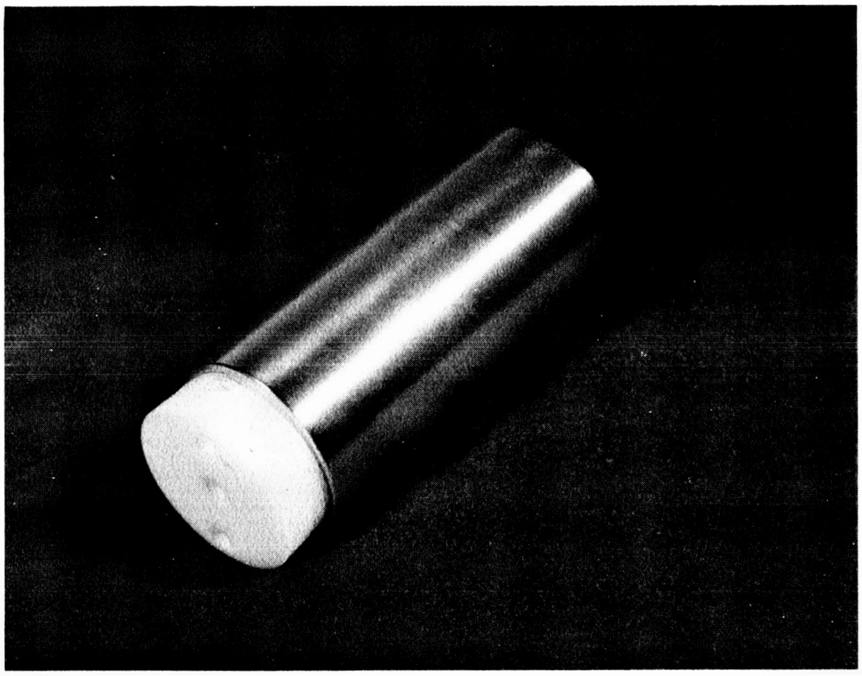
C2601

Figure 4. Cylindrical Cell, Design #2



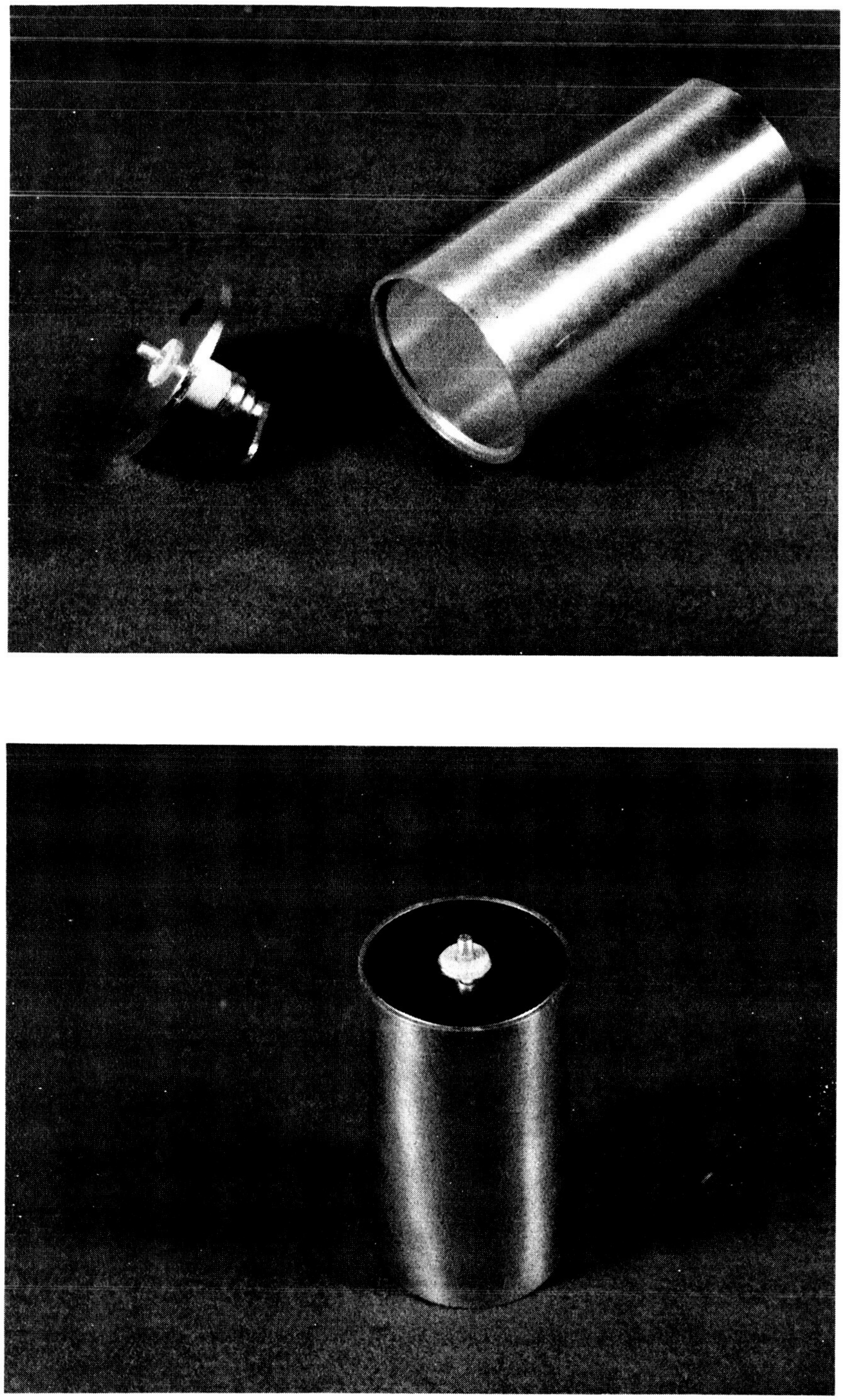
c2600

Figure 5. Cylindrical Cell, Design #3



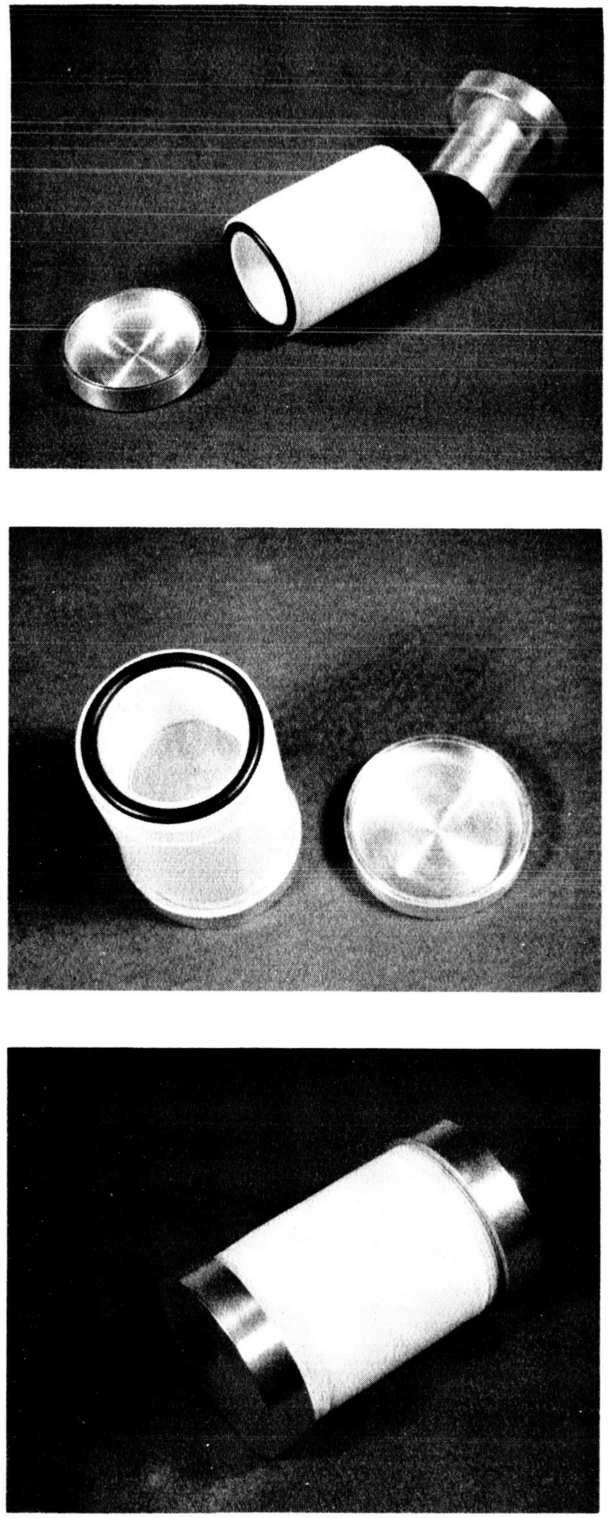
c2599

Figure 6. Cylindrical Cell, Design #4



c2598

Figure 7. Cylindrical Cell, Design #5



C2603

Figure 8. Cylindrical Cell, Design #6

### 2.3.2 Cell Design and Assembly

The design approach consists of a separator cup, which contains the silver electrode and which is placed at the center of the cylindrical case (Figure 9). The positive plate is a cylindrical slug of silver powder of the proper design parameters, pressed around a silver collector. The silver wires are attached to the positive terminal in the cover (if plastic), or to the cover itself (if metal) by means of solder.

As an improvement, KT material is added around and on the top of the silver slug.

### 2.3.3 Separator Cup

A typical separator cup is shown in Figure 10. The cups are made of the same inorganic materials used in the flat separator configuration. Porosity and thickness were kept identical so that the electrical area resistivity in KOH remains as close as possible to the one obtained for flat separators. The lateral area exposed to the passage of ions was arbitrarily selected to be 19 $cm^2$ until electrical polarization data could be obtained as well as mechanical data relative to the best sealing approach.

A cup was submitted to the sterilization procedure by itself at 145°C for 108 hours. No visual damage was noted.

### 2.3.4 Sealing of Cell

Four cylindrical cells were assembled with models #2, 3, 5, and 6.

The cells, models #2, 3, and 6, were sealed with Teflon tape on the threads.

The positive wire lead is brought up through the center hole of the cover which is screwed first onto the case, loosely revolving around the positive wire. Through this hole, the cell is then pressure-tested to determine the integrity of the seal, then the hole is plugged with solder. Models #2 and #3 leaked between Teflon insulator and cover at one point only around 10 psi.

Model #6 held its seal satisfactorily.

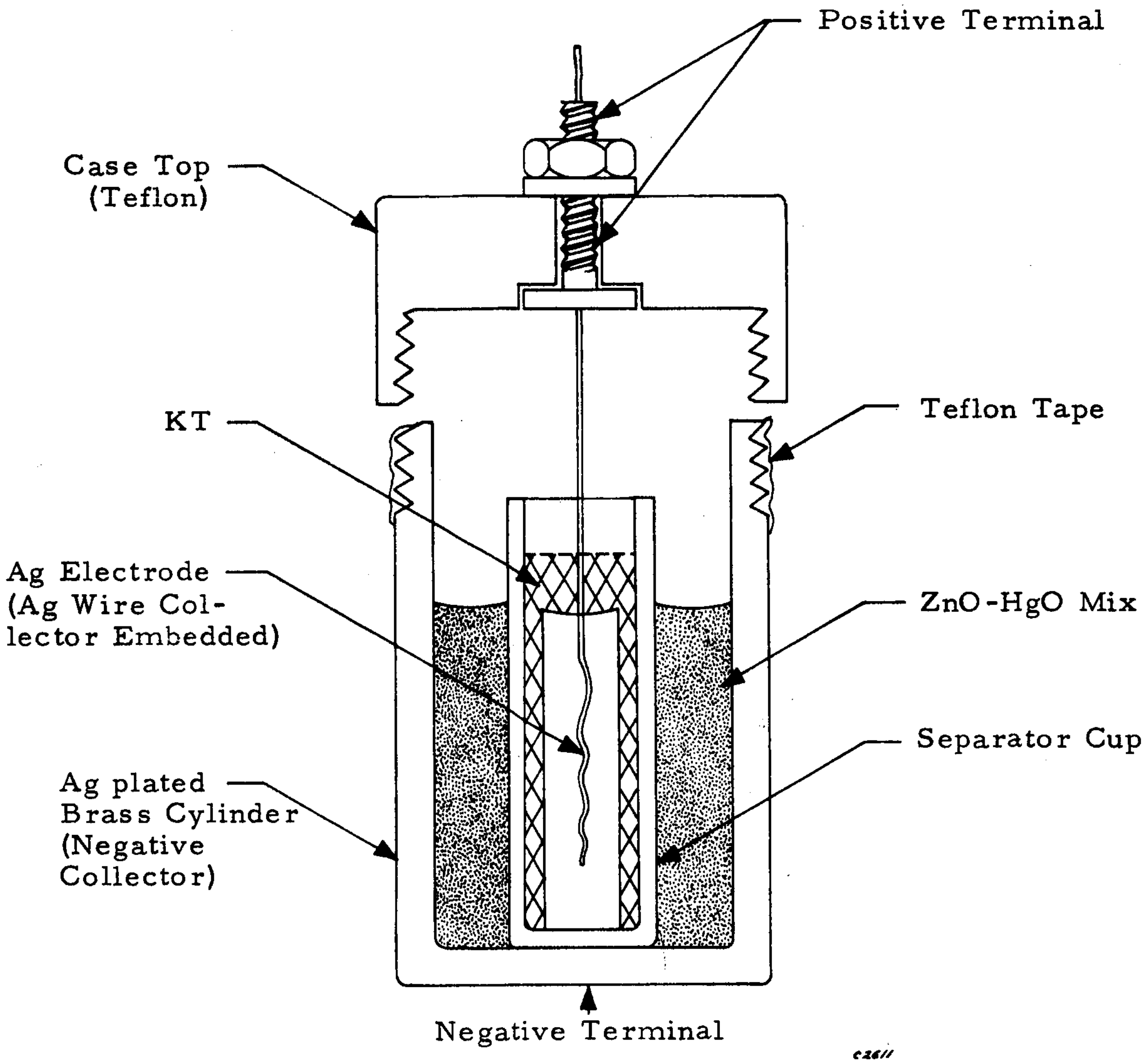
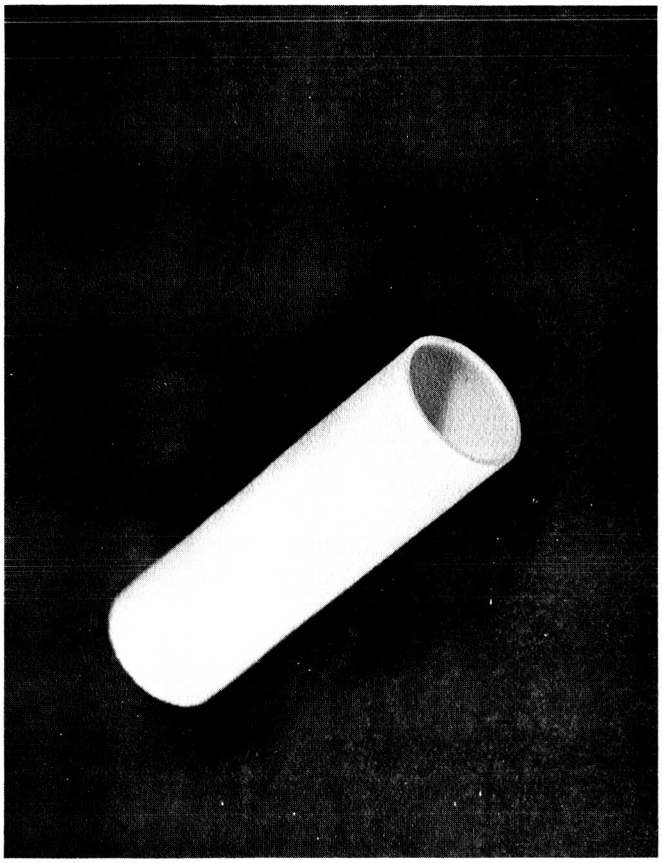



Figure 9. Typical Cylindrical Cell Assembly



C2604

Figure 10. Separator Cup

Model #5 (welded cover with ceramic seal) was not pressure-tested because no provision was made in the cover. Eventually a small hole will be left in the cover for filling and pressure-testing and will be plugged with solder.

Models #5 and #6 were submitted to the sterilization procedure inside a dry sealed vessel flushed with nitrogen and provided with a pressure gauge. After stabilization at 145°C, the pressures reached respectively 6.5 psig and 7 psig and remained constant throughout the entire test (108 hours). The fact that the pressure increase in the vessel (from 14.7 psia to 21.7 psia) was directly proportional within error limits to the temperature rise in degrees Kelvin (from 298°K to 418°K) proves that it was due exclusively to gas expansion and not to KOH vapor pressure, which would have been present, should the sealed cells have leaked. This was confirmed by the fact that there was no trace of alkali after sterilization on the exterior of the sealed cells and that their weights were found unchanged.

## 3.0 ELECTRICAL

### 3.1 Wafer Configuration Design

Samples of 3620-09 inorganic separator used in building wafer assemblies are shown in Figure 11 — one before sterilization, one after sterilization, and one after sterilization and cycling.

Two identical cells coded A-22-1 and A-22-2 were built using a 3420-09 inorganic separator and KT interseparator on both the positive and negative electrodes and filled with 45% KOH at the same time. Cell model is shown in Figure 12.

Cell A-22-1 was submitted to heat-sterilization without formation, then charged and discharged. On the other hand, cell A-22-2 was given a formation cycle (charge and discharge) first, then heat-sterilized.

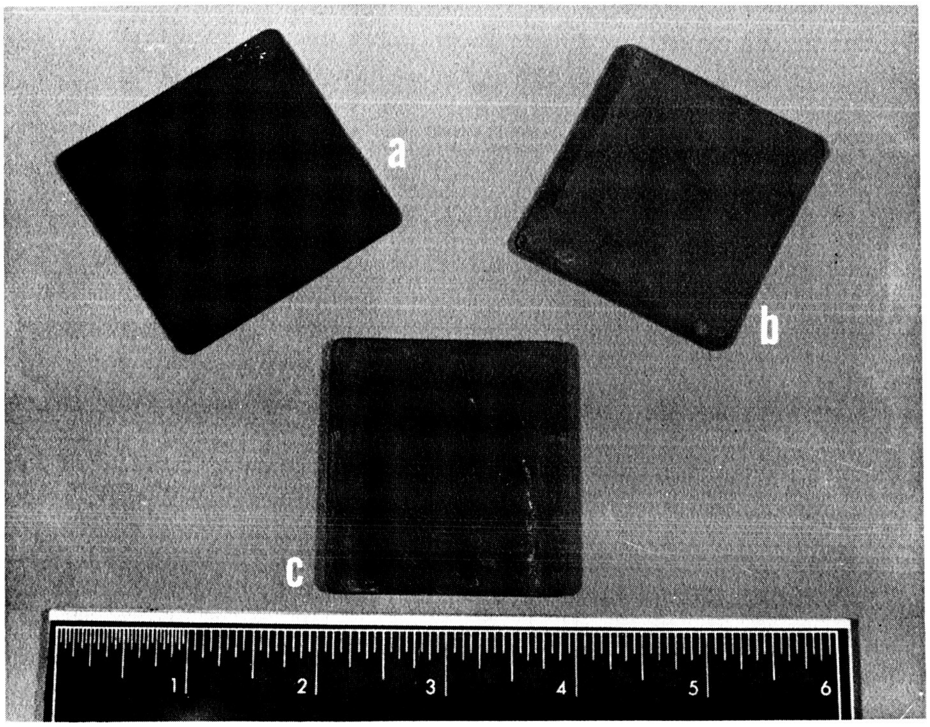
All charges were carried out at 100 mA and 2.10 V for total capacity determination.

Pressure and gas analyses were recorded for each pressure vessel.

Data are summarized in Table I. As expected, the pressure is higher in the preformed cell and hydrogen evolution much higher. In anticipation of high pressure build-up, the pressure vessel containing the preformed cell was evacuated. The maximum reached was approximately 55 psig, compared to 27 psig for the unformed cell. These data are preliminary and will be repeated on several cells to ascertain the maximum pressure and to establish the minimum safe pressure margin needed by the cell case and the seals.

The hydrogen evolution in preformed cells may be largely reduced by using a higher amalgamation.

After the duty cycles, the cells were placed on a simulated automatic cycling regime. The equivalent capacity of the duty cycle (0.3 Ah) is removed and put back on a one-hour cycling period as follows: discharge at 0.6 A for 1/2 hour; recharge at 0.72 A for 1/2 hour, thus simulating a low-orbital flight regime. Characteristic curves are given in Figures 13 and 14 for their duty cycles and in Figures 15 and 16 for their continuous automatic cycling until failure. Their actual capacity was approximately 2 Ah.



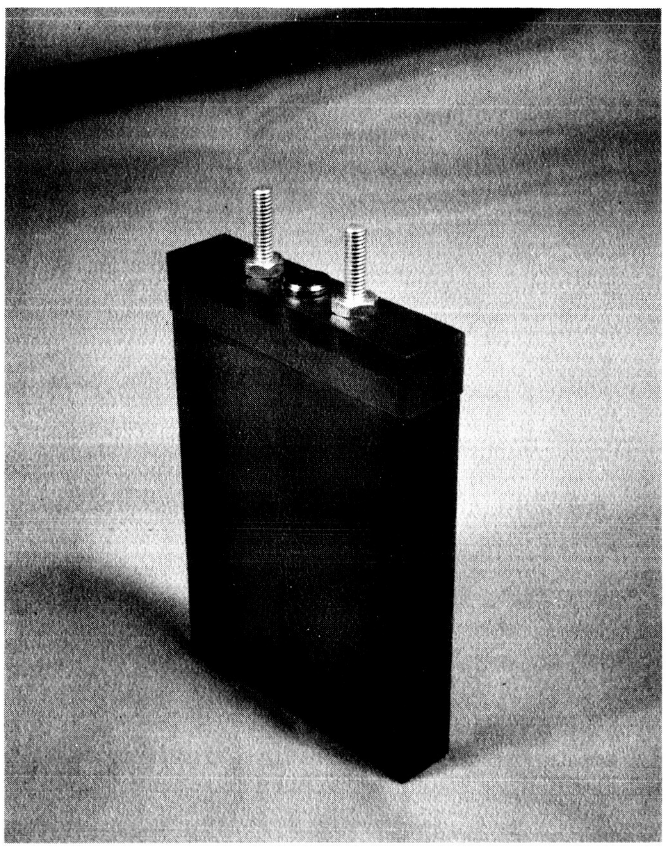

a. Before Sterilization

b. After Sterilization

c. After Sterilization and Continuous Cycling (274 Cycles)

C2621

Figure 11. Flat Separator Before Sterilization, After Sterilization, and After Cycling



C2597

Figure 12. Plastic Cell Assembly

TABLE I

UNFORMED VS. PREFORMED CELL DATA
$2^+/1^-$ WAFER, KT INTERSEPARATOR

| | A-22-1, Unformed | A-22-2, Preformed |
|---|---|---|
| Cycle 1 (charge & discharge) | | |
| Output to 1.0 V | | 2.2 Ah |
| 2 A pulse: voltage | | 1.18 V |
| 2 A pulse: power | | 2.36 W |
| Sterilization at 145°C | 104 hrs | 98 hrs |
| Initial pressure (before sterilization) | 760 mm Hg | 51 mm Hg |
| Maximum pressure (during sterilization) | 2,160 mm Hg | 3,600 mm Hg |
| Gas Analysis | | |
| $N_2$ | 93.5% | 16% |
| $O_2$ | 3.0% | trace |
| $H_2$ | 3.5% | 82% |
| $CH_4$ | trace | 2% |
| Cycle 1 (charge & discharge) | | |
| Output to 1.0 V | 2.5 Ah | |
| 2 A pulse: voltage | 0.96 V | |
| 2 A pulse: power | 1.92 W | |
| Cycle 2 | | |
| Output | 2.30 Ah | 1.90 Ah |
| 2 A pulse: voltage | 0.97 V | 1.03 V |
| 2 A pulse: power | 1.94 W | 2.06 W |
| Cycling Regime (0.3 Ah) at 25°C | | |
| Discharge: 1/2 hr x 0.6 A | | |
| Charge: 1/2 hr x 0.72 A | | |
| Cycles to Failure | 274 | 167 |

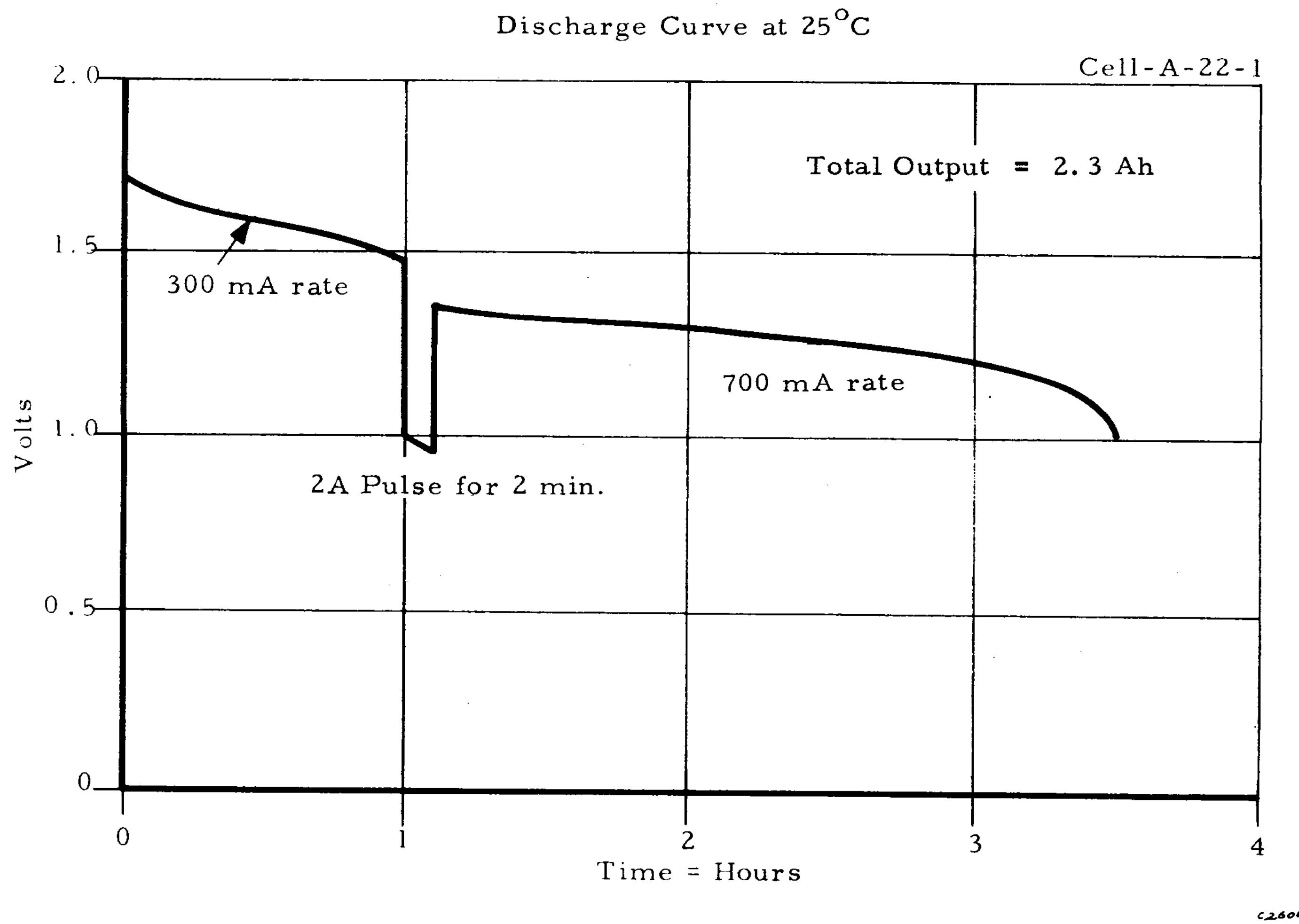



Figure 13. Standard Design: Cell Sterilized, Unformed – Nominal Capacity: 2 Ah

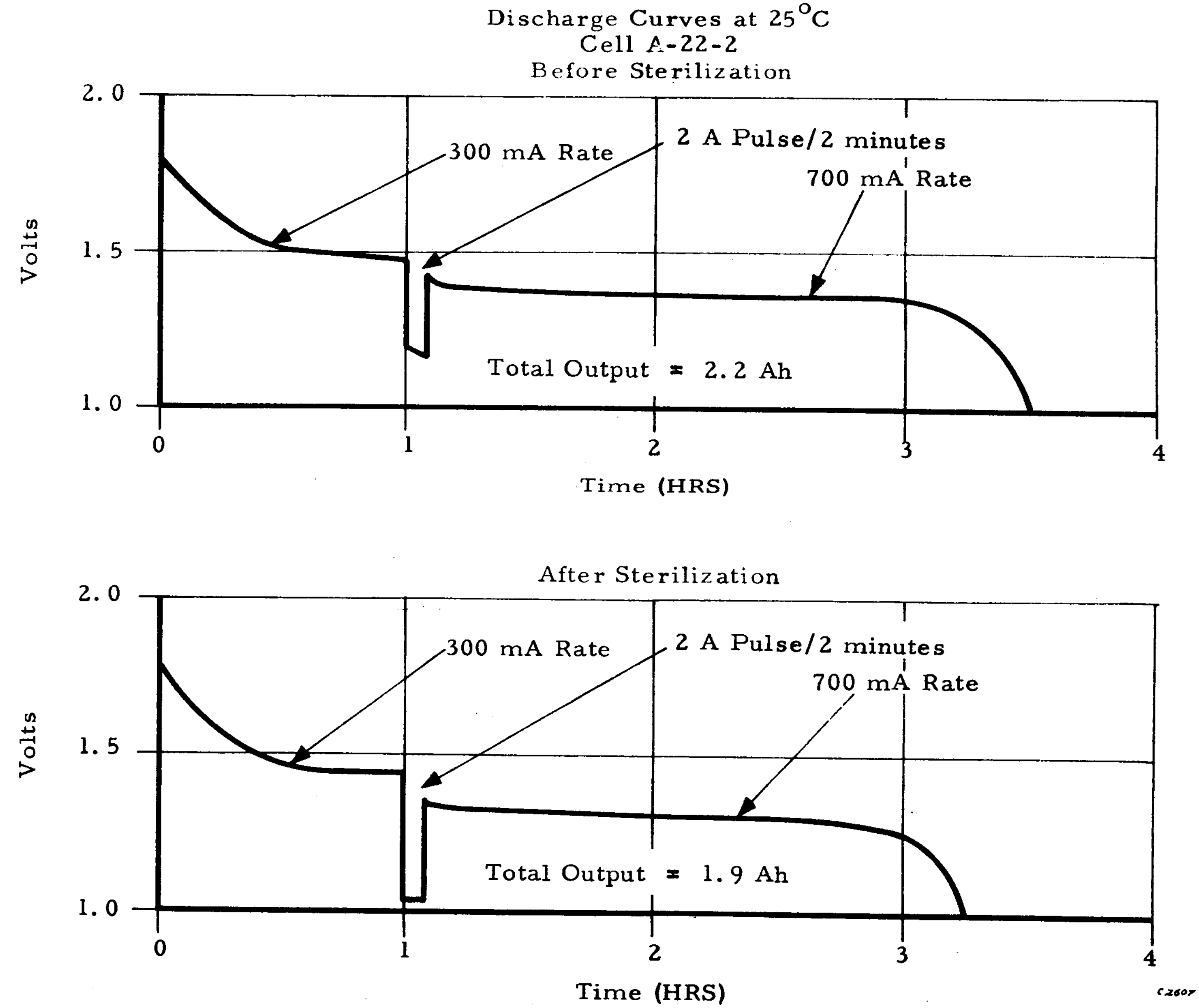



Figure 14. Standard Design Cell Sterilized After Formation and Discharge — Nominal Capacity: 2 Ah

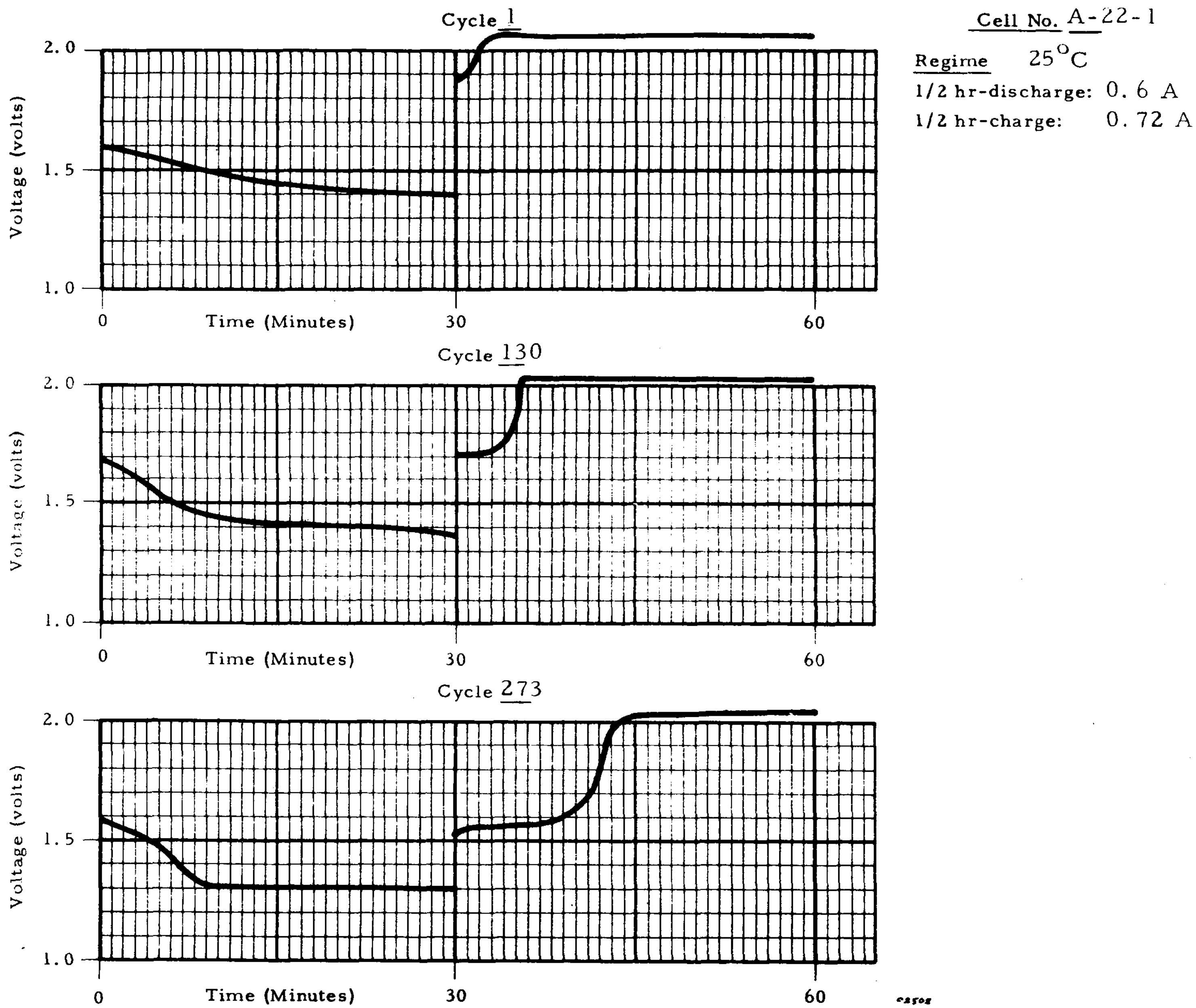
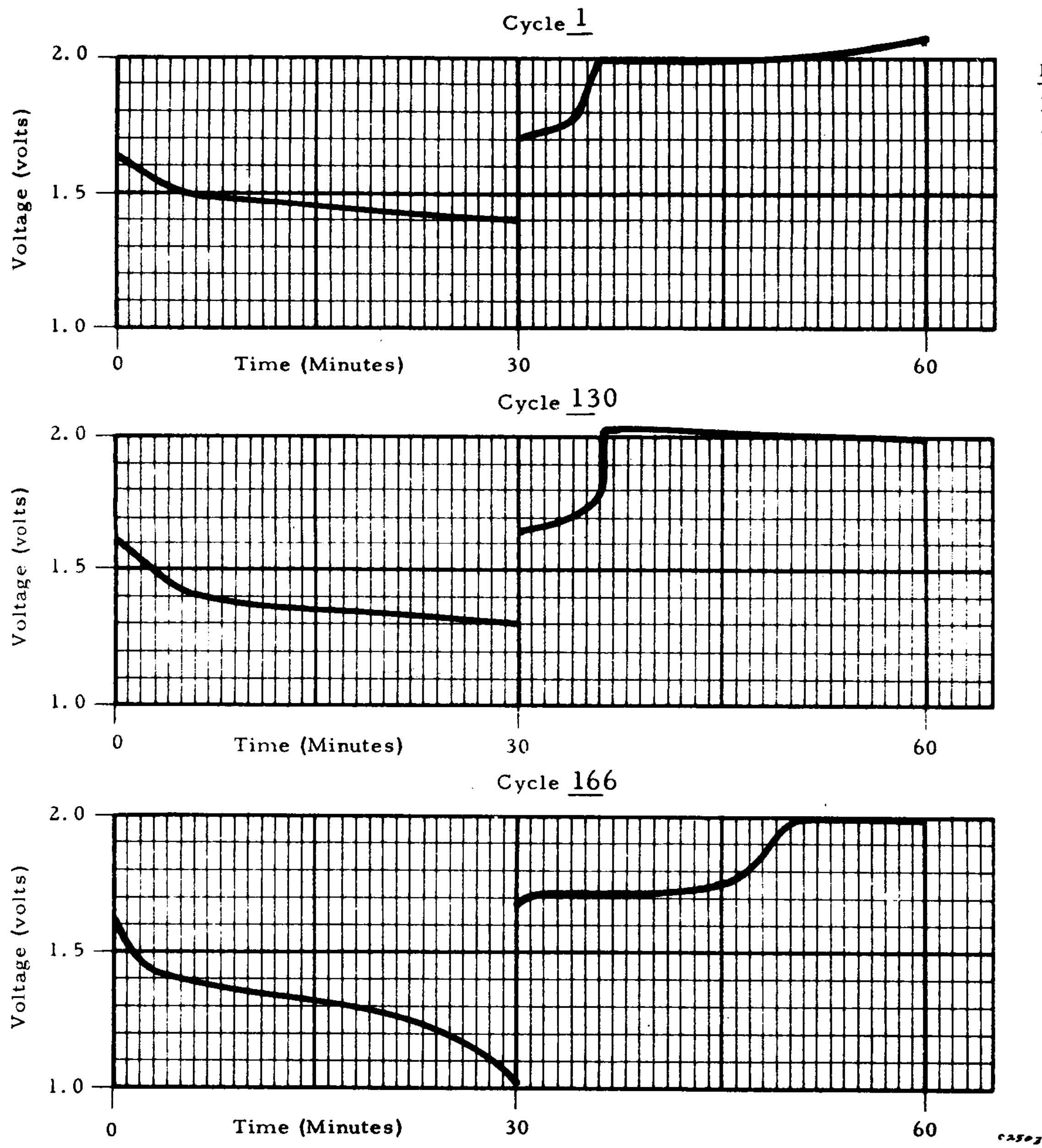



Figure 15. Characteristics of Cell Sterilized, Unformed, on Automatic Cycling




Cell No. A-22-2

Regime 25°C

1/2 hr-discharge: 0.6 A

1/2 hr-charge: 0.72 A

Figure 16. Characteristics of Cell Sterilized, Preformed, on Automatic Cycling

### 3.2 Separator Box Design

Another type of assembly was tried where no sealant was used. The separator consisted of one single rectilinear vessel in the form of the wafer used, with two flat sides as regular separators. This integral piece is made by pressing the inorganic material isostatically in a mold and machining it to the proper dimensions (Figures 17 and 18).

#### 3.2.1 First Run

Two cells were built with a one ampere-hour nominal capacity. One cell was sterilized unformed and one cell was used as control and not sterilized.

Control: A-20-2

Output: 1.30 Ah
2A-pulse voltage: 1.28 V
2A-pulse power: 1.56 W
Automatic cycling regime: 162 cycles

Test Cell: A-20-1

Sterilized unformed; evacuated: 25 mm Hg
Maximum pressure during sterilization: 2180 mm Hg
Gas analysis: $N_2$ = 91%, $O_2$ = 9%
Output: 1.10 Ah
2A-pulse voltage: 1.13 V
2A-pulse power: 2.26 W
Automatic cycling regime: 141 cycles

Figure 19 shows voltage characteristics of the two cells.

#### 3.2.2 Second Run

Again two cells were built and tested as follows: one cell left unformed, then sterilized and one cell formed, discharged, then sterilized. Each cell was subsequently recharged and discharged on a duty cycle.

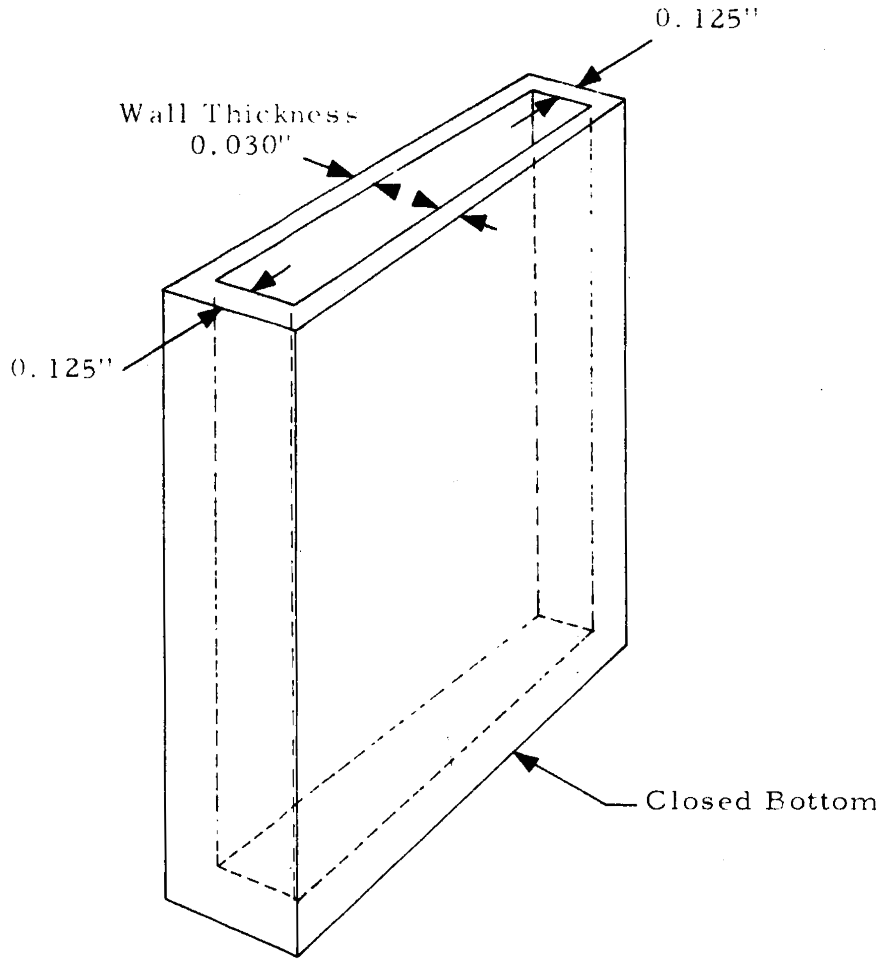
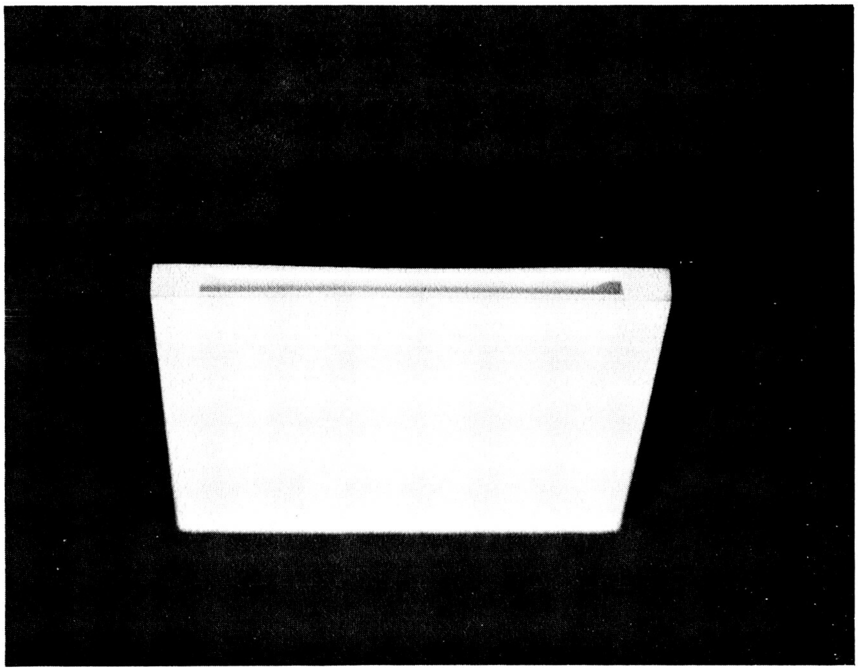


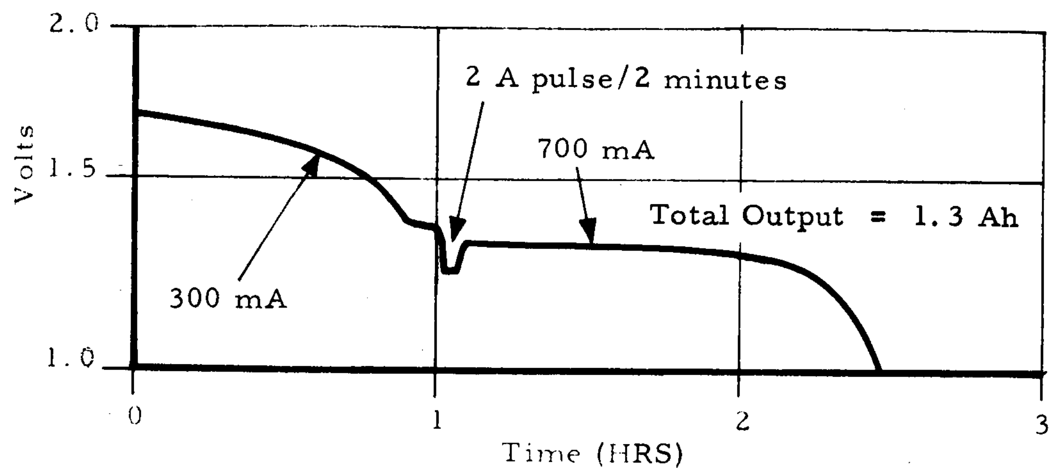

Figure 17. Separator Box



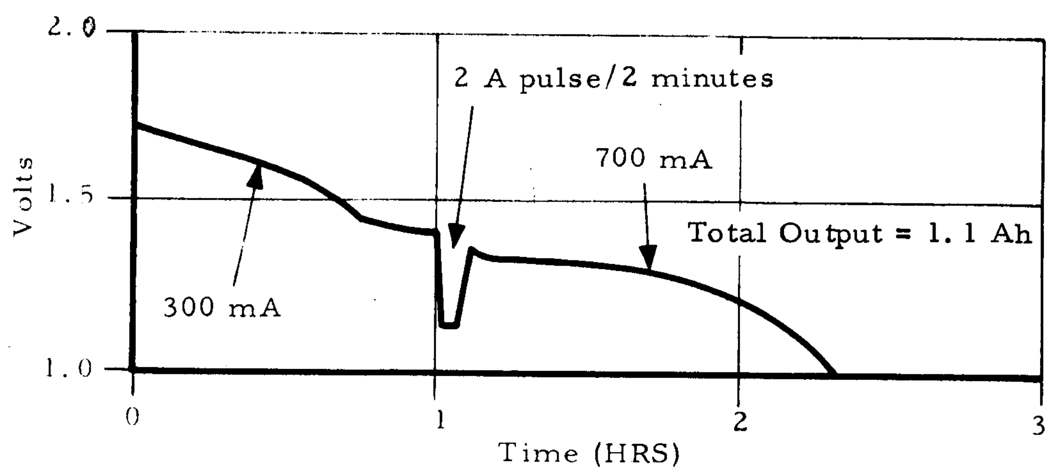
c2605

Figure 18. Sterilized Separator Box

Discharge Curve at 25°C




Unsterilized Control Cell A-20-2




Sterilized Cell (A-20-1)
116 hrs @ 145°C

Figure 19. Box Design — Nominal Capacity: 1 Ah

Results:

Cell A-39-1: Unformed

Sterilized at 145°C for 111 hours

Charged and discharged

Output: 1.2 Ah

2A-pulse voltage: 1.29 volts

2A-pulse power: 2.58 watts

Cell A-39-6: Formed and discharged

Output: 1.1 Ah

Sterilized at 145°C for 108 hours

2A-pulse voltage: 1.23 V

Charged and discharged

Output: 0.9 Ah

2A-pulse voltage: 1.06 volts

2A-pulse voltage: 2.12 watts

Discharge characteristics are shown in Figures 20 and 21, respectively.

### 3.3 Cylindrical Cell

Electrical testing of the cylindrical cells is in process and no data could be reported at the time of this writing.

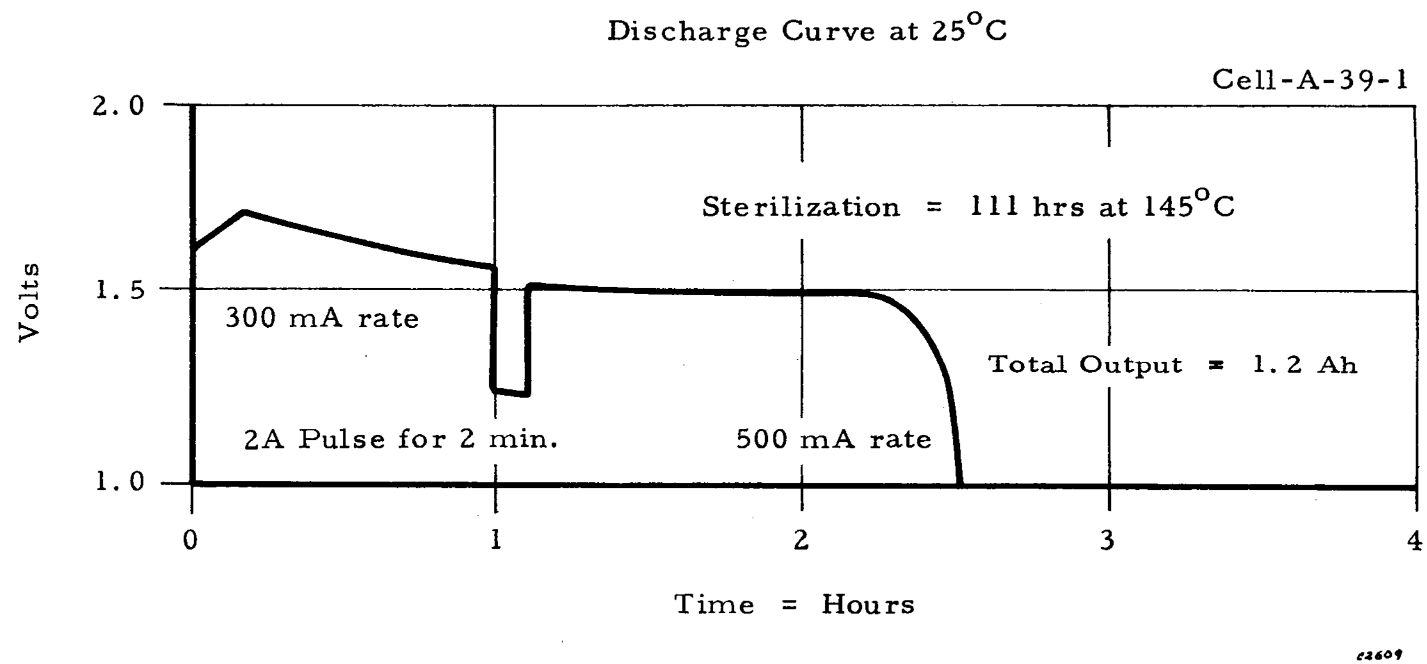



Figure 20. Box Design: Cell Sterilized, Unformed — Nominal Capacity: 1 Ah

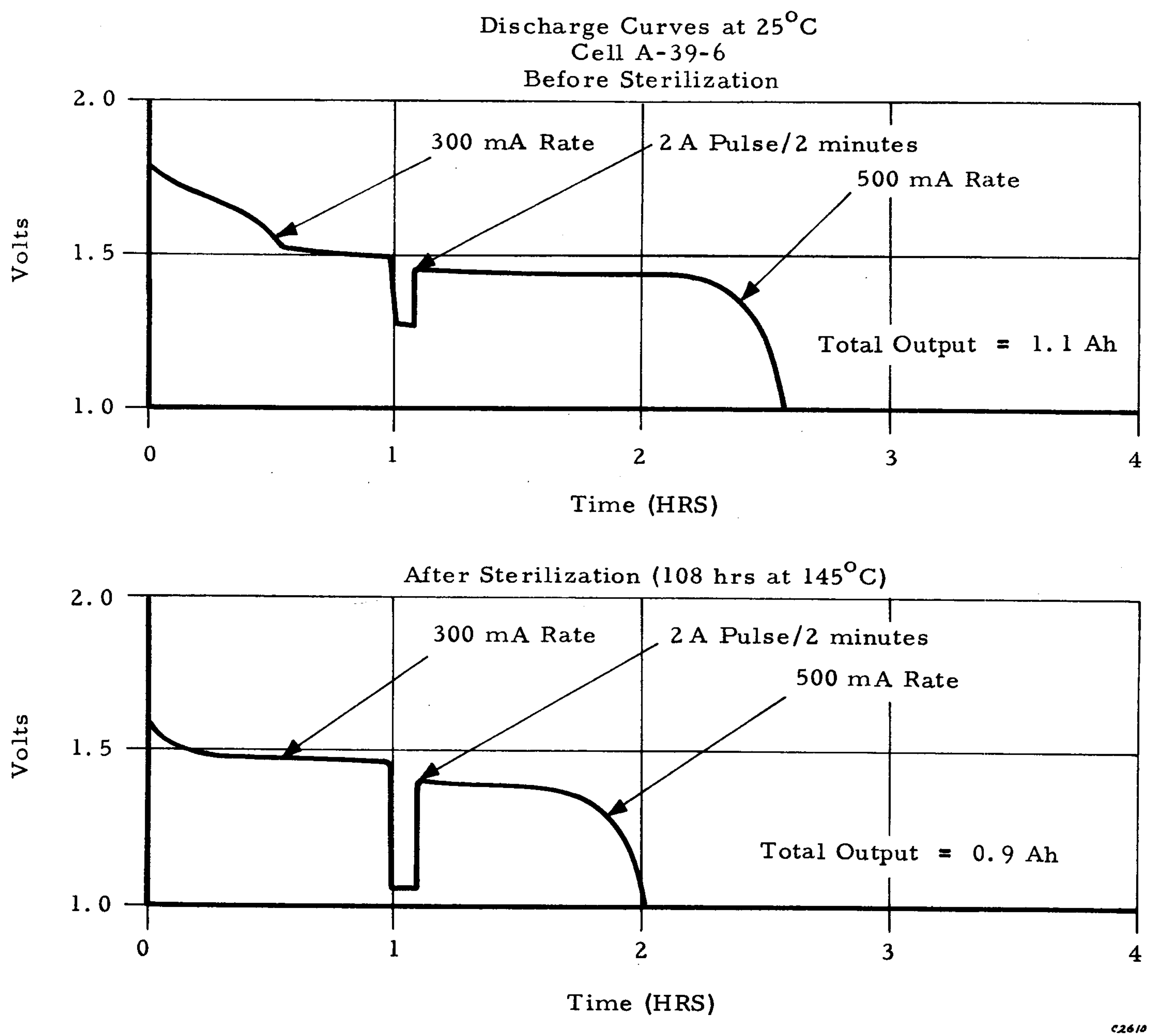



Figure 21. Box Design Cell Sterilized After Formation and Discharge – Nominal Capacity: 1 Ah

# 4.0 MISCELLANEOUS

## 4.1 Inorganic Separators

Carbonation of electrolyte due to the inorganic separator 3420-09 reported in the first quarterly report, page 39, Table VI,[1] was considered doubtful and tests were repeated. The separator samples used were handled for too long during absorption and resistivity measurement before being sealed in the pressure vessel. This may have resulted in heavy $CO_2$ pick up. Tests repeated under carefully controlled conditions without wet handling showed no evidence of carbonation, both for the 3420-09 separator as well as for another inorganic separator (coded 3420-25) also being considered for sterilization as a back-up. This is also supported by the fact that the electrolyte of a sterilized cell was not found to be carbonated to an extensive amount.

## 4.2 Interseparator

### 4.2.1 KT

The sterilization of KT sheet (potassium titanate) was repeated in 30% KOH because of an apparent discrepancy in the vapor pressures in 45% and 30% KOH, reported in the first quarterly report. The respective values reported in Tables IV and V of that report (pages 35 and 36) were 2310 and 1330 mm of Hg – the second value being lower instead of higher as expected. The repeat in 30% KOH gave a pressure of 3260 mm of Hg, which is comparable to other tests.

### 4.2.2 Coating 4561-7

It is an organic-inorganic coating on the silver electrode, used as an interseparator, mentioned in the first quarterly report (pages 6 and 26). Its KOH absorption was only 7 mg/cm$^2$, but was capable of sterilization (sterilized for 130 hours at 145$^{\circ}$C) and may be considered as a promising candidate.

## 5.0 CONCLUSIONS

The heat sterilization of an electrochemical cell in the two different configurations investigated, rectilinear and cylindrical, can be considered feasible with the use of an inorganic separator shaped in the form of a container for either electrode. This will make unnecessary the introduction of an organic sealant and thus will help reduce pressure and hydrogen content. A flat inorganic box or a cylindrical cup can be manufactured to the desired separator specifications.

The hermetic sealing of the cell case under sterilization conditions is being investigated also in both configurations. Some encouraging results were obtained with the rectilinear plastic case through ultrasonic welding and subsequent epoxy potting. The cylindrical metal case passed the seal test in two designs and may appear more reliable.

## 6.0 WORK PLANNED

In the next quarter, work will be continued on the two configurations described above with respect to seals.

Electrical data will be accumulated on wet stand over the remainder of the program, on performance at various temperatures and on repeated cycling.

## REFERENCES

1. Development of One Ampere-Hour Heat Sterilizable Silver-Zinc Cell, Astropower Laboratory Report SM-49109-Q1, Contract NAS 2-3819, October 1966.

2. Development of an Inorganic Separator for a High Temperature Silver-Zinc Battery, Contract NAS 3-7639.