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FIRST QUARTERLY REPORT

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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FIRST QUARTERLY REPORT

DEVELOPMENT OF A LOW TEMPERATURE BATTERY FOR SPACE PROBE APPLICATIONS

William F. Meyers (Principal Investigator)

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

November 15, 1964

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SUMMARY

The first objective of this program is to obtain 2.1 watt, 72 hour, reserve battery performance over the temperature range +20°C to -73° by modification of existing Livingston Ammonia Battery designs.

During the first quarter, cell test chambers were obtained and tested. Numerous difficulties associated with hermetic seals below -55°C were encountered. Cell tests were made in spite of these difficulties, and improved seals are being developed.

Cyclic load and recording systems were evolved to provide for the specified electrical requirements on a single cell and/or a five series cell battery basis.

The usual start-up problems were also encountered with continuous operation of mechanical refrigeration equipment at the lower temperatures. This was temporarily resolved by the installation of refrigerated liquid CO_2 equipment.

Despite the loss of many tests due to the above difficulties, 33 useful tests are reported giving a preliminary coverage of the operation of $Mg/NH_3 \cdot KSCN$ cells with selected cathodes as follows:

Cathode	Best Results Obtained
1. Mercuric Sulfate	103 hours at -73°C
2. meta-Dinitrobenzene	70 hours at -55°C
3. Sulfur	12 hours at -55°C

It appears that mercuric sulfate in a bobbin cell will be capable of meeting the Objective I of this program, and a design for five-cell batteries is being studied.

INTRODUCTION

The purpose of this program is to obtain 72-hour discharge at a specified power level over the temperature range of +20° C to -73° C from ammonia electromotive cells by modification of present Livingston ammonia battery designs. Some tests had been performed in laboratory test vehicles. Both single cells and complete batteries utilizing liquid ammonia as the solvent had demonstrated exceptional ability over a wide temperature range.

The initial phase of this work comprised efforts to construct single cells capable of cyclic operation at 0.3 watts per cell for 54 minutes and 1.5 watts per cell for 6 minutes alternating continuously for a 72-hour period. During this first quarter, preliminary investigations were conducted in laboratory test vehicles using magnesium anodes, 25 weight per cent KSCN in liquid ammonia electrolyte, and three different cathodic materials: meta-dinitrobenzene, mercuric sulfate, and sulfur. Since adequate discharge life is the primary factor in this first objective, it is encouraging to report that $HgSO_4 \cdot 2NH_3$ provided 103 hours at -73° C under the required cyclic load in an inverse bobbin structure.

Prior to the construction of cyclic load program units, initial full size cells were tested under 10Ω fixed load to approximate the average of the cyclic load based on a nominal two volts per cell. Following the construction of cyclic load programmers, nominal loads of 3Ω and 15Ω were adopted for full size cells subject to later adjustment depending upon the actual operating voltages and optimized utilization of the vehicle volume.

Two reusable cell holders of different geometry, termed vehicles, were used in the majority of the tests.

The internal volume of the slender cylindrical A-601 vehicle is 24 $inches^3$. Achievement of the specified 30 watt hour output within the maximum net volume (permitted by this cell vehicle) would represent 1.25 watt hours per cubic inch. The aim has been to attempt the requirement in less than this volume.

The internal volume of the short thick cylindrical A-622 vehicle is 34 $inches^3$. This was usually assembled with flat parallel plate electrodes scaled down to one-fifth the total number indicated. The remainder of the vehicle volume was blocked out with inert solids, and the nominal load resistance increased from the above 3/15Ω to the range 10/50Ω to 20/100Ω for meta-dinitrobenzene and as high as 50/250Ω for sulfur in the smaller A-606 vehicle. Despite the somewhat larger volume of the A-622 vehicle, the lower density of meta-dinitrobenzene may result in a higher energy per unit weight than $HgSO_4$ above.

In addition to consideration of three cathodic materials, two types of cell construction were utilized. The solvated mercuric sulfate was tested in the bobbin structure because of its intrinsically greater current handling capabilities. Meta-dinitrobenzene and sulfur were tested in flat cell structures to reduce cathode current density and to provide for the convenient installation of ion-exchange membranes.

Investigation of the use of ion-exchange membranes to extend the capabilities of the above cell types is also under study. The membrane studies which have been completed with sulfur indicate that the use of either a cationic or anionic membrane is detrimental when used with sulfur. However, the use of an anionic membrane has greatly extended the performance of the Mg/KSCN:NH_3/m-DNB: - NH_4SCN:C cell.

In order to present the rather substantial amount of data involved in the many cells tested under varying conditions, a general tabulation is presented in Table I, pages 9 through 17. The tests in this table were designed to determine the general effects of numerous physical, chemical, and electrical variables. Replication was considered to be of secondary importance in the initial research. In the future, confirmation of some of the preliminary results will be necessary. Many of these data may be considered as guide lines for the planning of future experiments. The tests in this table are grouped according to tasks within Objective I.

QUANTITATIVE DESCRIPTION OF PROGRESS

Single Cell Tests

The first goal was to develop electrochemical systems that would meet the specified electrical requirements of 0.3 watts per cell for 54 minutes and 1.5 watts per cell for six minutes, cyclically, for a total of 72 hours at -73°C without activated wet stand.

The best single cell results obtained in the first quarter were as follows:

Cathode	Best Results Obtained	Cell #
1. Mercuric sulfate	-73°C, 103 hours	7C
2. meta-Dinitrobenzene	-55°C, 70 hours	2319
3. Sulfur	-55°C, 12 hours	2205

In order to present the rather substantial amount of data involved in the many cells tested under varying conditions, a general tabulation is presented in Table I, pages 9 through 17. The tests in this table were designed to indicate the general effects of numerous physical, chemical and electrical variables. To further define the individual tests conducted, the purpose, design, results, and conclusions for each cell are listed separately, in some detail, in the Appendix. These cell summaries are arranged for convenience in the same order as the logic of Table I. Many of these data may be considered as guide lines for the planning of future experiments. The tests in these tables are grouped according to tasks within Objective I.

NOTES TO TABLE I

[1] Load shown as A/B represents cyclic of A Ω for six minutes and B Ω for 54 minutes.

[2] S. S. = stainless steel case
Ag. P. S. = silver-plated steel case

[3] M-1365 Webril; #50 Whatman filter paper; or Whatman Extraction Thimble

[4] Based on two electron change for meta-Dinitrobenzene.

[5] Finned and fluted, see Figure 7 , page 43.

[6] Finned

TABLE I

ELECTROCHEMICAL

Objective I

Magnesium-

Test Number:	A	2051	2078
Refer to Appendix, page:	1	1	1
Vehicle:	A-601	A-601	A-601
Percent of Vehicle Volume Utilized:	60	60	60
Configuration:	Bobbin	Bobbin	Bobbin
Net Cell Volume (inches^3):	14.4	14.4	14.4
Load Ω [1]:	10	10	10
Temperature:	24°C	-40° to -73°C	-73°C
Hours to End Voltage:	54	17	0
Anode (AZ31B Magnesium):	Rod	Rod	Rod
Anode Area cm^2:	71	71	71
Cathode:	$HgSO_4$**	$HgSO_4$**	$HgSO_4$**
Cathode Collector [2]:	S. S.	S. S.	S. S.
Separator [3]:	Webril	Webril	Webril
Ion Exchange Membrane:	---	---	---
Initial Open Circuit Voltage:	2.29	2.35	1.85
Initial Closed Circuit Voltage:	2.08	2.05	1.82
End Voltage:	1.50	1.80	1.80
Initial Anode Current Density (mA/cm^2)*:	2.9	2.9	---
Initial Cathode Collector Current Density (mA/cm^2)*:	1.0	1.0	---
Theoretical Cathode Coulombs/gram [4]:	580	580	580
Observed Cathode Coulombs/gram:	205	50	---
Cathode Coulombic Efficiency:	35%	9%	---
Watt Hours/Inch^3 of Net Cell:	1.21	0.44	0

*Based on the lighter load if cyclic.

**175 grams $HgSO_4 \cdot 2NH_3$ + 75 grams carbon.

CELL TESTS

Group A

Mercuric Sulfate Couple

2096	2166	7C	1C	6C	8C	2C	3C
2	2	2	3	3	3	4	4
A-601	A-601	A-601	A-601	A-601	A-601	A-622	A-622
60	60	60	60	60	60	46	46
Bobbin	Bobbin	Bobbin	Bobbin	Bobbin	Bobbin	Bobbin	Bobbin
14.4	14.4	14.4	14.4	14.4	14.4	16.4	16.4
10	3/15	3/15	10	10	50/250	10	10
24°C	24°C	-73°C	-73°C	-73°C	-73°C	-55°C	-73°C
87	33	103	24	72	168	9	24
Note[5]	Note[5]	Note[5]	Note[5]	Note[5]	Note[5]	Note[6]	Note[6]
142	142	142	142	142	142	25.6	25.6
$HgSO_4$**	$HgSO_4$**	$HgSO_4$**	$HgSO_4$**	$HgSO_4$**	$HgSO_4$**	$HgSO_4$**	$HgSO_4$**
S. S.	S. S.	S. S.	S. S.	S. S.	S. S.	Ag P.S.	Ag P.S.
Webril	Webril	Webril	Webril	Webril	Webril	Webril	Webril
---	---	---	---	---	---	---	---
2.24	2.37	2.20	2.20	2.34	2.30	2.30	2.24
2.19	2.25	2.15	2.04	2.25	2.28	2.13	1.72
1.50	1.50	1.50	1.50	1.50	1.80	1.50	1.50
1.5	1.1	1.0	1.4	1.6	0.06	8.3	6.7
1.0	0.7	0.7	1.0	1.1	0.04	1.9	1.6
580	580	580	580	580	580	580	580
322	122	360	89	266	40	33	89
55%	21%	62%	15%	46%	7%	6%	15%
2.06	0.83	2.39	.52	1.77	0.29	0.33	0.43

TABLE I Continued

ELECTROCHEMICAL CELL TESTS

Objective I Group A Continued

Magnesium-Mercuric Sulfate Couple

Test Number:	9C	10C	4C#	5C
Refer to Appendix, page:	4	4	4	4
Vehicle:	A-622	A-622	open cup	open cup
Percent of Vehicle Volume Utilized:	46%	46%	---	---
Configuration:	Bobbin	Bobbin	Bobbin	Bobbin
Net Cell Volume (inches^3):	16.4	16.4	---	---
Load Ω [1]:	3/15	50/250	200	200
Temperature:	-73°C	-73°C	-55°C	-55°C
Hours to End Voltage:	42	---	7	18
Anode (AZ31B Magnesium):	Note[5]	Note[5]	Exmet	Exmet
Anode Area cm^2:	25.6	25.6	---	---
Cathode:	$HgSO_4$**	$HgSO_4$**	$HgSO_4$***	$HgSO_4$**
Cathode Collector[2]:	Ag P.S.	Ag P.S.	Graphite	Graphite
Separator[3]:	Thimble	Thimble	Webril	Webril
Ion Exchange Membrane:	---	---	---	---
Initial Open Circuit Voltage:	2.28	2.30	2.30	2.38
Initial Closed Circuit Voltage:	2.15	2.25	1.45	2.24
End Voltage:	1.5	---	1.0	1.0
Initial Anode Current Density (mA/cm^2)*:	5.60	---	2.98	4.35
Initial Cathode Collector C.D. (mA/cm^2) *:	1.30	---	3.28	4.84
Theoretical Cathode Coulombs/gram[4]:	580	580	580	580
Observed Cathode Coulombs/gram:	134	---	21	80
Cathode Coulombic Efficiency:	23%	---	4%	14%
Watt Hours/Inch^3 of Net Cell:	0.85	---	---	---

*Based on the lighter load if cyclic

**175 grams $HgSO_4 \cdot 2NH_3$ + 75 grams carbon

***7 grams of $HgSO_4 \cdot 2NH_3$

#94% liquid NH_3 + 6% Toluene

TABLE I

ELECTROCHEMICAL

Magnesium-

	Group B-1		
Test Number:	2057	2074	2089
Refer to Appendix, page:	5	5	5
Vehicle:	A-622	A-622	A-622
Percent of Vehicle Volume Utilized:	< 20%	< 20%	< 20%
Configuration:	Flat Cell	Flat Cell	Flat Cell
Net Cell Volume (inches^3):	5.5	5.5	5.5
Load Ω [1]:	20/100	20/100	20/100
Temperature:	25°C	25°C	25°C
Hours to End Voltage:	42	50	117
Anode (AZ31B Magnesium):	Sheet	Sheet	Sheet
Anode Area cm^2:	135	135	135
Cathode grams of $HgSO_4 \cdot 2NH_3$:	---	---	---
Cathode grams of meta-Dinitrobenzene:	16.2	16.2	16.2
Cathode grams of Sulfur:	---	---	---
Cathode Collector [2]:	S.S.	S.S.	S.S.
Separator [3]:	Whatman	Whatman	Whatman
Ion Exchange Membrane:	---	---	---
Initial Open Circuit Voltage:	2.18	2.24	---
Initial Closed Circuit Voltage:	2.15	2.20	2.16
End Voltage:	1.70	1.70	1.50
Initial Anode Current Density (mA/cm^2)*:	0.16	0.16	0.16
Initial Cathode Collector Current Density (mA/cm^2)*:	0.16	0.16	0.16
Theoretical Cathode Coulombs/gram [4]:	1150	1150	1150
Observed Cathode Coulombs/gram:	210	280	600
Cathode Coulombic Efficiency:	18%	24%	52%
Watt Hours/Inch^3 of Net Cell:	0.43	0.43	1.04

*Based on lighter load if cyclic.

Continued

CELL TESTS - Objective I

meta-Dinitrobenzene Couple

Group B-2		Group B-3		Group B-4		Group B-5
2128	2145	2273	2300	2258	2290	2319
5	6	6	6	7	7	7
A-622	A-622	A-622	A-622	A-622	A-622	A-622
< 20%	< 20%	< 20%	< 20%	< 20%	< 20%	< 20%
Flat Cell	Flat Cell	Flat Cell	Flat Cell	Flat Cell	Flat Cell	Flat Cell
4.0	4.0	4.0	4.0	4.0	4.0	4.0
20/100	10/50	10/50	10/50	10/50	10/50	10/50
-55°C	-55°C	-73°C	-73°C	-73°C	-73°C	-55°C
94	59.3	32.5	30.0	15.0	8.7	69.8
Sheet	Sheet	Sheet	Sheet	Sheet	Sheet	Sheet
135	135	135	135	135	135	135
---	---	---	---	---	---	---
16.2	16.2	19.0	19.0	16.2	21.4	16.2
---	---	---	---	---	---	---
S.S.	S.S.	S.S.	S.S.	S.S.	S.S.	Ag Exmet
Whatman	Whatman	Whatman	Whatman	Whatman	Whatman	Whatman
SB6407	SB6407	SB6407	SB6407	SB6407	SB6407	SB6407
---	---	2.25	2.31	2.18	2.36	2.28
2.22	2.20	2.24	2.28	2.11	2.20	2.27
1.50	1.50	1.50	1.50	1.50	1.50	1.50
0.16	0.3	0.3	0.3	0.3	0.3	0.3
0.16	0.3	0.3	0.3	0.3	0.3	0.3
1150	1150	1150	1150	1150	1150	1150
518	628	285	285	155	83	784
45%	55%	25%	25%	15%	7%	68%
1.20	1.52	0.85	0.80	0.35	0.17	1.90

TABLE I

ELECTROCHEMICAL

Magnesium-meta-Dinitrobenzene Couple

Group B-6

Test Number:	2169	2190	2195	2224
Refer to Appendix, page:	7	8	8	8
Vehicle:	A-622	A-622	A-622	A-622
Percent of Vehicle Volume Utilized:	$<$ 20%	$<$ 20%	$<$ 20%	$<$ 20%
Configuration:	Flat Cell	Flat Cell	Flat Cell	Flat Cell
Net Cell Volume ($inches^3$):	4.0	4.0	4.0	4.0
Load Ω [1]:	10/50	10/50	10/50	10/50
Temperature:	-55°C	-55°C	-55°C	-55°C
Hours to End Voltage:	40.3	33.3	33.6	41.5
Anode (AZ31B Magnesium):	Sheet	Sheet	Sheet	Sheet
Anode Area cm^2:	135	135	135	135
Cathode grams of $HgSO_4 \cdot 2NH_3$:	---	---	---	---
Cathode grams of meta-Dinitrobenzene:	13.7	19.3	21.4	21.4
Cathode grams of Sulfur:	---	---	---	---
Cathode Collector [2]:	S.S.	S.S.	S.S.	S.S.
Separator [3]:	Whatman	Whatman	Whatman	Whatman
Ion Exchange Membrane:	SB6407	SB6407	SB6407	SB6407
Initial Open Circuit Voltage:	2.03	2.17	2.19	2.25
Initial Closed Circuit Voltage:	2.05	2.07	2.10	2.19
End Voltage:	1.50	1.50	1.50	1.50
Initial Anode Current Density (mA/cm^2)*:	0.3	0.3	0.3	0.3
Initial Cathode Collector C.D. (mA/cm^2)*:	0.3	0.3	0.3	0.3
Theoretical Cathode Coulombs/gram [4]:	1150	1150	1150	1150
Observed Cathode Coulombs/gram:	592	313	314	299
Cathode Coulombic Efficiency:	33%	27%	27%	26%
Watt Hours/$Inch^3$ of Net Cell:	0.78	0.66	0.66	0.63

*Based on lighter load if cyclic.

Continued

CELL TESTS - Objective I

Magnesium-Sulfur Couple			Magnesium-Mixed Cathode Couples			
	Group C			Group D		
2205	2204	2209	2056	2129	2136	2179
9	9	9	10	10	10	10
A-606	A-606	A-606	A-601	A-601	A-601	A-622
< 20%	< 20%	< 20%	60%	60%	70%	< 20%
Flat Cell	Flat Cell	Flat Cell	Bobbin	Bobbin	Bobbin	Flat Cell
0.66	0.66	0.66	14.4	14.4	14.4	4.0
50/250	50/250	50/250	10	10	10	10/50
-55°C	-55°C	-55°C	24°C	24°C	24°C	-55°C
12.5	9.5	7.7	1.0	0	26.1	9.2
Sheet	Sheet	Sheet	Rod	Rod	Rod	Sheet
28	28	28	71	71	71	135
---	---	---	26.3	26.3	26.3	---
---	---	---	---	---	---	13.0
3.23	3.23	3.23	60	60	60	7.2
S. S.	S. S.	S. S.	S. S.	S. S.	Ag wire	S. S.
Whatman	Whatman	Whatman	Whatman	Webril	Webril	Whatman
---	SA6404	SB6407	---	---	---	SB6407
2.22	2.11	2.16	---	0.4	2.12	2.18
2.21	2.10	2.19	2.28	0.1	2.50	2.00
1.50	1.50	1.50	1.50	1.50	1.50	1.50
0.3	0.3	0.3	---	---	3.5	0.3
0.3	0.3	0.3	---	---	---	0.3
6030	6030	6030	---	---	---	≈ 2890
154	114	95	---	---	84	87
2.6%	1.9%	1.58%	---	---	---	8%
0.39	0.28	0.24	---	---	0.64	0.21

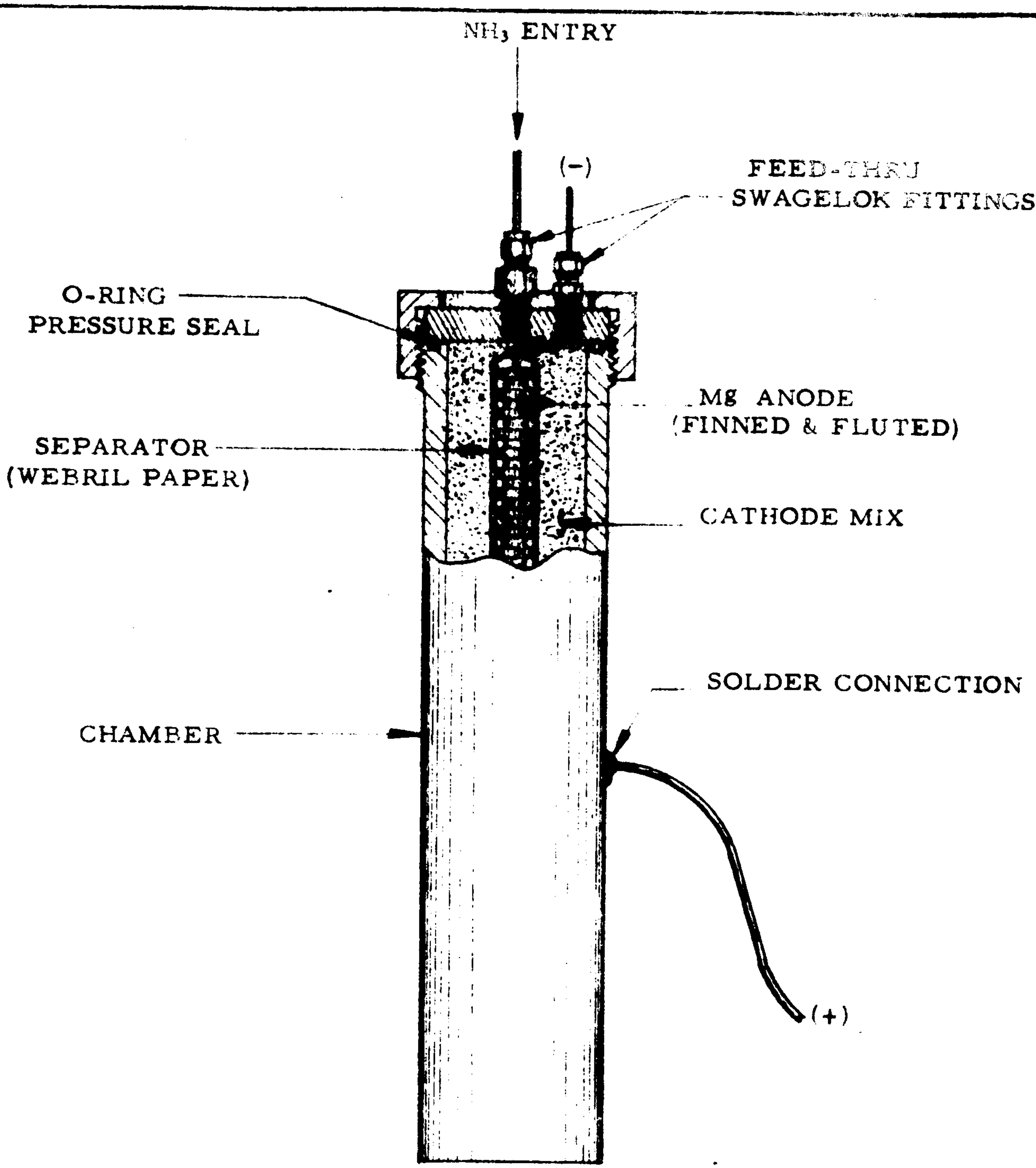
In view of the favorable results obtained from mercuric sulfate, current efforts are being concentrated on this cathodic material. In the meta-dinitrobenzene (m-DNB) cells the flat-plate type of construction has provided optimum results. The mercuric sulfate cathode has been investigated thus far only in bobbin configuration, but techniques for making flat-plate cells are being developed.

Group A tests refer to the efforts at evolving a $Mg/KSCN:NH_3/$ - $HgSO_4 \cdot 2NH_3$ bobbin cell (see Figure 1, page 21 and Figure 2, page 23).

A study of Table I indicates that this system shows much promise for relatively good performance at -73°C and that a considerable proportion of the future effort should be directed toward work with ammoniated $HgSO_4$ in both the bobbin and flat-plate configurations.

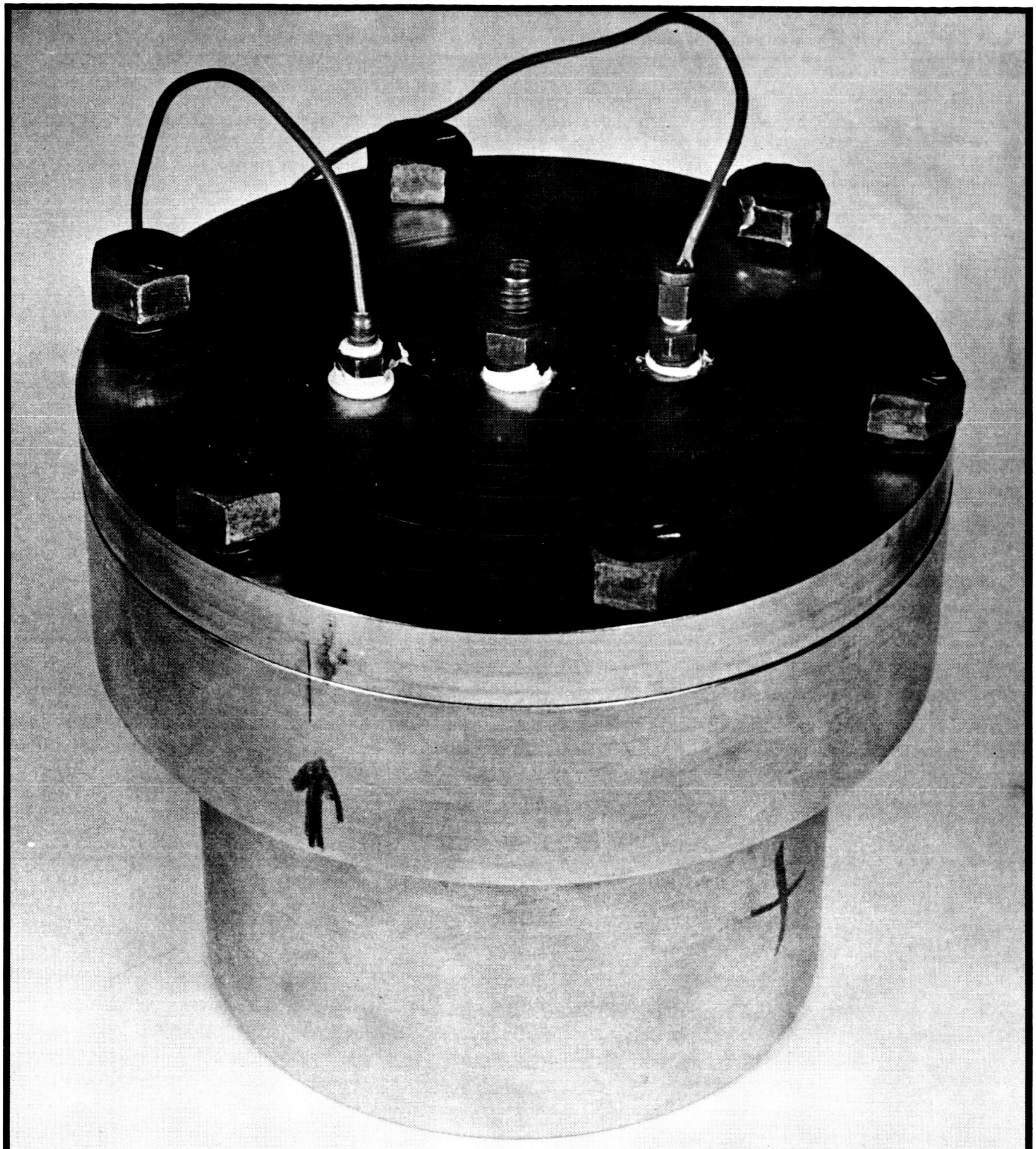
Group B, further sub-divided below, similarly treats m-DNB in a flat cell structure designed to reduce electrode current density. The vehicle generally used for these tests was assigned the number A-622 shown in Figures 2, 3, and 4, pages 23, 25, and 27. This chamber is capable of holding five parallel flat plate cells. The tests of Group B listed in Table I are single cell tests where 80 per cent of cell volume was blocked out with plastic. The cyclic load resistance was adjusted according to net cell volume.

B-1. (Tests 2057, 2074, and 2089) This sub-group indicates that a cut-off voltage of 1.5 volts provides a realistic target for this cathodic material.



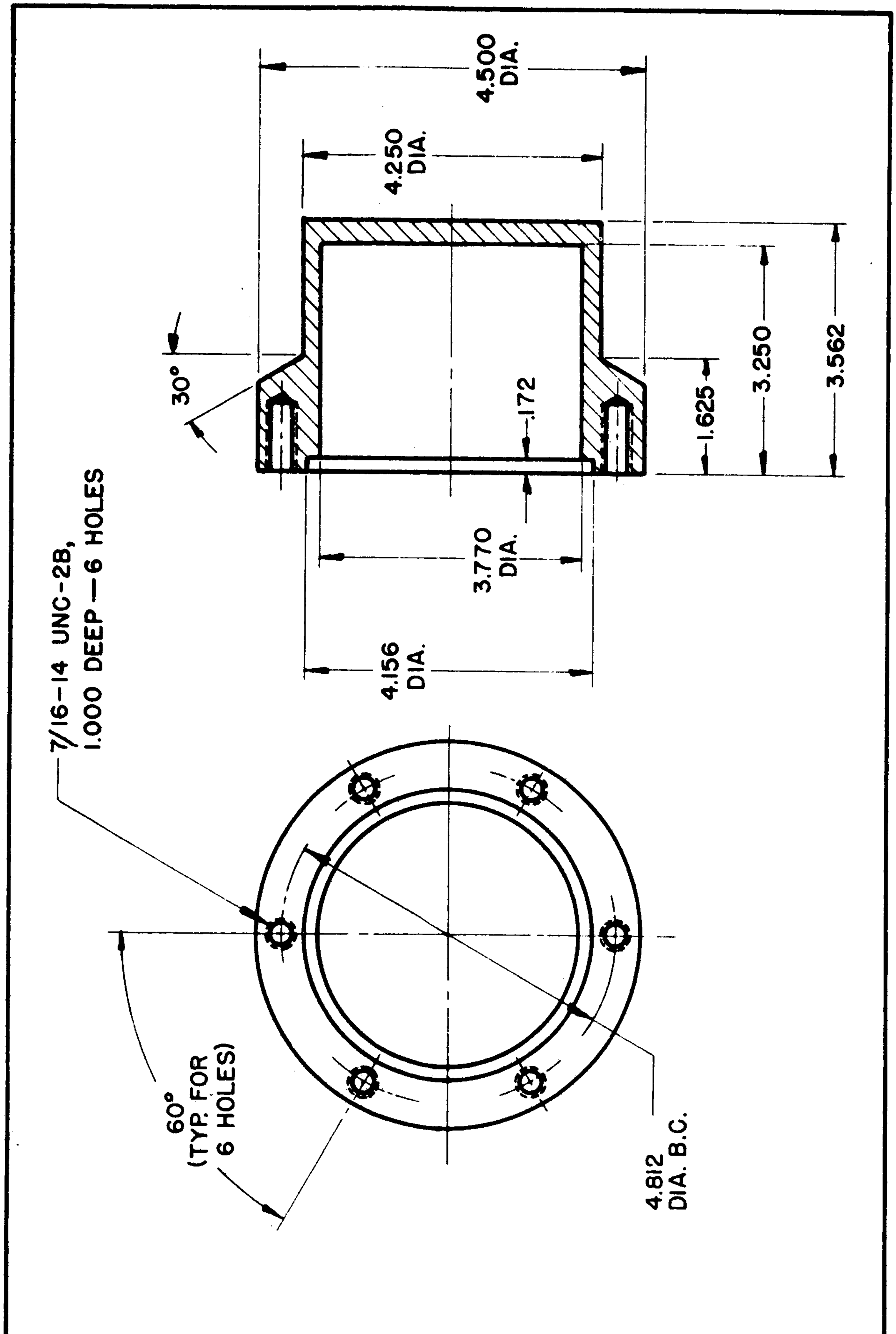
A-601 TEST VEHICLE

FIGURE 1



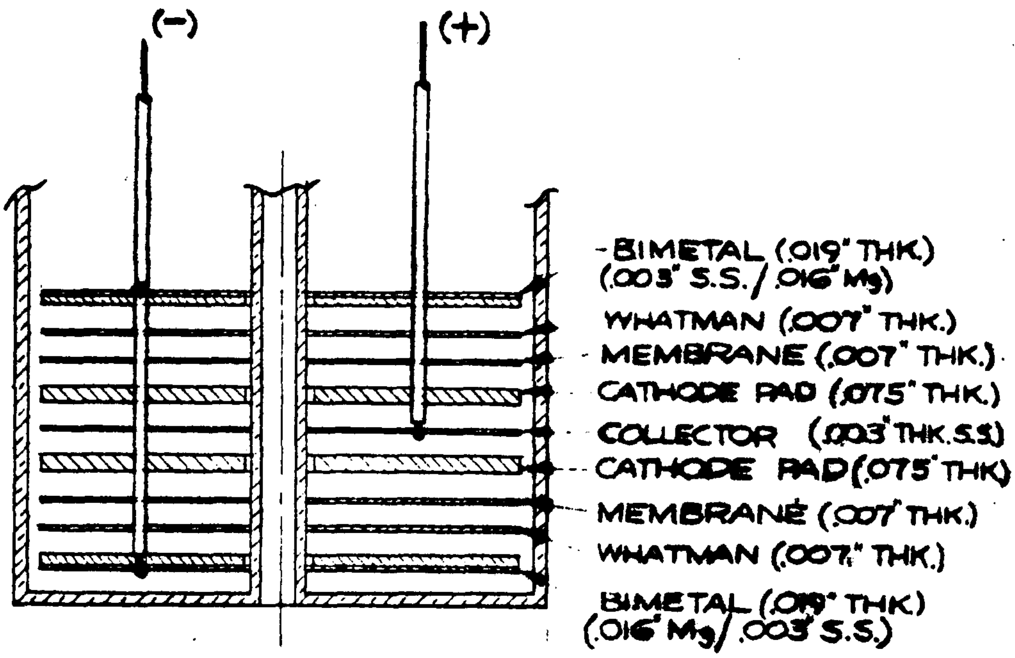
A-622 TEST CHAMBER

FIGURE 2



A-622 TEST CHAMBER

FIGURE 3



ASSEMBLY DRAWING OF A-622 FLAT-PLATE CELL

FIGURE 4

B-2. (Tests 2128 and 2145) A higher drain rate reduced the life of the cell, but yielded a better coulombic efficiency.

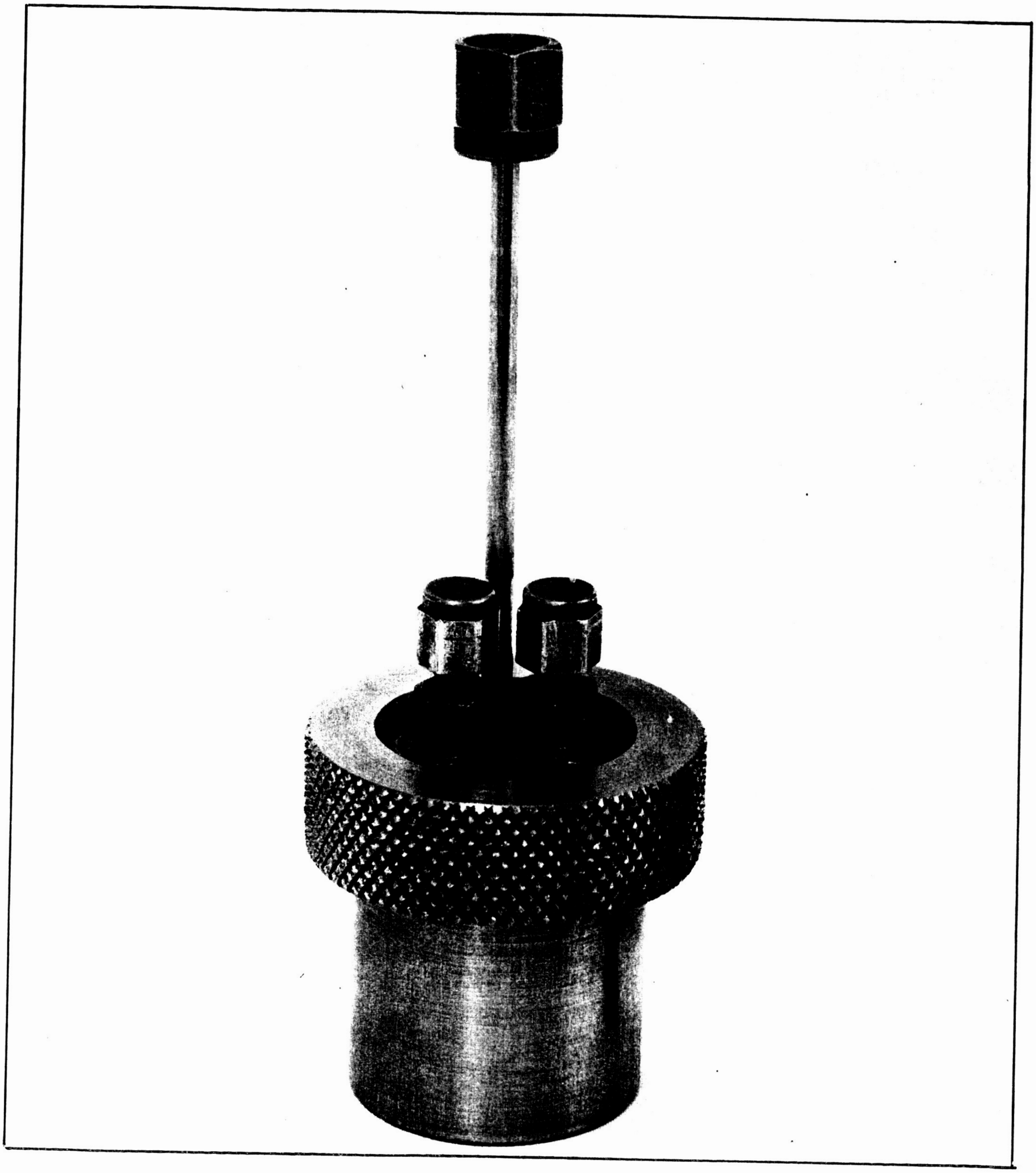
B-3. (Tests 2273 and 2300) The addition of 4 per cent of silver powder to the cathode improved the coulombic efficiency and doubled the run time. Compare with No. 2258.

B-4. (Tests 2258 and 2290) A reduction in operating temperature from -55°C to -73°C appears to have been responsible for great reduction in cell life and efficiency. Compare with No. 2145.

B-5. (Test 2319) The substitution of a silver Exmet cathector for stainless steel seems to have improved the cathodic efficiency and the run time. Compare with No. 2145.

B-6. (Tests 2169, 2190, 2195, and 2224) The purpose of this sub-group was to verify the cathode mix ratio 45:45:10, m-DNB: carbon: paper, respectively, as an optimum for this particular cell and vehicle configuration. The results confirm this ratio as optimum. Compare with No. 2145.

Group C. Three cells (Nos. 2205, 2204, and 2209) were run at -55°C using sulfur as the cathode reactant in the presence of an acid and a basic membrane separately. These tests were conducted in a third vehicle, designated A-606, which is defined in Figure 5, page 31. Since only one-fifth of the volume was utilized, and since the A-606 vehicle is even smaller than the A-622, a loading schedule of 50Ω for 6 minutes and 250Ω for 54 minutes was used to comply



A-606 TEST CHAMBER

FIGURE 5

with the specified power requirements. Sulfur appears to perform very inefficiently under these test conditions; and the use of ion-exchange membranes, both acid and basic, proved to be detrimental.

Group D. (Nos. 2056, 2129, 2136, and 2179) Group D comprised cells tested in both the A-601 vehicle and the A-622 vehicle for the purpose of examining mixed cathodes, i. e., sulfur : mercuric sulfate and meta-dinitrobenzene : sulfur mixtures. The capability of the S : $HgSO_4$ system seems to be much less than that of $HgSO_4$: $2NH_3$, and the mixture of m-DNB and sulfur is definitely inferior to m-DNB alone (see No. 2145).

Considerably more tests were run, but difficulties with sealing at -73°C have resulted in the loss of many of these tests. The problem of leakage was particularly damaging to an initial series of active wet stand tests.

MERCURIC SULFATE CELL PROCEDURE AND DISCUSSION

In order to evaluate the 72-hour low temperature potentialities of the mercuric sulfate system (Mg/25%KSCN: NH_3/$HgSO_4 \cdot 2NH_3$), new designs in cell construction were considered to obtain initial performance. Finned-fluted and multiple-channeled magnesium anodes were constructed to increase the effective anode surface area per volume of solid electrodes (see Figure 7, page 43). Satisfactory and uniform activation was obtained with the cells tested. These cells were of the bobbin configuration and arranged in a cylindrical fashion with the anode in the middle of the cathode mixture. The inside surface of the steel test vehicle acted as the cathector. Webril paper, No. 1365 M, was used to separate the anode from the cathode components. See Figure 1, page 21.

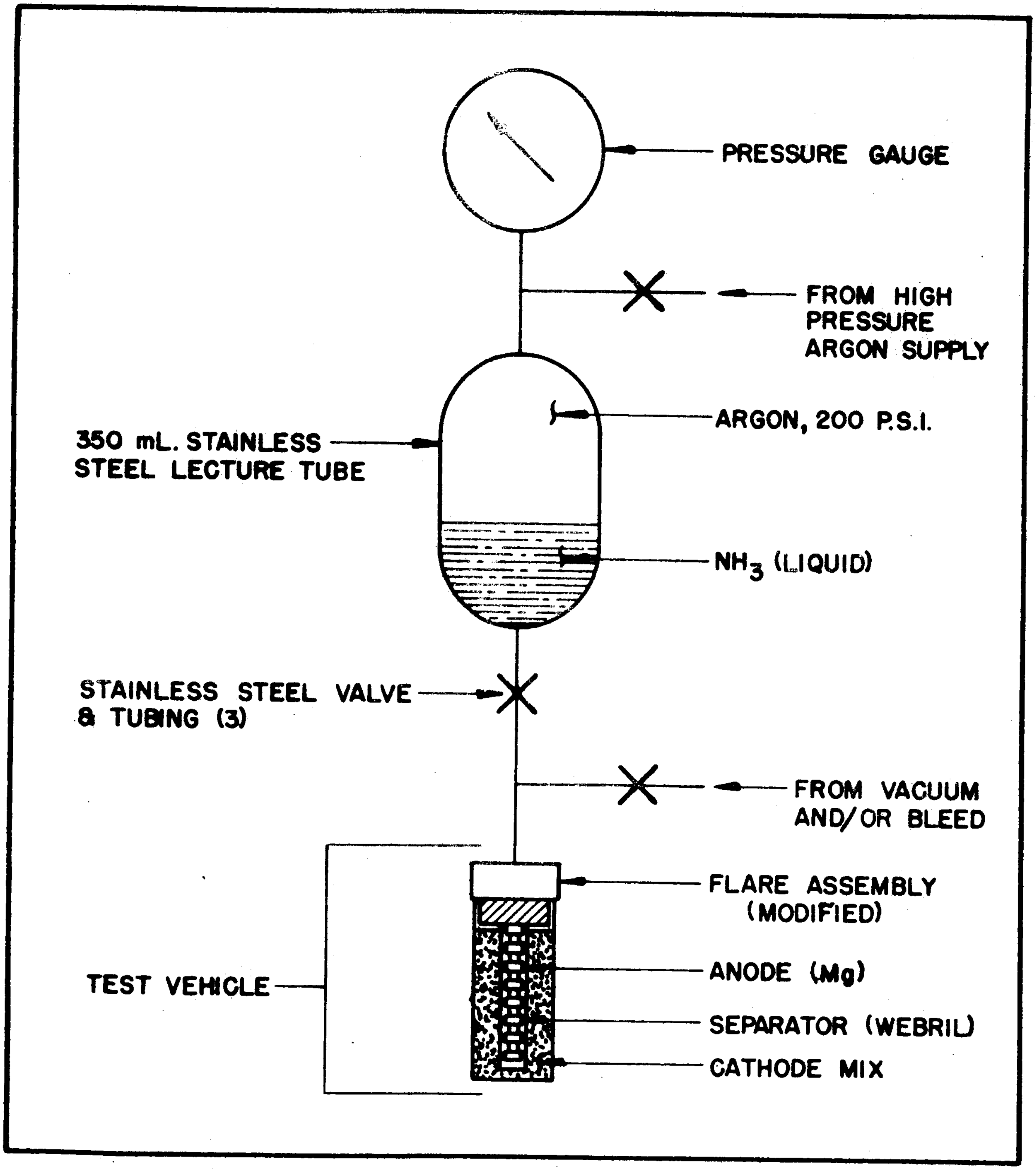
The top of the Mg anode contained a small copper rivet to which was soldered a silver wire. A piece of polyethylene tubing was placed around the silver wire for insulation. Epoxy was then applied around the soldered joint and polyethylene tubing for insulation of the joint from the KSCN-NH_3 electrolyte. Webril paper (two layers) was wrapped around Mg anode and sealed with acetone.

A 7 : 3 ratio of $HgSO_4 \cdot 2NH_3$ and Dixon air-spun carbon was ball-milled for two hours. This mix was packed around the insulated Mg anode. In these cells, 175 grams of $HgSO_4 \cdot 2NH_3$ and 75 grams of carbon, along with 25 grams of KSCN were utilized.

Following installation of the cells within vehicles, the vehicle and contents were evacuated to less than 0. 5 mm of Hg total pressure.

Each cell was activated with liquid ammonia at +200 pounds per square inch argon pressure at room temperature and discharged under load at the preselected temperature (see schematic, Figure 6, page 39). Prior to ohmic loading, the cells were allowed to remain on open circuit voltage in the cold temperature chamber until thermal equilibrium was reached. To prevent the release of excess heat within the cell during activation with liquid ammonia, pre-ammoniated mercuric sulfate ($HgSO_4 \cdot 2NH_3$) was used as the cathode depolarizer rather than unsolvated $HgSO_4$. Prior to activation, each cell was tested for leaks in a water bath using 600 pounds per square inch gauge of argon gas.

Post-mortem examinations of the magnesium-mercuric sulfate cells revealed that reasonably uniform corrosion of the finned-fluted anodes had occurred during the electrochemical discharge period. See Figure 7, page 43, for pictures taken before and after discharge.



SCHEMATIC OF THE MANIFOLDING OF THE A-601 TEST VEHICLE

FIGURE 6

META-DINITROBENZENE AND SULFUR CELLS PROCEDURE AND DISCUSSION

Investigations of the systems Mg/KSCN: NH_3/m-DNB: NH_4SCN: -C: paper and Mg/KSCN: NH_3/S: C: paper were limited to flat cell designs because past experience with these couples has indicated that they do not perform efficiently in the bobbin configuration at the higher drain rate.

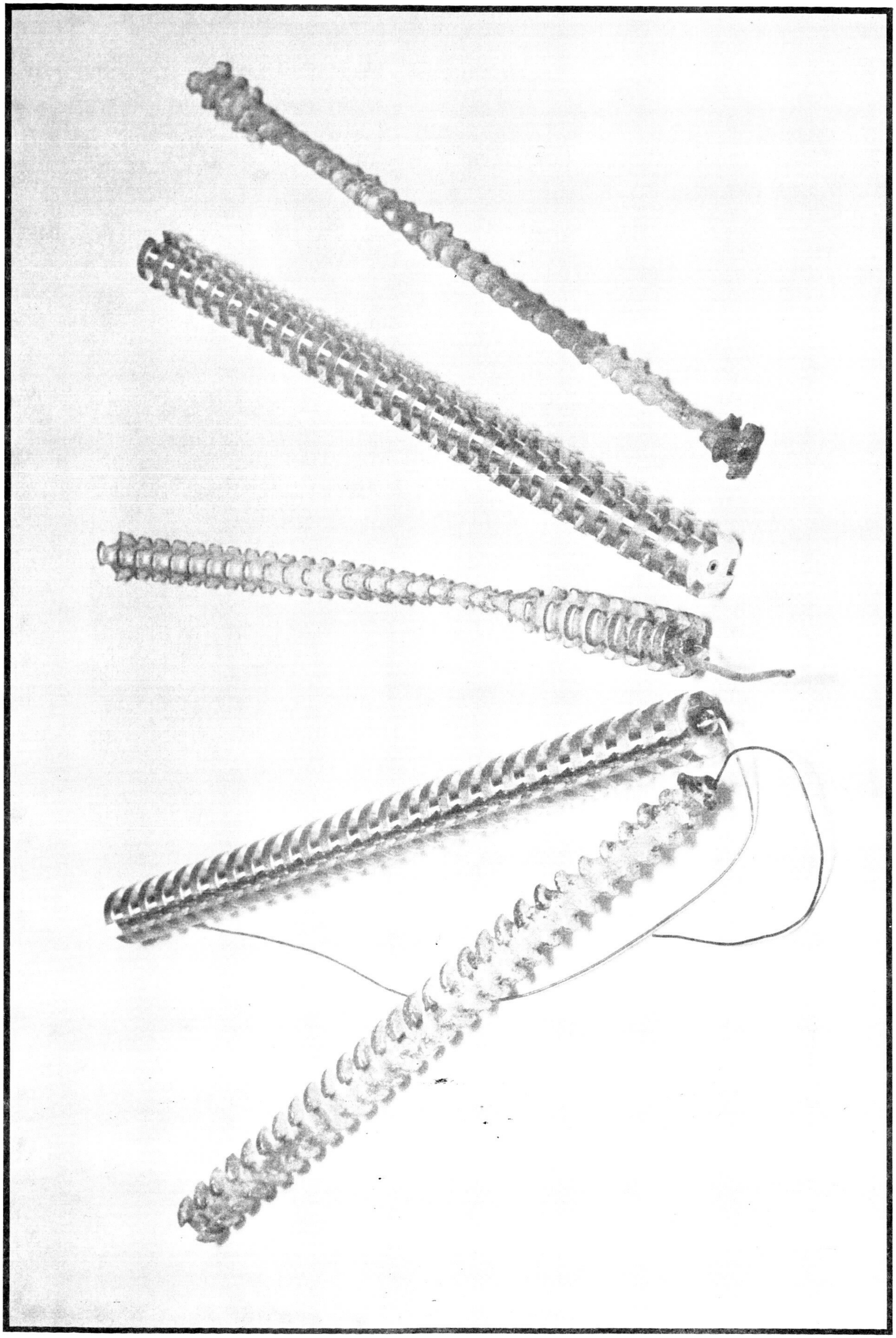
PREPARATION OF THE FLAT CATHODE PADS (META-DINITROBENZENE)

The composition of the cathode is predetermined to meet the requirements of the desired test.

The various ingredients are weighed in the correct proportions and placed into the blender jar, water added, and blended for five minutes.

The resulting slurry is molded into a sheet on a Williams Sheet Paper machine. Individual cathode pads are then cut from the sheet with a cutting rule die, dried, salted with NH_4SCN solution, and re-dried. The separator paper is salted with KSCN solution and dried.

Following installation of the cells within vehicles, the vehicle and contents were evacuated to less than 0. 5 mm of Hg total pressure.



FINNED AND FLUTED MAGNESIUM ANODES
BEFORE AND AFTER DISCHARGE

FIGURE 7

The cells were activated with liquid ammonia + 400 pounds per square inch gauge argon pressure under load. In all cases where the cyclic load was used, the cells were activated during the low drain portion of the cycle.

In order for a membrane to perform, it is mandatory that positive edge seals be made. Otherwise, ionic migrations may take place around the membrane; and its contribution to cell performance will be negated.

Membrane tests for this quarter have been confined to flat cell structures because practical techniques have been developed at this facility for sealing them into this type of cell.

One cathode membrane combination that has shown promise is $Mg/KSCN: NH_3/m\text{-}DNB: NH_4SCN: C$: paper utilizing strong base membrane SB 6407 (anionic) as shown in Figure 4, page 27.

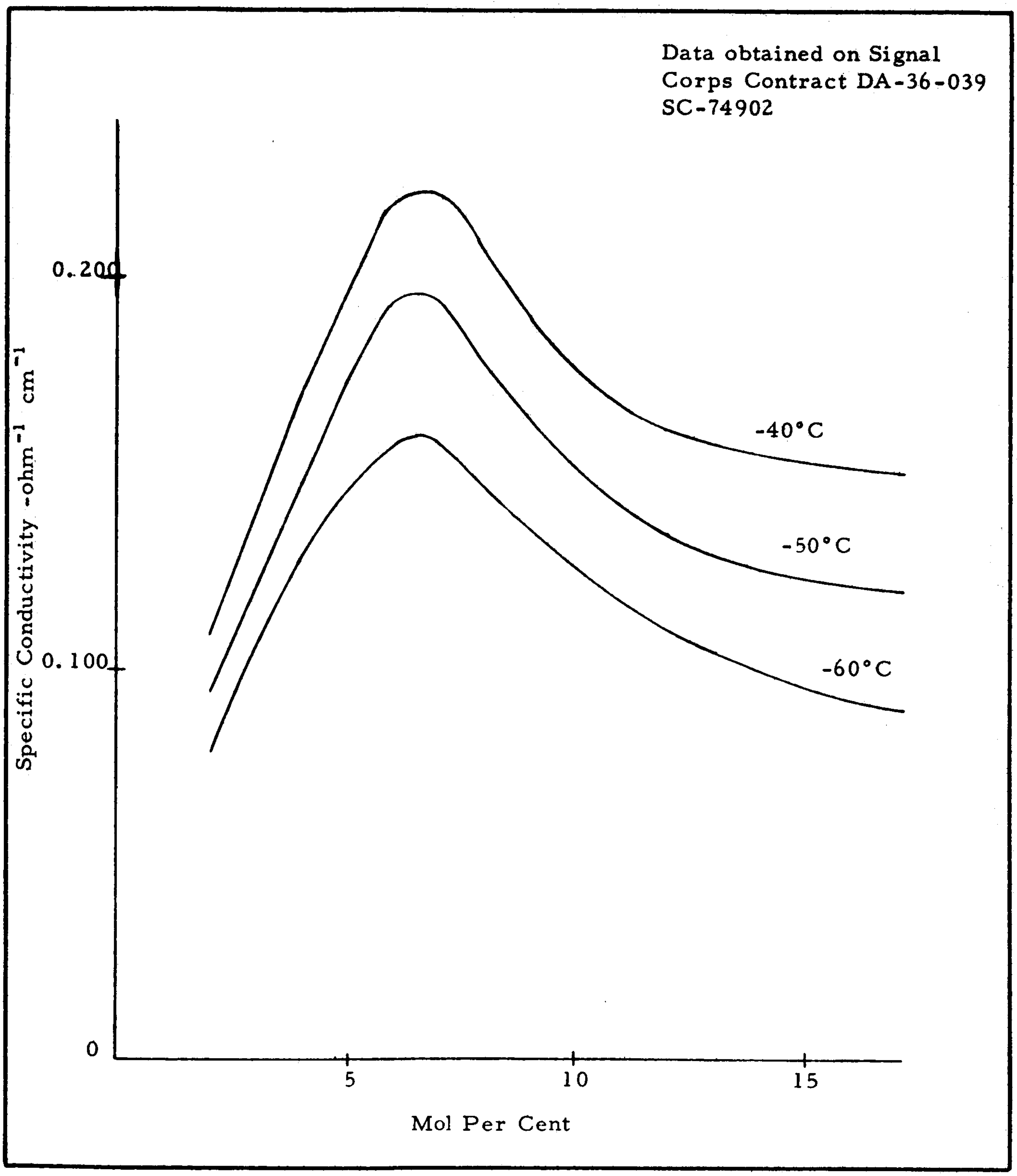
The purpose of an anionic membrane in these cells is to allow free transference of anions ($[SCN]^-$) and to inhibit transfer of cations ($[Mg]^{++}$, $[NH_4^+]$, and $[K]^+$).

Since this cell exhibits superior performance with the membrane, it may be postulated that exclusion of magnesium and/or potassium ions from the catholyte and exclusion of ammonium ions from the anolyte are beneficial.

ELECTROLYTE

Based on a previous knowledge of the specific conductance of KSCN in liquid ammonia, 25 weight per cent ($\approx$5.5 mol per cent) KSCN was selected as the standard test electrolyte for all three couples. The specific conductances of various KSCN concentrations in liquid ammonia at -40°C, -50°C, and -60°C are presented in Figure 8, page 49.

Since the cells tested to date have been activated with ammonia, rather than completed electrolyte, the requisite salt has been incorporated within the cell structure. In the meta-dinitrobenzene cells, some of the KSCN was replaced with NH_4SCN to provide a more favorable media with respect to the cathode.



SPECIFIC ELECTRICAL CONDUCTIVITY OF THE SYSTEM NH_3(l):KSCN

FIGURE 8

WORK TO BE DONE

In the second quarter, a major effort will be concentrated on completing Article I, Phase I, Paragraph B. 4 of the Scope which states that at least three five-cell batteries shall be tested at each temperature: +20°C, -20°C, -40°C, -73°C, and -90°C if feasible. The units shall be discharged at 1.5 watts for 54 minutes and 7.5 watts for 6 minutes alternating continuously for 72 hours.

Despite the fact that the major objectives of this program do not include a consideration of the cell container, the problem of leakage at -73°C indicates that an improvement in the sealing technique or the elimination of the need for sealing the low temperature cells is required. Both paths of action are being actively investigated, and a plastic battery case is being evolved, expecially for the continuation of research with $HgSO_4$ bobbin cells. A more complete presentation of the subject of cell test vehicles will be provided in a subsequent report.

Since the $HgSO_4$ cathode in the form of a bobbin yielded the best performance, it will also be tested in flat cells in order to reduce current density and to permit the convenient use of ion-exchange membranes. Mercuric sulfate is stable in contact with many organic liquids. Therefore, flat cathode discs will be formed as paper from a slurry of mercuric sulfate, graphite and paper pulp in a medium petroleum distillate.

Selected first quarter tests will be repeated to observe reproducibility and to confirm certain tentative conclusions.

Ion-exchange membrane studies will be conducted with both the mercuric sulfate and meta-dinitrobenzene cathodes.

In accordance with the requirements of Article I, Phase II, Paragraphs C.1 (a), (b), and (c) of the Scope, the study of active wet stand, Objective II of this program, will be initiated during the second quarter.

- APPENDIX -

ELECTROMOTIVE CELL TESTS - OBJECTIVE I

Refer to Table I
Pages through

GROUP A - MAGNESIUM-MERCURIC SULFATE CELLS

Test No. A

Purpose: To design a $Mg/25\%KSCN:NH_3/HgSO_4 \cdot 2NH_3$ cell with a 72-hour discharge at room temperature.

Design: Bobbin

Results: This cell was discharged at a constant load of 10 Ω for 54 hours until a voltage of 1.5 was reached. A cathode efficiency of 35% was obtained.

Conclusions: The geometry and size of A-601 chambers appeared to be promising for construction of long-discharge single cells.

Test No. 2051

Purpose: To determine the effect of increased compactness of cathode material upon cell performance.

Design: Bobbin

Results: Cell ran only 17 hours to 1.8v at a constant load of 10Ω because it was only partially activated due to the decreased porosity of cathode mixture. The post-mortem examination indicated that only the upper third portion of the cell was completely saturated with ammonia.

Conclusions: Pressure greater than 2,000 pounds per square inch should not be used in pressing the cathode mix into the final bobbin assembly.

Test No. 2078

Purpose: To determine the effect of low temperature (-73°C) on the cell performance.

Design: Bobbin

Continued on next page

GROUP A - MAGNESIUM-MERCURIC SULFATE CELLS Continued

Test No 2078 Continued

Results: Cell did not activate

Conclusions: Failure was due to an internal short between anode and cathode.

Test No. 2096

Purpose: To improve the activation time. To increase the cell efficiency by increasing the effective anode surface area.

Design: Bobbin

Results: Cell ran 87 hours to 1.5 volts at a constant load of 10Ω. It activated immediately, and a 55 per cent cathode efficiency was obtained. This cell was identical to Cell A except for the anode design.

Conclusions: Finned-fluted Mg anode provided for rapid activation and for an increase in the cell efficiency.

Test No. 2166

Purpose: To determine the effect of cyclic loading on the cell's electrochemical discharge characteristics.

Design: Bobbin

Results: The cell voltage was above 1.5 for 33 hours during the 3Ω portion of the cycle. The voltage was 2.18 for the 15Ω loading period. The cell was allowed to discharge for 65 hours at which time the respective high and low voltages were 1.90 and 1.35.

Conclusions: A comparison with No. 2096 shows that a constant 10Ω load yielded 87 hours versus 33 hours under cyclic loading.

Test No. 7C

Purpose: To determine the effects of cyclic ohmic loading on the cell's discharge characteristics at low temperature.

Design: Bobbin

Results: Cell ran 103 hours to 1.5 volts. It was identical in design to Cell No. 2166. This cell exceeded the

Continued on next page

GROUP A - MAGNESIUM-MERCURIC SULFATE CELLS Continued

Test No. 7C Continued

specified power level and time required for a single cell by this contract.

Conclusions: Good performance, cathode efficiency of 62 per cent was obtained.

Test No. 1C

Purpose: To determine the effect of low temperature on the cathode efficiency under a heavy load.

Design: Bobbin

Results: Cell ran only 24 hours to 1.5 volts at constant load of 10Ω. Electrolyte leaked from cell.

Conclusions: Butyl rubber "O" rings are not suitable at -73°C.

Test No. 6C

Purpose: To determine the effectiveness of silicone rubber "O" rings at -73°C.

Design: Bobbin

Results: Cell ran 72 hours to 1.5 volts at constant 10Ω load. Some leakage of electrolyte was still encountered.

Conclusions: Silicone rubber "O" rings are slightly better than butyl rubber.

Test No. 8C

Purpose: To determine the low discharge rate capacity of the mercuric sulfate system at -73°C. To establish the functional life of silicone "O" rings at -73°C in an ammonia - KSCN atmosphere.

Design: Bobbin

Results: The electrochemical system Mg/25%KSCN:NH_3/-$HgSO_4 \cdot 2NH_3$ was capable of performing for seven days at low cyclic drain rates (50Ω/250Ω) to 1.8 volts.

Conclusions: This system has excellent stability at low drain rates for extensive periods of time. The silicone "O" ring plus Teflon tape provided an excellent seal.

GROUP A - MAGNESIUM-MERCURIC SULFATE CELLS Continued

Tests No. 2C and 3C

Purpose: To evaluate A-622 type chamber for construction of single cells with 72-hour discharge. To determine the effect of a decreased anode area on cell performance.

Design: Bobbin

Results: Channeled anode was not suitable.

Conclusions: A decreased anode surface area was not conducive to a 72-hour cell.

Tests No. 9C and 10C

Purpose: To further evaluate the A-622 vehicle as a chamber for construction of single cells with a 72-hour discharge.

Design: Bobbin

Results: No. 9C ran only 42 hours to 1.5 volts under cyclic loading. No. 10C did not run. Poor for bobbin configuration.

Conclusions: The A-622 chamber was not found suitable for construction of 72-hour bobbin type cell.

Tests No. 4C and 5C

Purpose: Preliminary investigation of the effect of inert miscible solvents on the physico-chemical properties of KSCN-NH_3 solutions.

Design: Bobbin

Results: Inconclusive

Conclusions: None

GROUP B - MAGNESIUM-META-DINITROBENZENE CELLS

Sub-Group B-1 Reduction in End Voltage

Test No. 2057

Purpose: Test cathodic efficiency of the system Mg/KSCN: - NH_3/m-DNB : C at 80 per cent voltage regulation.

Design: Flat Cell

Results: Cell ran 42 hours to 1.7 volts.

Conclusions: None

Test No. 2074

Purpose: Replicate of Test No. 2057

Design: Flat Cell

Results: Cell ran 50 hours to 1.7 volts.

Conclusions: 80 per cent regulation results in $\approx$24 per cent cathodic efficiency.

Test No. 2089

Purpose: Test cathodic efficiency of the system Mg/KSCN: - NH_3/m-DNB: C at 70 per cent voltage regulation.

Design: Flat cell

Results: Cell ran 117 hours to 1.5 equivalent to 52 per cent cathodic efficiency.

Conclusions: Wider voltage regulation results in a very high gain in cathodic efficiency in this system. See Test Nos. 2057 and 2074.

Sub-Group B-2 Variation of Drain Rate

Test No. 2128

Purpose: Test the effect of Gelman SB6407 on the system Mg/KSCN:NH_3/m-DNB:NH_4SCN:C under cyclic load of 20/100Ω.

Design: Flat Cell

Results: Cell ran 94 hours to 1.5 volts.

Conclusions: None

GROUP B - MAGNESIUM-META-DINITROBENZENE CELLS Continued

Sub-Group B-2 Variation of Drain Rate Continued

Test No. 2145

Purpose: Test the effect of SB6407 at double the drain rate of Test No. 2128 (cyclic load of 10/50Ω).

Design: Flat Cell

Results: Cell ran 59.3 hours to 1.5 volts.

Conclusions: Addition of strong base membrane to this system is more beneficial at higher drain rates. Higher coulombic efficiencies were obtained.

Sub-Group B-3 Effects of Silver Powder

Test No. 2273

Purpose: Test the effect on cell performance at -73°C when silver powder constitutes 4 per cent of the cathode.

Design: Flat Cell

Results: Cell ran 32.5 hours to 1.5 volts.

Conclusions: Repeat test.

Test No. 2300

Purpose: Replicate of Test No. 2273.

Design: Flat Cell

Results: Cell ran 30 hours to 1.5 volts.

Conclusions: Addition of silver powder to cathode to increase conductivity seems to enhance performance. See Test No. 2258 on the following page.

GROUP B - MAGNESIUM-META-DINITROBENZENE CELLS Continued

Sub-Group B-4 Effects of Reduced Temperature

Test No. 2258

Purpose: Test capability of the system Mg/KSCN NH_3 /m-DNB:C at -73°C.

Design: Flat Cell

Results: Cell ran 15 hours to 1.5 volts.

Conclusions: System capability seems to be depressed at this temperature. See Test No. 2145 which ran 59.3 hours at -55°C.

Test No. 2290

Purpose: Replicate of Test No. 2258

Design: Flat Cell

Results: Cell ran 8.7 hours to 1.5 volts.

Conclusions: Leaking chamber contributed to short run time.

Sub-Group B-5 Comparison of Silver Exmet versus Stainless Steel Sheet

Test No. 2319

Purpose: Test effect of silver Exmet cathector versus standard stainless steel sheet cathector.

Design: Flat Cell

Results: Cell ran 69.8 hours to 1.5 volts.

Conclusions: Cell performs better with Silver Exmet cathector. See Test No. 2145, page 6 of this Appendix, which ran 59.3 hours.

Sub-Group B-6 Variation in Cathode Mix Ratio

Test No. 2169

Purpose: Test the effect of shifting the mix ration of m-DNB:C: - paper from 45:45:10 to 38:58:4.

Design: Flat Cell

Results: Cell operated 40.3 hours to 1.5 volts.

Conclusions: This mix ratio inferior to standard. See Test No. 2145 which ran 59.3 hours.

GROUP B - MAGNESIUM-META-DINITROBENZENE CELLS Continued

Sub-Group B-6 Variation in Cathode Mix Ratio Continued

Test No. 2190

Purpose: Test the effect of shifting the mix ratio to 54:40:6.

Design: Flat Cell

Results: Cell operated 33.3 hours to 1.5 volts.

Conclusions: As above. See Test No. 2145, page 6 of this Appendix.

Test No. 2195

Purpose: Test the effect of shifting the mix ratio to 59:36:5.

Design: Flat Cell

Results: Cell operated 33.6 hours at 1.5 volts.

Conclusions: As above. See Test No. 2145.

Test No. 2224

Purpose: Replicate of Test No. 2195.

Design: Flat Cell

Results: Cell operated 41.5 hours to 1.5 volts.

Conclusions: As above See Test No. 2145.

GROUP C - MAGNESIUM-SULFUR CELLS

Test No. 2205

Purpose: Test effects of ion-exchange membranes on operating characteristics of the $Mg/KSCN:NH_3/S:C$ system. This cell is the control, i.e., contains no membrane.

Design: Flat Cell

Results: Cell ran 12.5 hours to 1.5 volts.

Conclusions: None

Test No. 2204

Purpose: Test effect of Gelman Strong Acid 6404 membrane on the system $Mg/KSCN:NH_3/S:C$.

Design: Flat Cell

Results: Cell ran 9.5 hours to 1.5 volts.

Conclusions: Cell operates better without strong acid membrane. See Test No. 2205 above.

Test No. 2209

Purpose: Test effect of Gelman Strong Base 6407 membrane on the system $Mg/KSCN:NH_3/S:C$.

Design: Flat Cell

Results: Cell ran 7.7 hours to 1.5 volts.

Conclusions: Cell operates better without strong base membrane. See Test No. 2205 above.

GROUP D - MAGNESIUM-MIXED CATHODE CELLS

Test No. 2056

Purpose: Test operating characteristics of the system Mg/KSCN: -NH_3/S:$HgSO_4$:C.

Design: Bobbin

Results: Cell failed after one hour. Cause of failure unknown.

Conclusions: Repeat test.

Test No. 2129

Purpose: Same as Test No. 2056.

Design: Bobbin

Results: Cell failed to activate. Cause of failure unknown.

Conclusions: Repeat test.

Test No. 2136

Purpose: Same as Test No. 2056 above.

Design: Bobbin

Results: Cell operated 26.1 hours to 1.5 volts.

Conclusions: The capability of this system is considerably less than that of the mercuric sulfate system.

Test No. 2179

Purpose: Test operating characteristics of the system Mg/KSCN: -NH_3/m-DNB:S:C.

Design: Bobbin

Results: Cell operated 9.2 hours to 1.5 volts.

Conclusions: This combination of depolarizers is inferior to m-DNB alone. See Test No. 2145 , page 6 of this Appendix.