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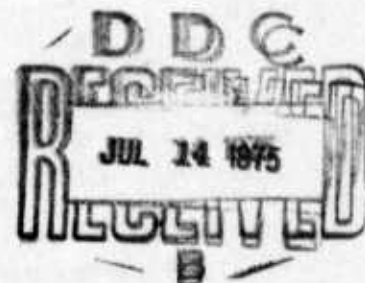
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AFAPL-TR-75-18

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ADVANCED ALUMINUM-CHLORINE BATTERY FOR EXPENDABLE ECM DEVICES

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FEBRUARY 1975



TECHNICAL REPORT AFAPL-TR-75-18

FINAL REPORT FOR PERIOD 15 SEPTEMBER 1972 — 15 FEBRUARY 1975

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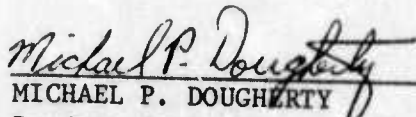
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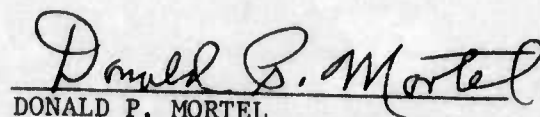
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This technical report has been reviewed and is approved for publication.


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1. INTRODUCTION

The aluminum anode is of interest in energy storage systems because of its potential (-1.66 volt vs. SHE) and its low equivalent weight. Making it even more attractive is its low cost and availability.

Aluminum electrodes are difficult to handle because of a surface layer of oxide. Once the oxide is removed then a corrosion reaction occurs in aqueous media which leads to oxidization of aluminum. Some oxide may form again which reduces the reaction rate and the voltage.

To avoid these complications, the aluminum anode has recently been investigated in a molten salt system.⁽¹⁾ In the molten salt the electrode is used as a secondary electrode.

It had been found in this laboratory that the oxide layer can be removed totally, and then some parts of the surface not allowed to reoxidize by partially amalgamating the surface. In addition to having just an active surface, another phenomenon was observed. Aluminum anodes in aqueous solutions yield open circuit potentials about 1.1 volts below the thermodynamic value. When the surface is partly amalgamated the open circuit voltage increases so that the electrode is now about 0.4 volts below the theoretical value. While in this state the electrode is termed "activated" or "promoted."

Once activated the aluminum corrodes but at a relatively slow rate. In a primary system not requiring stand, but requiring a high rate discharge, the efficiency of the electrode may reach 80%. The polarization of the electrode is quite low. Discharges at current densities of 0.5A/in^2 take place with less than 0.1 volt polarization of the anode.

Thus, the prospects of using aluminum as an anode in a high energy density system is promising. The question of the cathode naturally arises.

(1) J. Giner and G. Holleck, NASA CR-1541, March 1970

One's first thoughts go to group 8 of the periodic table. The only halogen of interest is chlorine. Fluorine is too reactive and too costly. Bromine is heavy enough to make the watt-hour per pound figure unattractive. Oxygen is precluded because it causes a severe change in pH which ultimately causes a deactivation of the anode. Sulfur offers only a low potential and a low watt-hour per pound figure. Based on a voltage of 2.6, the theoretical specific energy is 707 WH/lb.

The materials that are suitable for fabrication of a chlorine electrode structure are carbon, titanium, Hastalloy C and teflon. Graphite has been reported to swell and disintegrate.¹ The titanium, Hastalloy and carbon do yield about 1.08 volts versus a calomel electrode when chlorine is bubbled over them. The value 1.08 volts is the theoretical value. Other materials including gold, platinum and tungsten yield much lower potentials indicating corrosion and mixed potentials.

Gas electrodes have certain inherent disadvantages. Solid electrodes are generally more satisfactory. To retain the advantages of the high specific energy, certain cathodes were found that hold some sort of promise from the point of view of being strong oxidizing agents and having relatively low equivalent weight. These were lead chromate, potassium persulfate and calcium peroxide.

The goal of this contract to WPAFB was to develop this activated aluminum anode into a reserve type battery system for Electronic Counter Measure Devices. The requirements were to be operational from -60°F, to have a voltage of 28 volts and deliver 2A. The entire battery was to occupy a volume no greater than 6 in³. This report covers the work done during the program.

2. PROGRAM OBJECTIVE

The objective of this program was to provide advanced battery technology leading to the development of an improved primary power source, utilizing the activated aluminum anode, for expendable ECM Jammers. This battery system, when fully developed, was expected to yield energy densities of 60 WH/lb and 6 WH/in³ at the 45 minute discharge rate.

3. PROGRAM TASKS

The program was divided into a set of tasks which are presented and discussed below.

Cathode Structure and Chlorine Cathode

The use of an optimized composite structure is essential in obtaining an electrochemically efficient gas-diffusion Cl_2 electrode. Furthermore the electrode structure must be "light" and "reliable" for the high energy density and high power density battery. "Thin" composite electrode structure employed in the present investigation consists of two teflon (TFE)-bonded activated carbon layers which are supported on a porous titanium plaque. The Ti plaque also serves as the current collector.

The task was therefore to characterize the optimum loading levels (mg) for the composite layers and the optimum pressure for sintering the TFE in the electrode structure. The optimum loading levels and the sintering pressure was evaluated based on the actual electrode performance which follows. The electrode size was 2.625" x 0.925" (rectangular) with an active geometric area of about 2 in². This electrode had the actual single electrode size envisioned for the ECM reserve battery.

Anode Activation

The novel method of activating Al anode by amalgamating its surface yields a voltage increase of about 0.5 to 0.7 volts. This electrode activation requires a finite time which is also the time required to remove the Al surface oxide films by Hg^{++} and Cl^- ions and to amalgamate the surface by the chemical displacement reaction of Hg^{++} ions in solutions. For example, the full activation of an Al untreated surface requires a time varying from 5 minutes (for Al type 1199) to 30 minutes (for Al type 1100) in aqueous NH_4Cl solution containing $5 \times 10^{-3} M HgCl_2$. The activation time is dictated by the Al surface conditions and the Hg^{++} ion concentration in the solution.

Alternatively the once-activated Al exhibits a rapid activation time, even after it is exposed to air which reacts rapidly with the amalgamated surface. The objective of this task was therefore to investigate the proper method of cleaning the Al surface and to evaluate the optimum Hg^{++} ion concentration needed for a shortest electrode activation time. Prefabrication Activation and In Situ Activation were investigated on 1100 type Al which is commercially available and inexpensive.

CaCl_2 Aqueous Electrolyte

The selection of aqueous CaCl_2 solution for the present investigation is based on (1) the low eutectic temperature, i.e., -67°F for 29.8 wt.% CaCl_2 solution, (2) the low Al corrosion rate in the solution, e.g., 1.9 mA/in^2 , and (3) a reasonably good electrolyte conductivity, 0.17 mho/cm at 32°F .

The aim of this task was to determine (1) the optimum CaCl_2 concentration in the electrolyte for the required cell performance, and (2) the minimum electrolyte volume required to sustain the required cell voltage and capacity. The best Cl_2 cathode structure and the best Al activation method found in the previous tasks were utilized in determining the optimum concentration.

Separators

With the close spacing between the electrodes, a separator might have been needed to avoid accidental shorts. This task was therefore aimed at determining (1) the separator material suitable for the present system, (2) the wet-out time, and (3) the specific electrolyte absorption.

Cathode Selection

There are several high energy oxidants or cathode active materials, in addition to gaseous Cl_2 , which are potentially promising for high energy battery application. Among those materials are $\text{K}_2\text{S}_2\text{O}_8$, PbCrO_4 , and CaO_2 . A list of pertinent properties for these materials is given below.

<u>Oxidants</u>	<u>Density (g/cc)</u>	<u>mp (°C)</u>	<u>Solubility g/100gH₂O</u>	<u>Eq. wt. g/Eq</u>	<u>Theoretical* WH/lb</u>
K ₂ S ₂ O ₈	2.49	d<100°	5.0(20°)	135	280
PbCrO ₄	6.3	844°	7 x 10 ⁻⁶ (20°)	108	274
CaO ₂	?	d 275°	Sl. Sol.	36	?

*Based on an activated Al anode.

The selection of K₂S₂O₈ is based on its commercial availability, while PbCrO₄ is selected because of its low solubility. Alkali chromates are quite soluble in aqueous solutions. The properties of CaO₂ are not well known because of its strong reactivity. These materials are solids at room ambient temperature and are therefore easier to handle compared to gaseous Cl₂.

This task was to evaluate the feasibility of utilizing the above oxidants as the cathode active materials in an activated Al cell. The experimental procedures consist of (1) fabrication of porous cathode, impregnated with the reactants. This involves the selection of appropriate current collector materials and the proper method of fabricating the cathodes, e.g., compositions of cathode mixture, pressure for compaction, etc., and (2) testing and evaluation of the cathodes.

The remainder of the program effort involves the construction and the testing of the single cell module and the design of a breadboard battery.

4. SUMMARY

A) Review of Work Completed

During the program, work on the activated aluminum anode reserve battery system for expendable ECM Jammers has established the following:

- i. The choice of chlorine to serve as the cathode for this battery system.
- ii. A titanium based active carbon coated electrode to serve as catalyst-conductor for gaseous chlorine reduction. The voltage of this chlorine electrode during a 45 minute discharge at 0.5 amps/in² maintains itself between 0.4 and 0.5V vs. a saturated calomel electrode; a polarization of about 0.7 volts.
- iii. A plastic cathode housing compartment with a 1/16" recess cavity providing for Cl₂ gas space. The gas was lead into the space through two inlet ports at the top of the compartment.
- iv. The choice of an aluminum alloy (Al 1100) to serve as the anode material.
- v. An etching and preactivating procedure which results in an aluminum to calomel reference voltage of -1.4 to -1.5V at the 45 minute discharge rate. (Etching in Tucker solution for 30 seconds, and predischarging in 30% CaCl₂ + .1MHg⁺⁺ + 1 NHCl for 15 minutes at 0.5 amps/in².)
- vi. The initial choice of an electrolyte for the aluminum chlorine battery based on the requirement of cell voltage and freezing point. The cell voltage at the 45 minute discharge rate (0.5 amps/in²) was 2.0V in this electrolyte. The electrolyte, 30% CaCl₂ + .1M Hg⁺⁺ + 1NHCl also showed a freezing point below -65°F.
- vii. Determination of the behavior of the Al-Cl₂ cell in limited electrolyte, and as a result development of alternate electrolyte choices; 25% CaCl₂ aqueous and 15% CaCl₂-alcoholic.
- viii. A filter paper separator which does not significantly lower cell voltage and which is inert to electrolyte, chlorine and reaction products.

- ix. Investigation of alternate cathode materials, CaO_2 , $\text{K}_2\text{S}_2\text{O}_8$ and PbCrO_4 on various current collectors. Although some encouraging results were achieved with $\text{K}_2\text{S}_2\text{O}_8$ combined with a graphite current collector by means of spraying and impregnation, the amount of development required to improve this cathode to the present level of chlorine electrode would be beyond the scope of this contract. These three cathode materials have been investigated and the work indicated that the composite chlorine electrode was superior.

B) Problems Encountered and Methods Used to Solve Them

- i. A major problem arose when chlorine electrodes which were made according to the previously defined specification did not exhibit the same voltage as their predecessors under $0.5/\text{in}^2$ ampere load. Instead of 0.4 to 0.5V vs. calomel these electrodes gave a voltage of 0.2 to 0.3. Modification of electrode manufacturing techniques including using a thin titanium tab to achieve a more even surface, rotating electrodes in 45° increments during spraying, using more porous titanium, varying thickness of titanium and using different fabrication techniques (e.g. layer weight and sintering pressure) did not significantly improve the polarization of the chlorine electrodes. The problem was solved when a fresh batch of Darco carbon was used in fabricating the electrodes. Of a batch of 8 electrodes made with the fresh carbon five gave half-cell potentials of 0.5V, two gave 0.45V and one showed 0.4V at a current density of 0.5 amperes/ in^2 . Small improvements in Cl_2 electrode potentials had resulted out of using the new batch titanium and rotation during spraying. These methods were incorporated into the standard procedure of making electrodes.
- ii. Reference Electrode for Low Temperature Testing.
Because the calomel electrode freezes at low temperatures it was found unsuitable as a reference. A silver-silver chloride electrode was tried but was unstable in CaCl_2 . An aluminum reference was not found satisfactory because the aluminum reference underwent slow

activation in the electrolyte which contained mercury and hence a constantly changing potential. A chlorine reference was found suitable at low temperatures. The electrode consisted of a plexiglas tube with one end completely covered by a piece of titanium-carbon teflon coated material. Chlorine was passed through the open end of the tube from the same source which fed the chlorine counter electrode.

iii. Aluminum Activation at Low Temperatures.

A minimum ambient temperature of 32°F was shown to be required in order to rapidly activate the aluminum electrode. At temperatures below 32°F activation time exceeded 20 minutes. In order to properly activate the aluminum, a heating tape is required to raise the chlorine vapor pressure in the final design of the EMC battery and will also serve to raise the battery temperature to 32°F. The inefficient energy of the discharge will supply sufficient heat to maintain the battery temperature above 32°F during the discharge.

iv. Behavior of Aluminum Chlorine System in Limited Electrolyte Volume.

The characteristics of the aluminum and chlorine electrodes were established in excess electrolyte. The choice of electrolyte was based on cell performance in an excess amount of said electrolyte. In order to meet the weight and volume requirements of the 56 watt-42 watt-hour reserve battery a very limited amount of electrolyte must be used.

A problem heretofore not considered arose in limited electrolyte testing. During the discharge aluminum reacts to form $AlCl_3$ both by corrosion and electrochemical oxidation. The $AlCl_3$ formed coordinates with 6 waters to form $AlCl_3 \cdot 6H_2O$. The source of that water is the electrolyte. $AlCl_3 \cdot 6H_2O$ must also be dissolved and this requires additional water. $CaCl_2$ also tends to form hydrates which require water for formation and dissolution. It was calculated that for every gram of aluminum consumed almost 8cc of water are required. Because of the poor efficiency of aluminum in the originally

chosen electrolyte, a modification of that electrolyte was necessary. The modification was accomplished by reducing both the acid and mercury ion concentration in the electrolyte by an order of magnitude.

Further modifications such as additional decrease of mercury ion concentration and the use of organic solvents have reduced the volume of electrolyte required in the cell by increasing the efficiency of the aluminum.

By internal storage of electrolyte the volume of a 56 watt-42 WHr ECM battery could be decreased to almost half. From open circuit corrosion data of Al 1100 in 25% CaCl_2 it would be possible to allow each cell to contain its electrolyte directly in contact with aluminum. The corrosion of the aluminum is so slight that only 10% of the total weight of each anode would be consumed during a ten-year dormant stand.

5. CATHODE STRUCTURE DEVELOPMENT

A) Objective

To determine the conditions of construction which will yield minimum polarization for the chlorine electrode. The conditions investigated included loading levels of carbon and teflon layers, compression and necessity for gas distribution. Optimum conditions of construction were studied to characterize this electrode with respect to polarization, utilization of chlorine, discharge life and effective surface area at room and cold temperatures.

B) Experimental

1. Cathode Fabrication Procedure

The basic substrate is a porous titanium plaque (40% porosity, 10 μ mean pore size) 0.010" thick. The plaque is cut into a desired size and onto which a solid Ti lead (0.008" thick) is resistance

welded (Unitek 1-132-02, at about 40 W-sec. setting) to the Ti plaque, forming a positive terminal. For a strong, adherent spot weld, the Ti lead must be cleaned in an aqueous solution of 1 Vol. % HF and 15 Vol.% HNO_3 .

Spraying of the first layer of 50% TFE + 50% active carbon is made with a conventional air brush gun at a 60 lb air pressure. The spray solution is a mixture of TFE dispersed aqueous solution (DuPont TFE 30, 60% solids, 5.7% wetting agent), Darco activated carbon, and methanol. Typically for a 50% C + 50% TFE layer the mixture is prepared as follows:

3g activated carbon is first dispersed in a 75 ml MeOH solution, into which 3.3 ml TFE 30 is slowly added while the solution is under a mild stirring.

To avoid a possible coagulation of TFE, the TFE 30 must be added last in the mixing and the mixture is maintained under a mild agitation. The thickness of the composite 50% carbon layer varies between 0.003" to 0.010" (before pressing) in the loading levels between 60 mg to 200 mg on a 0.925" x 2.625" Ti plaque.

The electrode is vacuum dried (at about 10 μ Hg pressure, 60°C) to remove the solvents before being pressed at room ambient temperature. This cold-press allows for compacting the composite (C + TFE) layer and for intimate contacts between Ti substrate and carbon and carbon powders.

75% C + 25% TFE layer is sprayed onto the 50% carbon layer in a similar manner except the spraying mixture contains 1.1 ml TFE 30 per 3g carbon.

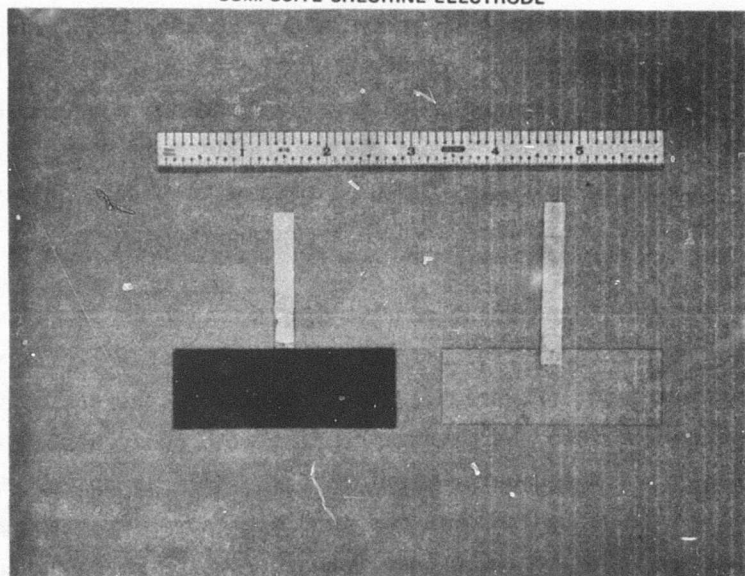
After the desired loading levels and number of composite layers are made, a thin porous TFE layer (loading level 50 to 100 mg) is sprayed onto the back surface of the Ti plaque. This TFE back layer (which faces the gas phase) is to ensure that the cathode structure will be free from solution flooding.

The last step in the fabrication is the sintering of TFE in the cathode structure. This is done at about 300°C under a press. Sintering must be performed in an inert atmosphere (Ar or He) or in vacuum to avoid oxidation and nitration of Ti. The electrode is now ready to be glued into a cathode housing and to be tested in a laboratory cell for its polarization performance.

Previous findings based on 0.030" thick Ti substrate have shown that two most important parameters which governed the cathode performance were respectively the solid loading levels of composite layers and the sintering pressure. These two variables are therefore selected for the optimization of the cathode structure.

Figure 1 shows the porous Ti substrate with a Ti lead attached (at right) and the processed composite electrode (at left). The electrode dimension is 2.625" x 0.925" which will have an effective geometric surface area of about 2 in² in the cathode housing. This is the actual single electrode size envisioned for the ECM reserve battery.

COMPOSITE CHLORINE ELECTRODE



Left: Front surface of a composite electrode

Right: Porous titanium substrate

Figure 1.

Composite Chlorine Electrode

ii. Porous Ti Plaques

The plaques are supplied by Gould Laboratories, Cleveland, Ohio. The porosity and the mean pore size are quoted by the supplier to be 40% and 10 microns respectively.

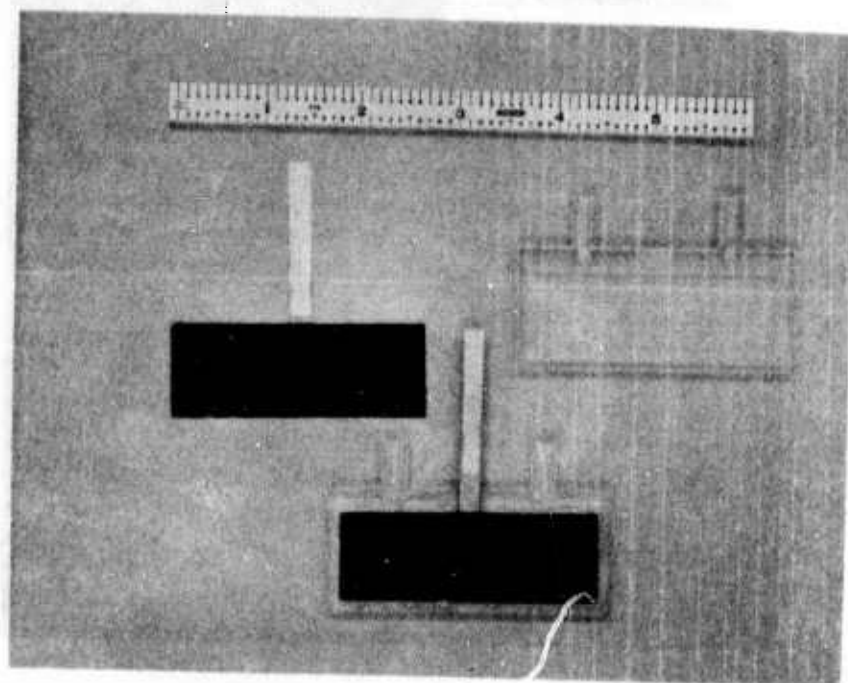
The electrical resistance of a 0.013" thick plaque (specimen dimension 1" x 3") was about 9.6 m Ω as determined by a two-probes (probe separation 2.05") dc method. This yields an effective specific resistivity of about $1.5 \times 10^{-4} \Omega \text{ cm}$. Similar measurements on a 0.031" thick plaque (also 40% porosity and 10 microns pore size) yielded 4.3 m Ω or a specific resistivity of about $1.7 \times 10^{-4} \Omega \text{ cm}$. Therefore the resistance of Ti plaque increases by a factor of 2.2 when plaque thickness is decreased from 0.031" to 0.013". However this resistance is quite negligible compared to that of electronic and electrolytic resistance inside the composite layers.

iii. Chlorine Cathode Compartment and Test Cell

The fabricated composite electrode was placed inside a plastic cathode housing compartment (Figure 2.) The periphery of the composite electrode was sealed into the plastic housing with epoxy glue. A 1/16" recess cavity in the housing provides for a Cl₂ gas space. The gas was led into the space through the two inlet ports at the top. A Gas Flowmeter Valve Assembly (air range 0.2 to 90 ml/min) was placed between the Cl₂ gas cylinder and the cathode compartment to control and monitor the flow rate. The complete cathode compartment had a dimension of 2 7/8" x 1 1/4" x 3/16" excluding the two gas inlet ports.

The test cell for the evaluation of composite Cl₂ electrode performance is shown in Figure 3. The cell was made of Lucite plastic and had a separate reference electrode compartment. The cell compartment and the reference compartment were electrolytically connected via a 1/16" diameter hole drilled in 3/8" diameter rod. The tip of the hole was situated close to the Cl₂ electrode surface in the cell compartment.

COMPOSITE ELECTRODE AND HOUSING

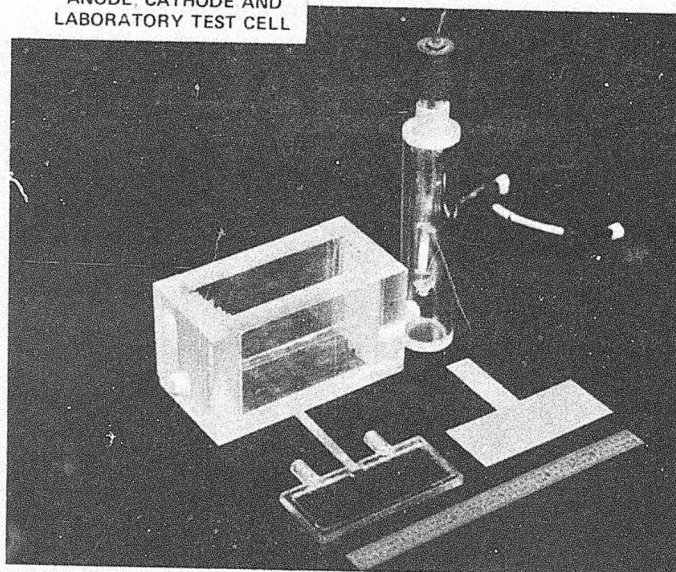


Top row: A composite electrode (left) and an electrode housing, (right).

Bottom row: A sealed chlorine electrode compartment

Figure 2. Chlorine Electrode Compartment

ANODE, CATHODE AND
LABORATORY TEST CELL



Electrodes:

Chlorine composite	(Cathode)
Aluminum	(Anode)
Sat'd Calomel	(reference)

Figure 3. A Laboratory Test Cell and the Electrodes

Saturated calomel electrode served as the reference with an Al electrode (Type 1100, dimension 1 1/8" x 2 13/16" x 0.025") serving as the anode. Figure 4 shows the assembled laboratory cell.

Optimization of Electrode Fabrication

The fabrication procedure defining layer weight, cold pressure after first layer and sintering pressure was varied until an electrode with minimum polarization was manufactured. The goal was for an electrode that polarized 0.4 volts at a current density of 0.5 amps/in². This corresponds to a half cell potential of 0.6 volts vs. the calomel reference. Tests of chlorine electrodes of different fabrication techniques were done in the cell shown in Figure 4. Al 1100 was the counter electrode, 30% CaCl₂ the electrolyte and a saturated calomel electrode served as reference. Discharges were run for a period of one hour at 0.5 amps/in². Chlorine to reference voltage was monitored throughout the discharge.

iv. Characterization of Optimum Chlorine Electrodes

Once the optimum fabrication procedure for the chlorine electrodes was determined, electrode characterization such as (a) polarization at various current densities, (b) life of the electrode, (3) utilization of chlorine, and (d) effective surface area, were measured.

a) Polarization: The open circuit potential and the potential between the chlorine electrode and the reference electrode were determined at currents ranging from 0.5 amperes to 3.0 amperes at increments of 0.5 amperes, first in ascending then in descending order. The flow rate of the chlorine gas was maintained at 25 ml/min. throughout the test. As before the tests were carried out in ~ 30% CaCl₂ with Al 1100 serving as the anode.

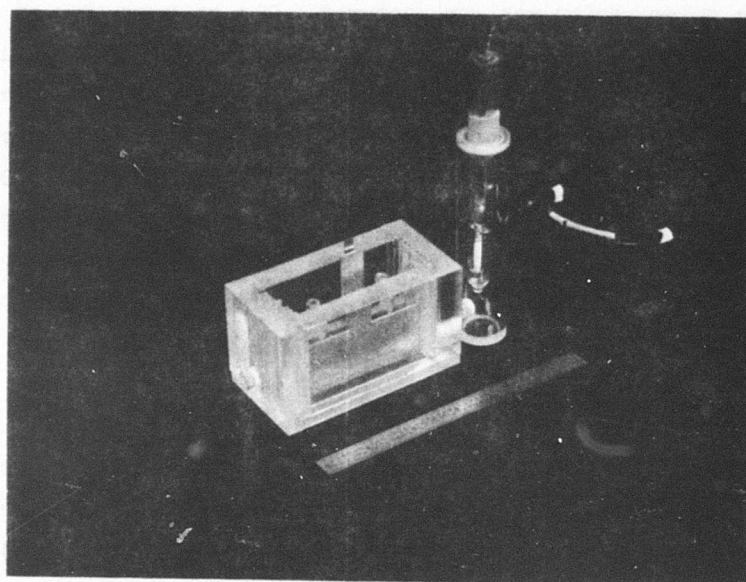


Figure 4. A Complete Laboratory Cell

b. Electrode Life. The active life of the Cl_2 electrode was determined at a discharge rate of one ampere against Al 1100 in 30% CaCl_2 .

The active life of the Cl_2 electrode is defined as the length of the voltage plateau region during discharge. Once the voltage vs. time plot hits a knee and then decreases sharply with time the active life of the electrode is over. Because of the limited capacity of the Al electrode the counter electrode had to be replaced twice so as to assure current distribution over the entire chlorine electrode.

c. Utilization of Chlorine. This test required the calibration of the flowmeter to measure true chlorine flow rate. The calibration on the meter is for air. The chlorine flow rate at a fixed setting on the flowmeter was determined by displacing water in a burette. The water was first saturated with chlorine. The apparatus is simple and is as shown in Figure 5. An Al-chlorine cell was set up and discharged at 1 ampere. The chlorine to reference potential was measured at chlorine flow rates (as read on the flowmeter) of 5, 6, 7, 8, and 10 ml/min. Each flow rate was maintained for a period of 1/2 hour or until Cl_2 to reference potential dropped sharply.

d. Effective Surface Area. The effective surface area of the chlorine electrode was measured by a determination of its double layer capacitance. The double layer capacitance is directly proportional to the effective area of an electrode.

An Al- Cl_2 cell with a calomel reference was set up. At the rest potential of the chlorine electrode (1.02V vs. calomel) a square wave pulse 13 mV peak to peak and 500 m sec. wide was supplied by a waveform generator. This signal was fed into the appropriate external input of a potentiostat which maintained the potential of the working (chlorine) electrode vs. the reference. The working electrode voltage vs. the reference was measured by a digital voltmeter. The current-time response of the cell to the voltage step

CALIBRATION OF FLOWMETER

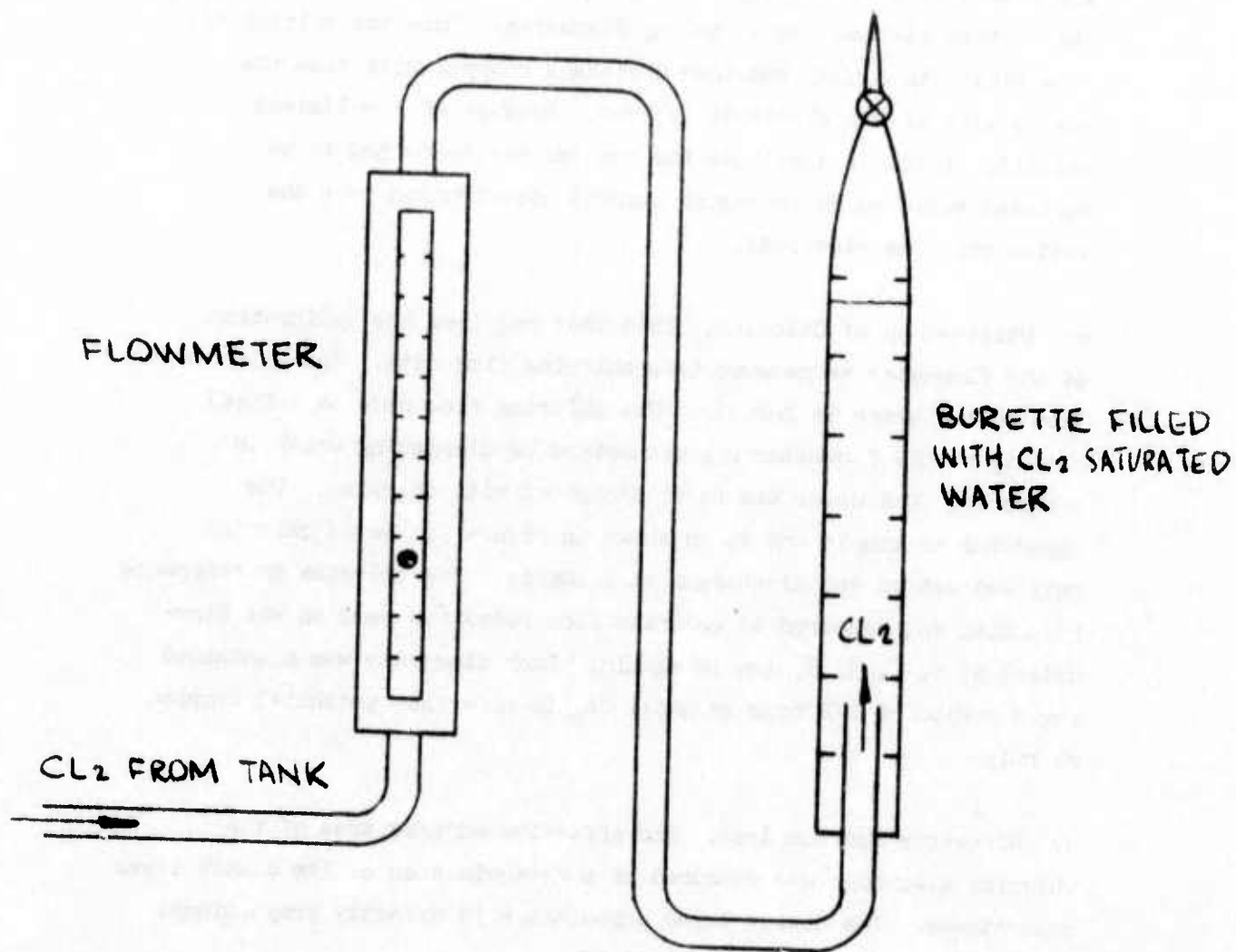


FIGURE 5

was measured by a storage oscilloscope by recording the voltage drop across a 100 ohm resistor. The current vs. time curve was directly photographed from the oscilloscope. The charge capacity of the double layer ($Q = \int_0^t i dt$) was determined by tracing the photographed curve on graph paper and then weighing a cut out of the curve. From the value of Q , the capacitance of the double layer can be calculated. By comparing the capacitance of the Cl_2 electrode with that of a smooth piece of nickel the effective area of the Cl_2 electrode can be calculated.

v. Reproducibility of Chlorine Electrodes

The batch of electrodes made after the characterization of optimum composition gave somewhat lower chlorine to reference voltages at the 0.5 amps/in² discharge rate.

The following steps were taken to upgrade chlorine electrode performance:

- a) Using a 4 mil tab instead of 8 mil to allow a more even compression of the electrode.
- b) A new batch of titanium with porosities of 42% and greater were used in making electrodes.
- c) Rotation of electrode in 45° increments while spraying to give a more even distribution of carbon and teflon.
- d) Using a fresh batch of Darco activated carbon.

C. Data and Discussion

i. Determination of Optimum Composition Cl_2 Electrode

After a series of fabrication and testing chlorine electrodes an optimum fabrication technique was chosen. The technique is outlined in Table 1. Electrodes made in this fashion gave a chlorine to calomel reference voltage of 0.4 to 0.5V at a discharge rate of 0.5 amps/in².

Table 1

Fabrication Specification for $C\ell_2$ Electrode

Weight of (50% C + 50% teflon)-layer -1	120 mg
Cold Pressure	800 psi
Weight of (75% C + 25% teflon)-layer -2	120 mg
Sintering Pressure	1500 psi

ii. Characteristics Optimum Cl_2 Electrode

a) Polarization Data

Figure 6 shows a plot of Cl_2 electrode to reference voltage vs. current. Since the effective area of the chlorine electrode is 2.0 sq. inch, current density is half of the current. At 1.0 amperes the chlorine voltage is 0.5V, as expected.

b) Electrode Life

Figure 7 shows a plot of the Cl_2 to calomel reference voltage vs. time at a discharge rate of 0.5 amps/in². Dips occurred in the curve due to a drop in chlorine gassing rate, (from 10 ml/min to 6 ml/min then readjusted to 10 ml/min) and replacement of aluminum counter electrodes. The life of the chlorine electrode at this current density was 6 hours during which time the Cl_2 to reference voltage dropped from 0.5V to 0.0V. The discharge was continued for an additional 48 minutes at the end of which the voltage had dropped to -.65V.

c) Utilization of Chlorine Gas

The calibration curve of the air flowmeter to chlorine gassing rate is shown in Figure 8. Plots of chlorine to reference voltage vs. time at a particular gas flow rate are shown in Figure 9. Discharges were at 1 ampere (0.5 amps/in²).

At a 100% utilization of chlorine gas 6.97 ml/min flow rate is required to sustain a current of 1.0 amperes as shown by the calculation below.

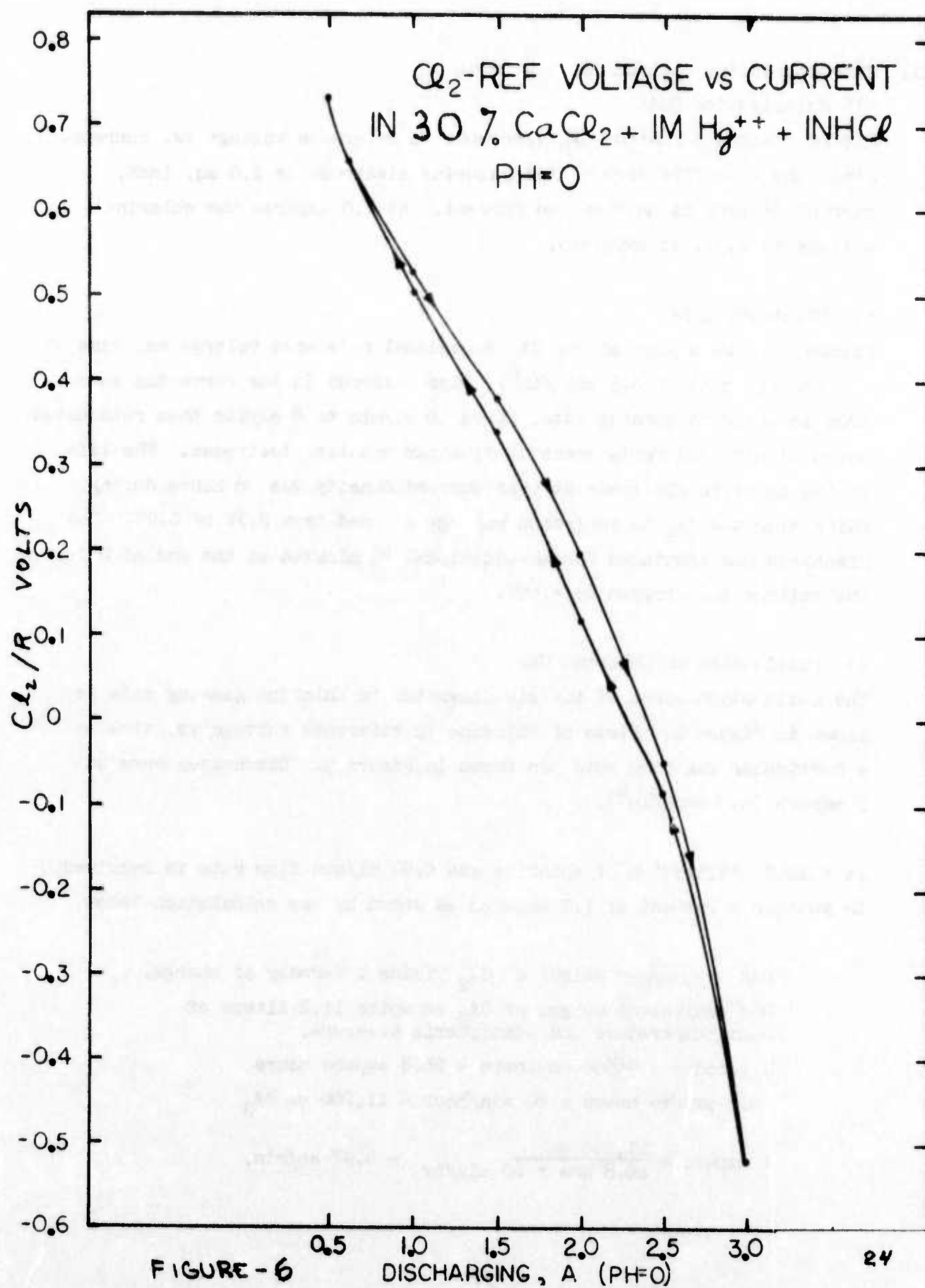
One equivalent weight of Cl_2 yields 1 faraday of charge.

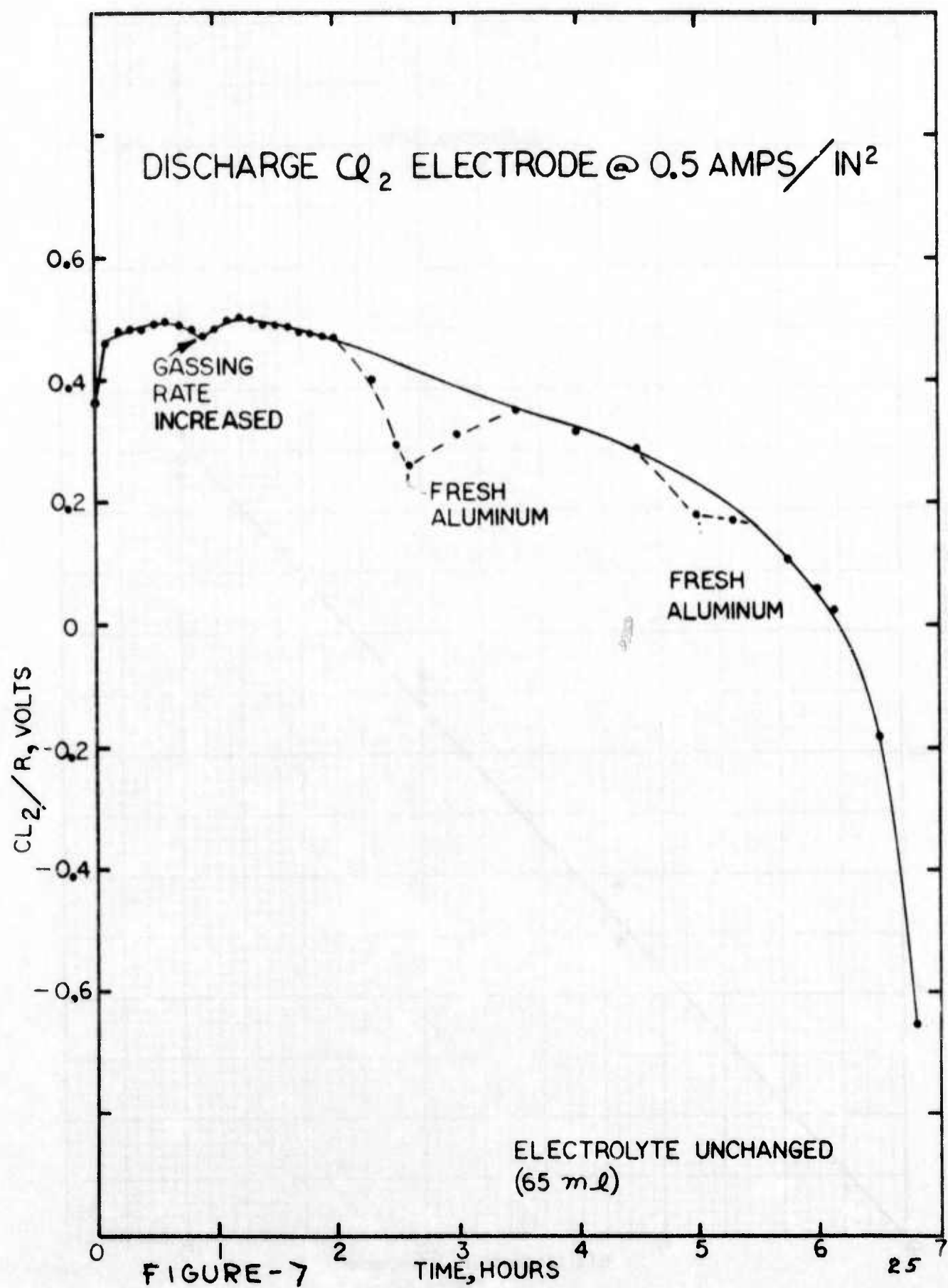
One equivalent weight of Cl_2 occupies 11.2 liters at room temperature and atmospheric pressure.

1 faraday = 96500 coulombs = 26.8 ampere hours

26.8 ampere hours x 60 min/hour = 11,200 cc Cl_2

1 ampere = $\frac{11,200 \text{ cc}}{26.8 \text{ hrs} \times 60 \text{ min/hr}}$ = 6.97 cc/min.





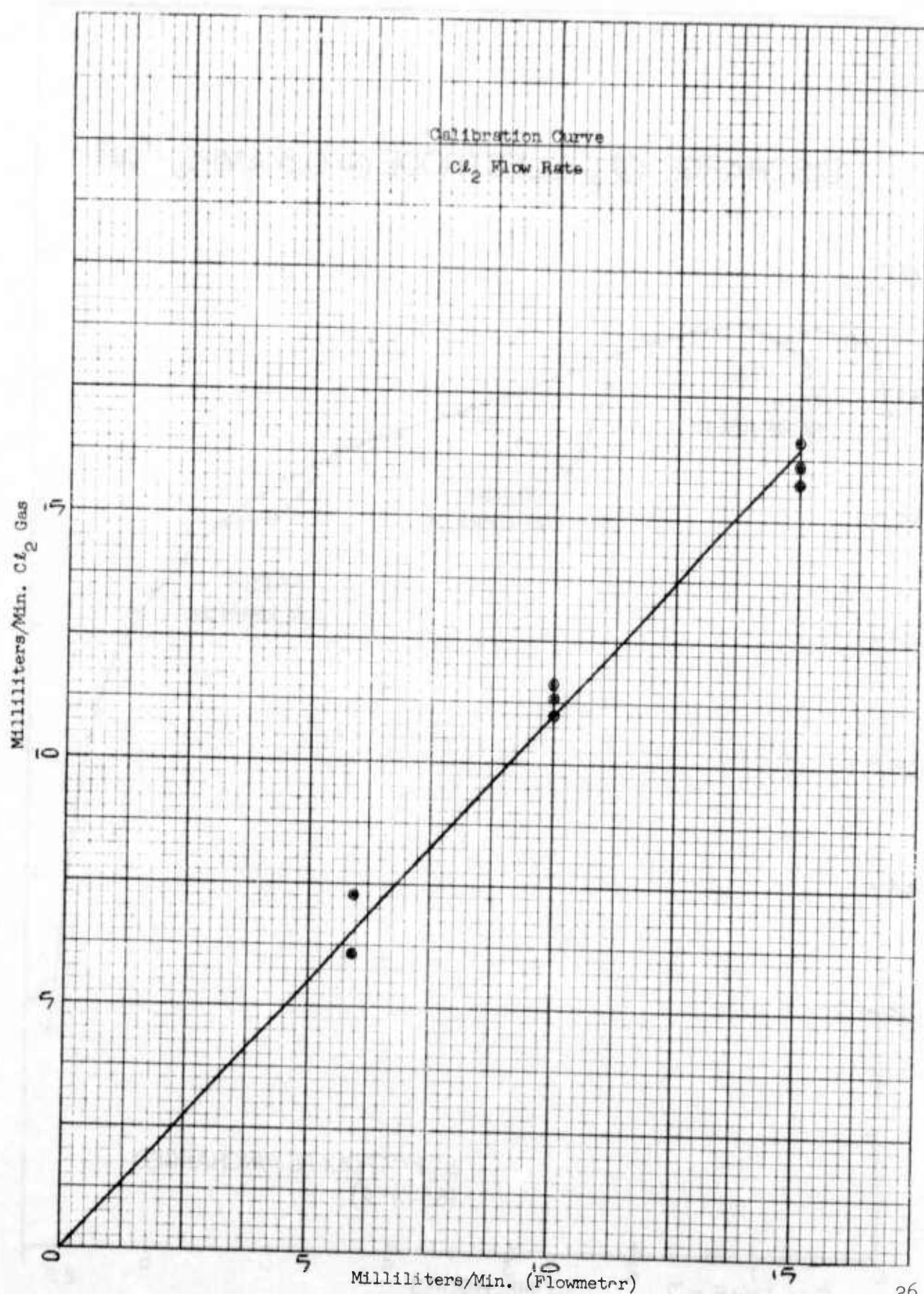


Figure 8

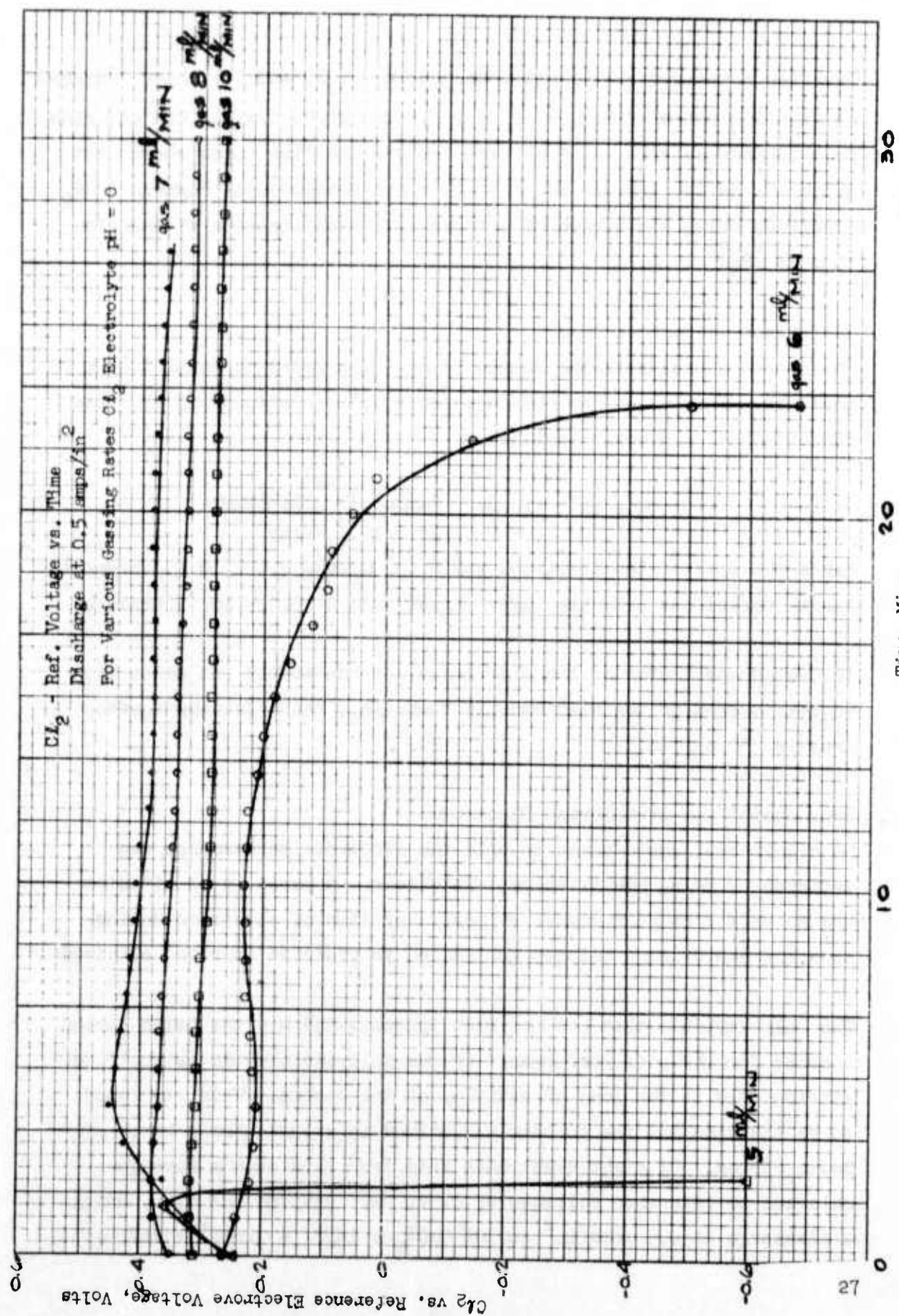


Figure 9

Time, Mins.

The flow rates set on the meter were 5, 6, 7, 8, and 10; these correspond to Cl_2 flow rates of 5.3, 6.4, 7.5, 8.6 and 10.9 cc/min. The chlorine to reference voltage vs. time plots at various flow rates shows that 7.5cc/min is the lowest flow rate that can continuously sustain a Cl_2 electrode being discharged at 1 ampere. The utilization of chlorine thus is $\frac{6.97}{7.5} = 93\%$.

d) Effective Surface Area

The charge capacity of the double layer Q was found to equal 3.84×10^{-4} coulombs. This value was obtained for a voltage step of 13 mV. The capacitance $C = \frac{Q}{V}$ was calculated as

$$2.95 \times 10^{-2} \text{ farads, } \frac{3.84 \times 10^{-4} \text{ coulombs}}{13 \times 10^{-3} \text{ volts}}$$

Since the area of the electrode was 2 in.², $C/\text{cm}^2 = 2.3 \times 10^{-3} \text{ farads/cm}^2$
Smooth nickel has a double layer capacitance of $2.0 \times 10^{-5} \text{ farads/cm}^2$

The roughness factor of the chlorine electrode is 115 and since the geometric area of the electrode is 2 sq. in., the effective surface area is 230 sq. in.

v. Reproducibility of Chlorine Electrodes

No significant improvement in chlorine electrode performance was achieved by using new titanium. Thickness and porosity of titanium had no effect on performance either. Rotation of electrode during spraying employing a thinner tab failed to yield an improved electrode.

The only variable that had not been investigated was the Darco carbon. A cause for the poor performance of the chlorine electrodes could be attributable to the loss of activity of the carbon. This was found to be the case and the problem was solved by using a fresh batch of Darco carbon. Of eight electrodes made from this carbon five gave chlorine to reference voltages of 0.5V, two .45V and one 0.4V during a discharge at 0.5 amps/in.² in 30% CaCl_2 + 1N HCl + .1M Hg^{++} electrolyte.

All electrodes made from that point on used the new titanium, the new carbon, and were sprayed turned in 45° increments.

6. ALUMINUM ANODE ACTIVATION

A) Objective

The theoretical potential of aluminum vs. a saturated calomel electrode is -1.93V. Because of the formation of Al_2O_3 at the surface of the electrode, passivation and severe polarization occur so that the measured potential under load is -.85V. By introducing mercury ions into the electrolyte solution amalgamation of the aluminum surface occurs breaking the oxide layer and raising the potential. The objective of anode activation is to determine the methods of activating aluminum electrodes within 10 seconds during a discharge at 0.5 amps/in². The activated voltage must be stable during 45 minutes of continuous discharge.

B) Experimental

i. Etching Aluminum 1100

The following etching solutions were used on acetone cleaned Al 1100. 15% KOH, 15% NaOH, 15% NaOH + 25 Vol% HCl, 25 Vol% HCl, 15% HNO₃ + 85% H₃PO₄, 15% NaHCO₃, 15% KOH followed by 15% HNO₃ and Tucker solution. Tucker solution consists of 30 ml-49% HF, 45 ml-37.5% HCl, 15 ml-70.5% HNO₃ + 10 ml distilled water. The electrode 2 13/16" x 1 1/8" x .025" was dipped in these solutions for time periods ranging from 15 seconds to 5 hours. Sandblasting aluminum was also used as a method of etching.

ii. Preactivation of Al 1100.

Both etched and unetched aluminum 1100 electrodes were preactivated. Preactivation involves the discharge of aluminum at 0.5 amps/in² against a chlorine counter electrode in 30% CaCl₂ + .1M Hg⁺⁺ electrolyte for a period of one hour. After preactivation Al is removed from solution and allowed to sit exposed to the atmosphere for a period of at least one week before being discharged again.

iii. Effect of Electrolyte pH on Aluminum Activation

Preactivated and insitu activated aluminum was discharged at 0.5 amps/in² in 30% CaCl₂ + .1MHg⁺⁺ electrolyte whose pH was adjusted to 8, 4, 1 and 0. Al to reference voltage was monitored during the hour of discharge.

iv. Behavior of Other Aluminum Alloys

Al 1199, 1095, 1060, 7075, and 5052 were discharged at 0.5 amps in 30% CaCl₂ + .1MHg⁺⁺ pH = 8 and pH = 0 electrolytes. All pieces were 2 13/16" x 1 1/8" in area and had been etched in Tucker solution for 30 seconds and then washed with deionized water prior to discharge. Aluminum to reference was monitored throughout discharge.

v. Effect of Method of Preactivation on Al Activation

The time of discharge and the pH of the discharging electrolyte used in preactivating aluminum were varied.

In pH = 0 electrolyte Al electrodes were discharged for 1 hour and for 15 minutes. One hour preactivation was performed in electrolytes of pH = 8, 1 and 0.5. All preactivation was done at 0.5 amps/in² in 30% CaCl₂ containing 0.1 MHg⁺⁺.

vi. Behavior of Aluminum in Cold Temperature

A determination of Al 1100 activation in cold temperature was undertaken. It was noted that calomel reference freezes at temperatures below 32°F and hence is unsuitable as a reference. Silver-silver chloride was shown to be unstable in CaCl₂. An aluminum reference was unsatisfactory because it underwent slow activation on open circuit resulting in an ever changing reference voltage. A chlorine reference was tried and found suitable at the low temperatures. This electrode consisted of a plexiglas tube with one end completely covered by a piece of titanium-carbon teflon chlorine electrode. Chlorine was

passed through the open end of the plexiglas tube from the same source which feeds the chlorine counter electrode. The rate of Cl_2 gassing was set at 20 ml/min to accommodate both the reference and counter electrodes. Room temperature tests in 30% pH = 0 electrolyte showed the chlorine reference to be .90V anodic to the calomel. To convert chlorine reference to calomel .90 volts must be added algebraically. Preactivated Al 1100 electrodes were discharged at 0.5 amps/in² for a period of one hour in 30% pH = 0 electrolyte at ambient temperatures of -20, -10, 0 + 10 + 32°F. Aluminum to chlorine reference was monitored through the discharge.

C) Results and Discussion

i. Etching of Aluminum

A 30 second etch in Tucker solution resulted in an aluminum to calomel reference voltage of -1.34V after only 5 minutes of discharge at 0.5 amps/in². None of the other etching techniques resulted in that rapid and that cathodic an activation of aluminum.

ii. Preactivation of Aluminum

Aluminum electrodes etched in Tucker solution and preactivated in 30% $\text{CaCl}_2 + .1\text{MHg}^{++}$ did not yield better results than were obtained when just etching in Tucker solution.

iii. Effect of pH on Aluminum Activation

Figure 10 shows a plot of aluminum to reference voltage during discharge at 0.5 amps/in² in electrolytes of pH = 8, 4, 1 and 0. In order to emphasize the voltage changes occurring during initial discharge the plot was made on semilog paper. Little difference exists among discharges in pH = 1, 4 and 8 electrolyte, with a maximum voltage of -1.4 not achieved until the end of discharge. In pH = 0 however, the aluminum to reference voltage reaches -1.4 after only 5 minutes of discharge. After 20 minutes of discharge a voltage of 1.50V is attained.

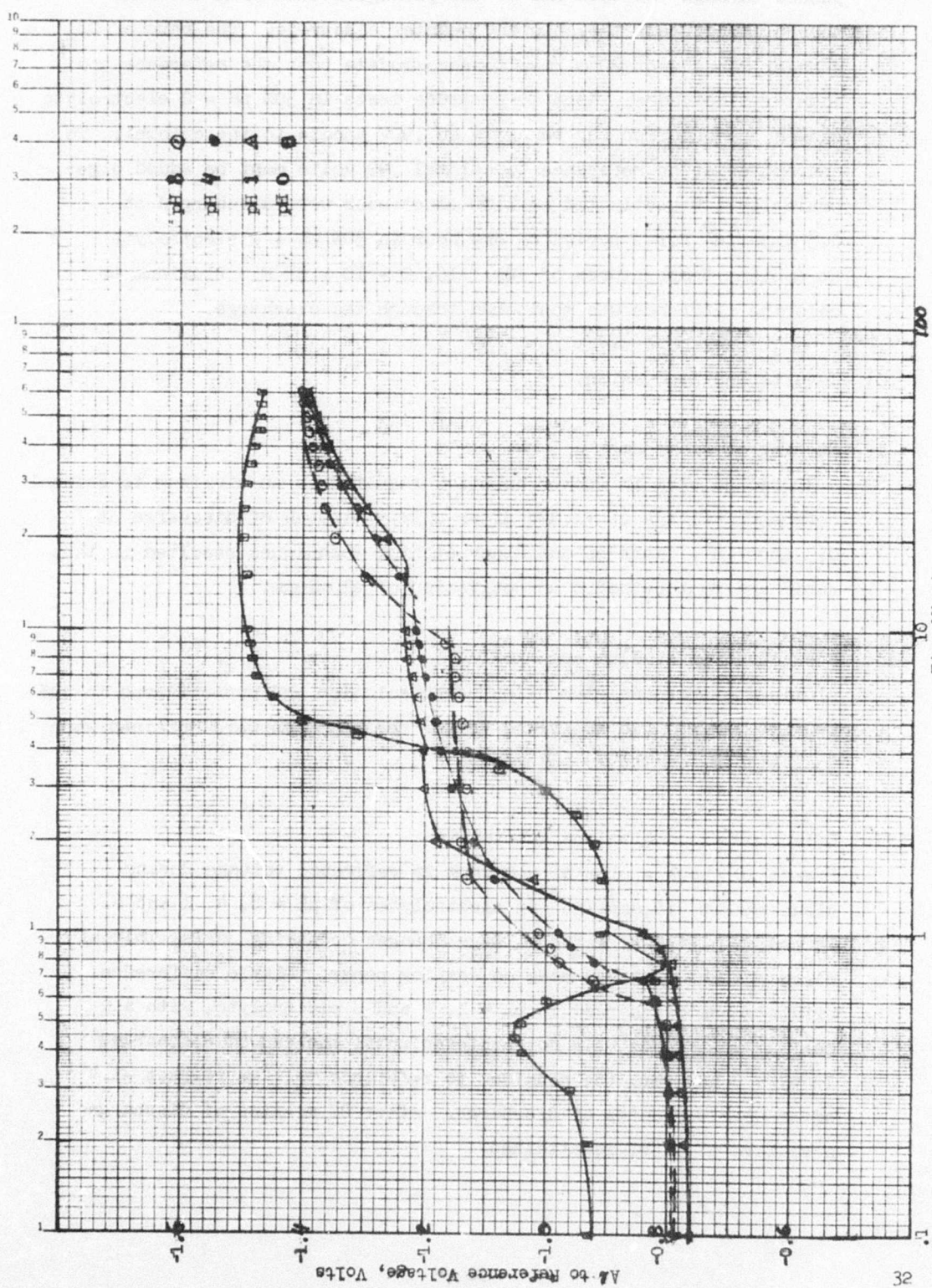


Figure 10-Effect of pH on Aluminum Alloy 1100

iv. Behavior of Other Aluminum Alloys

Figure 11 shows plots of Al to reference voltages comparing Al 1100 with Al 1060, 7075 and 5052. All four alloys activate fairly rapidly, with Al 1100 the most rapid.

Two very pure aluminums Al 1199 and Al 1095 were discharged in electrolytes of pH = 8 and 0. The alloys failed to activate above 1.35V and required one hour of discharge to attain that voltage.

v. Effect of Method of Preactivating Aluminum

Aluminum electrodes given various preactivation treatments were all discharged in 30% CaCl_2 + .1M Hg^{++} pH = 0 electrolyte at a discharge rate of 0.5 amps/in² against a chlorine counter electrode. Aluminum to calomel reference voltage was monitored. Plots of this are shown in Figures 12 and 13 for aluminum preactivated for different lengths of time and in various pH electrolytes. Again the plots are on semilog paper. Figure 12 compares the Al electrode preactivated at pH's of 0.5, 1 and 8. It can be seen that the electrode preactivated at pH = 0.5 activates the fastest. The time required to reach 1.40V for this electrode was 2 minutes. Figure 13 compares insitu activated Al 1100 electrodes, preactivated for 15 minutes, and preactivated for one hour in pH = 0 electrolyte. Even though the voltage level for the 15 minutes preactivated Al is slightly lower than that obtained with the electrode preactivated for 1 hour. The electrode preactivated for one hour lost structural integrity after 30 minutes of discharge. The time required for the 15 minute preactivated Al to reach -1.4V was 1.85 minutes.

Based on rapidity of activation, voltage level and structural integrity, the best method for preactivation is for 15 minutes in an electrolyte of pH = 0.

The method of pretreating aluminum for optimum discharge activation is degreasing in acetone, etching in Tucker solution for 30 seconds and discharging in 30% CaCl_2 + .1M Hg^{++} + pH = 0 electrolyte at 0.5 amps/in² for 15 minutes.

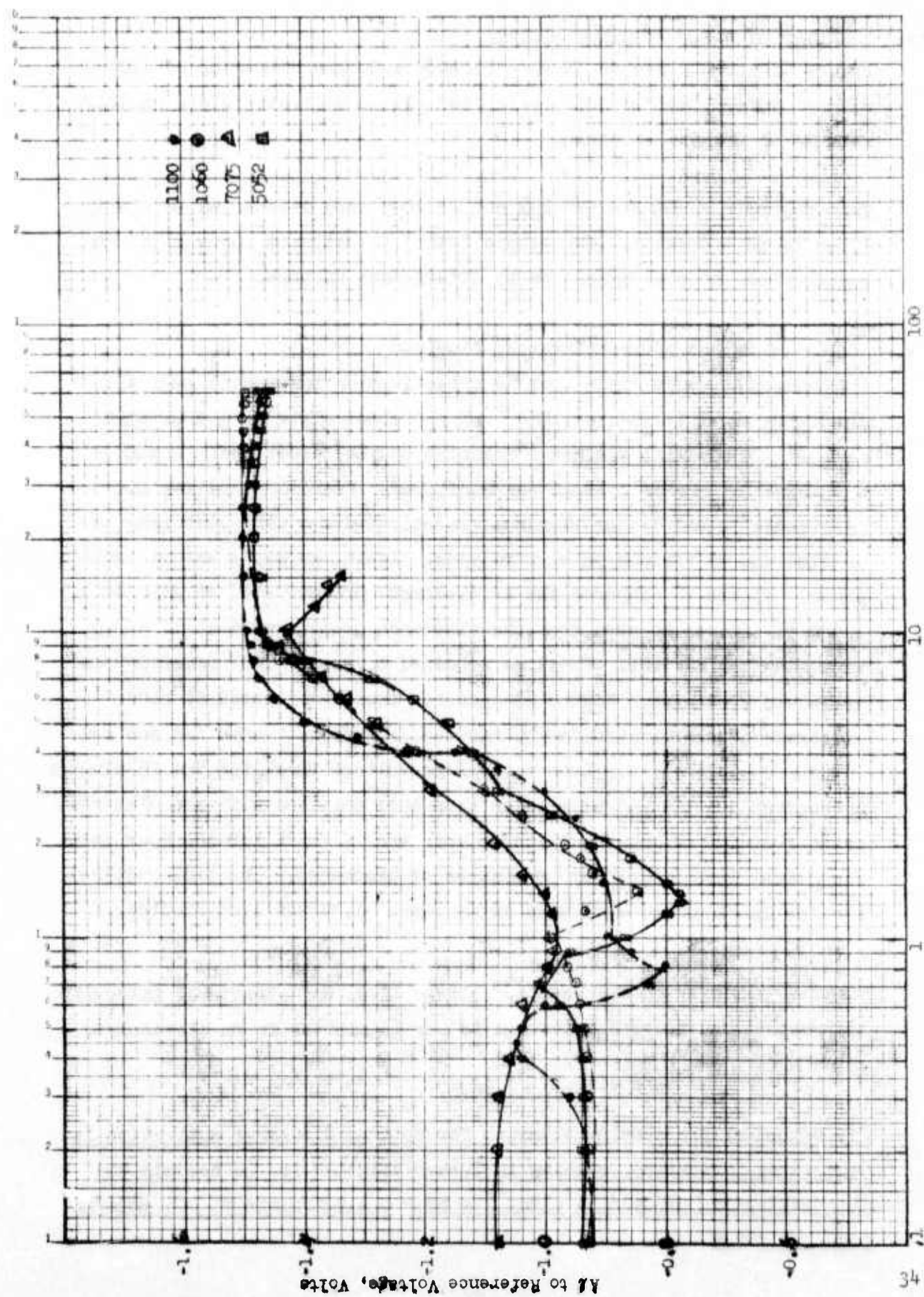


Figure 11 Behavior of Various Alloys in Electrolyte of pH 0

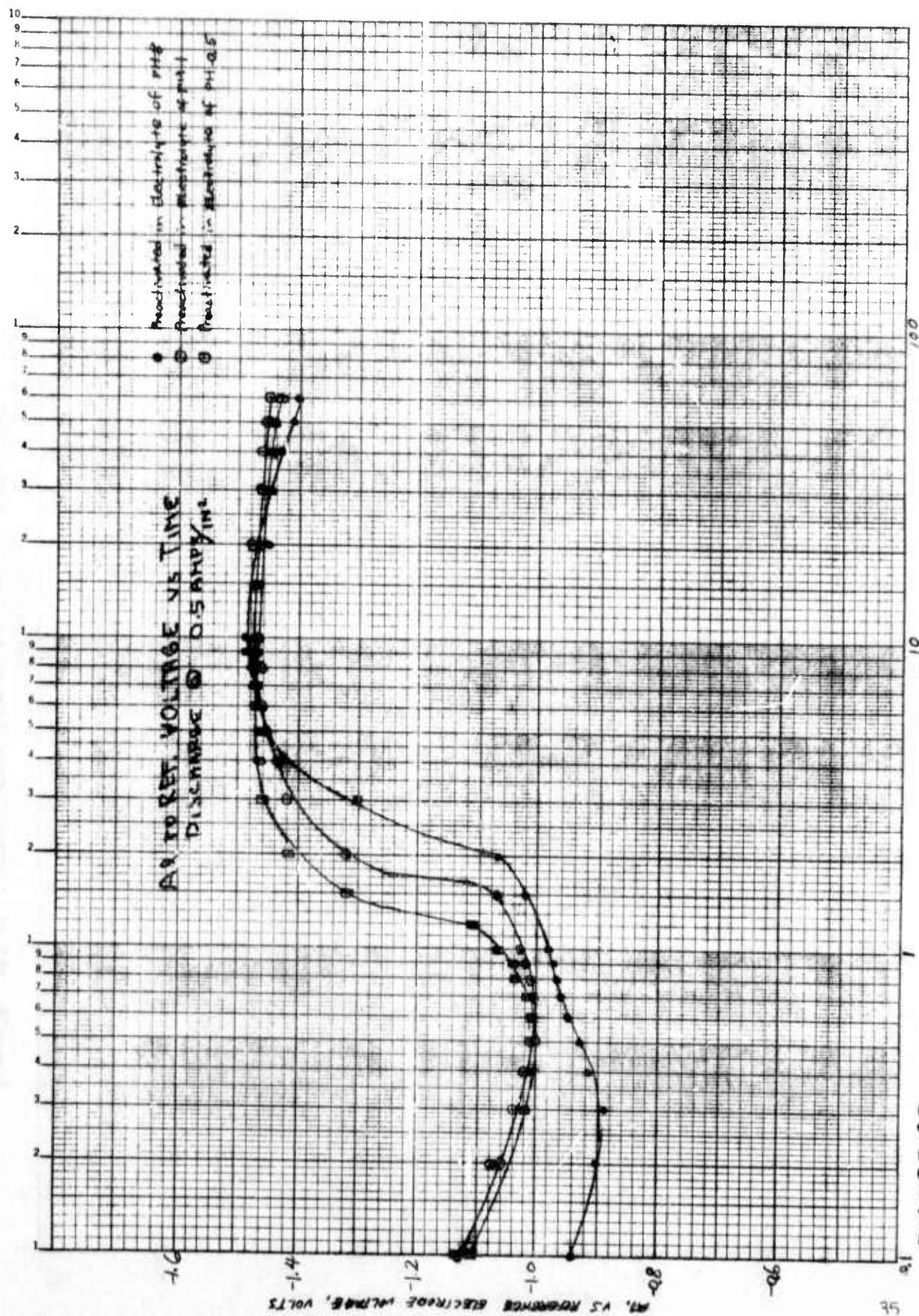


FIGURE-12
EFFECT OF

REACTIVATION TECHNIQUE

ON DISCHARGE CHARACTERISTICS

IN BATTERY OF NO. 1

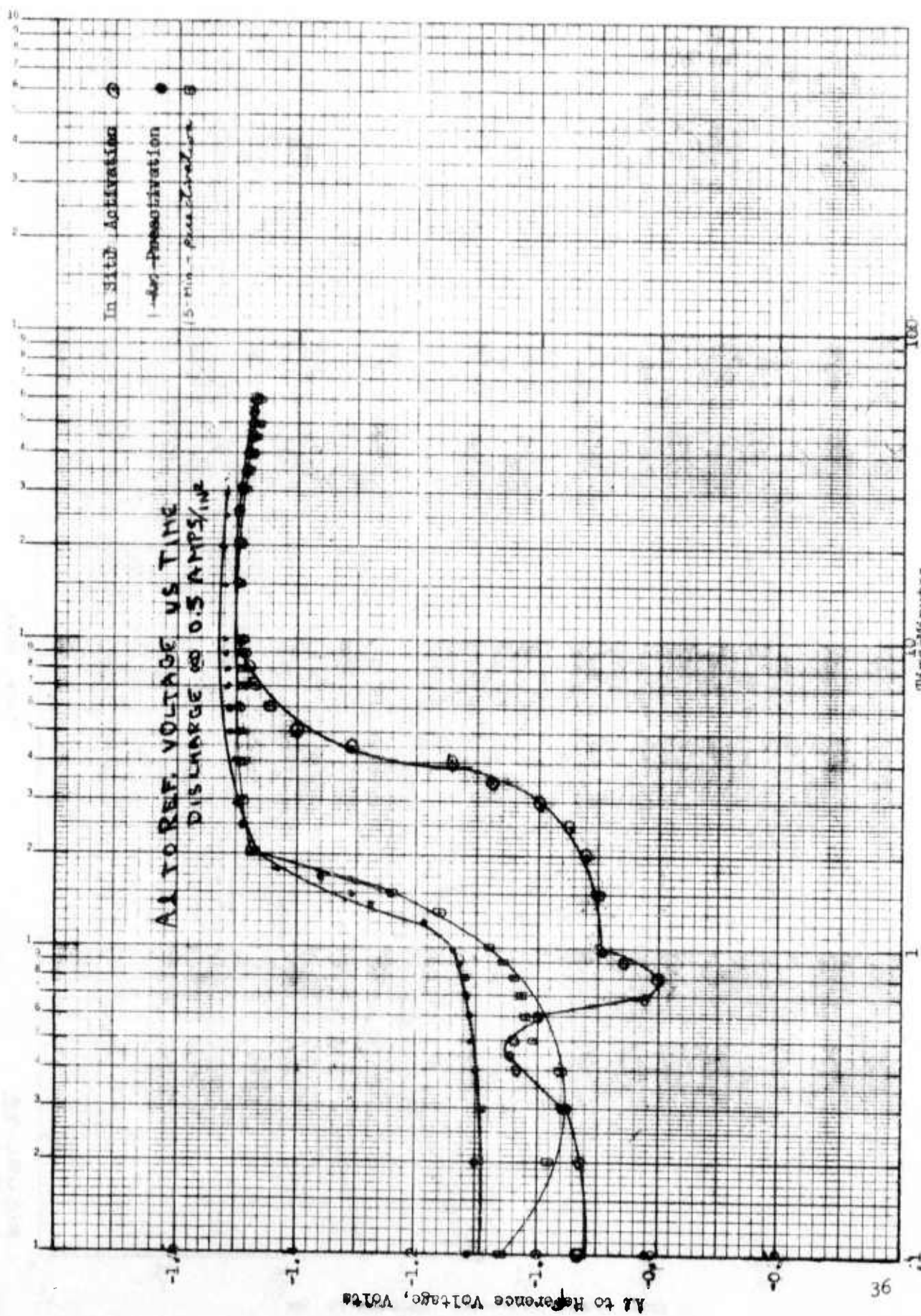


Figure 3. Effect of Preactivation Time on Al (1100) in Electrolyte of pH=0

vi. Behavior of Aluminum in Cold Temperature

Plots of the aluminum to chlorine reference during discharge at -20°F , -10°F , 0°F , $+10^{\circ}\text{F}$ and $+32^{\circ}\text{F}$ as well as room temperature are shown in Figures 14 and 15. At -20°F 50 minutes are required to fully activate aluminum. At -10°F 30 minutes are required, while at 10°F it takes 20 minutes to reach a maximum voltage of 2.35V. Ten minutes are necessary at 32°F for Al to chlorine reference voltage to reach -2.48.

From the standpoint of activation time and voltage level, 32°F is the minimum temperature wherein the aluminum chlorine system can operate without external heat sources. At ambients below 32°F heat will be supplied to the system by means of heating tape which is required to supply heat to raise chlorine vapor pressure. The tape will supply initial heat and the system will be kept warm by the heat energy of the electrochemical reaction (polarization voltage x current).

7. CaCl_2 AQUEOUS ELECTROLYTE

A. Objective

To determine (1) the optimum CaCl_2 concentrate in the electrolyte for the required cell performance with respect to voltage capacity and freezing point and (2) the minimum electrolyte volume required to sustain cell voltage and capacity.

B. Experimental

i. Determination of freezing points.

Four different concentrations of CaCl_2 solution were prepared; 15%, 20%, 25% and 30% by weight. The freezing points of the 15% and 20%

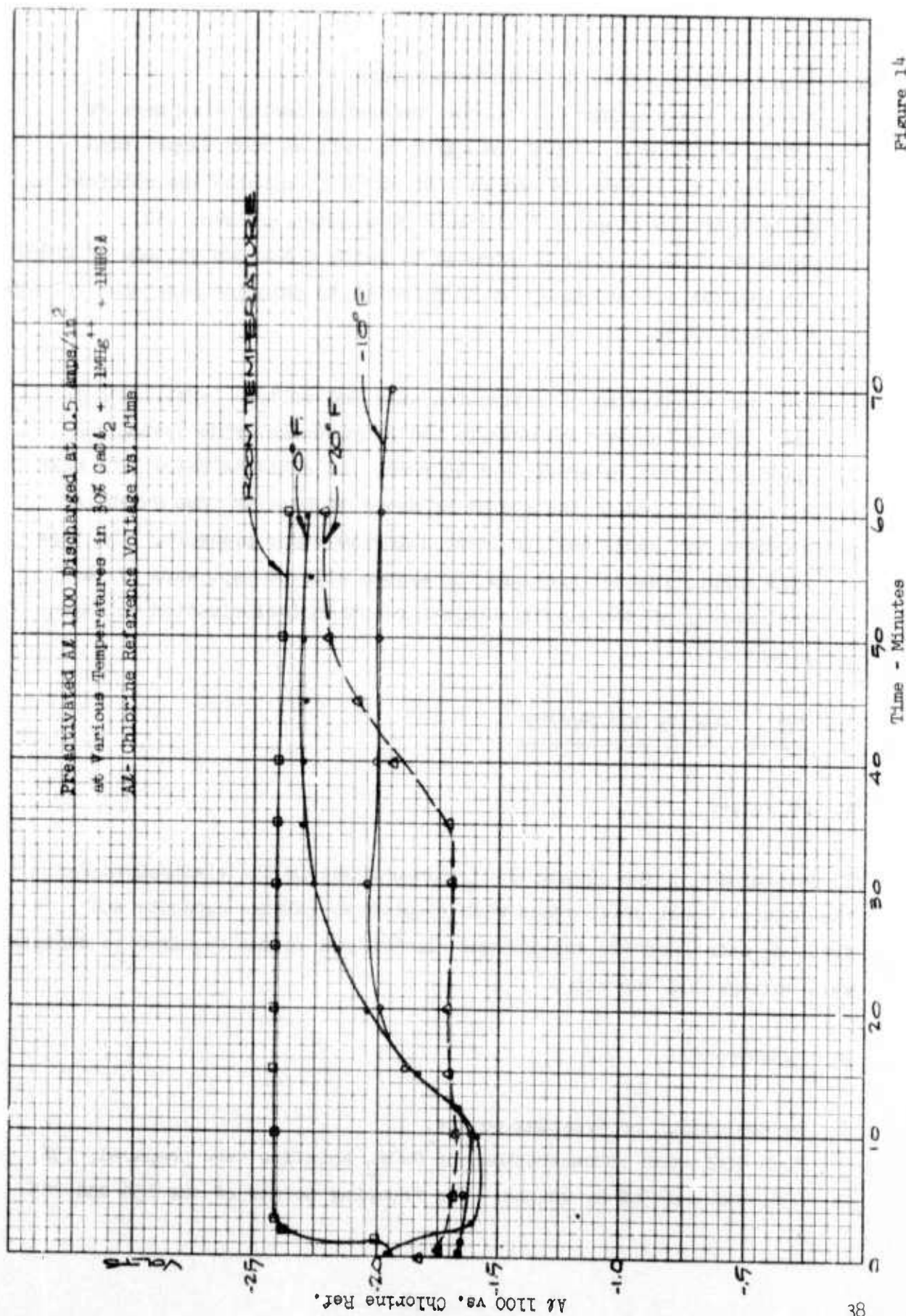


Figure 14

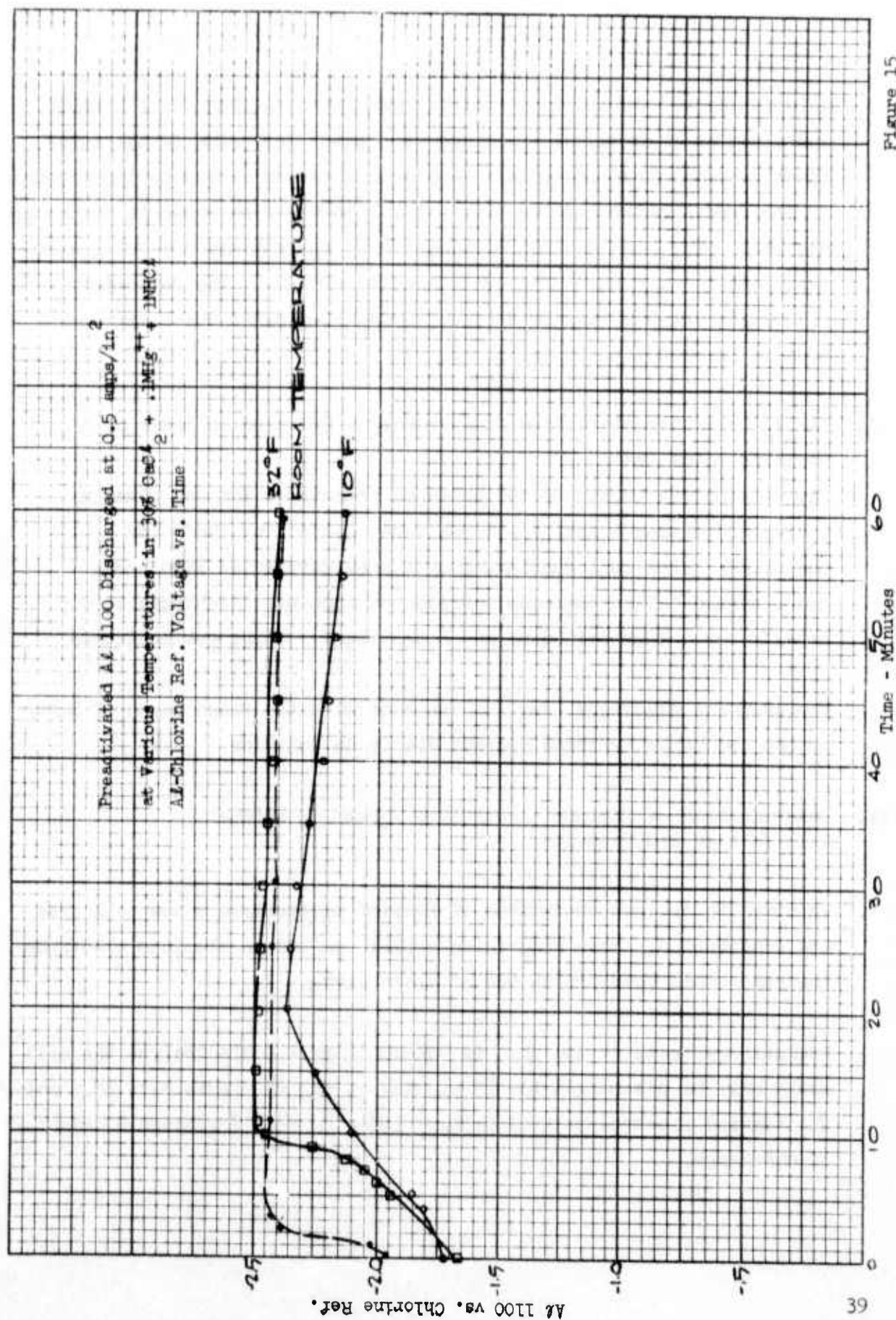


Figure 15

solutions were determined by cooling them in an environmental chamber and plotting thermocouple readings vs. time. The break in the curve identified the freezing point. Copper-constantan served as the thermocouple, and a reference junction set in ice water as shown in Figure 16 was used. The freezing and melting points for 25% and 30% CaCl_2 solution containing $.1\text{Mg}^{++}$ and 1NHCl were determined. The determination of melting point serves as a check to freezing point which may have been in error due to supercooling.

ii. Al-Cl_2 Cell Characteristics in Electrolyte Selected on Basis of Freezing Point Data.

The electrolyte chosen on the basis of freezing point and aluminum activation characteristics was 30% CaCl_2 containing 1NHCl ($\text{pH} = 0$) and 0.1Mg^{++} . A cell consisting of a preactivated Al 1100 anode and a carbon-teflon-titanium chlorine cathode was discharged at 0.5 amps/in^2 for a time period of one hour. Cell voltage was monitored.

The chlorine electrode used was one made with the fresh batch of Darco carbon and hence exhibits optimum electrode behavior.

iii. Determination of Minimum Electrolyte Volume to Maintain Cell Voltage and Capacity.

In order to achieve conditions of limited electrolyte a new cell case was constructed. When containing a chlorine and an aluminum electrode the case would hold 5cc to 6cc of electrolyte.

Preliminary tests showed that in 30% CaCl_2 $\text{pH} = 0$ electrolyte the cell could only be discharged for 23 minutes at the 45 minute rate (0.5 amps/in^2). Unacidified electrolyte (30% $\text{CaCl}_2 + .1\text{Mg}^{++}$) $\text{pH} = 8$ yielded 47 minutes of discharge.

FREEZING POINT MEASUREMENT
VIA COPPER CONSTANTAN THERMOCOUPLE
AND REFERENCE JUNCTION

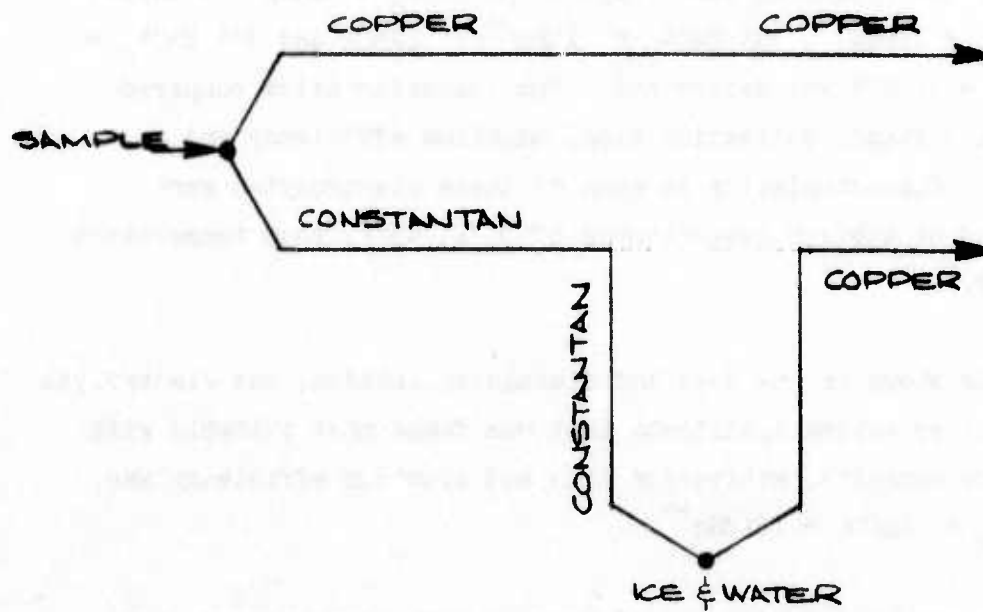


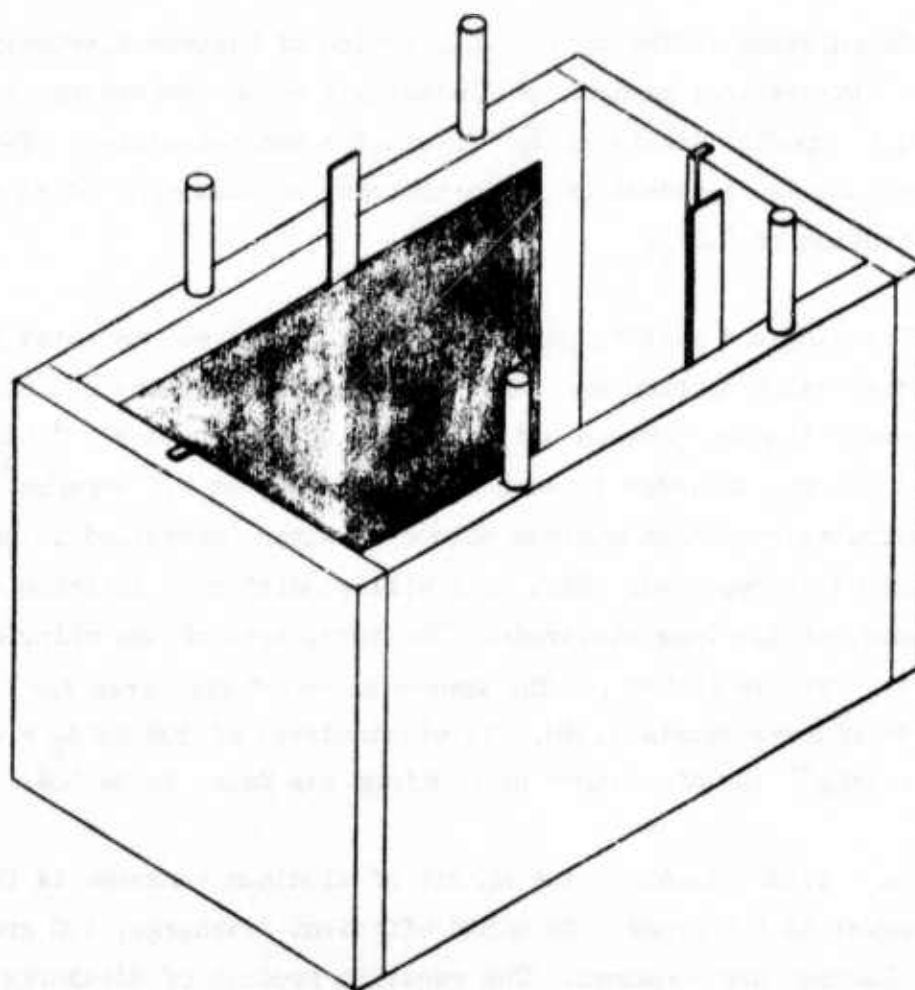
FIGURE 16

It was noted that at the end of charge the acid electrolyte had become very viscous apparently due to the buildup of AlCl_3 . It had been ascertained that the corrosion rate of Al in the acid was twice that of the unacidified form of the electrolyte. It was concluded that an alternate form of the electrolyte was necessary under limited volume conditions.

The performance of Al-Cl_2 cells (preactivated Al 1100 as anode) in 5cc of the following electrolytes $30\% \text{CaCl}_2 + .1\text{MHg}^{++} + 1\text{NHCl}$, $30\% \text{CaCl}_2 + .1\text{MHg}^{++}$, $30\% \text{CaCl}_2 + .1\text{MHg}^{++} + .1\text{NHCl}$ and $30\% \text{CaCl}_2 + .01\text{MHg}^{++} + .1\text{NHCl}$ was determined. The characteristics compared were cell voltage, activation time, aluminum efficiency and capacity. Characteristics in each of these electrolytes were determined at ambient temperatures of 32°F , 45°F , room temperature and 160°F .

As will be shown in the data and discussion section, the electrolyte under limited volume conditions that was found most suitable with respect to capacity, activation time and aluminum efficiency was $30\% \text{CaCl}_2 + .1\text{NHCl} + .01\text{MHg}^{++}$.

In the prototype cell for the 56 watt-42 watt hour battery, two chlorine electrodes will surround one aluminum electrode; the discharge for the 45 minute rate is 2 amperes. Such a prototype cell was constructed from two chlorine electrodes encased in their housing and joined facing each other with a space 0.275" apart, as shown in Figure 17. A .025" groove in the center of the spacer allowed for the placement of a pre-activated Al 1100 electrode $1-1/8"$ x $2-13/16"$ between the joined chlorine electrodes. With an aluminum electrode placed within the two chlorine electrodes container the volume of electrolyte contained was 10cc. This cell was discharged at 2 amperes until the cell voltage reached zero.



PROTOTYPE CELL I
CHLORINE BIELECTRODE

FIGURE 17

iv. Calculation of Theoretical Limitation of Minimum Electrolyte Volume

A theoretical minimum of electrolyte volume necessary to sustain a 0.5 amps/in² discharge for 45 minutes was calculated. The electrolyte volume is dependent on the efficiency of aluminum and on the concentration of CaCl_2 .

Freezing and melting point data, which will be presented in the discussion section show that for aqueous solutions of CaCl_2 any concentration between and including 25% CaCl_2 to 30% CaCl_2 is satisfactory. In order to sustain a discharge at 0.5 amps/in² for 45 minutes a certain minimum volume of water (contained in the electrolyte) is required. Each cell will consist of 2 chlorine electrodes and one aluminum electrode. The total area of the chlorine electrodes is 4 square inches. The ampere hours of discharge for 45 minutes equals 1.5AH. In electrolytes of 30% CaCl_2 + .1NHCl + .01MHg⁺⁺ the efficiency of aluminum was found to be 50%.

In a 1.5AH discharge the amount of aluminum consumed is theoretically equal to 0.5 grams. In a 50% efficient discharge, 1.0 grams of aluminum are consumed. The reaction product of discharge in the aluminum chlorine system is AlCl_3 . One gram of aluminum forms 4.9 grams of AlCl_3 . AlCl_3 reacts with all available water to form $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. For each gram of aluminum consumed 4 grams of water are required to form the hexahydrate $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. For each gram of aluminum 8.9 grams of the hexahydrate are formed. 8.9 grams $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ require 2.2 grams H_2O to completely dissolve it. Thus for a 45 minute discharge a minimum of 6.2 grams or 6.2cc of water are required. The volume of this electrolyte which would contain 6.2 grams of water is 6.8cc. In limited electrolyte as water is removed to associate with AlCl_3 , CaCl_2 tends to form a hydrate as is shown in the phase diagram in Figure 18. Since the cell becomes warm in limited electrolyte, the temperature inside the cell near the end of a 45 minute discharge is at least 60°C. At that temperature

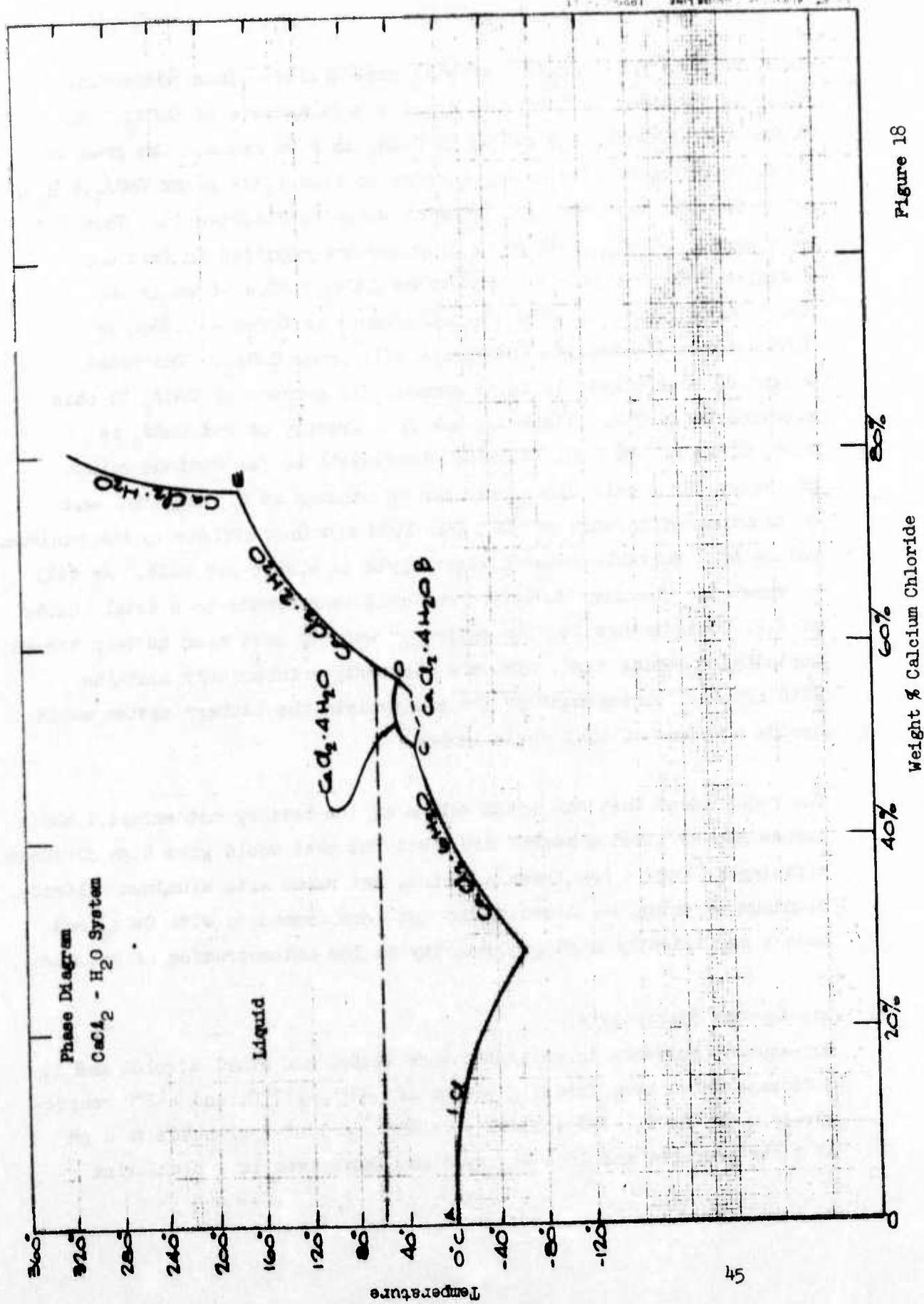


Figure 18

$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ is the hydrate that will crystallize. Thus additional water is required to form and dissolve this hydrate of CaCl_2 . In 6.88cc of 30% CaCl_2 the weight of CaCl_2 is 2.66 grams. One gram of CaCl_2 reacts with .324 grams of water to form 1.334 grams $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, which in turn requires .307 grams of water to dissolve it. Thus for each gram of CaCl_2 , .631 grams of water are required to form and dissolve $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. For .266 grams CaCl_2 1.68cc of water are required. The total water requirement is 6.2cc + 1.68cc or 7.88cc in an electrolyte containing 2.66 grams CaCl_2 . The total weight of electrolyte is 10.54 grams. The percent of CaCl_2 in this electrolyte is 25%. Since the specific gravity of 25% CaCl_2 is 1.24, 8.5cc of 25% CaCl_2 aqueous electrolyte is the minimum volume necessary for a cell discharged for 45 minutes at 0.5 amps/in² and an aluminum efficiency of 50%. For 100% aluminum efficiency the minimum volume of a suitable aqueous electrolyte is 4.25cc per cell. As will be shown in Section 11, 4.25cc per cell corresponds to a total volume of 7.21 cubic inches for the entire 56 watt-42 watt hour battery system including chlorine tank, with the electrolyte internally contained. With external containment of the electrolyte the battery system would occupy a volume of 11.1 cubic inches.

The requirement that the total volume of the battery not exceed 6 cubic inches necessitated a search for a solvent that would give high aluminum efficiency, have a low freezing point, not react with aluminum chloride, aluminum or chlorine, dissolve but not form compounds with CaCl_2 and have a sufficiently high conductivity at low concentration of solution.

v. Non-Aqueous Electrolyte

Non-aqueous solvents investigated were methyl and ethyl alcohol and 1, 3 dioxane which have freezing points of -98°C -117°C, and -42°C respectively. 30% CaCl_2 , 70% ethanol + .01M Hg^{++} acidified with HCl to a pH of 1 was prepared and 10cc was used as electrolyte in a bichlorine

electrode prototype cell. Preactivated aluminum served as the anode. Cell voltage was measured at open circuit and under load. A similar test was run with methanol. Because the initial results with alcohol only as the solvent were not encouraging, water-alcohol mixture were tried. The most promising of those was a solution consisting of 15% CaCl_2 + 65% H_2O + 20% CH_3OH ($\text{pH} = 1$, $\text{Hg}^{++} = .01\text{M}$). Discharge characteristics of $\text{Al}-\text{Cl}_2$ cell in limited and excess volumes of the electrolyte as well as freezing point and resistivity were determined.

vi. Internal Containment of Electrolyte

If electrolyte were present in the cells during the dormant stand of the battery it would reduce the overall volume of the 56 watt-42 watt-hour battery by at least 3.90 cubic inches.

The containment of electrolyte within the cell during stand could be accomplished in numerous ways such as:

- 1) Thin plastic bag within each cell containing electrolyte.
A pin breaks bag at the time of activation.
- 2) A thin, shatterable container around the aluminum electrode.
Thin gas lines go to the shatterable container of each from the chlorine tank. At the time of activation chlorine gas pressurizes all containers shattering them. Once shattered a valve closes off the chlorine gas and it is shunted to the chlorine electrode.
- 3) A compressible battery assembly and a separate compartment for all the electrolyte. During stand a spring compresses the battery. At activation spring is released and battery responds compressing the electrolyte compartment. The electrolyte then fills the newly created voids between the chlorine and aluminum electrodes. On the bottom of each cell there is a frangible opening which is shattered by the compressed electrolyte.
- 4) Cell containment of electrolyte made possible by low Al open circuit corrosion.

The electrolyte could be contained within the cell without elaborate mechanical devices provided that a) the aluminum corrosion rate in that electrolyte is sufficiently small < 0.1 mA as to assure sufficient aluminum available, after a 5 year stand, for a 45 minute discharge at 0.5 amps/in², and b) that the corrosion products do not have any detrimental effect on the chlorine electrode or aluminum activation.

Open circuit corrosion tests were conducted with the two most promising electrolyte 15% alcoholic solution of CaCl_2 and the 25% aqueous solution.

vii. Open Circuit Corrosion

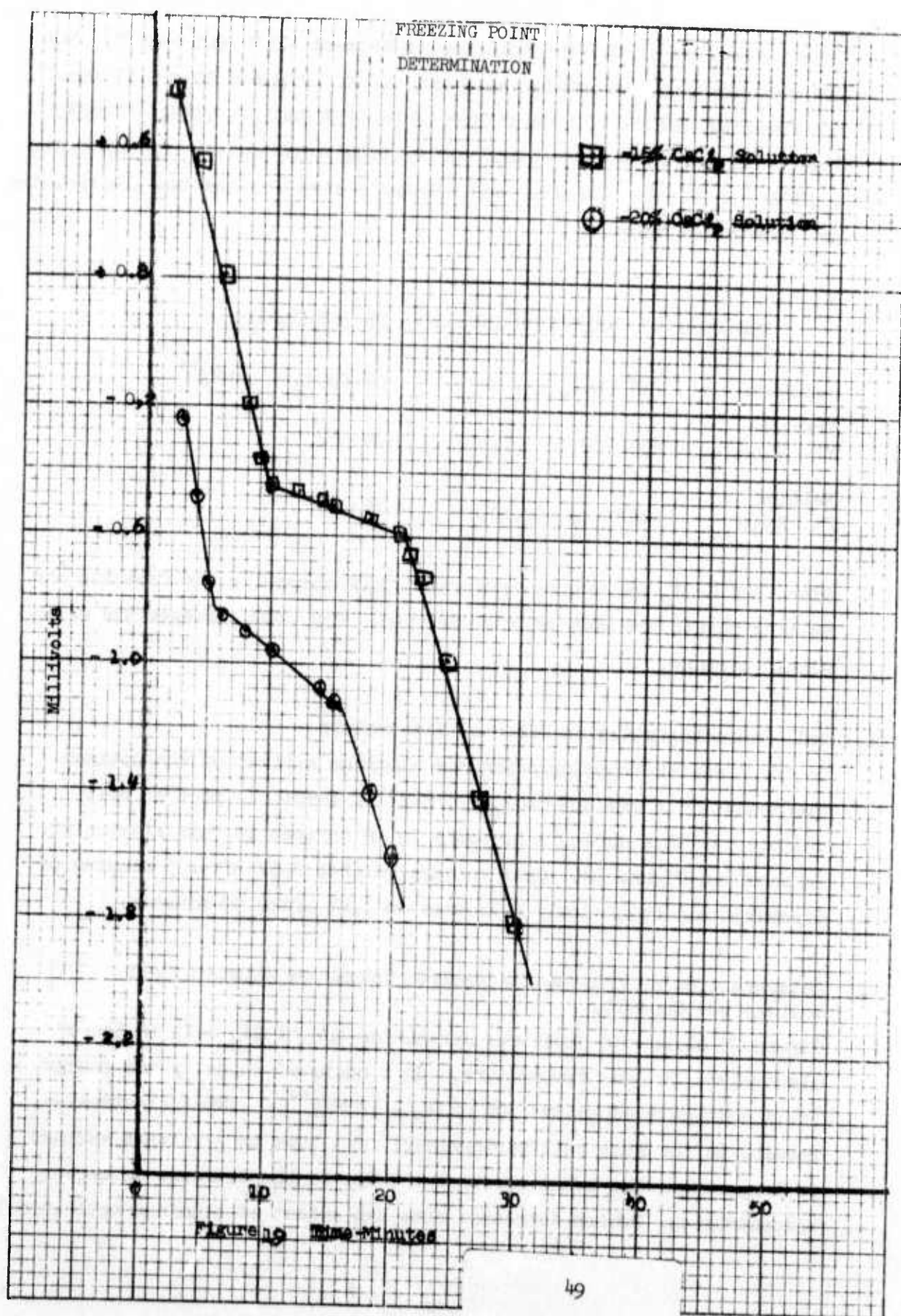
The open circuit corrosion rate of preactivated aluminum 1100 anodes ($2 \frac{13}{16} \times 1 \frac{1}{8} \times .025$) was measured in the 25% aqueous electrolyte and the 15% alcoholic electrolyte. For each electrolyte two levels of mercuric ions were used 10^{-4} M and 10^{-2} M. pH for all solutions was adjusted to unity.

A weighed aluminum anode was placed in each of the four solutions and corrosion allowed to take place. The anodes were removed, washed and dried and weight loss determined. The anodes were reimmersed in the respective solutions and the process repeated. The rate of weight loss was so calculated as to express it as a current.

C. DATA AND DISCUSSION

i. Determination of Freezing Points

Figure 19 shows a plot of thermocouples reading in millivolts vs. time for 15% CaCl_2 and 20% CaCl_2 . These two solutions being non-eutectic show a freezing point range. This range is indicated by the decrease in slope of the millivolt-time plot in the region of freezing. The



freezing region of the 15% solution is between $+11^{\circ}\text{F}$ and $+4.5^{\circ}\text{F}$. The 20% solution freezes between -9°F and -20°F . Figures 20 and 21 show the freezing and melting point curves for $25\% \text{CaCl}_2 + .1\text{MHg}^{++} 1\text{NHCl}$. Figures 22 and 23 show freezing and melting point curves for $30\% \text{CaCl}_2 + .1\text{MHg}^{++} + 1\text{NHCl}$. Freezing and melting points for the two electrolytes are summarized below.

FREEZING AND MELTING POINTS 25% AND 30% CaCl_2

Solution	$25\% \text{CaCl}_2 + .1\text{MHg}^{++}$	$30\% \text{CaCl}_2 + .1\text{MHg}^{++}$
Freezing Pt. Range	-55.7°F to -96.6°F	-72.5°F
Melting Pt. Range	-66°F to -70.5°F	-73°F

Since $30\% \text{CaCl}_2$ is near the eutectic 29.8% composite the freezing and melting points are very sharply defined. $25\% \text{CaCl}_2$ freezes and melts within a range.

ii. Cell Characteristics in Selected Electrolyte

On the basis of freezing point and aluminum activation the optimum electrolyte mix was $30\% \text{CaCl}_2 + .1\text{MHg}^{++} + 1\text{NHCl}$. A plot of cell voltage vs. time during a 0.5 amps/in^2 discharge in this electrolyte is shown in Figure 24. Cell voltage reaches 2.0V after 5 minutes of discharge and then slowly decreases to 1.85 after 60 minutes.

iii. Determination of Minimum Electrolyte Volume to Maintain Cell Voltage and Capacity.

Figure 25 shows the discharge curves for the $\text{Al}-\text{Cl}_2$ cell in 5cc of electrolyte at room temperature. On a basis of capacity and energy (cell voltage x capacity) $30\% \text{CaCl}_2 + .01\text{MHg}^{++} + .1\text{NHCl}$ electrolyte results in the best cell performance. The time to a voltage maximum is longer than the other electrolytes due to the decrease in mercury concentration, (which decreases rate and extent of aluminum activation).

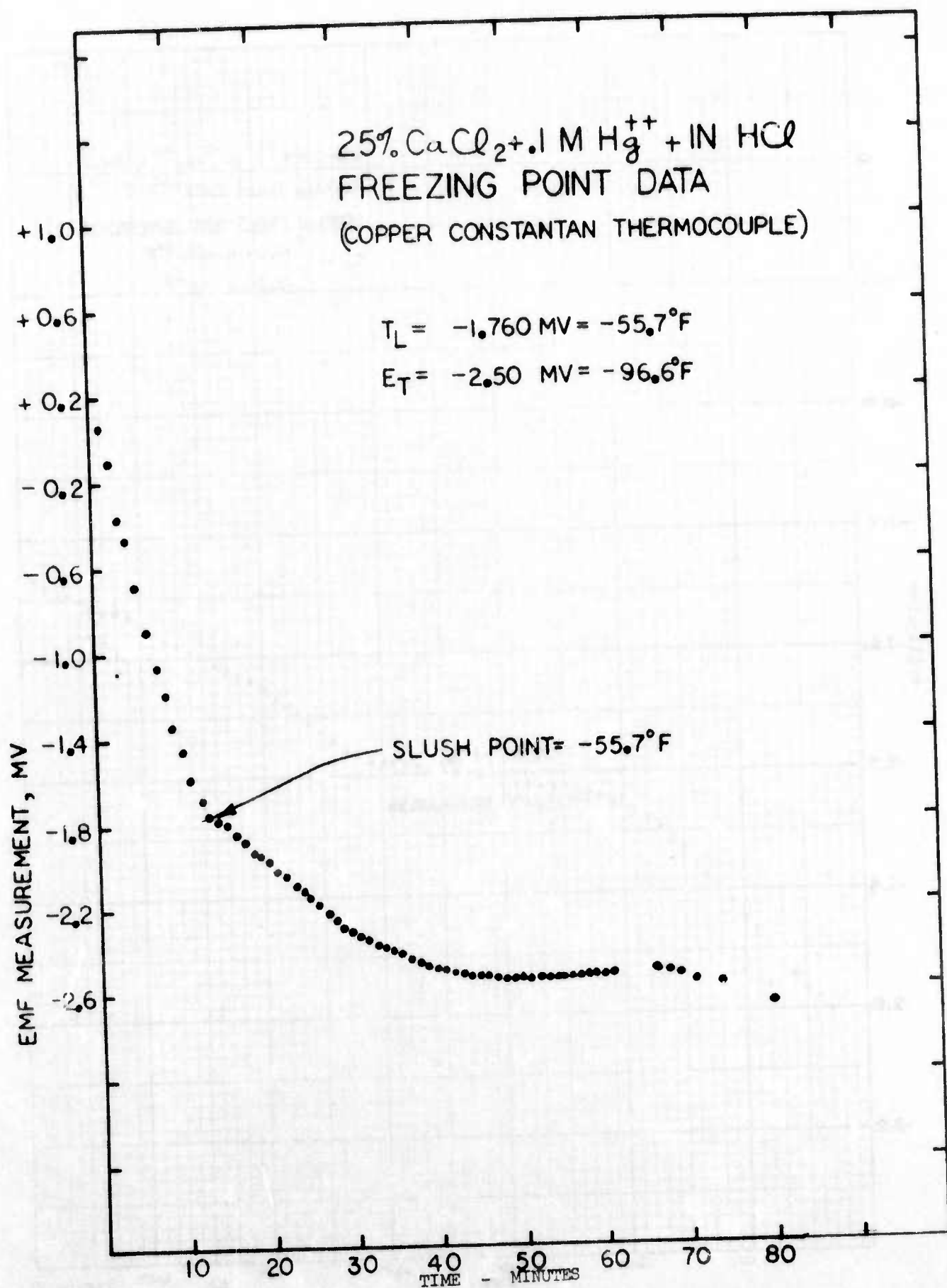


Figure 20

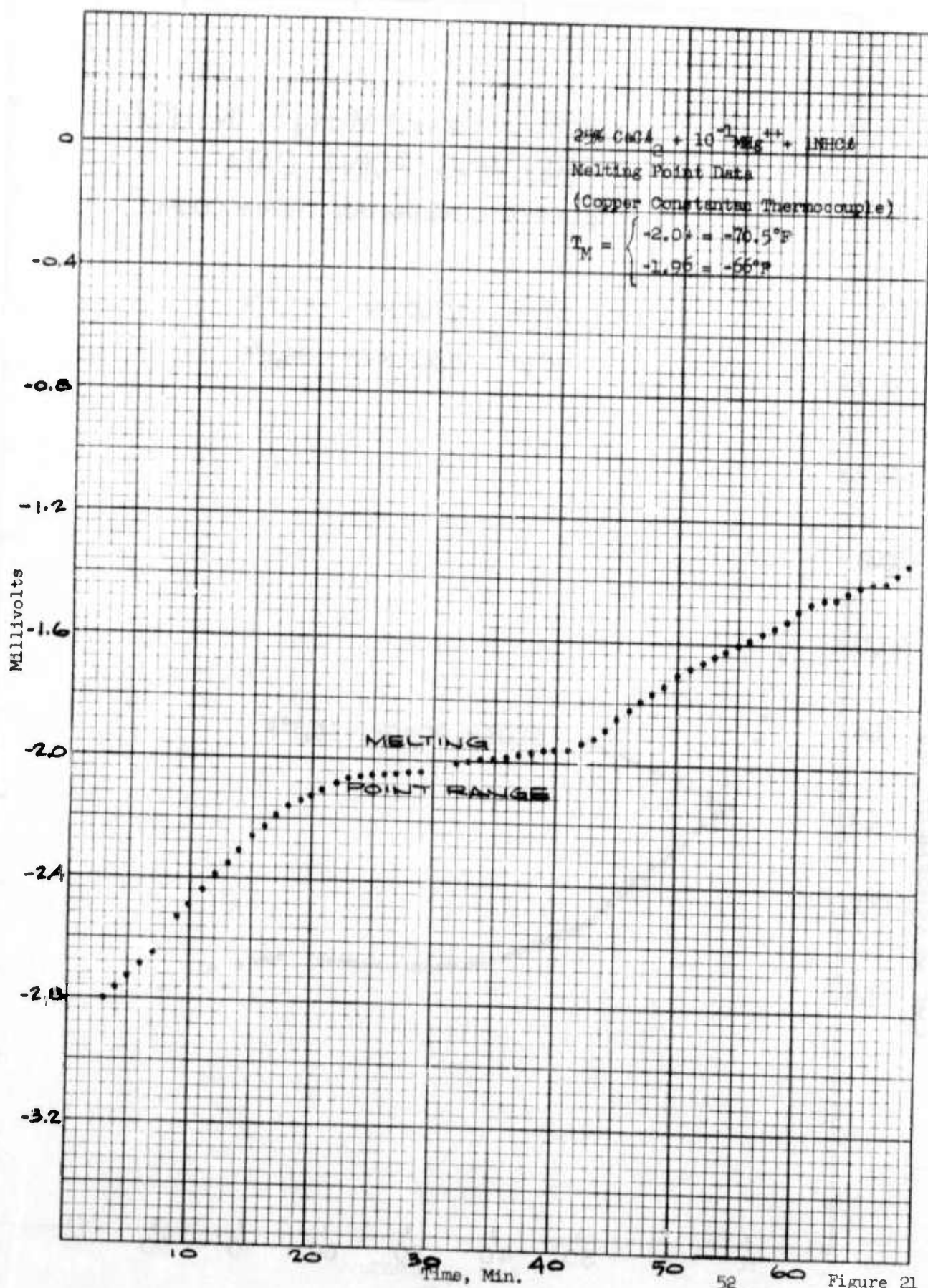
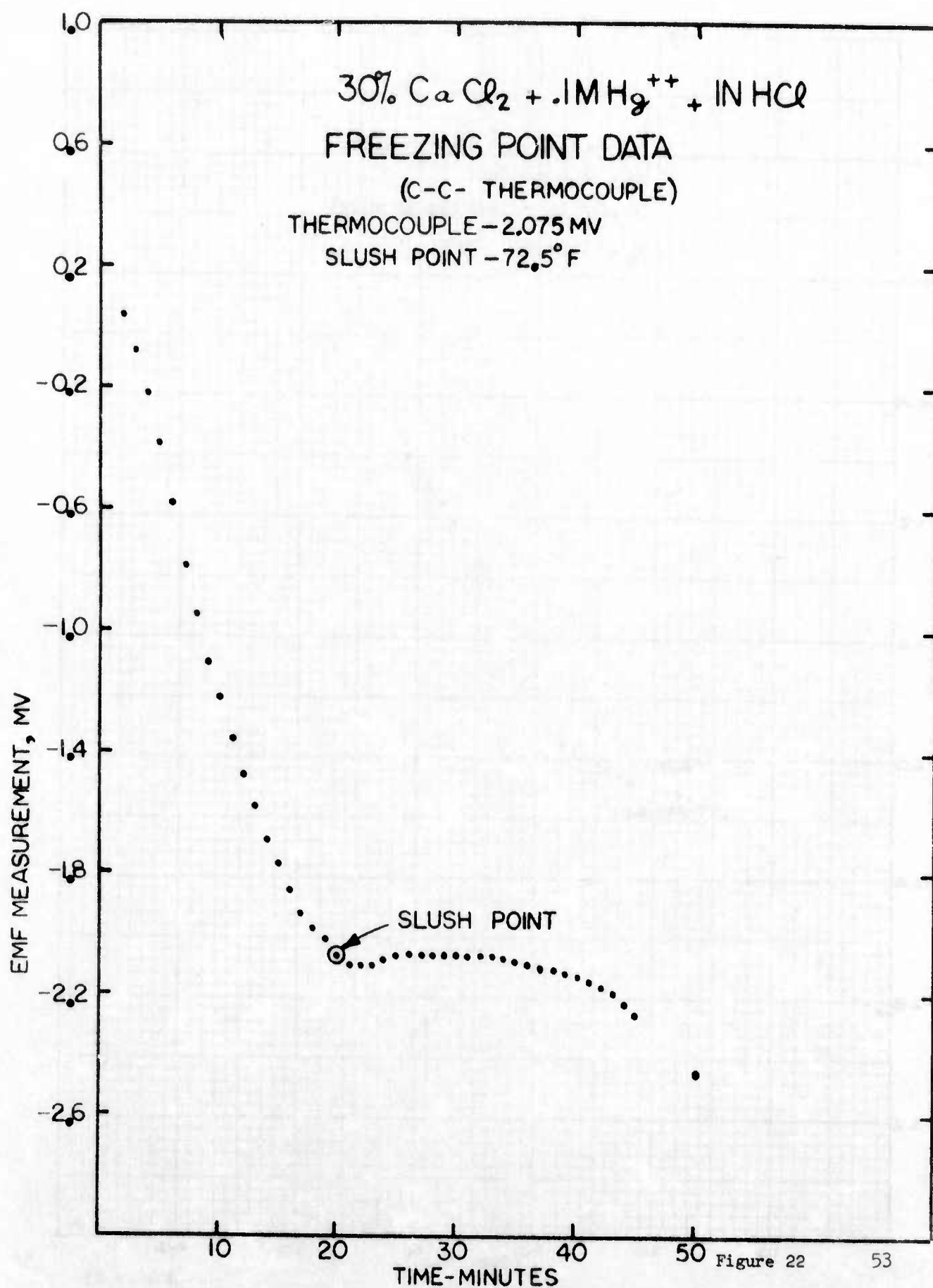


Figure 21



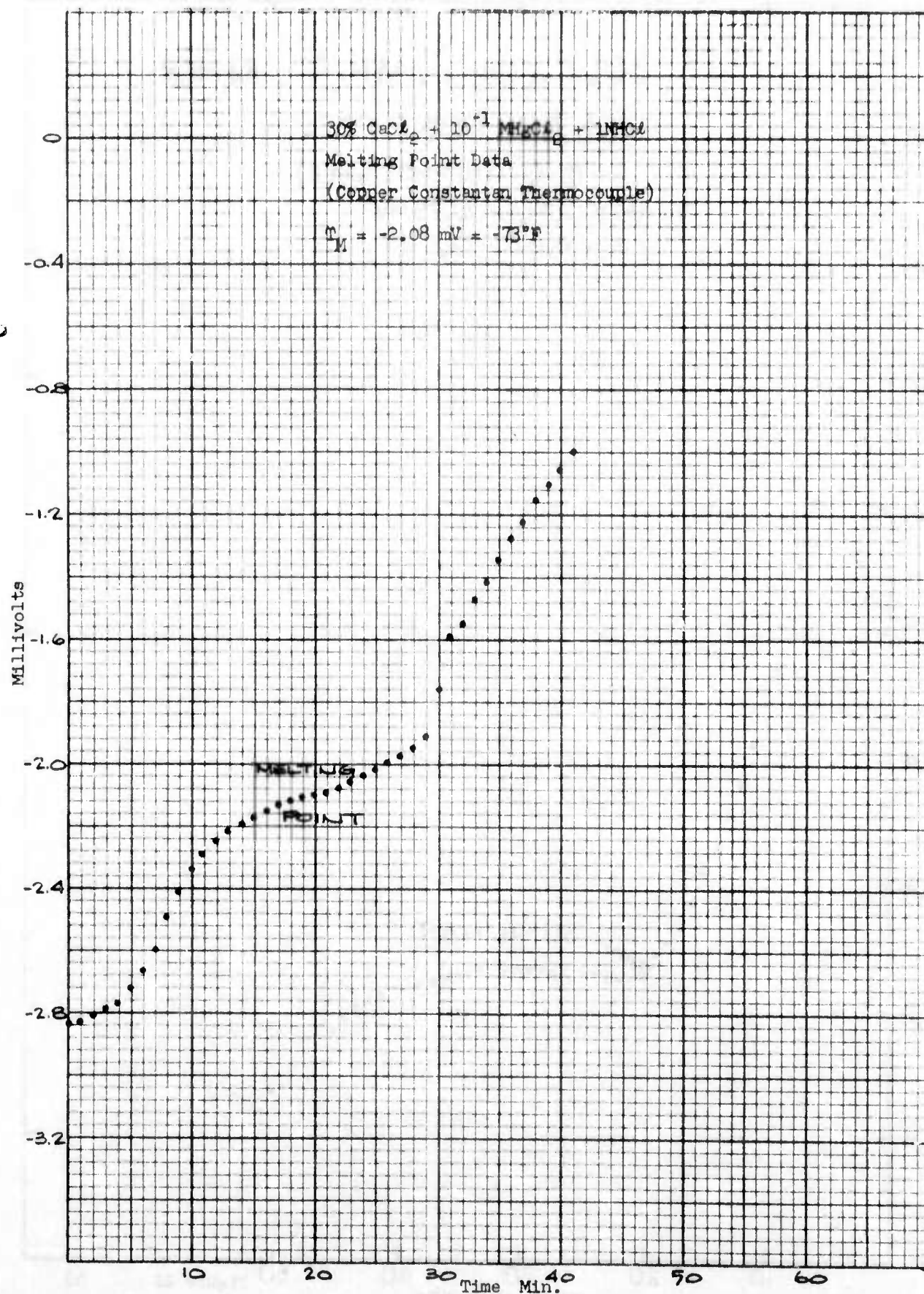


Figure 23

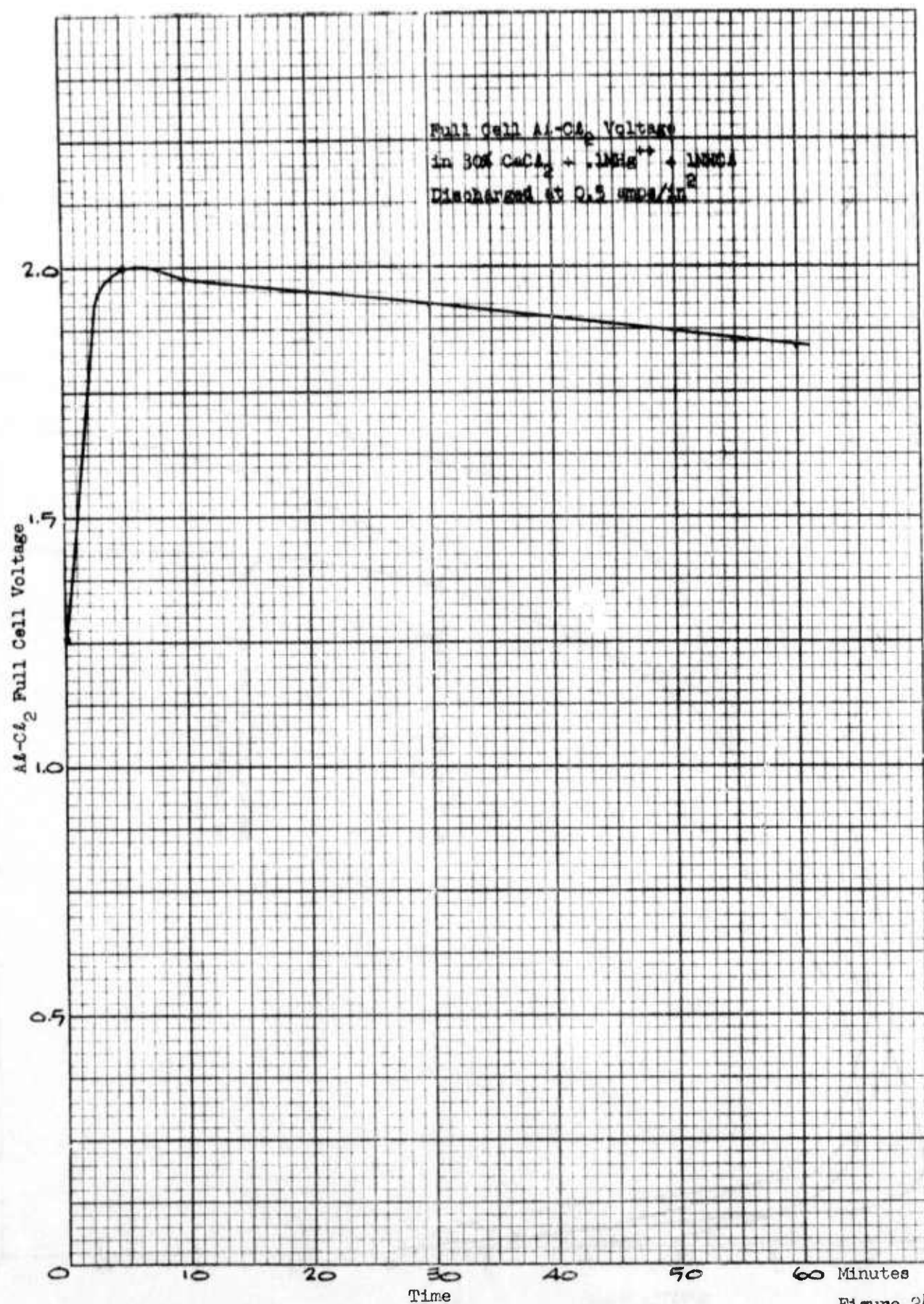
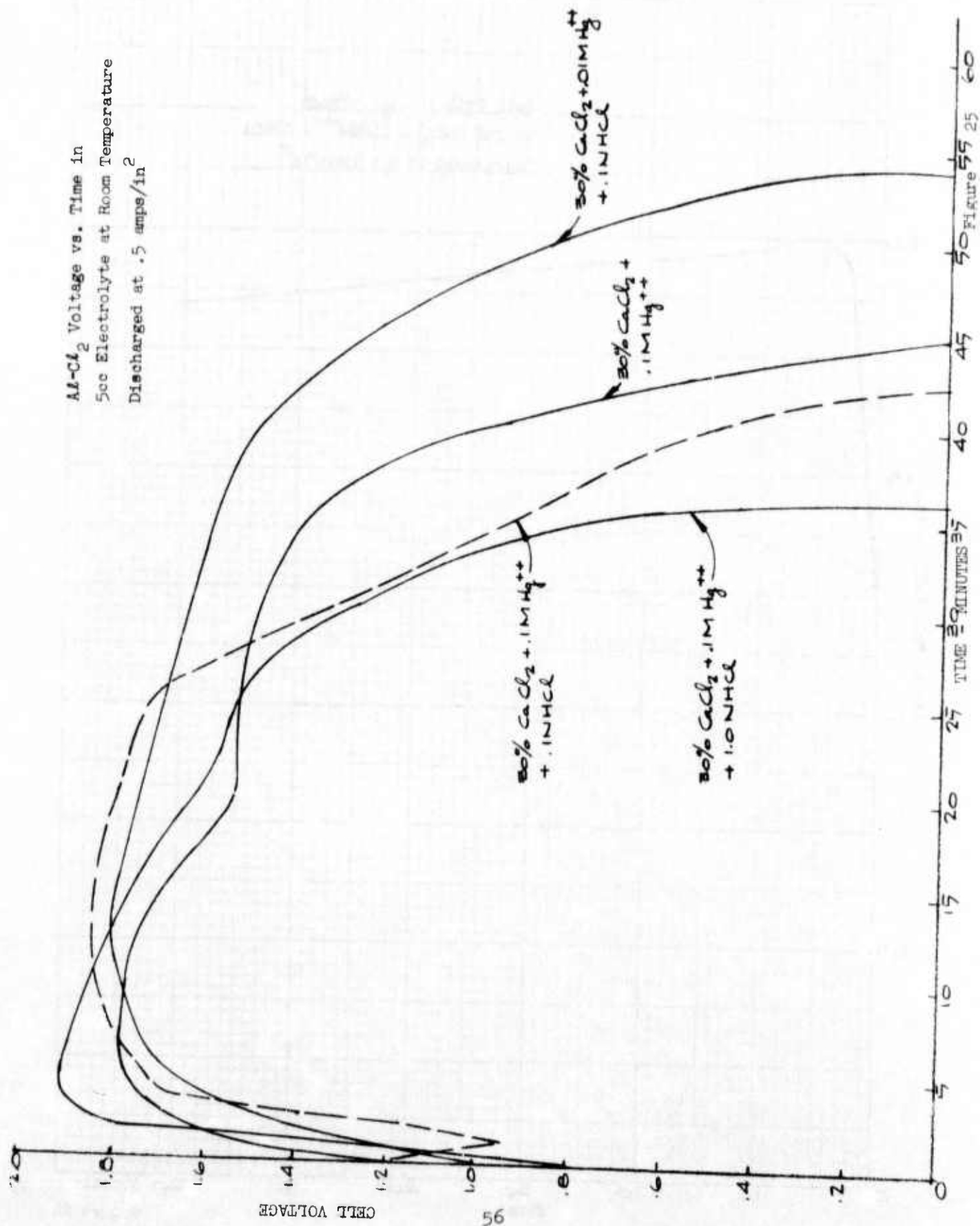


Figure 24

Al-Cl₂ Voltage vs. Time in
See Electrolyte at Room Temperature
Discharged at .5 amps/in²



Cell voltage, however, rises above 1.5V after 2 1/2 minutes into discharge and remains above that value until 40 minutes of discharge time has elapsed.

An AlCl_2 cell was discharged at 0.5 amps in 5cc of 30% CaCl_2 + .01M Hg^{++} + .1NHCl at 32°F. The initial cell voltage was 1.5 volts, but reached 0.0 volts in 12 minutes. No further discharges were attempted at 32°F since the optimum electrolyte at room temperature resulted in such poor performance at this temperature. Cell performance at 45°F in limited electrolyte was investigated and the results shown in Figure 26 indicate that the cell can be operated satisfactorily at that temperature. Thus at ambients below 45°F, heat will be supplied to the system by means of heating tape which is required anyway to raise the chlorine vapor pressure. The tape will supply initial heat and the system will be kept warm by the heat energy of the electrochemical reaction (polarization voltage loss x current).

A comparison of discharge curves in 5cc of various electrolytes indicates that from a capacity and energy standpoint 30% CaCl_2 + .01M Hg^{++} + .1NHCl and 30% CaCl_2 + .1M Hg^{++} + .1NHCl are superior to the other two electrolytes. From a standpoint of activation time and initial voltage level 30% CaCl_2 + 1NHCl + .1M Hg^{++} gives the best results but it falls far short with respect to capacity. 30% CaCl_2 + .1M Hg^{++} also gives a faster activation time and slightly higher voltage level but yields 20% less capacity.

It was necessary to maintain the chlorine gassing rate at 20-30cc per minute at this temperature in order to sustain the cell voltage. At room temperature the gassing rate was 10cc/minute. The utilization of chlorine at the lower temperature must be lower than at room temperature.

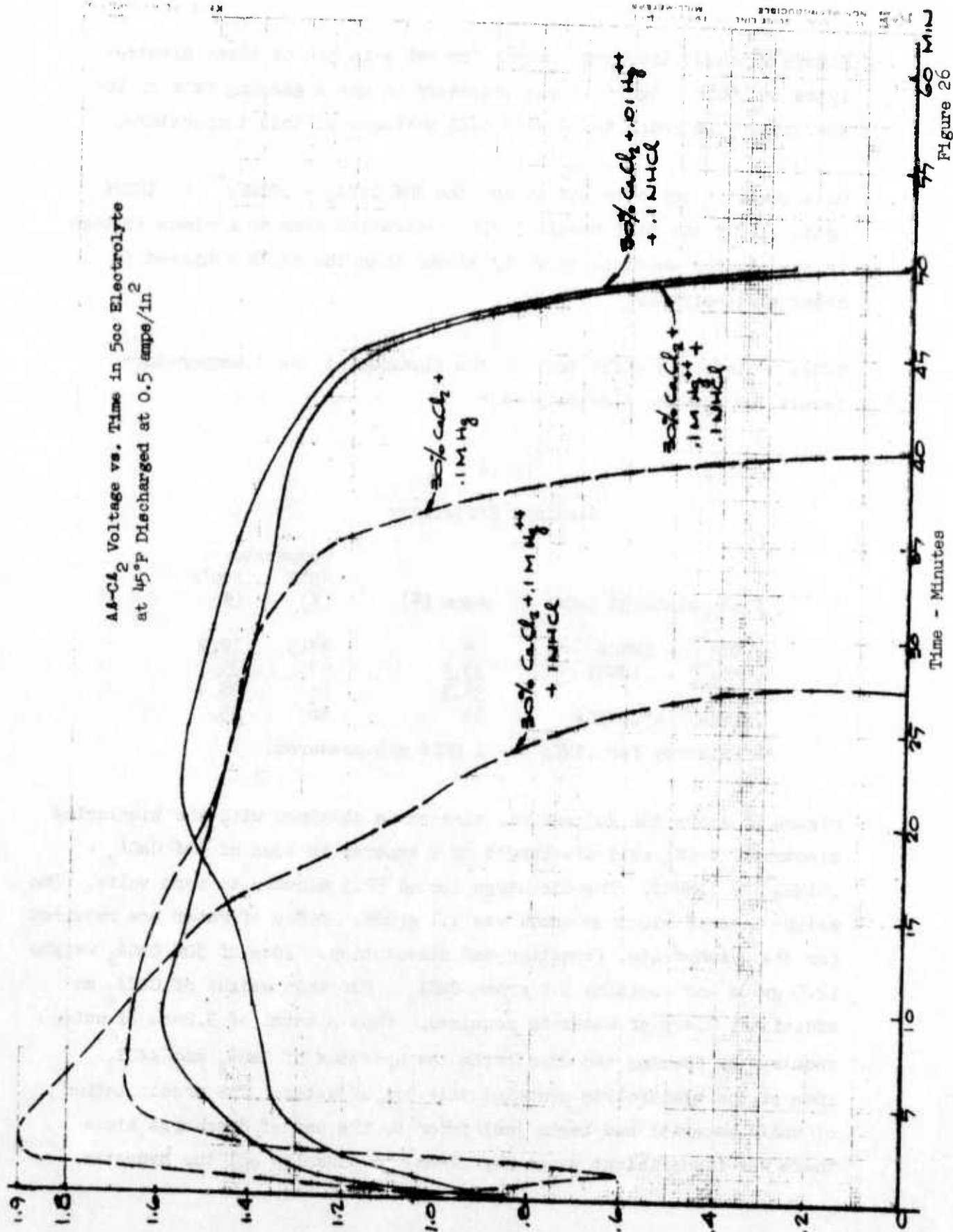


Figure 27 shows discharge curves for cells in 5cc of these electrolytes at 160°F. Again it was necessary to use a gassing rate of 20-30cc/minute in order to sustain cell voltages at this temperature.

On a basis of capacity and energy $^{++}$ 0% CaCl_2 + .01M Hg^{++} + .1NHCl again yields the best results. Activation time to maximum voltage is six minutes which is slightly slower than the cells achieved in other electrolytes.

Table 2 lists the efficiency of the aluminum at the 3 temperature levels for all the electrolytes.*

Table 2
Aluminum Efficiency

Electrolyte-30 CaCl_2 +	Room (%)	Temperature	
		45°F (%)	160°F (%)
.1M Hg^{++} + 1NHCl	*	44.5	19.9
.1M Hg^{++} + .1NHCl	33.5	57	35
.1M Hg^{++}	34.3	60	28.4
.01M Hg^{++} + .1NHCl	54	76	45.7

*Efficiency for .1M Hg^{++} + 1 NHCl not measured.

Figure 28 shows the voltage vs. time curve obtained with the bichlorine electrode Al- Cl_2 cell discharged at 2 amperes in 10cc of 30% CaCl_2 + .01M Hg^{++} + .1NHCl. The discharge lasted 52.5 minutes to zero volts. The weight loss of aluminum anode was 1.1 grams. 6.8cc of water are required for the hexahydrate, formation and dissolution. 10cc of 30% CaCl_2 weighs 12.9 grams and contains 3.9 grams CaCl_2 . For this weight of CaCl_2 an additional 2.4cc of water is required. Thus a total of 9.24cc of water required by forming and dissolving the hydrates of CaCl_2 and AlCl_3 . 10cc of the electrolyte contains only 9cc of water. The precipitation of solid material had begun just prior to the end of discharge since there was insufficient water (by .24cc) to dissolve all the hydrates.

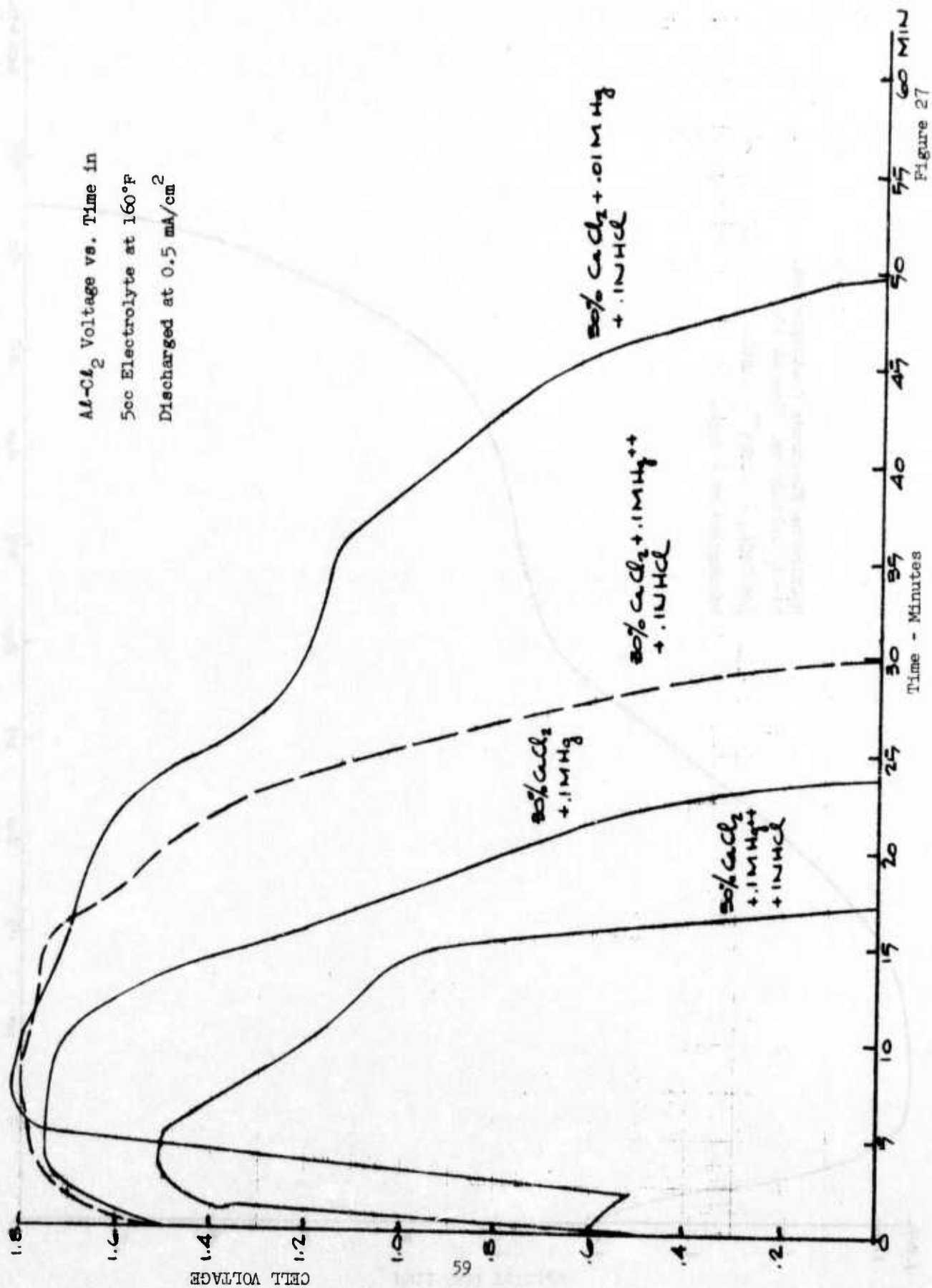
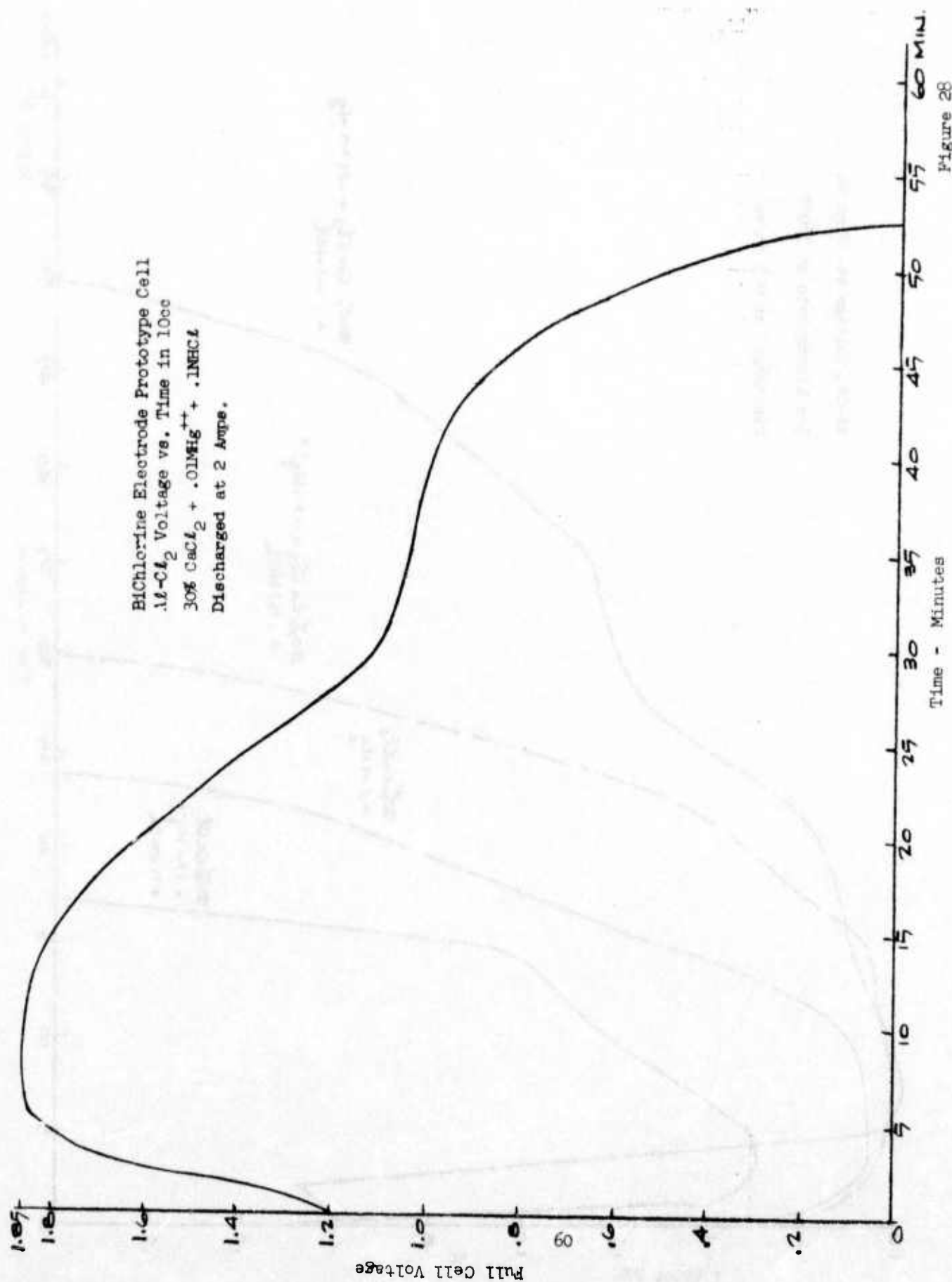


Figure 27



In a side experiment it was shown that the addition of water to a cell at the time that the cell voltage had dropped sharply causing a voltage recovery and an extension of discharge life.

iv. Theoretical Limitation of Minimum Electrolyte Volume.

This has been discussed in the Experimental Section B.

v. Non-Aqueous Electrolytes

Figure 29 shows the voltage vs. time curve of an Al-Cl₂ cell (preactivated Al 1100 anode) discharged in 6cc of 15% CaCl₂ + 20% CH₃OH + 65% H₂O, pH = 1, .01MHg⁺⁺ at a current density of 0.5 amps/in². The voltage was above 1.5V for the first minute of discharge to 37.5 minutes with a maximum voltage of 1.8V.

A discharge curve in 65cc of the same electrolyte at 0.5 amps/in² is shown in Figure 30. The aluminum efficiency was 68%. The gap between the aluminum and chlorine electrode was set at 3/8" and after 11 minutes the gap was decreased to 1/8". A cell voltage rise from 1.35V to 1.55V resulted. The resistivity of the electrolyte was calculated from these data.

$$\Delta V = .20V, i = 0.5 \text{ amps/in}^2$$

$$R = \frac{\Delta V}{i} = \frac{.20}{.5} = 0.4 \text{ ohms}$$

$$R = \frac{\rho l}{A}$$

$$0.4 \text{ ohm} = \rho \frac{.25" \times 2.54 \text{ cm/in}}{1 \text{ sq. in } (2.54)^2 \text{ cm}^2/\text{in}^2}$$

$$0.4 \text{ ohm} = \rho .1 \text{ cm}^{-1}$$

$$\rho = 4 \text{ ohm cm}$$

$$\text{conductivity} = \frac{1}{\rho} = 0.250 \text{ Mho/cm}$$

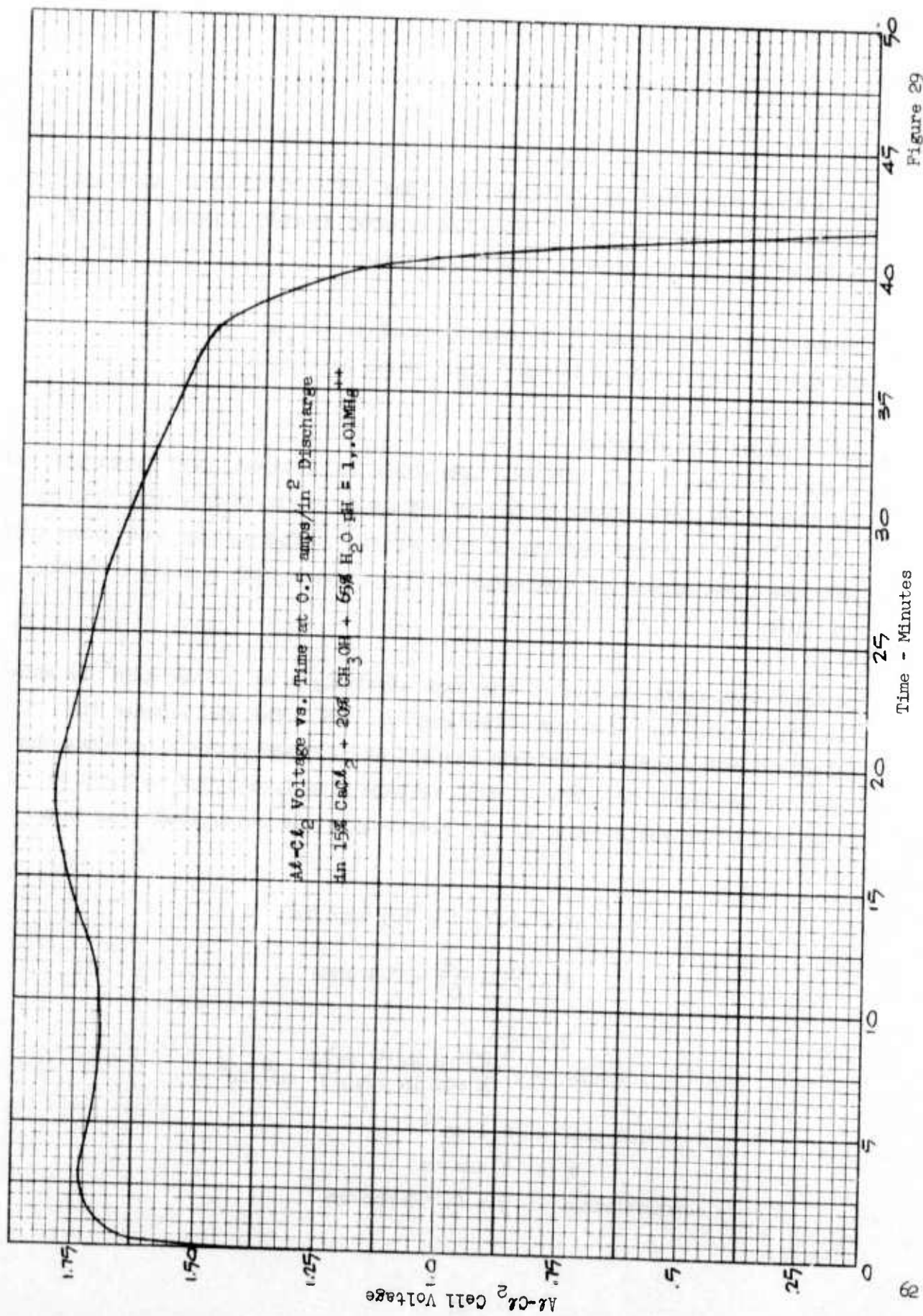


Figure 29

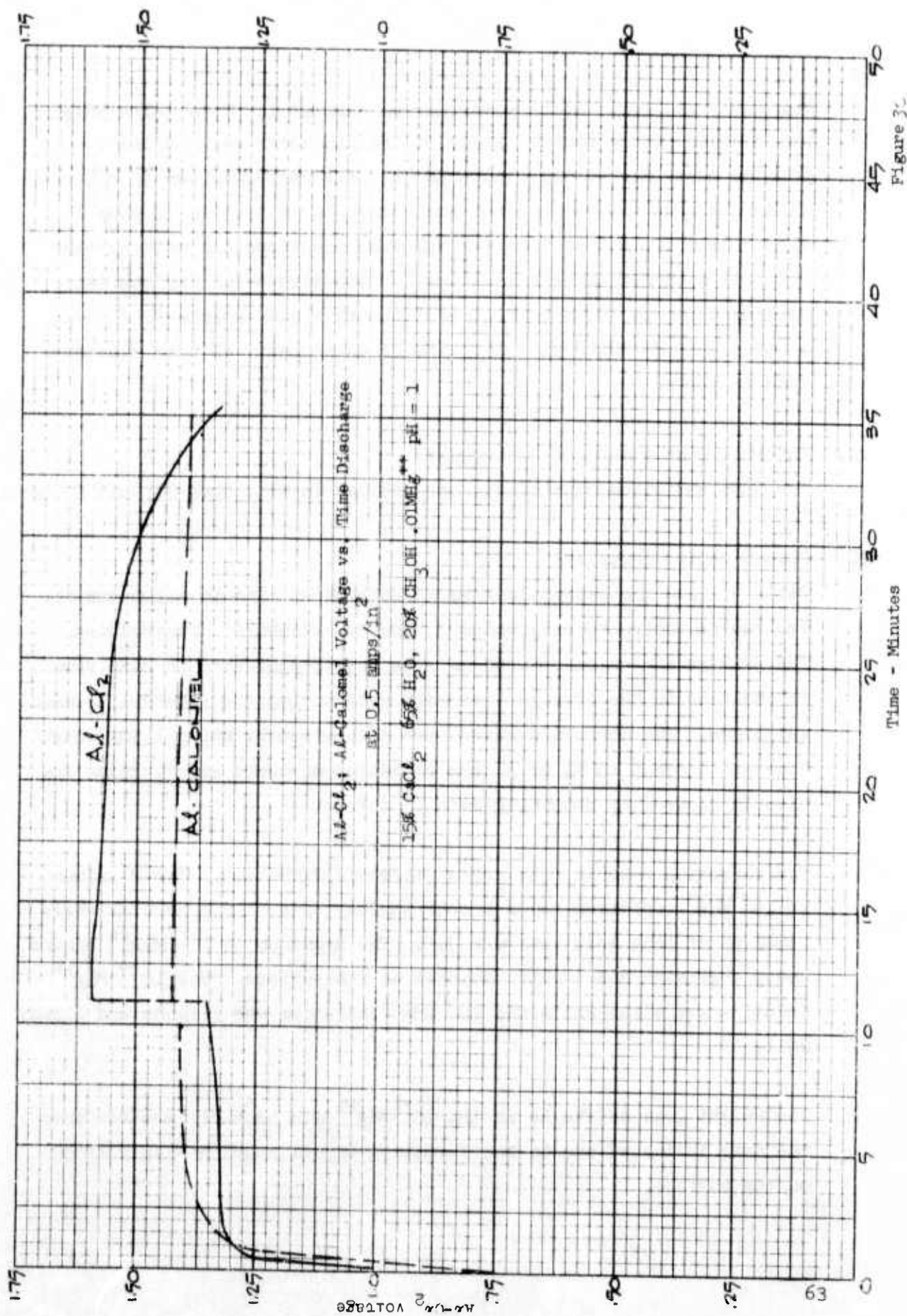


Figure 30

The data also shows Al to reference voltage of 1.35V, a value which was reached in the fourth minute of the discharge and remained there for the duration. A dip occurs in the cell voltage after 30 minutes while the aluminum voltage remains constant. A test in aqueous 15% electrolyte mix showed that the chlorine electrode had deteriorated but this occurred after a total use of 100 minutes in various tests. A Cooling curve is shown in Figure 31 for this electrolyte (15% CaCl_2 + 65% H_2O , + 20 CH_3OH pH = 1). The freezing point of this electrolyte is -60°F .

vi. Internal Containment of Electrolyte

The data and discussion of vi. is included in vii. Open Circuit Corrosion.

vii. Open Circuit Corrosion

Table 3 lists the weight loss as a function of time in solutions for the two preactivated electrodes in the two alcoholic electrolytes. The average corrosion rate in mA as a function of time is also shown in addition to the average corrosion rate during the interval between weighings. The corrosion rates were determined by multiplying weight loss of aluminum in mg by 3 thus obtaining mA-hours and dividing the time in hours thus obtaining rate as current.

The corrosion rate in both cases decreases with time. The aluminum in 10^{-4}MHg^{++} solution had a smooth surface after 162 hour soak while final pH of both solutions was 7.5. The aluminum in 10^{-2}MHg^{++} showed heavy corrosion and a white deposit on its surface. The 10^{-4}MHg^{++} solution was clear while the 10^{-2}MHg^{++} solution was viscous and cloudy white.

The weight loss of the Al in the 10^{-2}MHg^{++} was probably greater than the data indicated due to the formation of salts and probably $\text{Al}(\text{OH})_3$ on the surface.

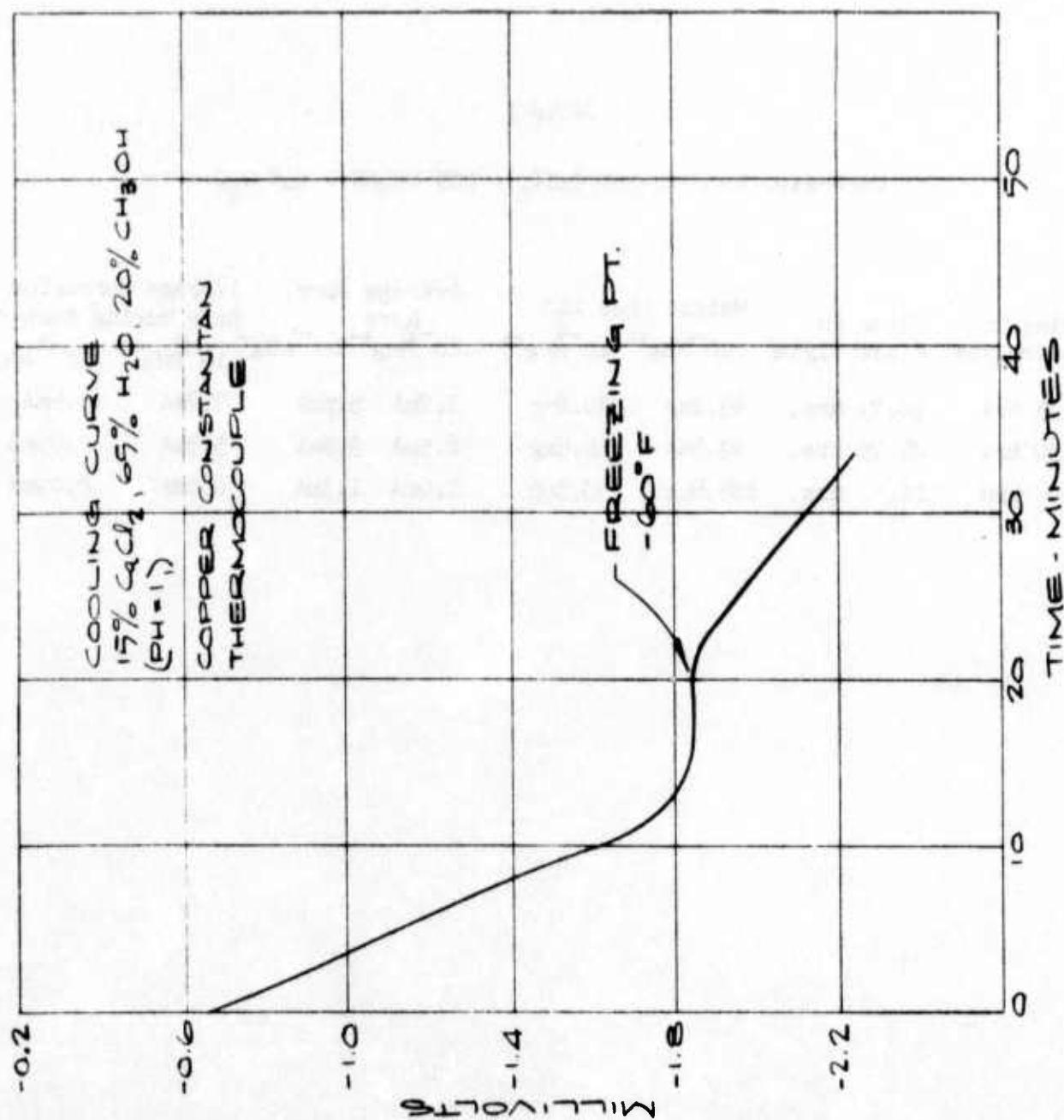


FIGURE - 31

Table 3

Corrosion Rate in 15% CaCl_2 + 20% CH_3OH + 65% H_2O

Time in Electrolyte	Δ Time in Electrolyte	Weight Loss AL		Average Corr. Rate		Average Corrosion Rate During Each ΔT	
		10^{-2} MHg^{++}	10^{-4} MHg^{++}	10^{-2} MHg^{++}	10^{-4} MHg^{++}	10^{-2} MHg^{++}	10^{-4} MHg^{++}
16.75 hrs	16.75 hrs.	43.2mg	30.6mg	7.7mA	5.5mA	7.7mA	5.5mA
48.50 hrs	28.75 hrs.	93.8mg	38.8mg	6.5mA	3.9mA	5.3mA	0.85mA
162.0 hrs	116.5 hrs.	102.8mg	49.3mg	1.9mA	1.3mA	0.22mA	0.09mA

Table 4 shows weight loss and corrosion rates for 25% CaCl_2 at both levels of mercury ion concentration.

The corrosion rate of the aluminum in the 25% CaCl_2 aqueous solution (10^{-2}MHg^{++}) is greater than in the 15% CaCl_2 solution containing the same level of mercury ion. The rate does not decrease significantly with time. As was the case with the 15% CaCl_2 methanol solution the 25% aqueous CaCl_2 solution was cloudy viscous with a white gelatinous precipitate. The alumina piece soaked in it showed an irregular surface due to the corrosion. The final pH was again 7.5. The 10^{-4}MHg^{++} solution was clear and its aluminum piece retained its smooth surface. The final pH of this solution was also 7.5.

The results indicate that in the case of a sufficiently low mercury ion concentration the open circuit corrosion rate especially in the case of the 25% aqueous CaCl_2 decreases rapidly with time and within a week is almost nonexistent.

Consider the corrosion rate of .01 mA observed in the time interval between 28 and 144.75 hours in solution. Even if that corrosion rate prevailed (it is expected to decrease even further with time) it would require 10^{+5} hours (over 10 years) before 0.33 grams or 10% of the aluminum weight were consumed.

At such a corrosion rate this electrolyte could easily be contained within the battery during its dormant stage without requiring any of the elaborate mechanical devices.

8. SEPARATORS

A. Objective

To find a separator for the Al-Cl_2 system which will not adversely affect cell voltages capacity and activation time. The separator should be chemically inert to chlorine, aluminum chloride and electrolyte, but be easily wetted by the electrolyte.

Table 4

Corrosion Rate in 25% CaCl_2 + 75% H_2O

Time in Electrolyte Hrs.	Δ Time Electrolyte Hrs.	Weight Loss Al		Average Corrosion Rate		Average Corrosion Rate During Each ΔT	
		10^{-2} MHg ⁺⁺ mg	10^{-4} MHg ⁺⁺ mg	10^{-2} MHg ⁺⁺ mA	10^{-4} MHg ⁺⁺ mA	10^{-2} MHg ⁺⁺ mA	10^{-4} MHg ⁺⁺ mA
28	28	118.3	1.6	12.7	0.17	12.7	0.17
144.75	116.75	529.4	2.0	11.0	0.05	10.6	0.01

B. Experimental

Three preactivated A&L1100 electrodes (2-13/16" x 1-1/8" x .025") were bagged with 5 mil polypropylene (RAI), 5 mil pellaon (Webril) and S and S 589 White Ribbon filter paper.

These electrodes were assembled into cells together with chlorine electrodes. The cells were discharged at 0.5 amps/in² in 66cc of 30% CaCl₂ + .1MHg⁺⁺ + 1NHCℓ electrolyte.

Pieces of S and S 589 White Ribbon filter paper (2-13/16" x 1-3/8") were placed into 30% CaCl₂ + .1Hg⁺⁺ electrolyte so that only 1/4" of its width was below the level of the electrolyte. The time to completely wet the separator material with electrolyte was recorded. This was done twice and then repeated twice in 30% CaCl₂ + .1MHg⁺⁺ + 1NHCℓ. (At the time of this investigation the optimum electrolyte composition in limited volume had not as yet been determined.)

The specific gravities of 30% CaCl₂ + .1MHg⁺⁺ and 30% CaCl₂ + .1MHg⁺⁺ + 1NHCℓ were determined by weighing a 10cc volume of each. The thickness of 1-3/8" x 2-13/16" piece of separator was measured and separator volume was determined. Next 1-3/8" x 2-13/16" piece of separator were submerged in electrolyte and maintained under vacuum. The weight of the electrolyte absorbed by the separator was determined by the difference of the previously weighed dry separator and the weight of the wet separator. This was done with 30% CaCl₂ + .1MHg⁺⁺ and 30% CaCl₂ + 0.1MHg⁺⁺ + 1NHCℓ. From the weight of electrolyte and the specific gravity the volume of electrolyte absorbed by the separator was determined.

The ratio $\frac{\text{cm}^3 \text{ electrolyte absorbed}}{\text{cm}^3 \text{ separator volume}}$ (specific electrolyte absorption) was calculated from the above data.

The specific electrolyte absorption was also determined for wetting of separator and capillary action (dipping a small fraction of separator in electrolyte).

C. Results and Discussion

Figure 32 shows voltage time plots with the 3 separator materials. Clearly the filter paper stands out as the best; and was characterized as described below.

The time required to completely wet separator by capillary action with 30% CaCl_2 + .1MHg⁺⁺ and 30% CaCl_2 + .1MHg⁺⁺ + 1NHCl is given in Table 5 below.

Table 5

Rate of Separator Wetting

Electrolyte	Run 1	Run 2	Average
30% CaCl_2 + .1MHg ⁺⁺	6.88 min.	6.59 min.	6.74 ± .15 min.
30% CaCl_2 + .1MHg ⁺⁺ + 1NHCl	5.97	5.87	5.92 ± .05 min.

It should be noted that the time required to wet the separator half way to the top was approximately one minute for each electrolyte. The wet out time would vary considerably as a function of the depth of separator immersion in electrolyte.

Table 6 gives the specific gravity, weight of electrolyte absorbed by vacuum impregnation and by capillary action for both electrolytes.

Table 6

Electrolyte Absorption

Electrolyte	Sp. Grav.	Weight Absorbed		Vol. Absorbed	
		Vac Impreg.	Cap. Action	Impreg.	Cap
30% CaCl_2 + .1MHg ⁺⁺	1.292	.539g	.498g	.42cc	.38cc
30% CaCl_2 + .1MHg ⁺⁺ + 1NHCl	1.282	.545g	.499g	.43cc	.39cc

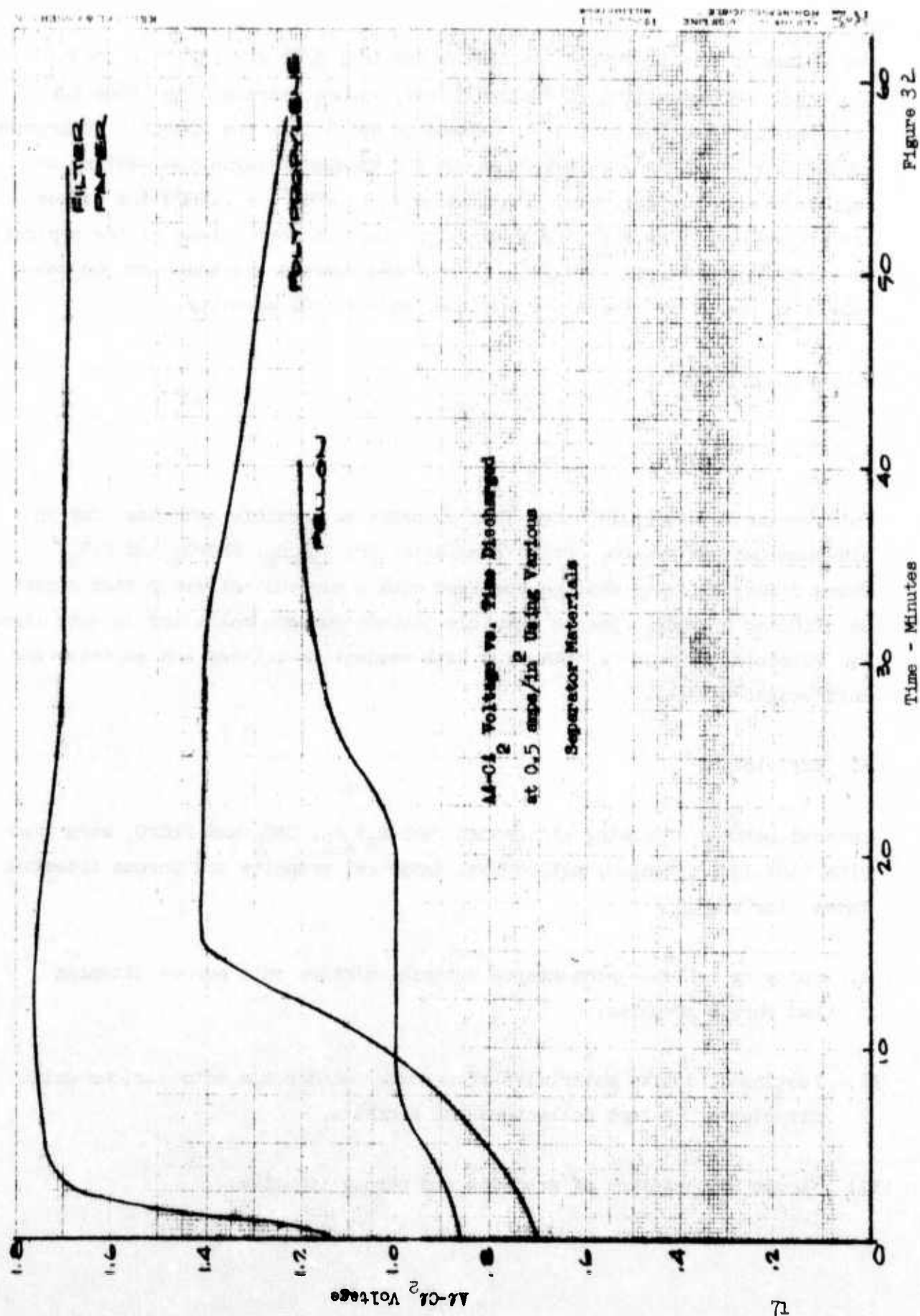


Figure 32

The volume of the separator test piece dry is $1 \frac{3}{8}'' \times 2 \frac{13}{16}'' \times .007'' = 0.44\text{cc}$. After wetting with electrolyte, volume increased to .48cc due to separator swelling to .0077''. Based on wet volume the specific absorption in 30% $\text{CaCl}_2 + .1\text{MHg}^{++}$ is 87%, and 80% for vacuum impregnation wetting and capillary rise respectively. For 30% $\text{CaCl}_2 + .1\text{MHg}^{++} + .1\text{NHCl}$ the values are 90 and 81%. The specific absorption based on pore volume of the separator is slightly greater in actuality since these numbers are based on the geometric volume of the separator and they assume 100% porosity.

9. CATHODE SELECTION

A. Objective

To investigate materials other than chlorine as possible cathodes for an aluminum battery system. Prime candidates are $\text{K}_2\text{S}_2\text{O}_8$, PbCrO_4 and CaO_2 . These strong oxidants must be combined with a current collector that cannot be oxidized by them. Once a feasible cathode-current collector is established its fabrication should be optimized with respect to voltage and capacity per unit weight (WH/lb).

B. Experimental

Several methods of making electrodes with $\text{K}_2\text{S}_2\text{O}_8$, CaO_2 and PbCrO_4 were used with tantalum, titanium, molybdenum, tungsten, graphite and porous titanium. These include

- i. Spraying teflon-carbon-active material mixture onto porous titanium and porous graphite.
- ii. Pasting of active material-carbon powder binder mix onto various grid structures, current collectors and graphite.
- iii. Vacuum impregnation of graphite and porous titanium.

Cathodes were combined with preactivated aluminum 1100 electrodes; open circuit and load potential were determined using 17% NH_4Cl + .1M HgCl_2 and 30% CaCl_2 + .1M HgCl_2 . The ammonium chloride electrolyte was used in conjunction with $\text{K}_2\text{S}_2\text{O}_8$ electrodes since CaSO_4 would precipitate if CaCl_2 electrolyte is used in conjunction with $\text{K}_2\text{S}_2\text{O}_8$.

C. Data and Discussion

The open circuit voltages vs. a preactivated Al 1100 obtained with pasted cathode-carbon binder mixes or various current collectors is presented in tabular form below.

Current Collector	Open Circuit Voltage vs. Al			
	$\text{K}_2\text{S}_2\text{O}_8$	CaO_2	PbCrO_4	
Graphite	*2.2	1.55	1.75	
Tantalum	*1.8	.65	1.65	*1.60
Titanium	*2.0	.80	1.20	*1.50
Tungsten	*1.7	.75	1.45	*1.70
Molybdenum	*1.75	.90	1.50	*1.70

*-in NH_4Cl electrolyte

The only cathode material that held some promise was $\text{K}_2\text{S}_2\text{O}_8$. The best capacity result was obtained with a vacuum impregnation of a saturated solution $(\text{NH}_4)_2\text{K}_2\text{S}_2\text{O}_8$ into porous graphite and then soaking in 50% KOH to precipitate $\text{K}_2\text{S}_2\text{O}_8$ within the pores of the graphite. The electrode yielded an open circuit of 2.1V against preactivated aluminum, and when discharged at 100 mA/in² in 5cc of 17% NH_4Cl yielded a voltage of 1.5 during the first 5 minutes. After 32 minutes of discharge the cell voltage decreased to .25 at which point the discharge was interrupted. The discharge curve is shown in Figure 33.

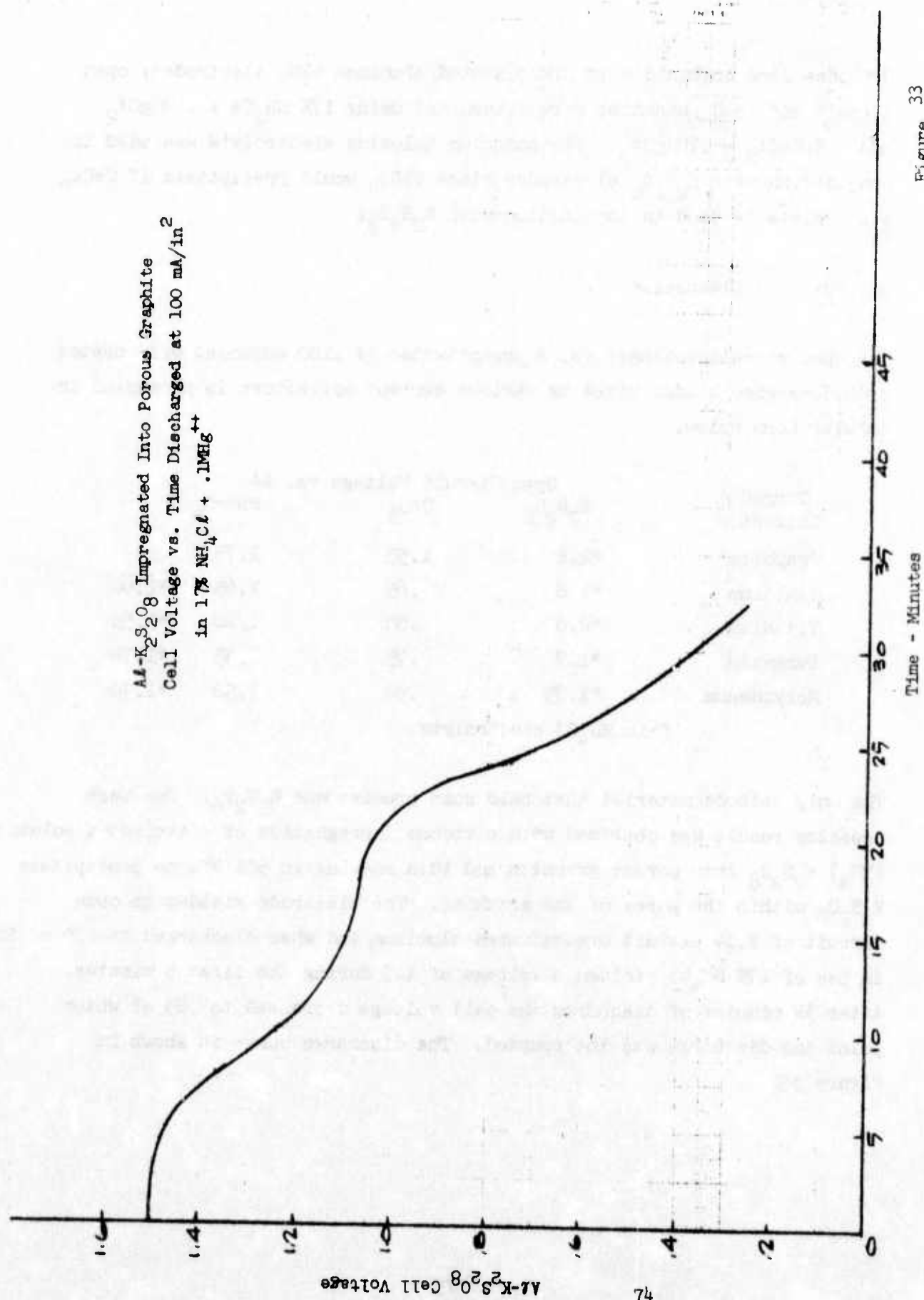


Figure 33

The utilization of the active cathode material was 15%.

Even though this cathode holds some promise, development work necessary to achieve characterization on the same level as the chlorine electrode was beyond the time scope of the contract.

10. SPECIAL TESTS - ALUMINUM ELECTRODE

A. Objective

The purpose of these tests was to further characterize the behavior of the aluminum electrode in lower mercury concentration electrolyte.

It was anticipated that under these conditions the efficiencies of the aluminum would be increased.

B. Experimental

i. Effect of Mercury Concentration on Aluminum Voltage and Efficiency

As was shown previously the amount of aluminum consumed during a discharge determines the amount of electrolyte needed in the $Al-Cl_2$ cell. If the efficiency of aluminum is doubled from 50% to 100% the amount of electrolyte required is cut in half. For this reason an investigation was undertaken to determine whether the aluminum efficiency could be increased without detrimentally affecting the activation time or activated voltage. All tests were performed with 65cc of 30% $CaCl_2$ aqueous electrolyte pH = 1 with varying amounts of Hg^{++} : 0.1M, .01M, .001M, .0001M and no Hg^{++}).

In all cases except one, the aluminum used for the tests was preactivated for 15 minutes in 65cc of 30% $CaCl_2$ pH = 0, .1M Hg^{++} . The one exception was where the preactivation took place with no Hg^{++} .

The tests consisted of a discharge at 0.5 amps/in² of the preactivated aluminum pieces in 65cc of 30% $CaCl_2$ pH = 1 against a chlorine electrode at each concentration of Hg^{++} , with calomel serving as the reference

electrode. Aluminum to reference voltage was monitored and aluminum efficiency was determined. A discharge with no mercury was performed with normally preactivated aluminum electrodes and also with an aluminum electrode that was preactivated in the absence of any Hg^{++} .

ii. Effect of Current Density on Aluminum Efficiency and Voltage

A $2\frac{13}{16}$ " x $1\frac{1}{8}$ " x .025" coupon of Al 1100 preactivated was discharged in 65cc of 25% CaCl_2 ($\text{pH} = 1$, 10^{-4}MHg^{++}) for approximately 5 minutes at each current density of 0.07; 0.13, 0.25, 0.375, 0.5, 0.375, 0.25, 0.13, 0.07 A amps/in² in that order. Cell voltage and aluminum to reference voltage were recorded. A similar test was run with 15% CaCl_2 alcoholic electrolyte.

C. Data and Discussion

i. Effect of Mercury Concentration on Aluminum Voltage and Efficiency

Coulombic efficiency of aluminum is a controlling factor in the amount of electrolyte necessary in a cell as was shown earlier in this report. The effect of mercury ion concentration in the electrolyte on the coulombic efficiency of aluminum at a discharge rate of 0.5 amps/in² in 65cc of 30% CaCl_2 $\text{pH} = 1$ aqueous electrolyte is shown in Figure 34. A plot of Al efficiency vs. Hg^{++} concentration in the range of .1M to .0001M was made on semilog paper. The efficiency is an inverse function of the logarithm of the mercury ion concentration. It should be noted that at Hg^{++} concentration of 10^{-4}M the efficiency reached 88.5% as opposed to 61.5% attained in a .1M Hg^{++} solution.

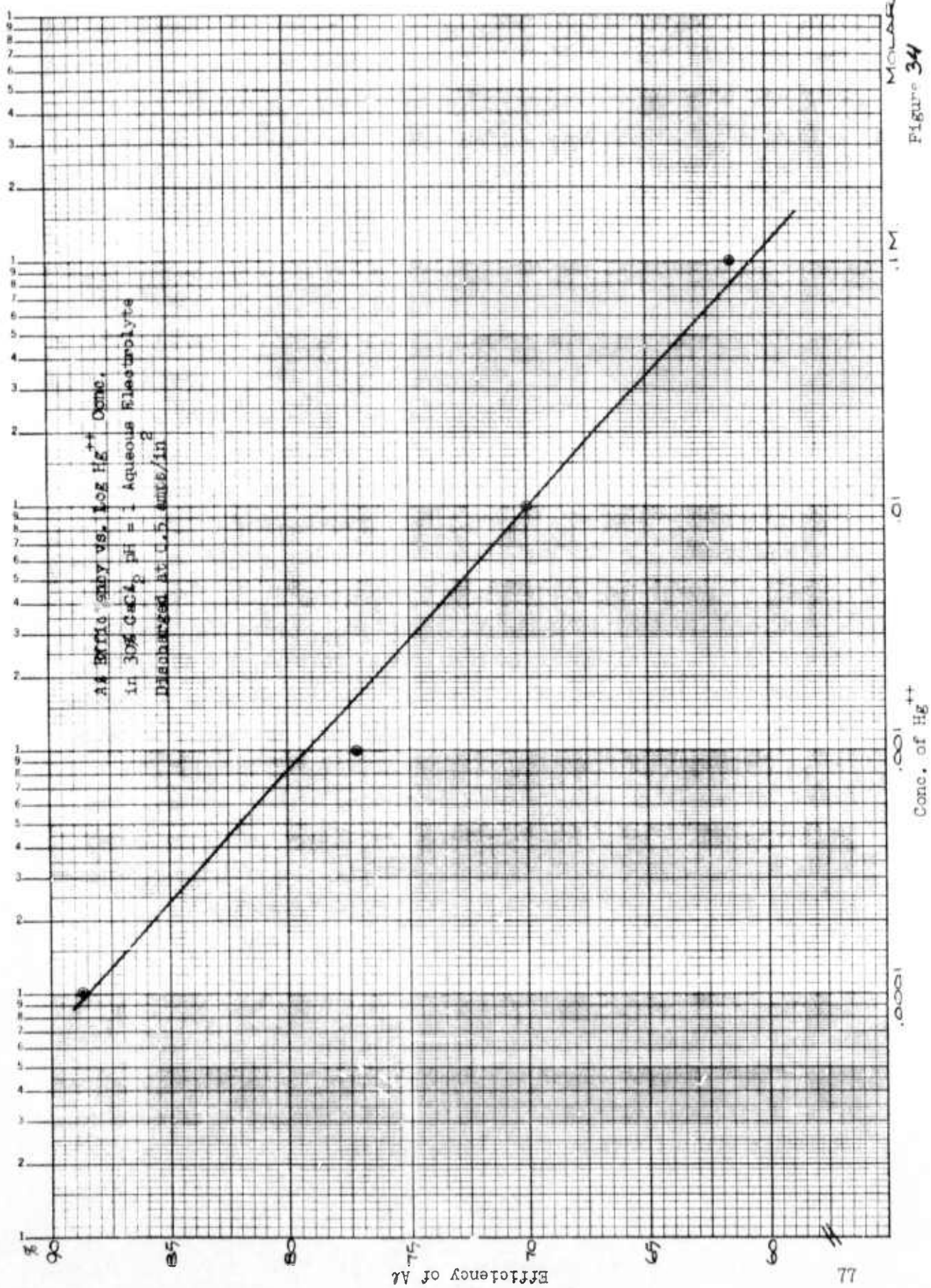


Figure 34

The efficiency obtained with no mercury present on a piece of aluminum which had been "preactivated" in the normal way was 65.5%. The efficiency obtained with a piece of aluminum "preactivated" without mercury and then discharged without mercury was 84%. The behavior of the aluminum in the absence of mercury with regard to coulombic efficiency cannot as yet be explained.

Figure 35 shows plots of aluminum to calomel reference voltage vs. time at a discharge rate of 0.5A/in^2 at various concentrations of mercury ion in 30% CaCl_2 pH = 1 aqueous electrolyte. All mercury containing electrolyte solutions activate the aluminum within minute of discharge. 10^{-3}M Hg^{++} results in the highest Al to reference voltage; 1.45V. 10^{-4}M Hg^{++} resulted in a voltage of 1.39. Thus it can be seen that low concentrations of mercury do not have significant adverse effects on either activation time or voltage, but do result in significant improvement in efficiency. The two aluminum electrodes which were discharged without mercury exhibited a voltage level below 1.0V. The electrode preactivated in the presence of mercury gave a higher voltage level than the one preactivated without mercury. The non-activation of the aluminum electrode which had been preactivated in the normal fashion is an unexpected result. The efficiency obtained for this electrode as mentioned before is also a surprise.

The most important result arising from these tests is that the efficiency of the aluminum electrode can be considerably increased to almost 90% at a discharge rate of 0.5 amps/in^2 by decreasing the mercury concentration without adversely effecting voltage.

Al to Calomel Voltage vs. Time Dis-
charged at 0.5 amps/in² in 65cc of
30% CaCl₂, pH = 1 Varying Hg⁺⁺
Concentration (Al Preactivated)

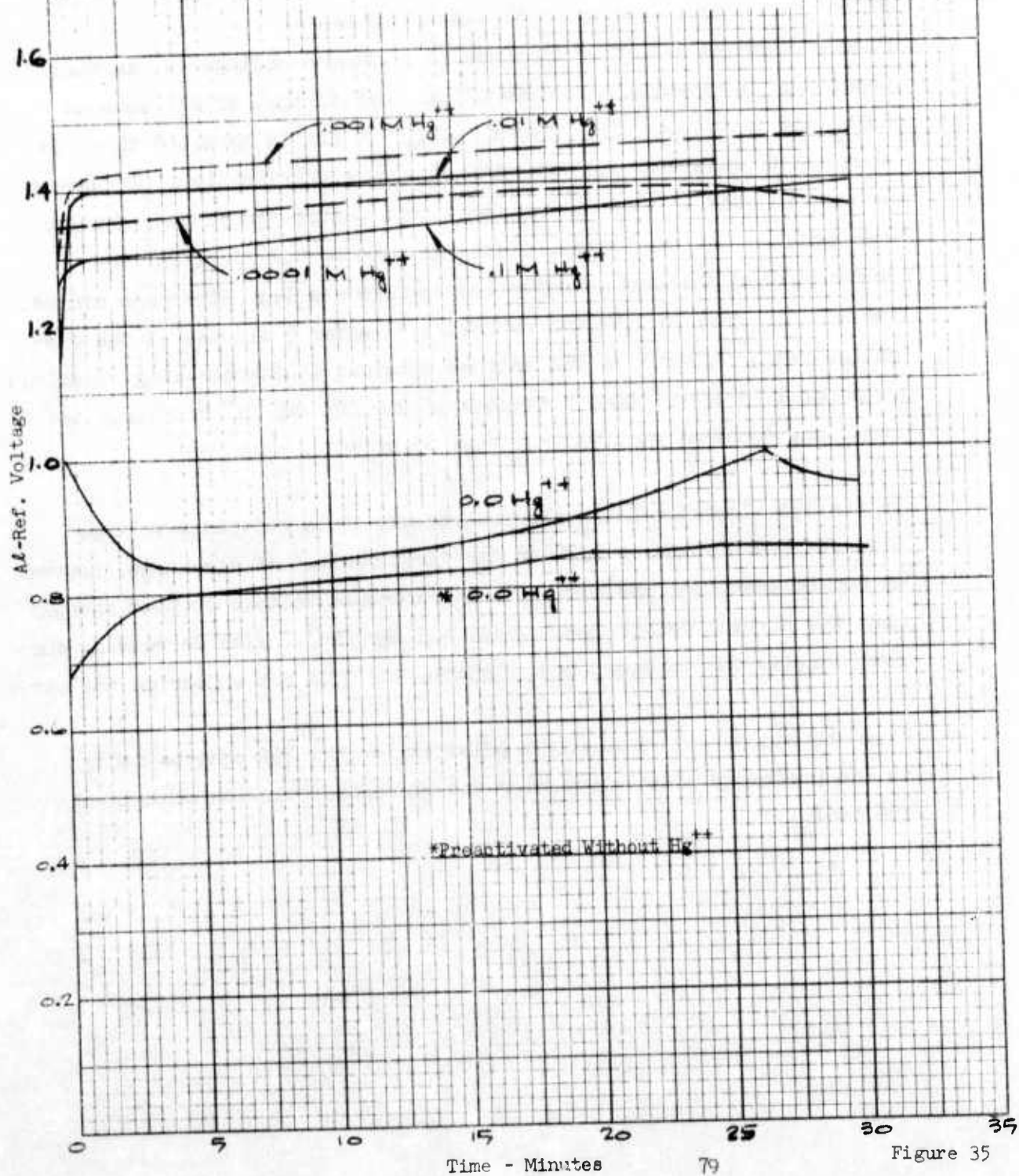


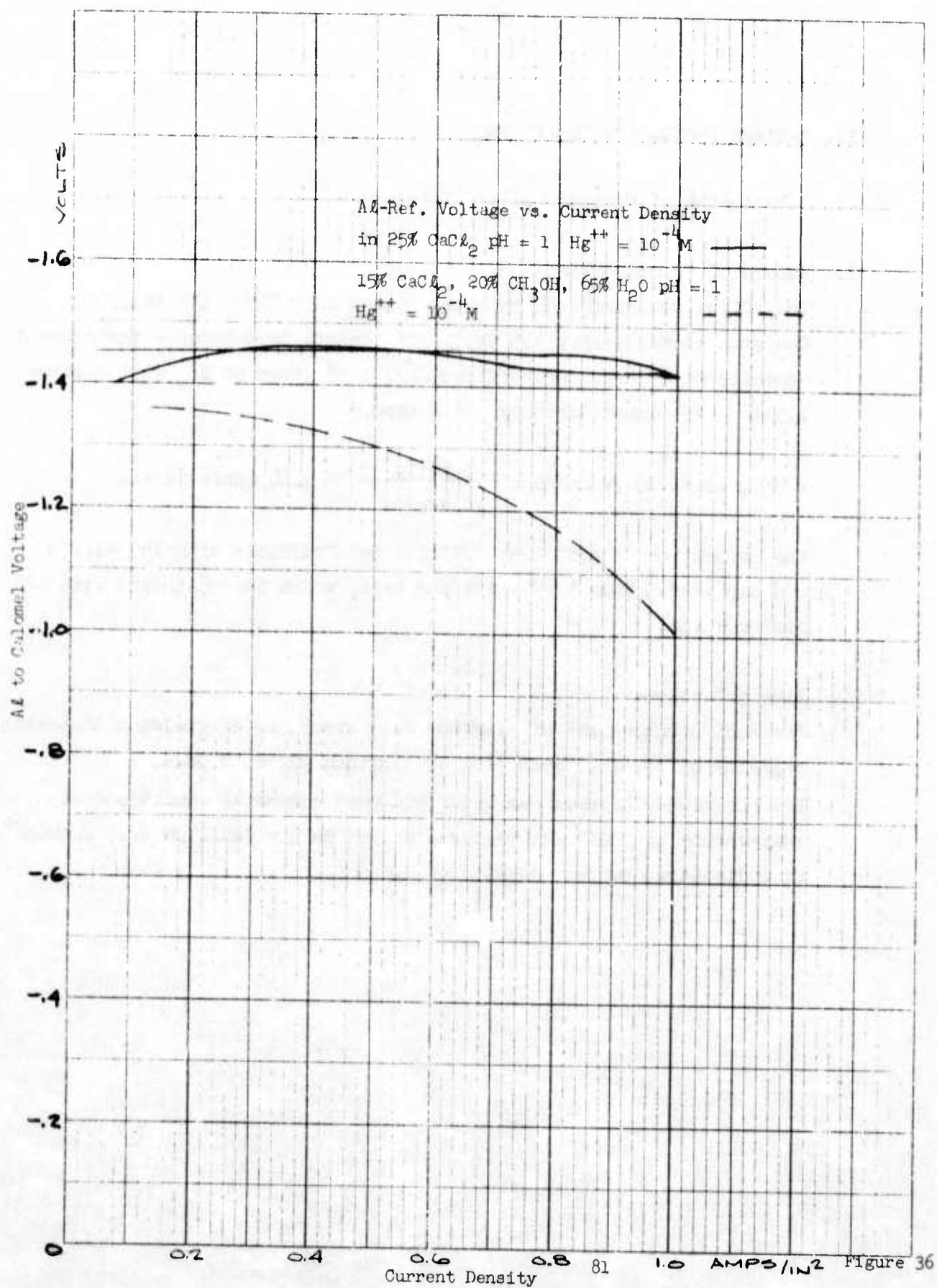
Figure 35

ii. Effect of Current Density on Aluminum Voltage

Figure 36 shows a plot of aluminum to reference voltage vs. current densities in ascending and descending order in 65cc of 25% aqueous CaCl_2 and in 65cc of 15% aqueous CaCl_2 . It should be noted that the aluminum to reference voltage did not vary significantly with current density nor did it vary during the time a particular current density was applied. At the initial discharge rate of 0.07 amps/in^2 the instantaneous aluminum to reference voltage was 1.3V after one minute. The voltage rose to 1.4V and reached 1.42 after 5 minutes at the discharge rate. After that the voltage remained steady reaching a maximum value of 1.45 after about 2 minutes of the $.13 \text{ amp/in}^2$ discharge and remaining constant at 1.45 from that point on.

In the 15% alcoholic CaCl_2 electrolyte the Al to reference voltage also reached a value of 1.36 at the first instant of discharge, however as can be seen from the curve the Al reference voltage dropped sharply when the current density went above 0.5 amps/in^2 . With decreasing current density the voltage was not stable and does not appear on the curve.

From the standpoint of aluminum polarization the 25% aqueous CaCl_2 is the preferred electrolyte over the alcoholic solution containing 15% CaCl_2 .



11. BATTERY DESIGN CONSIDERATIONS

A) Calculation of Minimum Battery Volume

i. Volume of Chlorine Tank

The effective density of chlorine (based on a 70% fill) is 1.09.

One gram atomic weight (35.5g) of Cl_2 reacts to deliver a theoretical capacity of 26.8AH. Proportionately, 1.98 grams of Cl_2 will deliver 1.5AH. (45 minute discharge at 2 amps.)

$$1.98 \text{ grams} / 1.09 \text{ grams/cc} \times \frac{15 \text{ cells}}{16.4 \text{ cc/in}^3} = 1.67 \text{ cubic inches}$$

The assumption is made that 28V will be attainable with 15 cells at a 2 amp load. Thus 1.87 volts per cell, which is consistent with past results.

ii. Aluminum Volume

The equivalent weight of aluminum is 9 grams, which yields a theoretical capacity of 26.8AH. Each gram of aluminum yields 2.98AH.

The efficiency of aluminum under the most corrosive conditions at a temperature of 160°F was measured as 45% in 30% CaCl_2 pH = 1, .01M Hg^{++} at a discharge current density of 0.5 amps/in².

The results presented in this report indicate that the efficiency of aluminum can be considerably improved by decreasing the mercury ion concentration in the electrolyte. The decreased Hg^{++} concentration does not adversely affect activation time nor aluminum voltage level.

For simplicity we will assume the worst case of Al efficiency as 50% and the best case as 100%.

At 50% efficiency a 45 minute 2 ampere (0.5 amps/in^2) discharge (1.5AH) will consume the equivalent of 3.0 AH of aluminum or 1 gram of aluminum. The density of aluminum is 2.7 grams/cc. The volume of 1 gram of aluminum is .370cc. For 15 cells $.370\text{cc} \times 15/16.4\text{cc/in}^3 = .338$ cubic inches.

At 100% efficiency half the aluminum weight and hence half the volume would be required. Thus at 100% efficiency total aluminum volume would be .169 cubic inches.

iii. Electrolyte

The electrolyte volume per cell was calculated previously as 8.5cc for 50% Al efficiency and 4.25cc for 100% Al efficiency. To convert to total volume for battery in cubic inches $8.5\text{cc} \times \frac{15}{16.4\text{cc/in}^3} = 7.80$ cubic inches for 50% Al efficiency and 3.90 cubic inches for 100% Al efficiency.

Thought has been given to contain the electrolyte within the cells rather than having a separate tank to store the electrolyte. With the storage tank, the volume necessary for the electrolyte would be double, since a volume allotment for the electrolyte in the cell and in the tank would have to be made. Another advantage to containing the electrolyte in the cell is that it could be heated by the heat paper used to warm the chlorine tank, which may allow a possibly higher freezing point electrolyte.

The containment of electrolyte within the cell during standby may be accomplished in numerous ways such as:

- 1) thin plastic bag in each cell containing sufficient electrolyte, at the time of activation the plastic bag is broken by the action of a pin;
- 2) A thin shatterable container around the aluminum electrode and the electrolyte contained within the cell exposed to the chlorine electrode. Thin gas lines go to the shatterable container of each cell from the chlorine tank at the time of activation. A valve sends chlorine gas into all the aluminum containers shattering them. Once shattered the valve closes and all chlorine gas is shunted into the chlorine electrodes;
- 3) A compressible battery assembly and a separate compartment for all the electrolyte. When a spring compressing the battery is released the electrolyte compartment is compressed by the expanding battery. The electrolyte then fills the newly created voids between the chlorine and aluminum electrodes. On the bottom of each cell there is a frangible opening which is shattered by the compressed electrolyte.

iv. Chlorine Electrode

The size of the chlorine electrode is 2.625" x .925" x .015". Two chlorine electrodes of adjacent cells will be placed back to back between a .010" space which will have an outer area dimension of 2.625" x .925" and an opening 2.5" x .800". The total thickness of electrodes and spacers will be .040". Each cell is associated with two chlorine electrodes surrounding an aluminum electrode. Hence, there will be a total of 15 bichlorine electrodes in the battery. The volume of each bichlorine electrode is .098 cubic inches or 1.47 cubic inches for the battery.

v. Total Volume 56 watt 42 WH Al-Cl₂ Battery

	100% Al efficiency cubic inches	50% Al efficiency cubic inches
Cl ₂ tank	1.67	1.67
Aluminum	.17	.34
Electrolyte	3.90	7.80
Cl ₂ electrode and spacer	<u>1.47</u>	<u>1.47</u>
	7.21 cubic inches	11.28 cubic inches

If the cell voltage can be raised to 2.0V, 14 cells will be necessary thus $14/15 (7.21) = 6.84$ cubic inches; $14/15 (11.28) = 10.50$ cubic inches for 100% and 50% Al efficiency respectively.

vi. Means of Decreasing Battery Volume

- a) Increasing Amount of Solvent per cc of Electrolyte: If the concentration of CaCl₂ were reduced to 15% the amount of water (or water-organic solvent mix) would rise from 70% to 85%. Further, the amount of water or other solvent necessary to form and dissolve CaCl₂.2 H₂O or CaCl₂.2 ROH would decrease. An aqueous 15% CaCl₂ solution has a freezing point range of 4.5 to 11°F. However, the addition of methanol, ethanol or some other low freezing point organic solvent which is miscible with water can lower the freezing point to the required value (-65°F). The solution containing 15% CaCl₂ + 65% H₂O + 20% methanol that was tested had a sufficiently low freezing point, (-60°F) and let us assume that CH₃OH and water react in the same way with AlCl₃ and CaCl₂ forming hydrates and alcoholates. One gram Al requires 6.2 grams of solvent (water-alcohol) to make and dissolve AlCl₃.6H₂O and AlCl₃.6ROH. 6.2 grams water-CH₃OH correspond to 85% of the electrolyte, hence $\frac{6.2}{.85} = 7.3$ grams of electrolyte necessary per gram aluminum consumed. 7.3 grams of electrolyte solution contain $(7.3) (.15) = 1.1$ grams CaCl₂ which requires .69 grams water-alcohol to make and dissolve CaCl₂.2 H₂O and CaCl₂.2 ROH. The specific gravity

of 15% CaCl_2 + 65% H_2O + 20% CH_3OH was measured as 1.08 grams/cc. The total weight of solvent is $6.2 + .7 = 6.9$ grams water-alcohol. The total weight of electrolyte is 6.9 grams $\text{H}_2\text{O}-\text{CH}_3\text{OH}$ + 1.1 grams $\text{CaCl}_2 = 8$ grams. $\frac{8 \text{ grams}}{1.08 \text{ gm/cc}} = 7.4\text{cc}$ of electrolyte per cell, per gram Al as compared to 8.5cc for the 25% CaCl_2 aqueous electrolyte. Thus a 1.1cc decrease per cell per gram Al results. In a battery operating at 0.5 amps/in² with an aluminum efficiency of 50% for 45 minutes using 15 cells the battery volume would decrease from 11.28 cubic inches to 10.25 cubic inches. For the same battery operation at 100% Al efficiency the volume would decrease from 7.21 to 6.70 cubic inches. For 14 cells at 50% and 100% Al efficiency the volumes would be 9.58 and 6.25 cubic inches respectively.

b) Decreasing Time of Operation

Consider another alternative using the existing aqueous electrolyte (effectively 25% CaCl_2) at 0.5 amps/in² for a shorter period of time. Based on the previous calculations it can be seen that the chlorine electrode volume will remain a constant, but the electrolyte, aluminum and chlorine tank will decrease proportionately. The number of cells will remain the same. The simplest way to perform the calculations is subtract the volume of the chlorine electrodes from the total volume and multiplying by the ratio $X/45$ minutes where x is the desired time of operation. This value then is added to the volume of the chlorine electrodes. Example: For 15 minutes of operation at an aluminum efficiency of 100%.

$$\begin{aligned} 7.21 \text{ cubic inches} &= \text{Battery volume for 45 min. } 0.5 \text{ amps/in}^2 \\ -1.47 \text{ cubic inches} &\text{ volume of chlorine electrodes} \\ \hline 5.74 \text{ cubic inches} & 5.74 \times \frac{15}{45} = 1.91 \text{ cubic inches} \end{aligned}$$

$$\begin{aligned} 1.91 \text{ cubic inches} \\ +1.47 \text{ cubic inches} \\ \hline 3.38 \text{ cubic inches} &\text{ battery volume necessary for 15 minutes} \\ &\text{at } 0.5 \text{ amps.} \end{aligned}$$

A plot of operation time and watt hours vs. the total battery volume is shown in Figure 37 for a battery discharged at 0.5 amps/in^2 (56 watts). Values are shown for both 100% Al utilization (efficiency) and 50% Al. The number of cells in the battery is set at 15.

A comparison of a 28 watt ($.25 \text{ amps/in}^2$) and a 56 watt ($.50 \text{ amps/in}^2$) battery volume vs. time and watt hours appears in Figure 38. The efficiency of aluminum is expected to be greater at the lower current density and a value of 75% is assumed for the 28 watt battery. The efficiency of 100% is assumed as the maximum value for the 28 watt battery as well. Due to the decreased current density of the 28 watt battery, the number of cells necessary is set at 13. The number of cells affects the volume of the Cl_2 electrodes, the Cl_2 tank, the aluminum and the electrolyte. The volume of all components per cell except the chlorine electrode are cut in half, with half the current density. It can be seen from the curve that a 28 watt battery occupying a volume of 6 cubic inches with an aluminum efficiency of 75% can deliver seventy minutes of operation. A 56 watt battery with a total volume of 6 cubic inches at an efficiency of 50% could run for about 21 minutes. At an aluminum efficiency of 100% the battery would have a life of 35 minutes. Based on recent experiments, the aluminum efficiency will be closer to 100% than 50% and the expected life of a 56 watt battery would be more than 30 minutes in 25% CaCl_2 aqueous electrolyte ($\text{pH} = 1$, $\text{Hg}^{++} = .0001\text{M}$).

C) Varying Current Density - Operating 45 Minutes

A plot was made of the volume a battery operating for 45 minutes vs. the current density for both 100% Al efficiency and varying Al efficiency. (The efficiency of aluminum is a function of current density. Thus at 0.1 amps/in^2 an efficiency of 90% is assumed. At .25, .375 and $.50 \text{ amps/in}^2$ the efficiency was assigned the values 75%, 60% and 50% respectively). The actual efficiency of the aluminum will be somewhere between the assigned values and 100%. It should be noted that because of varying current density

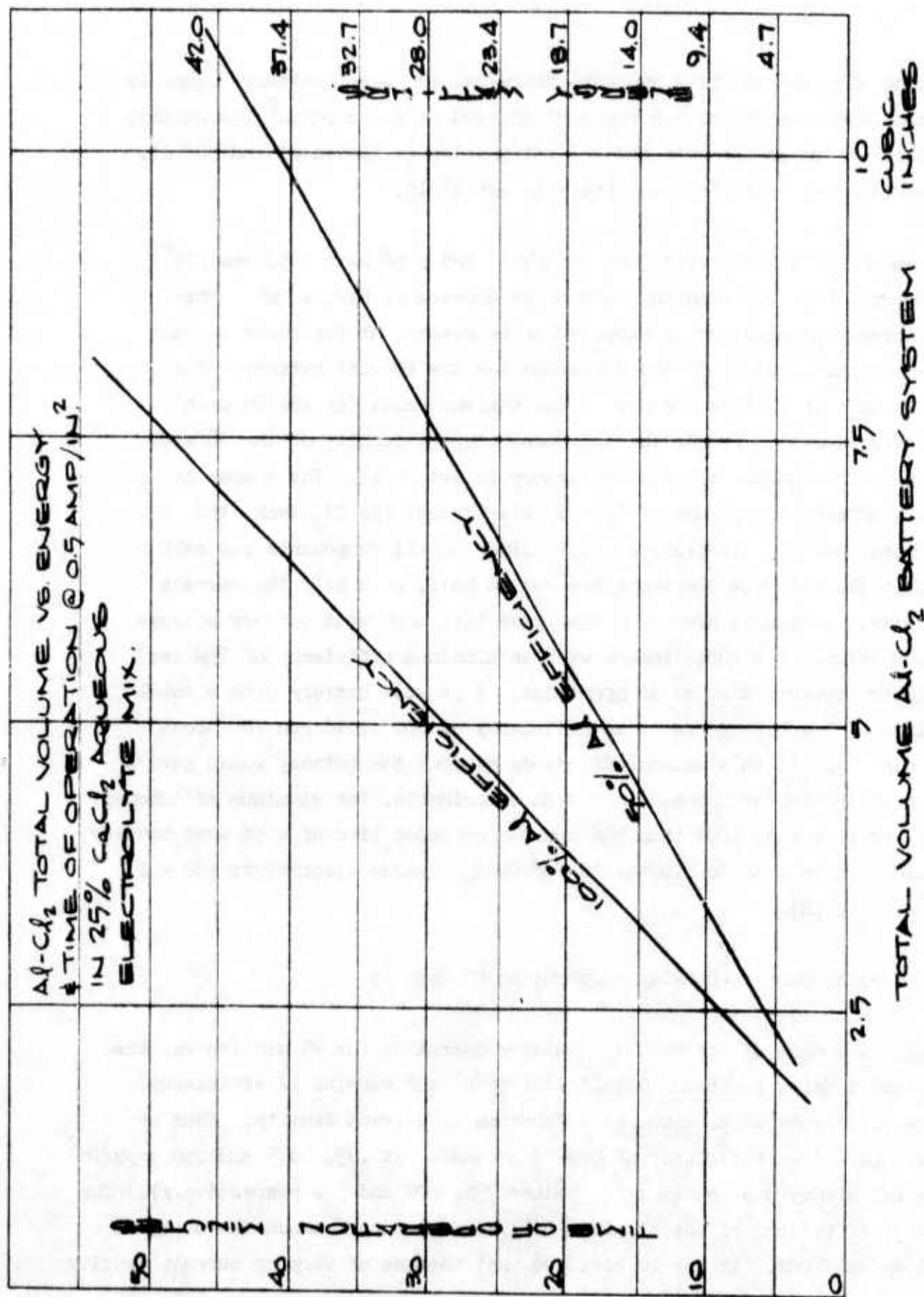


FIGURE-37

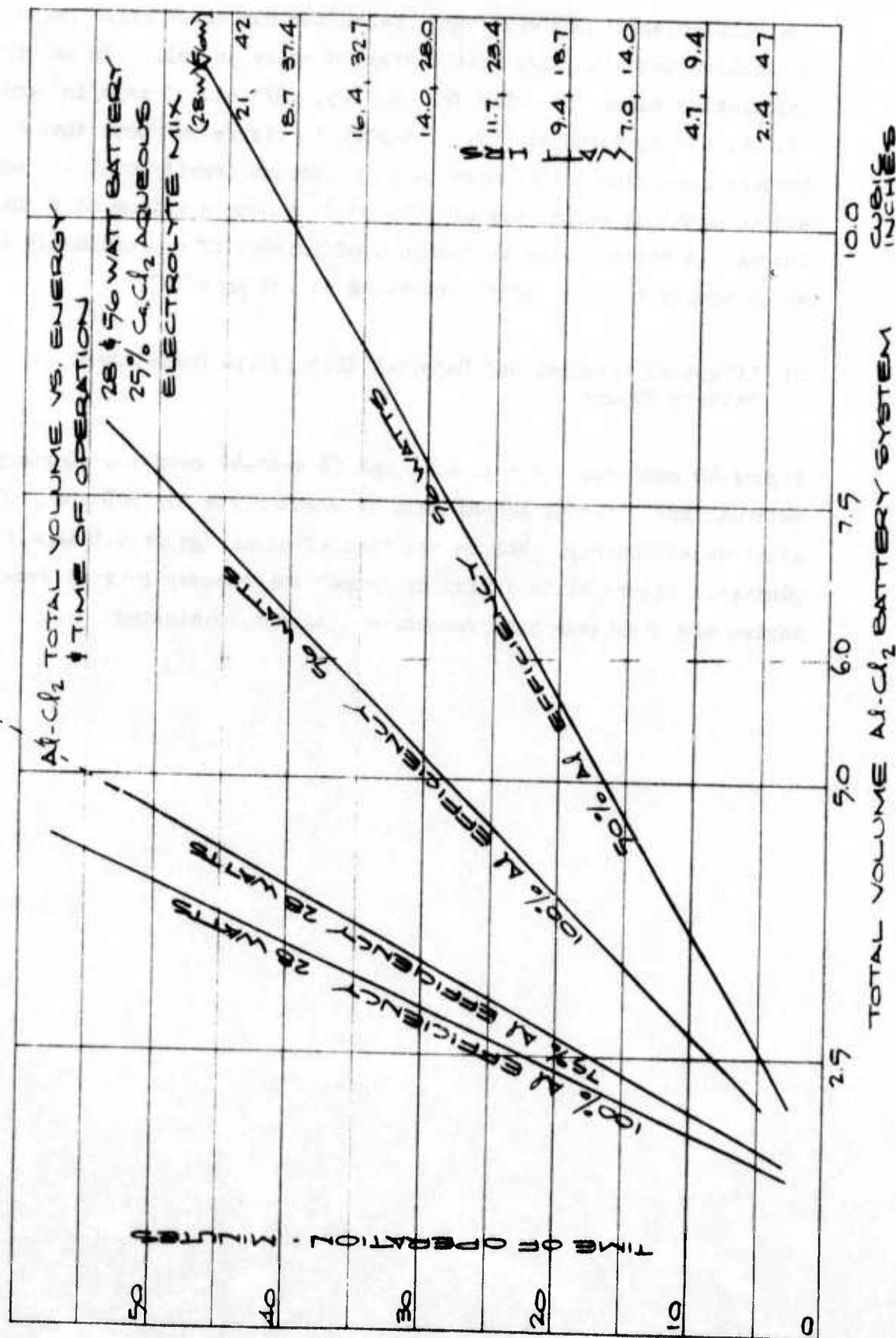


FIGURE-38

the cell polarization will vary, hence the number of cells necessary to achieve 28V will vary with current density as well. In making the calculation number of cells for .1, .25, .375 and .5 amps/in² are 12, 13, 14, and 15 respectively. The plot in Figure 39 shows that a battery operating for 45 minutes at a current density of 0.43 amps/in² and an aluminum efficiency of 100% would occupy a volume of 6 cubic inches. A battery with an aluminum efficiency of approximately 65% would occupy 6 cubic inches operating at .34 amps/in².

D) Effect of Internal and External Electrolyte Containment on Battery Volume

Figure 40 compares the volume of the 56 watt-42 watt hour battery with external and internal containment of electrolyte for 50% and 100% aluminum efficiency. Volume vs. time of discharge at 0.5 amps/in² is plotted. Figure 41 is a similar comparison however current density is varied and discharge time remains a constant 45 minutes.

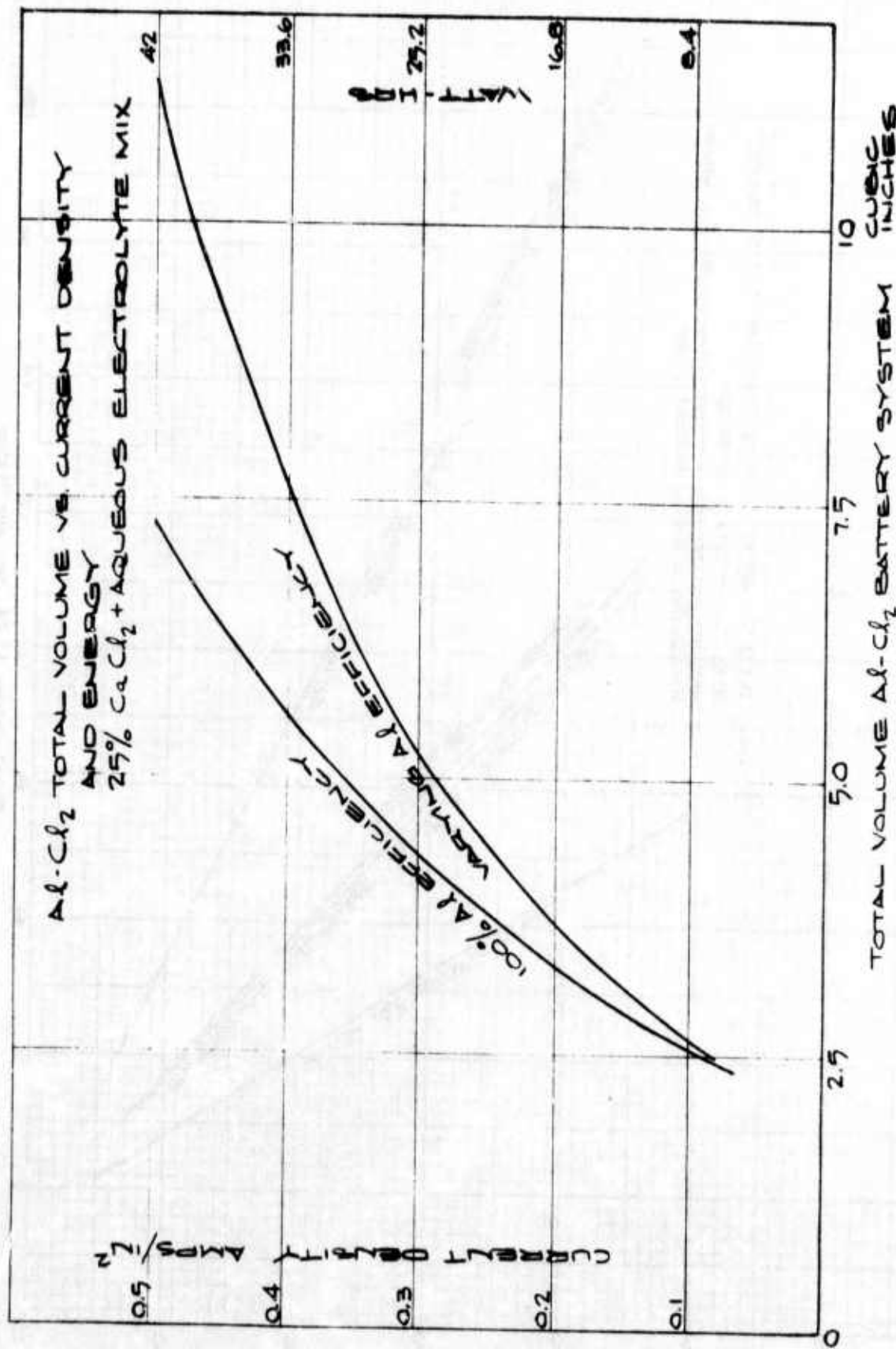


FIGURE 39

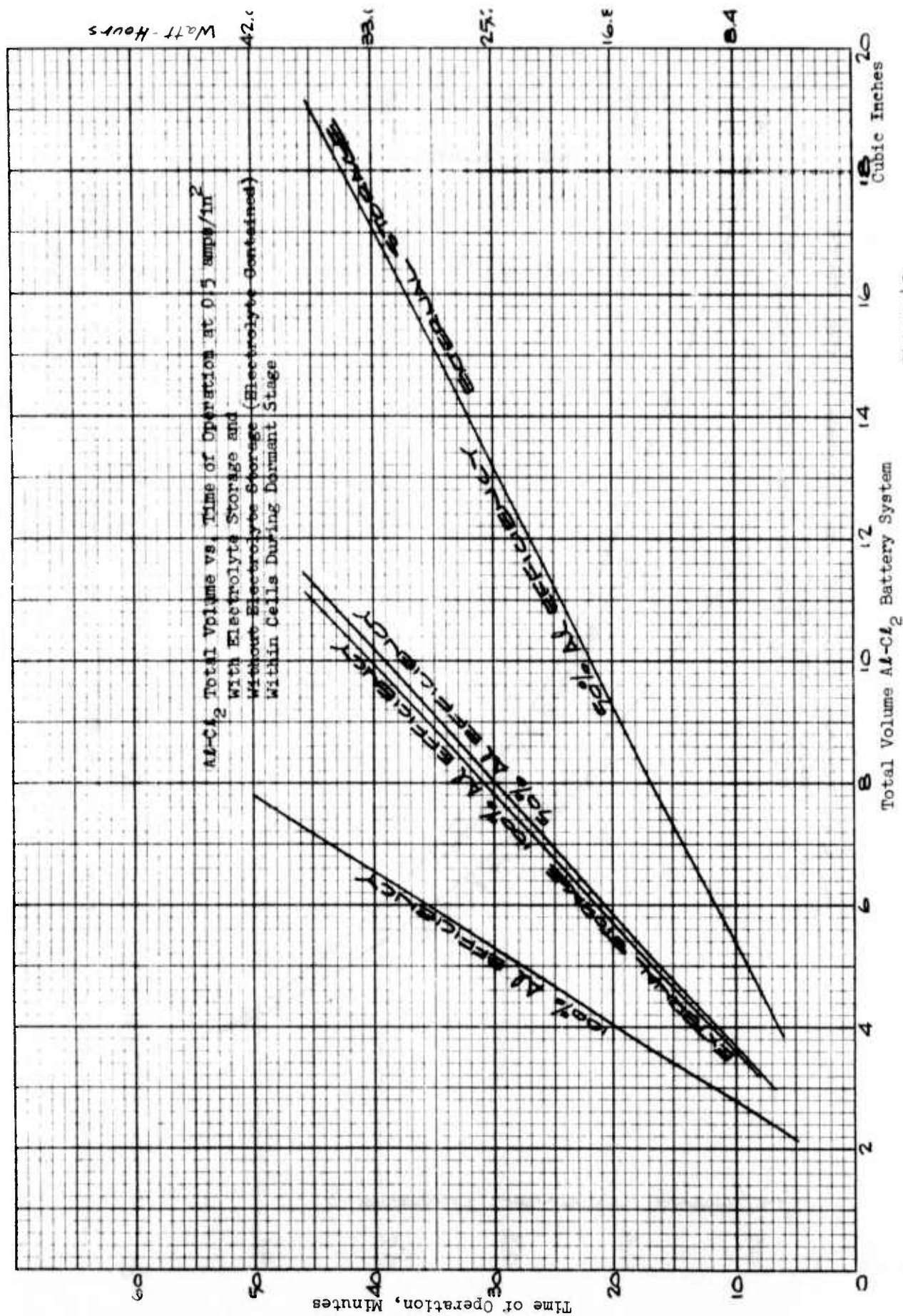


Figure 40

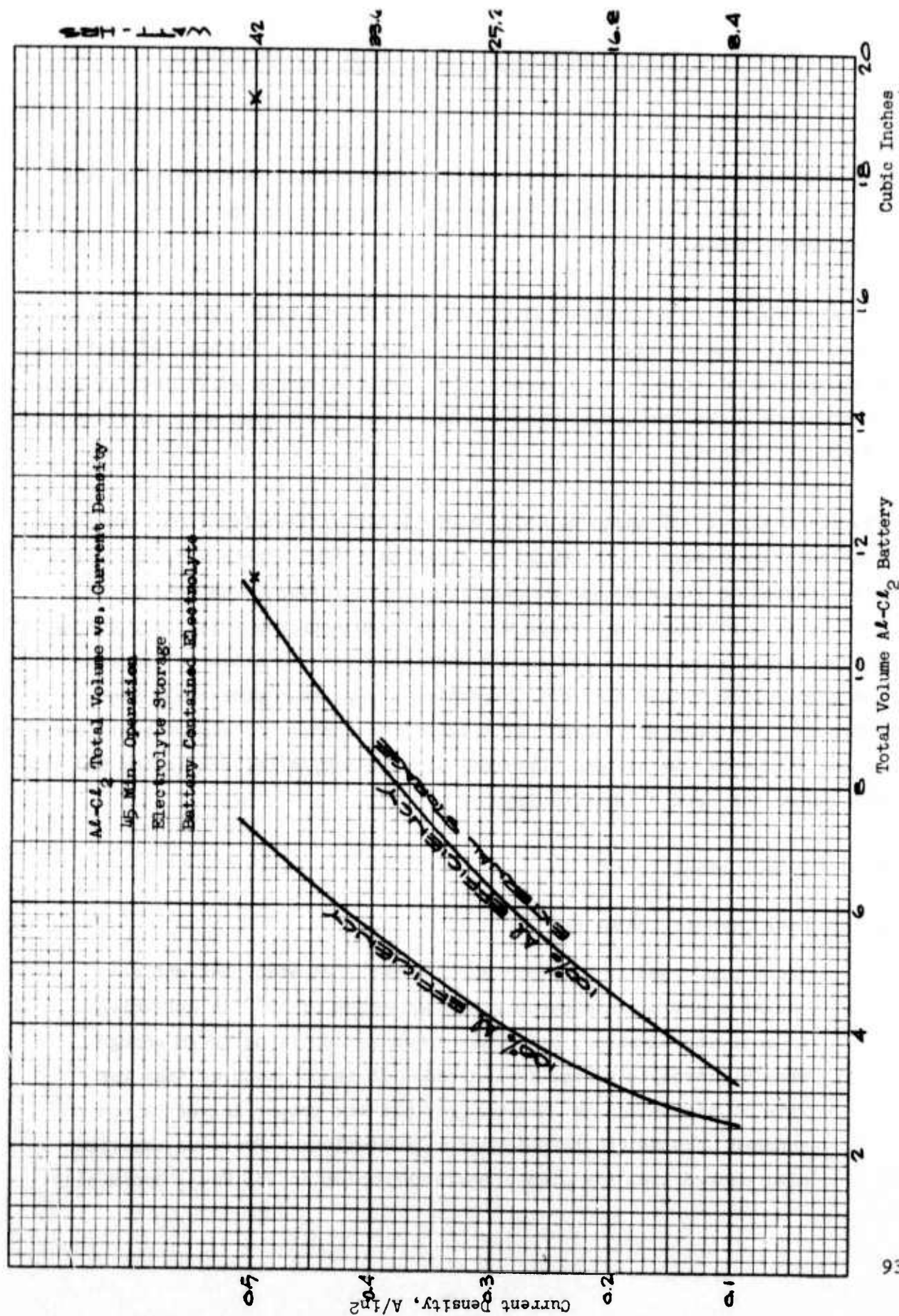


Figure 41

12. ADDITIONAL CaCl_2 ELECTROLYTE CHARACTERIZATION EXPERIMENTS

A) Objective

The purpose of this task is to define the electrolyte composition in such a way as to meet the cell performance requirements over the desired temperature range.

The electrolyte composition should be such that the open circuit corrosion rate of aluminum decreases to a rate of less than 30 microamps/in² within a short period of time (3 to 5 days). This would assure a sufficient amount of aluminum to be discharged when a cell is activated even after a stand in excess of 5 years.

Two electrolytes 25% aqueous CaCl_2 and 15% CaCl_2 alcoholic (20% methanol) meet the requirements with regard to freezing point. These were optimized with respect to their pH and mercury ion concentration. The goal is to produce an electrolyte mix which will give high aluminum efficiency during discharge and also have a low enough corrosion rate to allow for storage of the electrolyte within the cell compartment. As shown previously high efficiency and internal storage of electrolyte results in significant decreases in the volume of the system. Internal storage simplifies activation and also eliminates the need of manifolding.

B) Experimental

i. Open Circuit Corrosion

Tests performed in previous experiments indicated that while in excess electrolyte a mercury concentration of 10^{-4} is sufficient to activate aluminum, and that concentration is not high enough when electrolyte volume is limited. It is conjectured that the rate of activation is fast enough, but the proper degree is not reached because of stoichiometric limitations. Previous experiments also showed that the open circuit corrosion in 25% CaCl_2 containing

10^{-4} MHg⁺⁺ decreased to a level of 10 μ A. At that corrosion rate it would take over 10 years to consume 10% of the aluminum electrode. In another test the corrosion rates of preactivated aluminum in both the 15% CaCl₂ alcoholic and the 25% CaCl₂ aqueous electrolyte were studied at two higher levels of mercury concentrations 10^{-3} and 5×10^{-4} M.

Tests were performed using preactivated aluminum 1100 coupons cut to the size of the aluminum electrode to be used in the actual battery (1-1/8 x 2-13/16 x .025"). A weighed coupon was placed in 10cc of each of the four solutions and allowed to corrode. The coupons were removed, washed in water, dried and weight loss determined. They were then reimersed in their respective solutions. This was done twice at room temperature, and then the temperature at which the coupons were standing in electrolyte was increased to 160°F. At the elevated temperature the weight loss of the coupons was periodically checked using the same procedure as done at room temperature.

The weight loss data was used to calculate the corrosion rate expressed in years required to consume 10% of the weight of the aluminum coupon.

A refined method of studying the corrosion rates was introduced as a third generation experiment. Two preactivated aluminum coupons 1-1/8" x 2-13/16" x .025" were allowed to corrode in 15% CaCl₂ alcoholic and 25% CaCl₂ aqueous at a mercury concentration of 3×10^{-3} M. It was also shown that a 30% CaCl₂ solution yields better aluminum efficiency than the 15% CaCl₂ alcoholic or 25% CaCl₂ aqueous. On this basis two solutions of 30% CaCl₂ each containing 5×10^{-3} M mercury were prepared. One solution at an initial pH of unity, the other at a pH of 8. This time, however, the test was conducted in vacuum in the absence of any reacting gases with electrodes in an upright position and in 16cc of electrolyte.

Each cell in the 56W 28V battery will be completely sealed from the atmosphere and will either be filled with an inert gas or be in vacuum during its dormant stand. Data developed previously indicated that 3×10^{-3} M mercury was the lowest concentration which would activate aluminum in limited electrolyte volume. Therefore, this was the concentration tested in the measure of open circuit corrosion.

ii. Aluminum Efficiency and Cell Voltage as Affected by Mercury Concentration and Current Density.

The utilization of the aluminum anode and cell voltage was studied in limited electrolyte volume as a function of current density and mercury ion concentration.

Preactivated aluminum 1100 and standard chlorine electrodes were combined with 6cc of 25% CaCl_2 aqueous electrolyte pH = 1. The concentration of mercury ion in the electrolytes were steadily increased from test to test to determine the minimum concentration of mercury ions necessary to activate the aluminum electrode under these conditions. Mercury concentrations investigated were 10^{-3} , 2×10^{-3} , 3×10^{-3} , 5×10^{-3} and 10^{-2} M. All cells were discharged at 0.5 amps/in².

The effect of current density on cell voltage and aluminum efficiency were studied in 6cc of 25% aqueous CaCl_2 at mercury concentrations of 10^{-2} M. Discharges were run at current densities of 0.5 A/in², 0.375A/in², and .10A/in². These tests were run concurrently with the study of the effect of mercury concentration on cell characteristics.

Another set of discharges were performed using 6cc of the alcoholic 15% CaCl_2 electrolyte pH = 1. Preactivated aluminum and standard chlorine electrodes were used for these tests as well. The effect of current density on aluminum efficiency and cell voltage was determined in 6cc of this electrolyte at a mercury concentration of 10^{-2} M with current densities of 0.5 amps/in², 0.25 amps/in² and 0.1 amps/in².

The effect of mercury concentration on efficiency and the determination of the minimum concentration necessary to activate aluminum in 6cc electrolyte was determined. Mercury concentrations investigated were 3×10^{-3} and 5×10^{-3} , and from the experiment above 10^{-2} M. All discharges were performed at a current density of 0.5 amps/in².

In all tests the cell voltage was monitored continually during discharge. Aluminum was weighed before and after a particular discharge. From the aluminum weight loss and the discharge coulombs (current x time) the efficiency or utilization of aluminum was calculated. These tests were performed at room temperature.

Previous data had shown that efficiency of aluminum decreased with decreasing concentrations of CaCl_2 (whether the solvent was water or an aqueous-alcoholic mixture). Based on the phase diagram of CaCl_2 - H_2O system the aqueous electrolytes with a sufficiently low freezing point, range between 25% and 32% CaCl_2 concentration. Since 25% had been established in the above work as inferior to 30%, the lower end of the range of CaCl_2 concentration investigated in this new experiment was 28%. 35% CaCl_2 was also looked at as an electrolyte even though its freezing point is below that required. If 35% CaCl_2 proved feasible its freezing point could be considerably lowered by use of an aqueous-alcoholic solvent as was done before for 15% CaCl_2 .

The effect of pH and mercury concentration within the 28 to 35% CaCl_2 aqueous concentration range was also investigated. Al-Cl_2 cells were discharged at room temperature at 0.5 amps/in² in 6cc of various electrolytes each differing with respect to CaCl_2 concentration, mercury concentration and pH. Four levels of pH 1, 4, 8, 10; two levels of mercury concentration 5×10^{-3} and 3×10^{-3} M and four levels of CaCl_2 concentrations 28%, 30%, 32% and 35% were investigated. Table 7 lists the various electrolyte mixes in which discharges of Al-Cl_2 cells were performed.

Table 7

Composition of Electrolyte with Respect
to CaCl_2 , pH, Hg^{++} Concentrations

% CaCl_2	Hg^{++}	pH = 1	pH = 4	pH = 8	pH = 10
28	5×10^{-3}	x		x	
	3×10^{-3}		0		0
30	5×10^{-3}	x	x	x	x
	3×10^{-3}	x		x	
32	5×10^{-3}	x		x	
	3×10^{-3}		x		0
35	5×10^{-3}			x	
	3×10^{-3}				

x indicates compositions investigated

0 planned but not investigated

Cell performance in the various electrolytes was evaluated with respect to discharge life (to a 1 volt cut off) aluminum efficiency cell voltage and activation time. Data indicated that $3 \times 10^{-3} \text{M Hg}^{++}$ was not quite sufficient for full activation and did not result in extending the discharge life, even though efficiency was increased at that lower concentration. Because of this some of the planned tests at $3 \times 10^{-3} \text{M Hg}^{++}$ were not performed and instead electrolytes with a concentration of 10^{-2}M Hg^{++} were investigated. The following electrolyte mixes each containing 10^{-2}M Hg^{++} were investigated; 35% CaCl_2 pH = 8, 32% CaCl_2 pH = 8, pH = 1, 30% CaCl_2 pH = 1, 4 and 8.

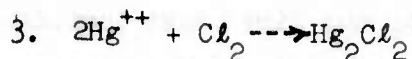
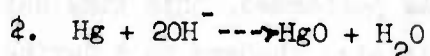
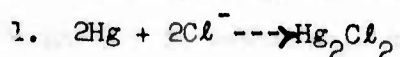
iii. Anode Activation Following Extended Exposure to Electrolyte.

The feasibility of internal storage of electrolyte depends on not only a low open circuit corrosion rate of aluminum, but also the capability of rapid aluminum activation once discharge is initiated. As a result of stand, either one or both of the following could occur: 1) an oxide layer is developed on the aluminum which renders it passive, 2) the electrolyte could lose its activating powers.

A test was conducted using the electrolyte and aluminum electrodes after they had completed the corrosion test as described in i. above. An aluminum chlorine cell was prepared with the aluminum electrode and electrolyte which had been on open circuit corrosion test for 120 hours and a chlorine electrolyte. The electrolyte used had an initial pH of 1 which had decreased to 4 during the open circuit corrosion test. The resulting $Al-Cl_2$ cell was discharged at 0.5 amps/in². Cell voltage was monitored. Another test was performed, this time using the electrolyte with an initial pH of 8 (this also changed to 4 during open circuit testing). Because the results of the first test indicated nonactivation of the aluminum (as will be further discussed in the experimental section) a fresh piece of preactivated aluminum was used along with the corroded electrolyte in construction and discharge of an aluminum chlorine cell. The purpose of this test was to see whether the electrolyte had maintained its activating powers or if the lack of activation shown in the previous test was a result of formation of a passivating oxide layer on the aluminum as a result of open circuit corrosion. As will be discussed later, the fresh aluminum failed to activate. With the discharge continuing, a few drops of concentrated $HgCl_2$ were added to the electrolyte. The voltage rise indicated aluminum activation. The discharge was interrupted and the corroded aluminum electrode was substituted for the fresh one. Discharge was continued. This latter test now compares the behavior of a fresh preactivated aluminum electrode with one that had undergone open circuit corrosion. The tests also indicated the effect of corrosion product in the electrolyte discharge on the life of a cell.

iv. Cell Characteristics in 2.5cc of Electrolyte

The effect of reducing electrolyte volume with respect to mercury ion concentration was evaluated. In the previous experiments the opposing dual effect of mercury ion concentration on cell capacity was discussed. To review, a relatively high concentration of mercury ion tends to decrease aluminum efficiency and hence decrease cell life, since a greater amount of aluminum and, hence, of electrolyte are consumed per ampere hour of capacity. The consumption of electrolyte (water) leads to a "drying out" of the cell and results in low cell capacity. On the other hand, at a concentration of $10^{-3}M$ the amount of mercury contained in 2.5cc is only 2.5 micromoles. Although this low concentration would result in an increase in aluminum efficiency, mercury is removed from solution by the formation of insoluble precipitates by the following reactions:



A voltage drop of 0.6V would occur when mercury on aluminum is consumed and there is insufficient mercury left in solution to sustain activation (a voltage drop less than 0.6V could be encountered due to partial activation at very low amounts of mercury ion).

From a screening of electrolyte varying in pH, $CaCl_2$ concentration and mercury ion concentration performed previously it was found that 35% $CaCl_2$ containing $10^{-2}M Hg^{++}$ seemed most promising. Its freezing and melting points were therefore determined and 2.5cc of this electrolyte was used in an aluminum chlorine cell discharged at 0.5 amps/in². Because the freezing point of this electrode was -28°F, a 35% $CaCl_2$ + 90% H_2O + 10% CH_3OH , $10^{-2}M Hg^{++}$ solution was prepared and 2.5cc used to discharge an aluminum chlorine cell at 0.5 amperes.

30% CaCl_2 had yielded good results with respect to cell life when evaluated in 6cc previously. Aluminum-Chlorine cells were prepared with standard chlorine electrodes and standard preactivated aluminum electrodes. These cells were discharged in 2.5cc of four different 30% CaCl_2 electrolytes. Composition with respect to pH and mercury ions was (1) pH = 8; $5 \times 10^{-2} \text{Hg}^{++}$, (2) pH = 1; 10^{-1}Hg^{++} , (3) pH = 1; 10^{-2}Hg^{++} and (4) pH = 1; $5 \times 10^{-3} \text{Hg}^{++}$.

C. DATA

1. Open Circuit Corrosion

Table 8 lists the weight loss of the two aluminum electrodes each contained in 10cc of 15% CaCl_2 alcoholic electrolyte. One electrolyte with 10^{-3}MHg^{++} , the other $5 \times 10^{-4} \text{MHg}^{++}$. For the first 93 hours corrosion was allowed to take place at room temperature. From the 93 hours to 190.5 hours the corrosion took place at a temperature of 160°F . Corrosion is compared on the basis of time required to consume 10% of the weight of the aluminum coupon which is taken to have a nominal weight of 3.0 grams. In some instances the coupon gained weight during a particular time interval and where this occurred time to corrode 10% was not calculated.

The data indicates that storage in both 5×10^{-4} and 10^{-3} concentration at 160°F in the 15% CaCl_2 alcoholic electrolyte results in a corrosion rate which would consume 10% of the aluminum in less than 0.2 years. At room temperature 10% of the aluminum would be consumed in 0.3 years, .2 years in 10^{-3} and 5×10^{-4} respectively. In both cases solutions turned cloudy and pH increased to 6.

Table 8

Open Circuit Corrosion in 15% CaCl_2 Alcoholic Electrolyte

Room Temperature

Time in Electro-lyte hrs	Weight Al grams		Δt	Δw mg		Years to 10% Weight Loss	
	10^{-3}MHg^{++}	$5 \times 10^{-4} \text{MHg}^{++}$		10^{-3}Hg^+	$5 \times 10^{-4} \text{Hg}^{++}$	10^{-3}MHg	$5 \times 10^{-4} \text{MHg}^{++}$
0	2.7054	2.3765	0				
24.5	2.7030	2.3718	24.5	-2.4	-4.7	0.37	0.17
93	2.7049	2.3797	68.5	-	-		
160°F							
115.75	2.6999	2.3720	22.75	-5.0	-7.7	.15	.10
139.0	2.6803	2.3571	23.25	-19.6	-14.9	.04	.05
163.5	2.7001	2.3825	24.5	-	-		
190.5	2.6829	2.3768	27	-	-		

Table 9

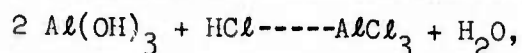
Open Circuit Corrosion in 25% CaCl_2 Aqueous Electrolyte

Time in Electro-lyte hrs	Weight Al grams		Δt hrs	Δw mg		Years to 10% Weight Loss	
	10^{-3}MHg^{++}	$5 \times 10^{-4} \text{MHg}^{++}$		10^{-3}Hg^+	$5 \times 10^{-4} \text{Hg}^{++}$	10^{-3}MHg	$5 \times 10^{-4} \text{MHg}^{++}$
0	2.5408	2.2697	0				
24.5	2.5200	2.2736	24.5	-20.8	+3.9	.04	
93.5	2.4885	2.2731	68.5	-31.5	-..5	.07	4.7
160°F							
115.75	2.3974	2.2668	22.75	-91.1	-6.3	.01	.123
139	2.3016	2.2663	23.25	-95.8	- .5	.01	1.7
163.5	2.2256	2.2600	24.5	-76.0	-6.3	.01	.13
190.5	2.1790	2.2556	27	-46.6	-4.4	.02	.21

Table 9 shows open circuit data obtained in 10cc of 25% CaCl_2 aqueous solution at the two levels of mercury concentration: 10^{-3}M and $5 \times 10^{-4}\text{M}$. Except for the first interval in the $5 \times 10^{-4}\text{MHg}^{++}$ electrolyte, weight losses were noted at all times when aluminum coupons were weighed. At the 10^{-3}M mercury level corrosion rate was exceedingly high and no significant slowing down occurred either at room or elevated temperatures. The time required to consume 10% of the aluminum at room temperatures reached .07 years; at 160°F it was .02 years. At the lower mercury concentration it would require 4.7 years to consume 300 mg of aluminum while at the elevated temperature the time required ranged from .12 years to 1.7 years. At the completion of the tests the pH of both solutions were measured as 6. The 10^{-3}M mercury solution was cloudy, the other was clear. The results may be understood as buffer reactions. The aluminum corrodes:



but the hydroxide reacts with the acid present,



changing the pH to a less acid value. When the acid is consumed there is an excess of Al(OH)_3 which yields the cloudy appearance. Hence, the greater the corrosion rate, the more cloudy the appearance.

Corrosion tests under vacuum were performed with an even higher mercury concentration. In both the 15% CaCl_2 alcoholic and the 25% CaCl_2 aqueous the corrosion of aluminum was studied at $3 \times 10^{-3}\text{M}$ mercury.

Table 10 shows the corrosion data again presented as time to consume 300 Mg or 10% of the aluminum electrode for 15% alcoholic solution.

Table 10

Corrosion in 15% CaCl_2 Alcoholic pH = 1, 3×10^{-3} MHg Under Vacuum

Time hrs.	Weight grams	Δt	Δw mgs	$\Delta w / \Delta t$	Time in Years to Consume 10%
0	2.9048		0		
16	2.7218	16	183.0	11.4mg/hr	.003
40	2.7046	24	17.2	.72mg/hr	.05
64	2.6901	24	4.5	.19mg/hr	.18
88	2.6841	24	6.0	.25mg/hr	.14

The corrosion rate decreases rapidly by almost two orders of magnitude but the maximum time to corrode 10% is less than 0.2 years.

Table 11 shows corrosion rate in 25% CaCl_2 aqueous pH = 1 Hg = 3×10^{-3} M.

Table 11

Time	Weight Al	Δt	Δw mg	$\Delta w / t$	Time to consume 10%
0	2.9652g				
16	2.8645	26	100.7	6.3 mg/hr	.005 years
40	2.8589	24	5.6	.23	.15 years
64	2.85566	24	2.3	.10	.34 years
88	2.8559	24	.7	.03	1.14 years

Again the corrosion rate decreases rapidly with time; more than two orders of magnitude. During the interval from the 64 hours until the 88th hour the corrosion rate was such that it would require 1.14 years to consum 300 mg of aluminum (10%). At that corrosion rate internal storage would be possible. This concentration of mercury is sufficient to activate aluminum in limited electrolyte.

Table 12 lists the weight loss of the aluminum electrodes contained under vacuum in 15cc of 30% CaCl_2 , $5 \times 10^{-3} \text{M Hg}^{++}$ pH = 1 electrolyte. As can be seen from the data the corrosion rate decreases by almost 2 orders of magnitude from the first day to the third day and more than 25 fold from the third day to the fifth day. The corrosion rate on the fifth day is such that 4.25 years would pass before another 300 mg corroded. Thus after that time period the aluminum electrode would weigh 2.3 grams which is more than sufficient for a 45 minute discharge at 2 amperes, which at an efficiency of 50% would consume 1 gram of aluminum.

Table 13 shows similar data for a 30% CaCl_2 + $5 \times 10^{-3} \text{M}$ mercury electrolyte mix at pH = 1. The corrosion rate decreases by 1 order of magnitude from the first to the third day, but shows an increase for the second to the third day. On the fourth day the corrosion rate is such that it would require almost 7 years to corrode an additional 10% of the aluminum electrode. However, during the fifth day the corrosion has apparently increased so that only 1.3 years would be required. Since we are dealing in tenths of milligram weight change an error due to aluminum loss in washing and drying could have occurred. The pH of the solution at the end of the experiment was 4 and was cloudy. The electrode was more pitted than the one allowed to corrode in the original pH = 8 solution.

Table 12

Open Circuit Corrosion in 30% $\text{CaCl}_2 + 5 \times 10^{-3} \text{Mg}^{++}$ pH = 8

Time in Electrolyte Hrs.	Al Weight Grams	Al Weight Loss Δ Grams	Time Interval Δ Hrs.	Corrosion Rate mg/hr	Time In Years To Consume 300 mg
0	2.9588				
18	2.6605	.2983	18	16.6	.002
44.67	2.6530	.0075	26.67	0.28	.12
72.5	2.6473	.0057	27.8	0.21	.16
93	2.6471	.0002	20.5	0.01	3.4
118	2.6468	.0002	25.0	0.008	4.25

Table 13

Open Circuit Corrosion in 30% $\text{CaCl}_2 + 5 \times 10^{-3} \text{Mg}^{++}$ pH = 1

0	3.0761				
18	2.7610	.3151	18	17.5	.002
44.67	2.7456	.0154	26.67	0.58	.058
72.5	2.6935	.0521	27.8	1.87	.018
93	2.6934	.0001	20.5	.0049	6.9
120	2.6927	.0007	27.0	.025	1.3

ii. Aluminum Efficiency and Cell Voltage as Affected by Mercury Concentration and Current Density

Figure 42 & 43 show voltage vs. time plots of $Al-Cl_2$ cells discharged in 6cc of 25% $CaCl_2$ electrolyte with various concentrations of mercuric ion ranging from $10^{-3}M$ to $10^{-2}M$. The voltage curves obtained in 5×10^{-3} and $10^{-2}M$ mercuric ion containing electrolyte are shown in Figure 42. Cell voltage reached 1.8V within 12 minutes of discharge in both cases. Figure 43 shows voltage curves obtained in electrolyte with mercury concentrations of 10^{-3} , 2×10^{-3} and 3×10^{-3} . The cell voltage level at these concentrations is lower than those shown in Figure 42. The different voltage levels are primarily a function of the degree of aluminum activation. The plateau voltage obtained in 6cc of the $10^{-3}MHg^{++}$ electrolyte is 1.1 which is 0.7V lower than the value attained in 10^{-2} and 5×10^{-3} mercury containing electrolyte. In 6cc of electrolyte containing 2×10^{-3} mercury ion voltage level is at 1.35, while at $3 \times 10^{-3}M$ mercury voltage level reaches 1.6V.

Table 14 lists the aluminum efficiency at each mercury ion concentration.

Table 14

Discharge Current Density	Mercuric Ion Concentration	Aluminum Efficiency
0.5 amps/in ²	10^{-3}	64%
0.5	$2 \times 10^{-3} M$	57%
0.5	3×10^{-3}	49%
0.5	5×10^{-3}	45%
0.5	1×10^{-2}	39%

Al-Cl₂ CELL VOLTAGE vs TIME
 Time Discharged @ 0.5 amps/in²
 in 6cc of 25% CaCl₂ pH = 1,
 various Hg⁺⁺ Concentrations

--- Hg⁺⁺ = 10⁻²M
 — Hg⁺⁺ = 5 x 10⁻³M

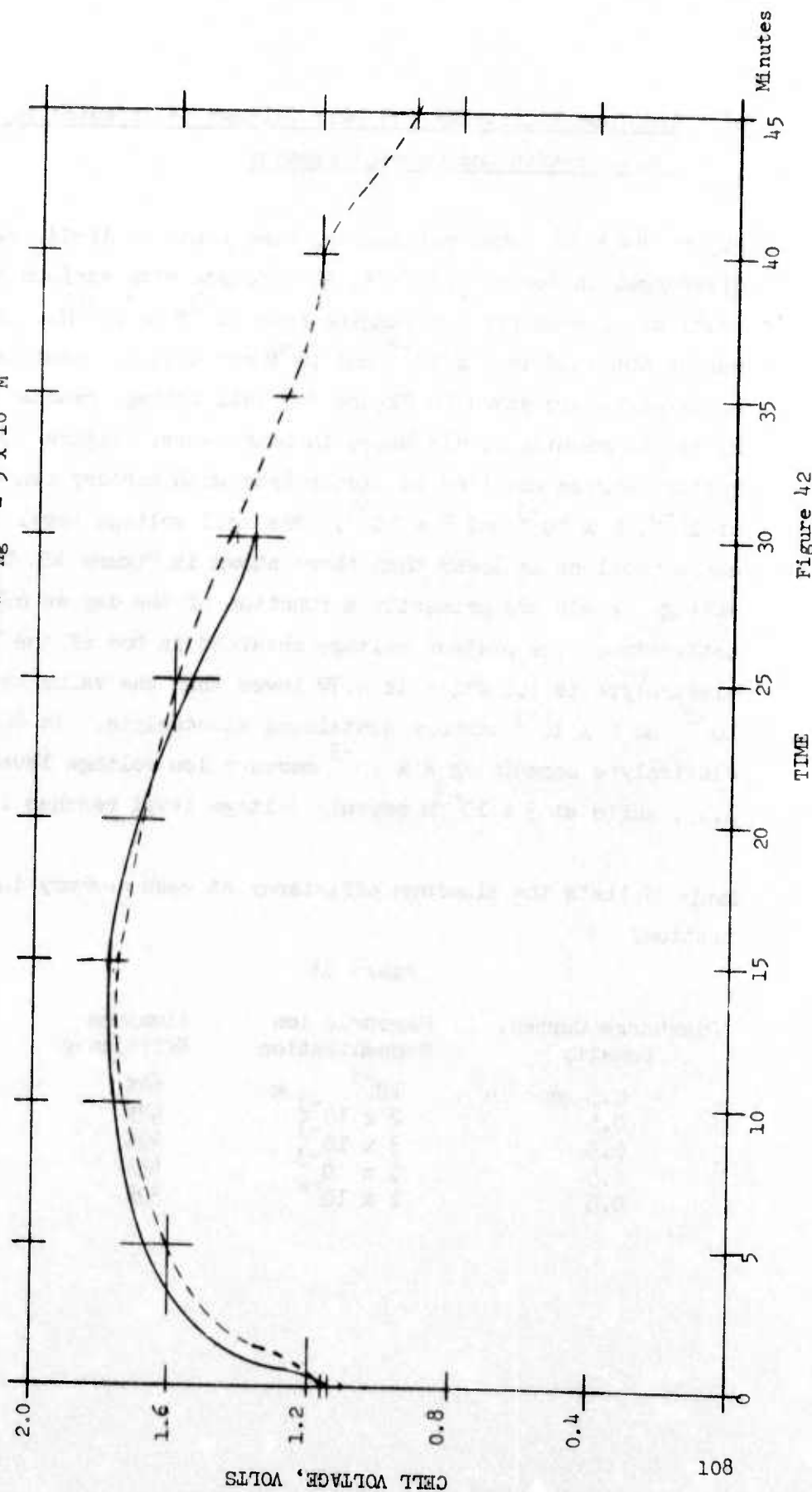


Figure 42

Al - Cl_2 CELL VOLTAGE vs TIME

6cc, pH-1, 25% CaCl_2 @ 0.5 amps/in²

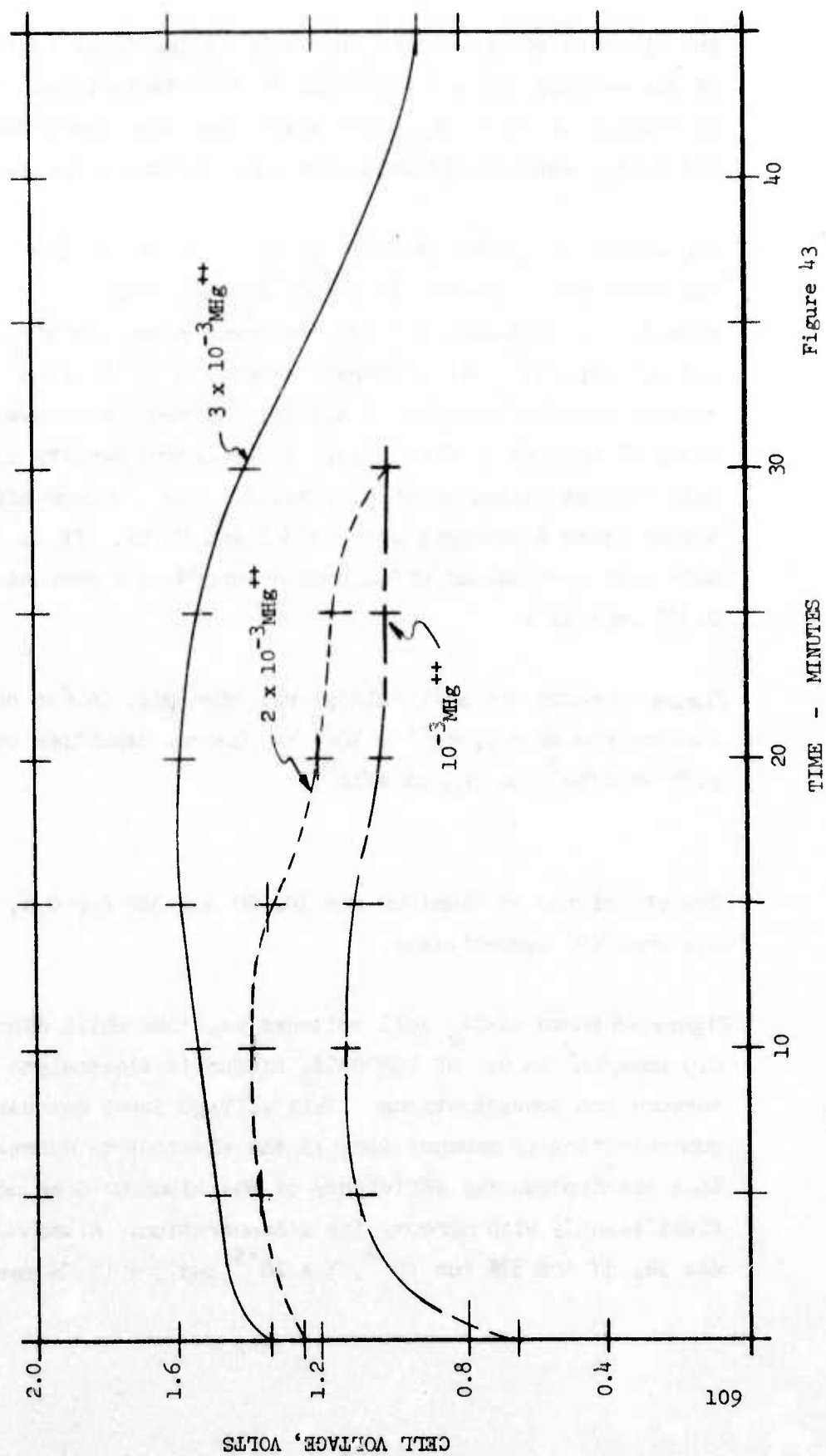


Figure 43

The aluminum efficiency is inversely proportional to the logarithm of the mercury ion concentration in the electrolyte. Further, the efficiency in 25% CaCl_2 aqueous is lower than previously found for 30% CaCl_2 when comparing at the same concentration level of mercury.

The effect of current density on cell voltage is shown in Figure 44. The electrolyte was 6cc of 25% CaCl_2 $\text{pH} = 1$ $\text{Hg}^{++} = 10^{-2}$. Cell voltage vs. time was plotted at current densities of 0.1, 0.375 and 0.5 amps/in². At a current density of 0.375 A/in² the cell voltage reached 1.6 after 6 minutes and remained above test value until 45 minutes of discharge. At a current density of 0.1 amps/in² cell voltage plateaued at 2.25 volts. The aluminum efficiencies obtained during these discharges were 39, 42 and 20.5%. It is interesting to note that the maximum efficiency occurred at a current density of 0.375 amps/in².

Figure 45 shows the cell voltage vs. time plot in 6cc of 15% alcoholic electrolyte $\text{pH} = 1$, $\text{Hg}^{++} = 10^{-2}$ at current densities of 0.1 amps/in², 0.25 amps/in² and 0.5 amps/in².

The efficiency of aluminum was 10, 20 and 32% for 0.1, 0.25 and 0.5 amps/in² respectively.

Figure 46 shows Al- Cl_2 cell voltages vs. time while discharged at 0.5 amps/in² in 6cc of 15% CaCl_2 alcoholic electrolyte at various mercury ion concentrations. Cell voltage level decreases as the concentration of mercury ions in the electrolyte decreases. In this electrolyte the efficiency of the aluminum does not vary significantly with mercury ion concentration. Aluminum efficiency was 32, 37 and 37% for 10^{-2} , 5×10^{-3} and 3×10^{-3} M mercury.

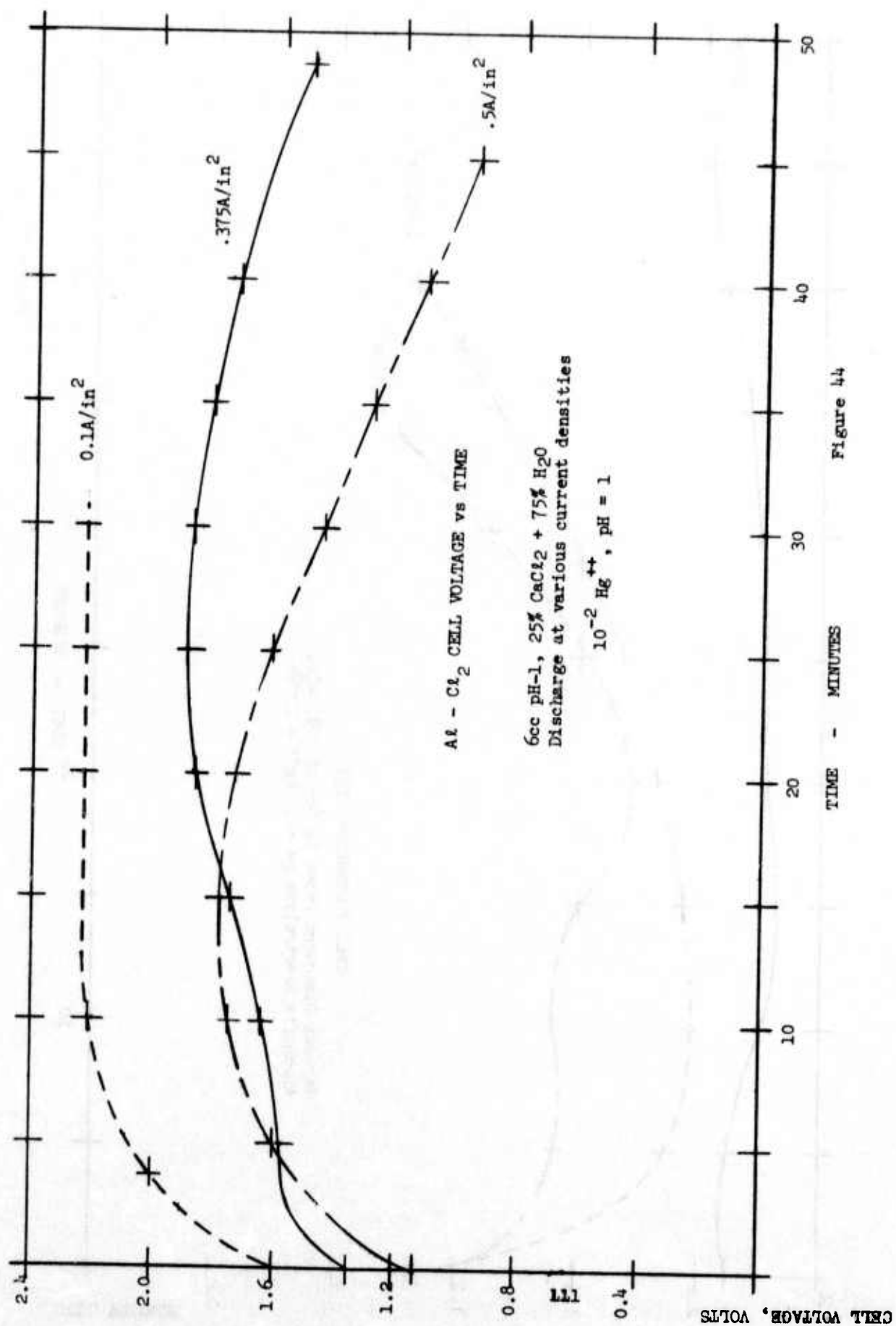


Figure 44

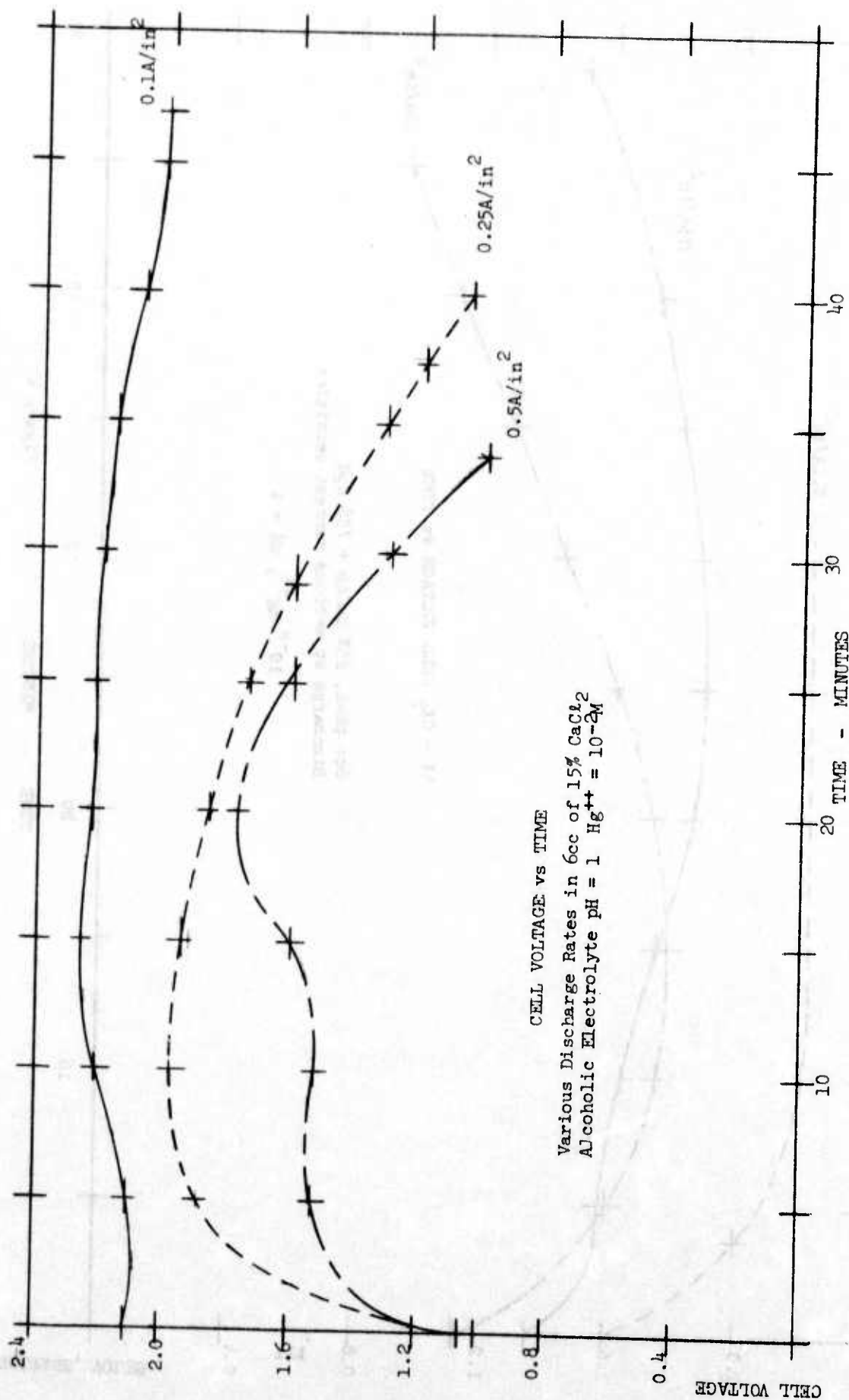


Figure 45

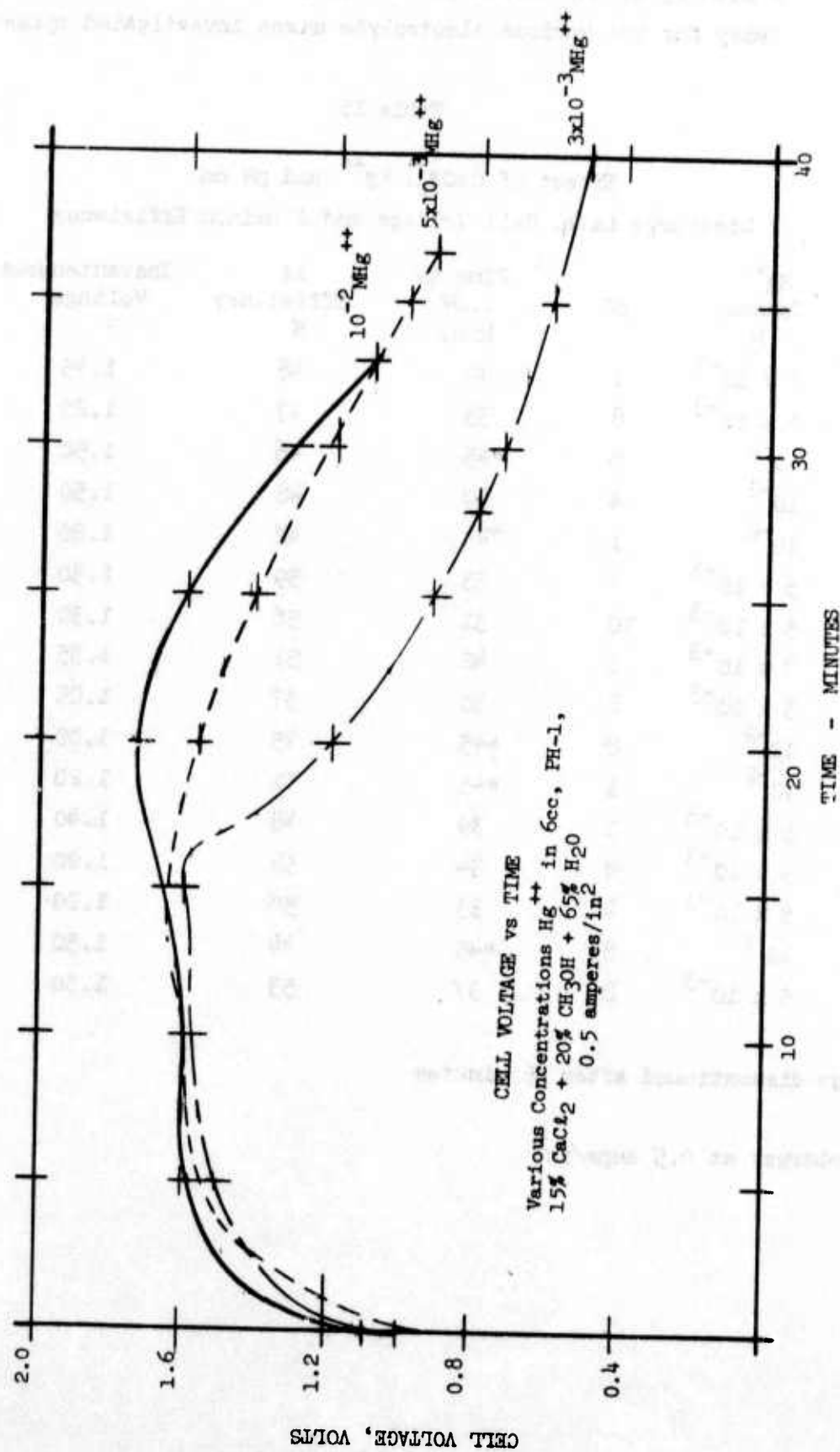


Figure 46

CELL VOLTAGE, VOLTS

A summary of the discharge voltages, time to 1.0V and aluminum efficiency for the various electrolyte mixes investigated appear in Table 15.

Table 15

Effect of CaCl_2 , Hg^{++} and pH on
Discharge Life, Cell Voltage and Aluminum Efficiency

CaCl_2 Concn. %	Hg^{++} Concn. M	pH	Time to 1.0V Min.	Al Efficiency %	Instantaneous Voltage V	Maximum Voltage V
28	5×10^{-3}	1	40	48	1.45	1.70
28	5×10^{-3}	8	33	47	1.25	1.60
30	10^{-2}	8	*45	46	1.50	1.70
30	10^{-2}	4	40	48	1.50	1.75
30	10^{-2}	1	*45	42	1.20	1.78
30	5×10^{-3}	4	33	59	1.30	1.80
30	5×10^{-3}	10	31	56	1.30	1.78
30	3×10^{-3}	1	42	51	1.35	1.65
30	3×10^{-3}	8	30	57	1.25	1.65
32	10^{-2}	8	*45	45	1.00	1.70
32	10^{-2}	1	*45	51	1.20	1.70
32	5×10^{-3}	1	39	48	1.40	1.55
32	5×10^{-3}	8	34	58	1.20	1.60
32	5×10^{-3}	4	33	56	1.10	1.55
35	10^{-2}	8	*45	44	1.50	1.75
35	5×10^{-3}	8	37	53	1.50	1.68

*Discharge discontinued after 45 minutes

All discharges at 0.5 amps/in²

The data shows that for a longer life at a high voltage level a mercury concentration of 10^{-2} M is necessary. It was previously shown that efficiency of the aluminum decreases with the log of the mercury concentration. The lower discharge life with the lower concentration of mercury is the result of the consumption of mercury ions as insoluble HgO or Hg_2Cl_2 during the discharge. At low mercury concentration 10^{-3} for instance, the amount of mercury contained in 6cc of electrolyte is 6 micro moles, at 10^{-2} this is raised to 60 micromoles. A voltage drop of 0.6V would occur when the mercury on the aluminum is consumed and there is not enough mercury left in solution to sustain activation. Mercury ion and mercury can be consumed, forcing insoluble precipitates, (hence removing these activating powers,) by the following reactions:

- 1) $2\text{Hg} + 2\text{Cl}^- \rightarrow \text{Hg}_2\text{Cl}_2$
- 2) $\text{Hg} + 2\text{OH}^- \rightarrow \text{HgO} + \text{H}_2\text{O}$
- 3) $2\text{Hg}^{++} + \text{Cl}_2 \rightarrow \text{Hg}_2\text{Cl}_2$

The second reaction is favored in basic media, the third and the first in acid. At a high mercury concentration the consumption of aluminum per ampere hour increases leading to an increased water consumption per ampere hour which has the net result of decreasing cell discharge life. Increasing the amount of mercury in the cell has two opposing effects on capacity. The optimum mercury concentration must be found empirically, and from all available data it is somewhere between 5×10^{-3} and 10^{-1} .

The effect of pH within the ranges investigated is not clear. A comparison of the 28% CaCl_2 - $5 \times 10^{-3} \text{MHg}^{++}$ tests at pH = 1 and 8, favor pH = 1. The 30% CaCl_2 - 10^{-2}MHg^{++} tests at pH = 1, 4 and 8 favor pH = 8 and the 32% CaCl_2 $\text{Hg} = 10^{-2}$ pH = 8 and 1 are about equal.

From the overall results the 35% CaCl_2 at 10^{-2}MHg^{++} seem most promising. Freezing point determination was made at the end of this experiment. The freezing point was -28°F , thus a small amount of alcohol would be necessary to lower freezing point. It should be noted that alcohol did not have any detrimental effect on cell performance when used to make 15% CaCl_2 electrolyte.

iii. Anode Activation Following Extended Exposure to Electrolyte

Figure 47 shows a plot of the cell voltage vs. time for an aluminum chlorine cell consisting of an aluminum electrode which had been exposed to 30% CaCl_2 electrolyte ($5 \times 10^{-3} \text{Hg}^{++}$, $\text{pH} = 1$) for a period of 120 hours, and 6cc of that electrolyte plus a fresh chlorine electrode. Discharge was performed at 0.5 amps/in^2 at room temperature. The maximum voltage achieved was 1.23 volts and the cell was over 1.00V from the beginning of discharge until 40 minutes into the discharge. At 45 minutes when the cell voltage had decreased to .75V a few drops of water were added to the cell and the voltage rose to 1.15 within 1 minute and then plateaued at 1.23V. The efficiency of the aluminum during discharge was 67%.

The following can be concluded from the data; 1. the aluminum did not activate, either because the mercury ion in the solution had been consumed leaving an insufficient amount to activate the aluminum, or the aluminum had found a passive layer on its surface during open circuit stand, or both. 2. the efficiency of the aluminum had increased to 67% due to these same factors, 3. the system is water limited as shown by the complete recovery of voltage upon the addition of a few drops of water.

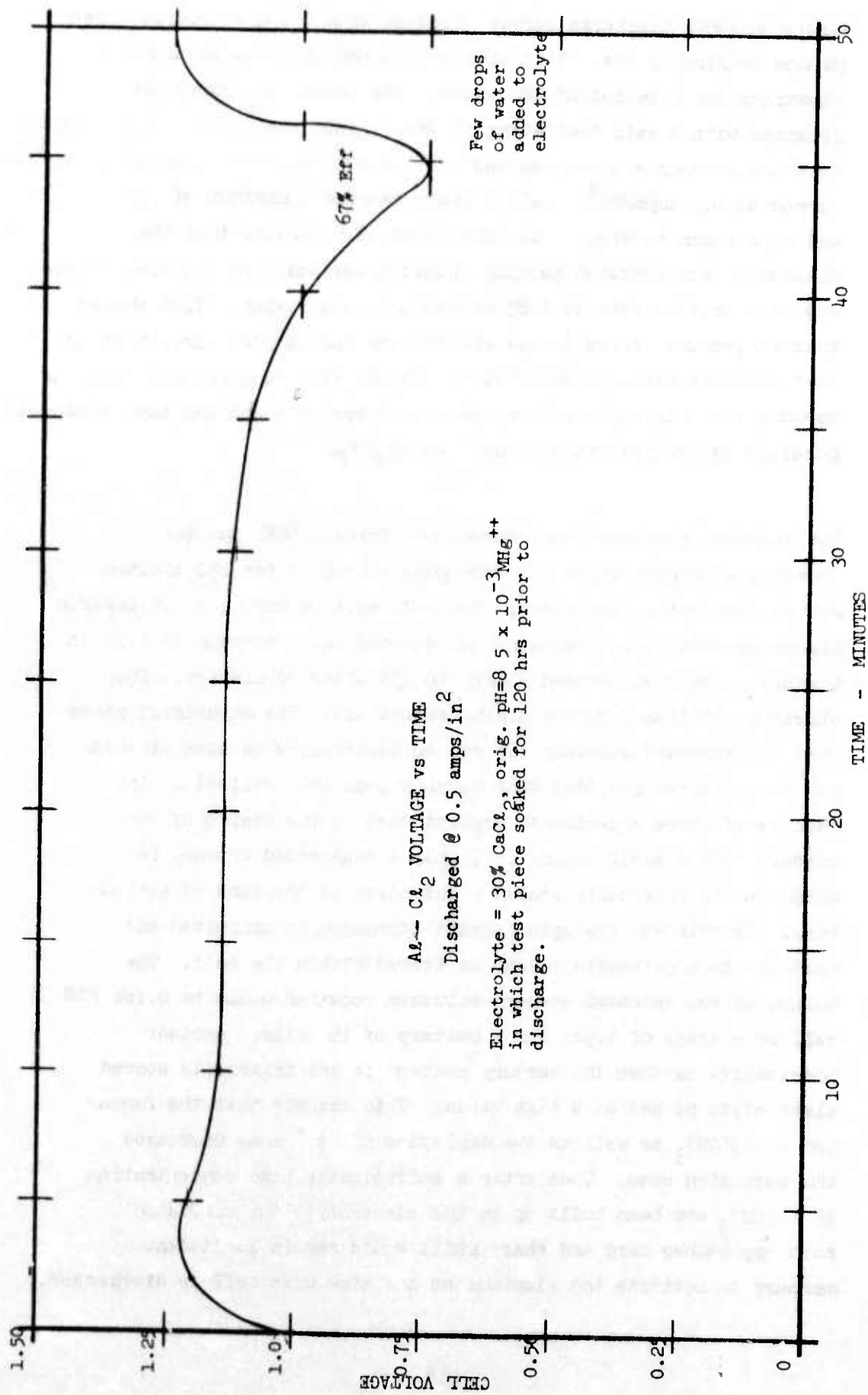


Figure 47

Figure 48 shows discharge curves obtained with the electrolyte whose pH was originally one. This electrolyte had corroded an aluminum electrode for a period of 120 hours. The solid line curve was obtained with a cell consisting of 6cc of said electrolyte and a fresh pre-activated aluminum electrode and a chlorine electrode. Discharge was performed at 0.5 amps/in². Cell voltage reached a maximum of 1.4 and then began to decay. At this point, 12.5 minutes into the discharge, concentrated mercury chloride was added to the electrolyte and cell voltage rose to 1.85 within a 5 minute span. This showed that no product formed in the electrolyte during open circuit stand that inhibits aluminum activation. It can also be concluded that the mercury ion originally present before corrosion stand had been consumed; possibly by precipitation as HgO or Hg₂Cl₂.

The aluminum electrode was removed (efficiency 60%) and the aluminum electrode which had undergone corrosion for 120 minutes was substituted in its place. The cell voltage during a 0.5 amps/in² discharge reached 1.70 within four minutes and a maximum of 1.75 in 5 minutes and then decayed slowly to 1.0V after 40 minutes. The aluminum efficiency during discharge was 61%. The experiment shows that the corroded aluminum exposed to electrolyte on open circuit can be activated provided that mercury ions are available. The results of these experiments suggest that in the design of the battery cell a small volume of highly concentrated mercury be added to the internally stored electrolyte at the time of activation. In this way the open circuit corrosion is minimized and most of the electrolyte volume is stored within the cell. The volume of concentrated mercury solution required would be 0.1cc PER cell or a total of 1.5cc for a battery of 15 cells. Another possibility is that the mercury content in the internally stored electrolyte be set at a high value. This assumes that the formation of Al(OH)₃ as well as the depletion of Hg⁺⁺ ions decreases the corrosion rate. Then after a sufficiently high concentration of Al(OH)₃ has been built up in the electrolyte the corrosion rate approaches zero and there still would remain sufficient mercury to activate the aluminum at the time when cell is discharged.

Al-Cl₂ VOLTAGE vs TIME
Discharged @ 0.5 amps/in²

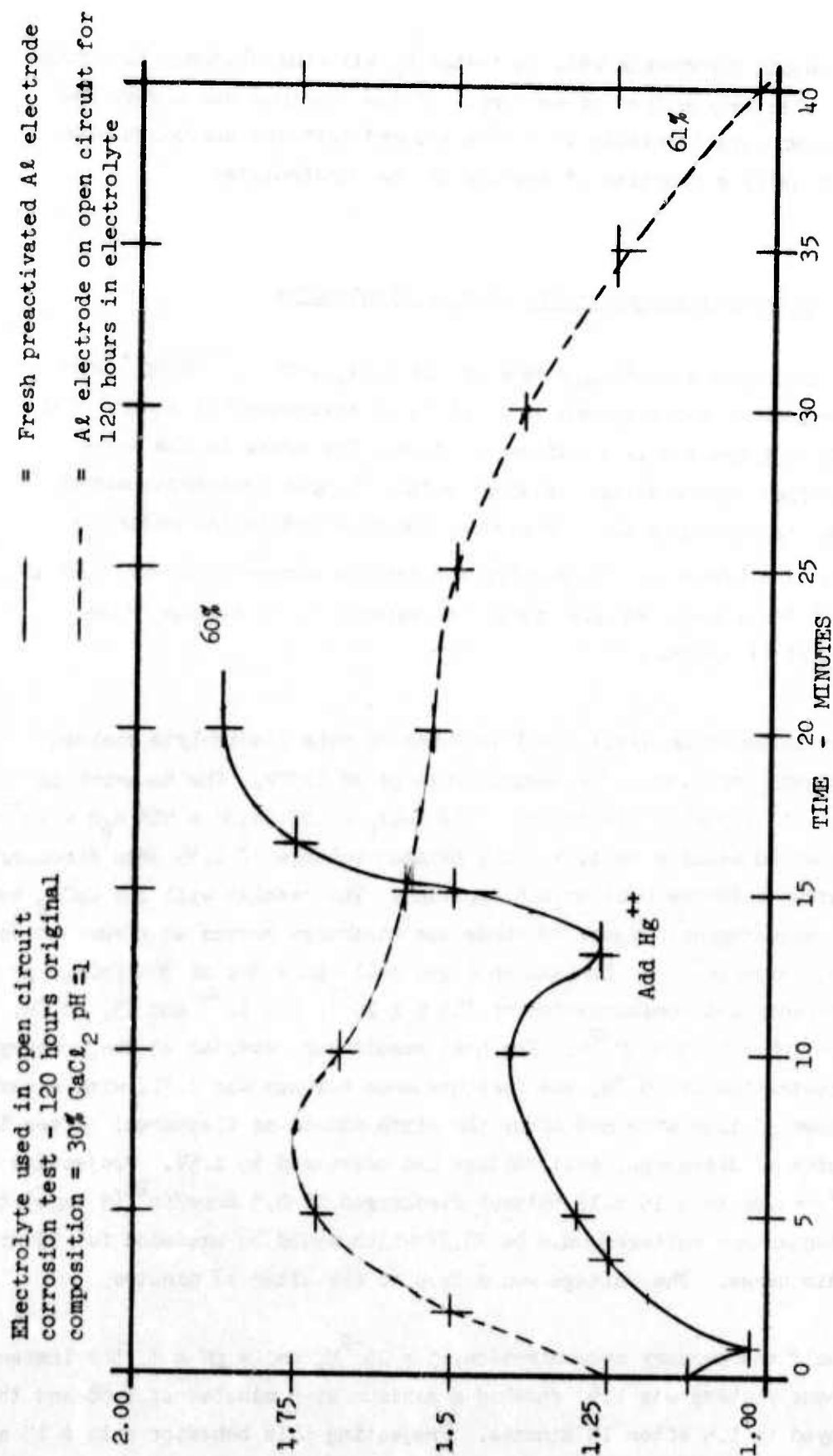


Figure 48

CELL VOLTAGE

This second hypothesis will be tested by allowing aluminum to corrode in an electrolyte free of mercury. If the aluminum has a very low corrosion rate initially it can be assumed that the corrosion rate is initially a function of mercury in the electrolyte.

iv. Cell Characteristics in 2.5cc of Electrolyte

The freezing and melting points of 35% CaCl_2 with 10^{-2}M Hg^{++} were determined by cooling (and warming) in an environmental chamber and plotting thermocouple readings vs. time. The break in the curve identified the freezing (melting) point. Copper constantan served as the thermocouple and a reference junction set in ice water was used. The breaks in the cooling and heating curves occur at -1.24 mV and -1.2 mV, respectively, which corresponds to an average value -1.22 mV or -38°F.

A discharge of an Al- Cl_2 cell in 2.5cc of this electrolyte yielded 13 minutes to 1.0V and a maximum voltage of 1.50V. The behavior in 2.5cc of alcoholic electrolyte (35% CaCl_2 + 10% CH_3OH + 55% H_2O + 10^{-2}M Hg) yielded 10 minutes to 1.0V and a maximum voltage of 1.45 when discharging an aluminum chlorine cell at 0.5 amps/in². The results with 30% CaCl_2 were more encouraging. Figure 49 shows the discharge curves at a current density of 0.5 amps/in² for aluminum-chlorine cells in 2.5cc of 30% CaCl_2 , pH = 1 at mercury ion concentration of (1) 5×10^{-3} , (2) 10^{-2} and (3) 10^{-1}M , and at (4) pH = 8, $5 \times 10^{-2}\text{M}$. The best result was obtained at the mercury concentration of 10^{-1}M , the instantaneous voltage was 1.70, with a maximum voltage of 1.92 attained after the sixth minute of discharge. After 18 minutes of discharge, cell voltage had decreased to 1.5V. Projecting this performance to a 15 cell battery discharged at 0.5 amps/in² (2 amps) the instantaneous voltage would be 25.5V which would be exceeded for 15 minutes of discharge. The voltage would drop to 24V after 17 minutes.

At half the mercury concentration, $5 \times 10^{-2}\text{M}$, and a pH = 8, the instantaneous voltage was 1.6, reached a maximum at 5 minutes of 1.88 and then decayed to 1.5 after 15 minutes. Projecting this behavior onto a 15 cell battery, 24 volts would be attained or exceeded during the first 13 minutes

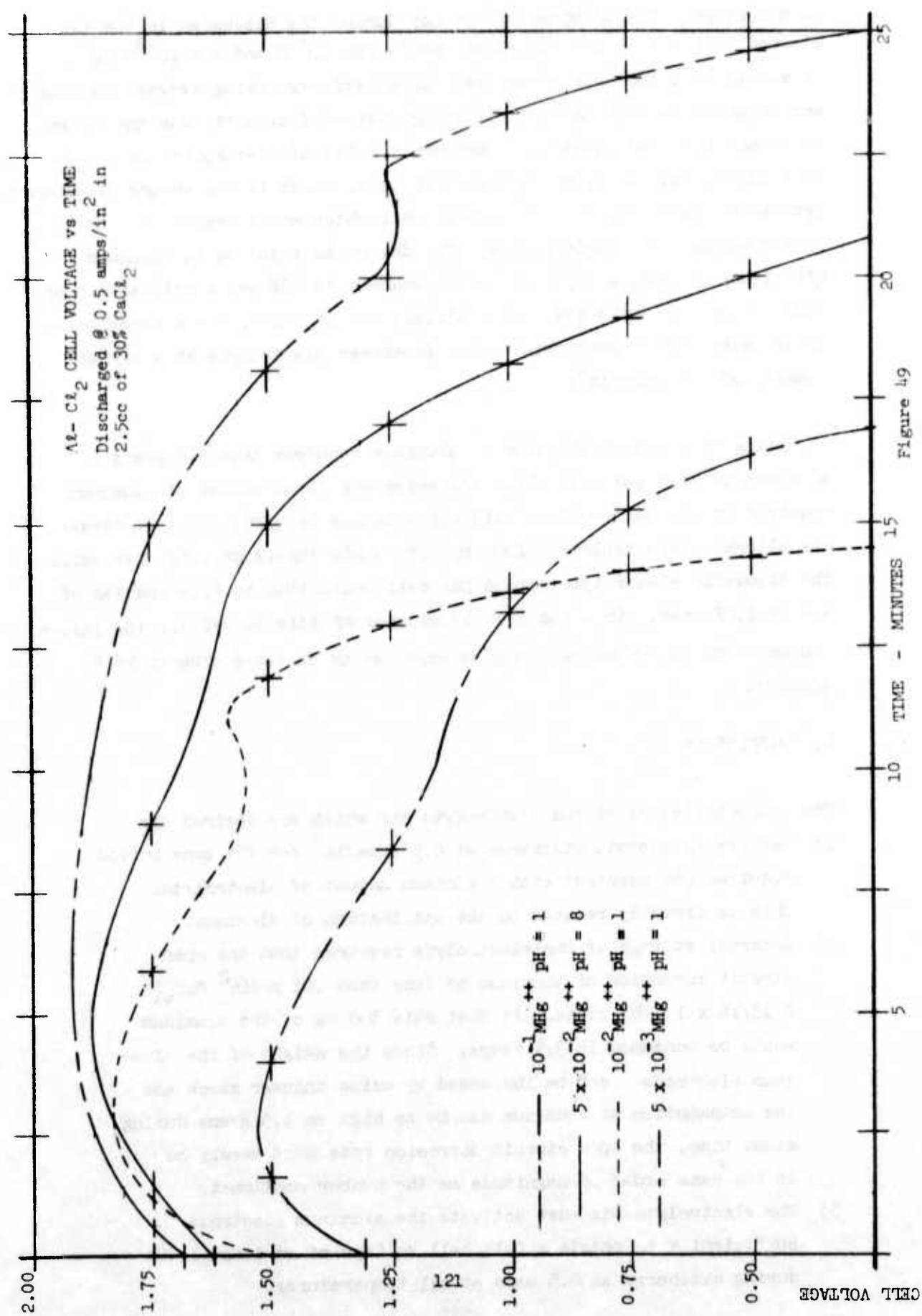


Figure 49

of discharge. The aluminum efficiency during the discharge in the two electrolytes was 33 and 36% respectively for $10^{-1}M$ and $5 \times 10^{-2}M Hg^{++}$. It should be noted that these tests were performed using excess aluminum and chlorine so that the only limiting factor of capacity was the volume of electrolyte and quantity of mercury. 2.5cc of electrolyte in a test cell corresponds to 4.2cc in a battery cell, which is the volume of electrolyte to be contained in each battery cell which would result in a total system volume of 6 cubic inches. The design is based on an aluminum efficiency of 50%, which must now be amended to 33% and a utilization of 100% for the chlorine gas. (The utilization of chlorine was established as at least 93% at room temperature in excess electrolyte at a current density of 0.5 amps/in²).

Adjusting to a 33% utilization of aluminum requires that 0.5 grams of aluminum be used per cell which increases the total volume of aluminum required in the battery from .113 cubic inches to .168. This decreases the allowable electrolyte volume by .055 cubic inches or .06cc per cell. The allowable electrolyte volume per cell would then be 4.14 instead of 4.2 or 1.5% less. On a basis of 17 minutes of life to 24V for the larger volume. The lower volume would be expected to decrease time to 16.4 minutes.

D. DISCUSSION

The characteristics of the electrolyte mix which are desired are

- 1) ability to sustain discharge at 0.5 amps/in² for the time period required (45 minutes) with a minimum amount of electrolyte. This is directly related to the utilization of aluminum.
- 2) Internal storage of the electrolyte requires that the open circuit corrosion of aluminum be less than .01 ma/in² for a $2 \frac{13}{16} \times 1 \frac{1}{8}$ " piece. At that rate 300 mg of the aluminum would be consumed in 3.4 years. Since the weight of the aluminum electrode can be increased by using thicker stock and the consumption of aluminum can be as high as 1.5 grams during stand time, the open circuit corrosion rate must merely be in the same order of magnitude as the number mentioned.
- 3) The electrolyte mix must activate the aluminum electrode sufficiently to obtain a full cell voltage of at least 1.7V during discharge at 0.5 amps at all temperatures.

In the above studies electrolyte compositions of 15% CaCl_2 + 20% CH_3OH + 65% H_2O , and 25% CaCl_2 + 65% H_2O were evaluated with respect to open circuit corrosion of aluminum cell voltage characteristic and aluminum utilization during discharge. The result indicates that the 25% CaCl_2 aqueous electrolyte is superior in all respects to the 15% CaCl_2 alcoholic electrolyte.

The 25% CaCl_2 aqueous electrolyte was chosen to be evaluated further because it had the highest water content and yet maintained a sufficiently low freezing point. For a given efficiency the greater the water content of an electrolyte the longer the life. For the same mercury concentration and pH aqueous 30% CaCl_2 results in a higher Al efficiency than 25% CaCl_2 (50% vs. 39%) when discharged at 0.5 amps/in². Thus 25% CaCl_2 contains 3% more water, but is about 11% less efficient. The 30% CaCl_2 is obviously preferable. Since we are limited by the freezing point of the electrolyte, the concentration range of CaCl_2 that can be worked with is from 25 to about 32%. It has been established in this study that the minimum concentration of mercury required to activate aluminum is $3 \times 10^{-3}\text{M}$. $5 \times 10^{-3}\text{M}$ has definitely been established as sufficient to fully activate aluminum.

Based on the above data 45 minutes, of useful capacity at 0.5 amps/in² can be obtained with 6cc of electrolyte. Translated into the limits of 6 cubic inches for the entire battery system, the useful capacity of the ECM battery operating at 2 amperes (above 24 volts) would be 15-20 minutes. On a watt-hour/in³ basis 2.3 to 2.8 could be expected. The battery delivering 20 minutes at 2 amps would weigh one third of a pound. Thus 56 watt-hrs/lb would be achieved. For 15 minutes 44 watt-hrs/lb would be obtained.

13. APPENDIX

As a result of the work described in this report a technical paper was prepared and presented at the Fall Electrochemical Society meeting in New York October 13-17, 1974. The title of the paper was: "Characteristics of the Aqueous $Al-Cl_2$ System as a High Energy Density Reserve Battery." A copy of this paper is presented in the Appendix because it does summarize the work accomplished and provides a conceptual six cubic inch battery design based on the study.

CHARACTERISTICS OF THE AQUEOUS $Al-Cl_2$
SYSTEM AS A HIGH ENERGY DENSITY
RESERVE BATTERY

P. F. Ritterman,* H. N. Seiger, Heliotek, Sylmar, California;
R. Marsh and M. Dougherty, Wright-Patterson Air Force Base,
Dayton, Ohio

The experimental and design work to be described in this presentation was directed toward demonstrating the feasibility of utilizing an aqueous aluminum-chlorine system as a reserve battery. The requirements for the ultimate reserve battery put forth by the Air Force Aero Propulsion Laboratory who sponsored this effort, was:

- 1) The entire battery system would not exceed a volume of 6 cubic inches.
- 2) The battery would deliver 2A at a voltage of 28 ± 4 volts.

Theoretically, aluminum offers many significant advantages for use as an anode material, as shown in the first slide (Figure A-1). Its voltage and low equivalent weight result in an extremely high energy density. Furthermore, the material is solid, inexpensive, plentiful, and easy to handle.

Past efforts have shown that the open circuit potential of aluminum is considerably less than its theoretical value. A voltage of -0.4 to -0.6 V vs. the standard hydrogen electrode has been observed. This corresponds to a voltage between -0.7 to -0.9 V vs. a calomel reference.

A discovery made three years ago at Heliotek resulted in a significant increase in both the observed open circuit and discharge potential of aluminum.

* TRW Systems Group, Redondo Beach, California

The voltage increase was brought about by the presence of a small amount of mercuric chloride dissolved in the electrolyte. Apparently an amalgamation occurs on the surface of aluminum resulting in an observed open circuit voltage of -1.2 V vs. S.H.E. (-1.5 V vs. calomel). The mechanism of this voltage increase has not as yet been determined. It may be related to inhibition of formation of an aluminum oxide coating as a result of the aluminum amalgamation, or it could be the result of an increase in the overvoltage of hydrogen on an amalgamated surface over that observed on aluminum. The increase in hydrogen overvoltage would result in an increased mixed potential between hydrogen evolution and Al dissolution. The determination of the true activation mechanism would have been an interesting study, but was beyond the scope of this investigation.

When aluminum is combined with a chlorine electrode in aqueous CaCl_2 containing $0.1\text{M}\text{HgCl}_2$ an open circuit potential of 2.5 to 2.6 volts is observed. The theoretical energy density of this system based on the observed open circuit potential is 710 Wh/lb and 39 Wh/in^3 . Based on active materials only, the cost per kWh delivered by this system is less than 20 cents.

Let us look briefly into the nature and characteristics of the chlorine electrode, the aluminum electrode, and the laboratory test cell. The electrode where chlorine gas is reduced to chloride ions is a composite gas diffusion cathode consisting of a sintered 40% porous titanium current collector, one side of which is coated with two layers of teflon bonded active carbon. This composite electrode is 15 mil thick. Figure A-2 shows the porous titanium substrate with a titanium lead attached along side the processed composite electrode. The electrode is sealed into a plastic housing compartment Figure A-3. A recess cavity in the housing provides for chlorine gas space, with the chlorine being lead into the space through two inlet ports at the top.

The anode is aluminum alloy 1100 and has its own integral tab. Prior to use in a cell, the aluminum is degreased in acetone and then etched in Tucker solution, which is a mixture of HF, HCl, and HNO_3 .

The electrochemical active area of the composite electrode is 2 in^2 . The aluminum electrode is slightly larger. The electrodes in the proposed design of the prototype will have the same area.

The anode, cathode and laboratory test cell are shown in Figure A-4. The interelectrode spacing was sufficient so that no separator was required. The test electrolyte was 30% CaCl_2 at a pH of 1 and containing 0.1 molar HgCl_2 .

Using the laboratory cell, polarization data was obtained for the chlorine electrode as shown in Figure A-5. The voltages are given relative to a saturated calomel electrode. Similar data was obtained for the aluminum electrode, both in the absence and presence of mercuric ion, as shown in Figure A-6. Notice that in neither case does the aluminum voltage change significantly with increase in discharge current density.

Utilization of active material at a discharge current density of 0.5 A/in^2 was 50% for the activated aluminum electrode, and almost 100% for the chlorine.

Another property of aluminum which is of interest is that a considerable time is required for this electrode to "activate" when discharged in mercury ion containing electrolyte. If the aluminum is preactivated, by means of discharging the electrode for a short period of time sufficient to amalgamate its surface, the electrode can be removed from the cell and be stored indefinitely. The subsequent activation time is accelerated. This can be seen in Figure A-7 comparing discharge voltage vs. time of an in situ and preactivated aluminum electrode. The in situ activated aluminum requires 10 minutes to reach a maximum voltage of 1.5 V vs. the calomel electrode, while preactivated aluminum attains the maximum voltage two minutes after the initiation of discharge.

A typical discharge curve at a current of 1A (0.5 A/in^2) for the full cell aluminum chlorine system is shown in Figure A-8. The aluminum was preactivated previous to discharge and chlorine gas at the rate of 10 ml/min was passed through the composite electrode.

The time of discharge or total ampere hours which an aluminum chlorine cell can deliver is a function not only of the weight (and volume) of active materials but also volume of electrolyte. To be more precise, it is the amount of water which limits the Ah output. The cell reaction as shown in Figure A-9 produces AlCl_3 which in turn reacts with water in the electrolyte producing $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. For every gram of aluminum consumed as a result of discharge current and corrosion, 6.2cc of water are required. In addition to this, 2.1cc are needed to keep the CaCl_2 in the electrolyte from crystallizing as a hydrate. Thus, a total of 8.3cc of water is required for every gram of aluminum electro chemically consumed.

A battery system occupying a volume of 6 in^3 was conceptually designed, based on experimental and calculated information regarding cell voltage, active material utilization and the relation of electrolyte volume to amount of aluminum consumed. When discharged at a current of 2 A, such a battery would operate for 20 minutes between voltages of 30 V to 24 V. The weights and volumes of the components of the battery system on a cell and battery level are tabulated in Figure A-10. Fifteen cells make up the battery. The components consist of the composite electrode including spacers, chlorine gas, electrolyte and aluminum electrodes.

A cross-sectional view of a single cell for the conceptual six (6 in^3) design is shown in Figure A-11. An individual cell will consist of two chlorine electrodes surrounding one aluminum electrode, and filled with 4.2cc of electrolyte.

A blowup view of a single cell is shown in Figure A-12. Note that electrodes of adjacent cells are back to back, separated by a 10 mil thick spacer which provides for chlorine gas space.

A half cell was constructed consisting of one chlorine electrode opposite one side of an aluminum electrode separated by 2.1cc of electrolyte. This is sufficient electrolyte to allow for cell operation of 20 minutes when discharged at 1 ampere. The aluminum electrode and chlorine supplied to the cell would allow it to operate well beyond the limitations placed on it by the amount of electrolyte.

A plot of cell voltage vs. time appears in Figure A-13. The voltage remains above 1.6 V for the first 17 minutes of discharge. Since the prototype battery is to consist of 15 cells, this corresponds to the lower limit of 24 V. Based on this result, the battery would yield 85% of its predicted capability within a six (6) cubic inch volume.

The energy density from this system could be increased by using a more dilute electrolyte. If it were possible to use pure water as the electrolyte, the energy density would increase by only 5% on a volume basis, but by 15% on a weight basis.

The size of the battery has an effect on the energy density because the weight and volume of the composite electrode remains the same as the capacity at a given current drain increases. Based on the cell discharge capacity of 17 minutes a projection of Wh/lb and Wh/in³ for this battery system was made vs. capacity at 2 A discharge. This is shown in Figure A-14. At a capacity of 4.5Ah, (2-1/4 hour discharge at 2A) the system would yield in excess of 70 Wh/lb and almost 3.4 Wh/in³.

The aqueous Al-Cl_2 system is a new system and still requires considerable study from a fundamental as well as hardware design basis. However, Al-Cl_2 is very promising, not only as a reserve battery, but also as a mechanically rechargeable system. Al-Cl_2 would have an excellent application where electrolyte would be continuously replaced, such as a sea water or torpedo battery system.

I wish to thank the Air Force Aero Propulsion Laboratory who sponsored this effort under contract F 33615-73-C-2018, my coauthors, and Mrs. Shu Tsai for her assistance in performing the laboratory experiments.

CHARACTERISTICS OF ALUMINUM

HIGH POTENTIAL	E = -1.86V
LOW EQUIVALENT WEIGHT	9 GRAMS PER EQUIVALENT
SOLID; DENSITY	2.7 g/cm³
INEXPENSIVE	\$0.50/LB (ALLOY 1100)
PLENTIFUL IN SUPPLY AND RESERVES	
HIGH THEORETICAL ENERGY DENSITY	2.2 kwh/LB

FIGURE A-1

COMPOSITE CHLORINE ELECTRODE

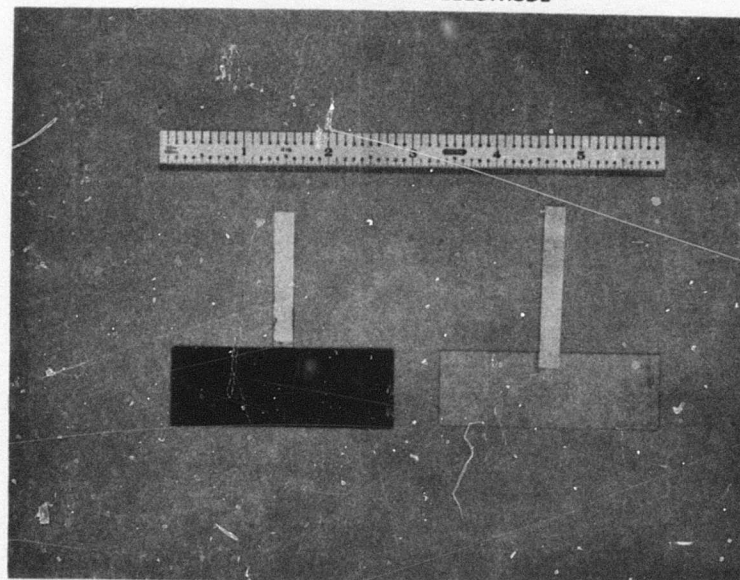


Figure A-2

COMPOSITE ELECTRODE AND HOUSING

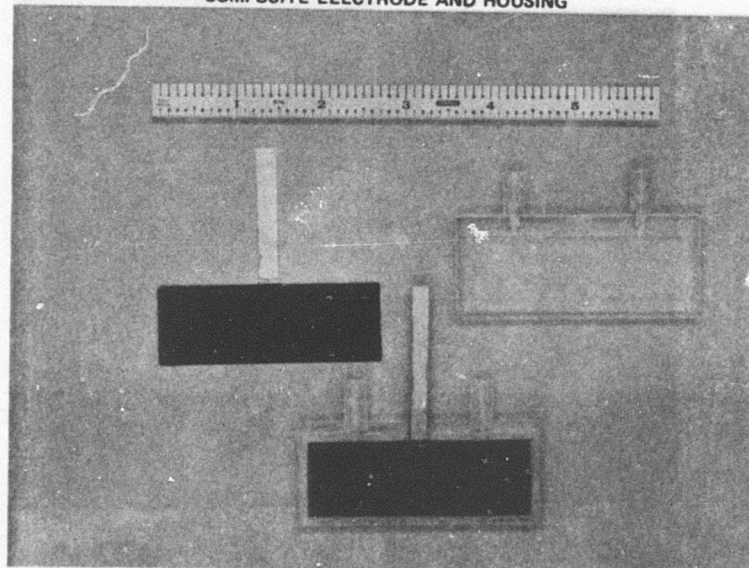


Figure A-3

ANODE, CATHODE AND
LABORATORY TEST CELL

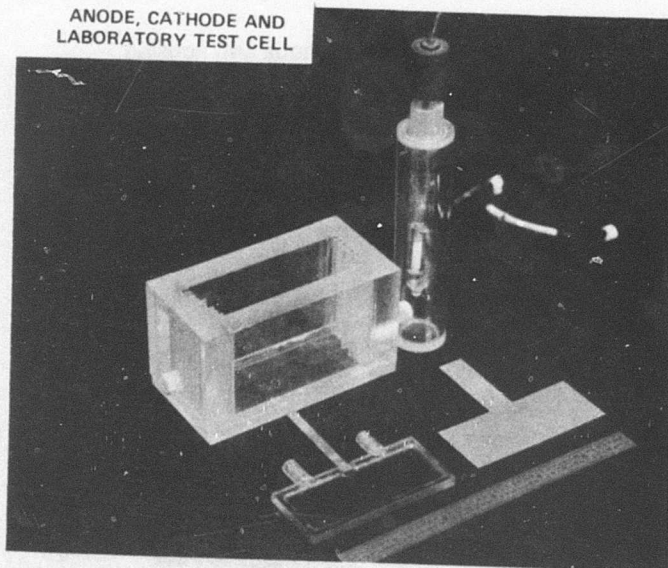


Figure A-4

Cl₂ TO CALOMEL REFERENCE VOLTAGE VERSUS CURRENT DENSITY

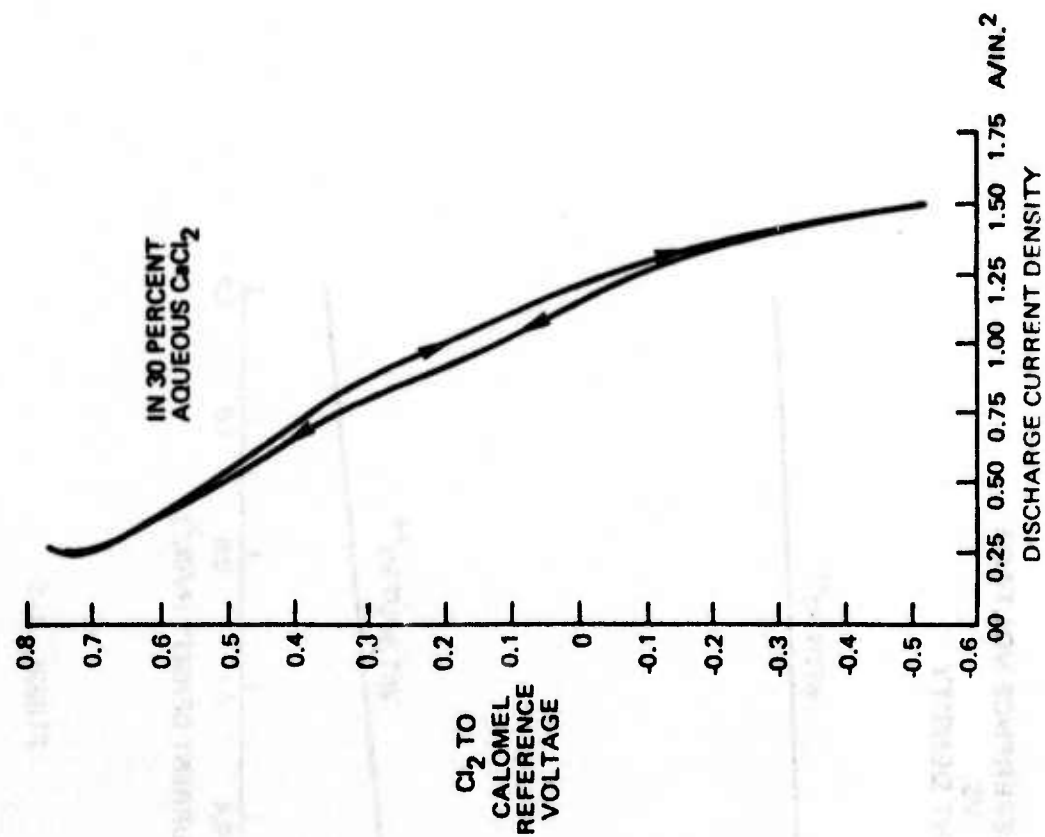


FIGURE A-5

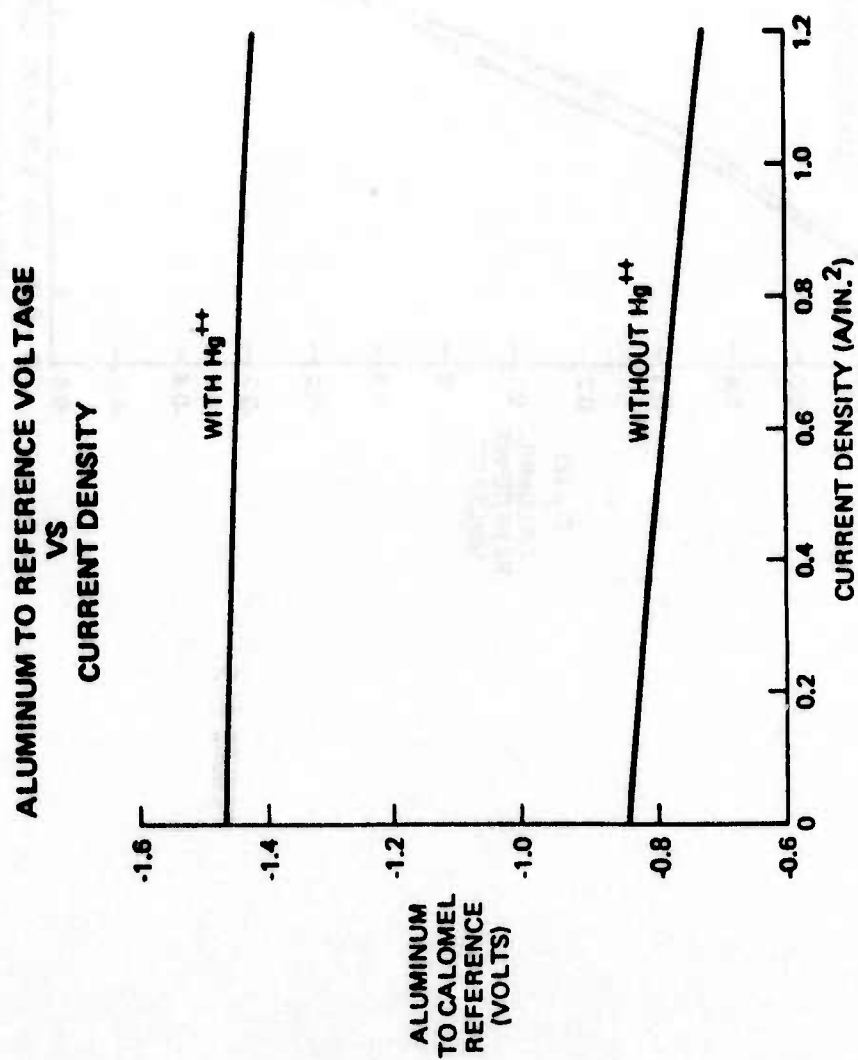


FIGURE A-6

FIGURE A-7

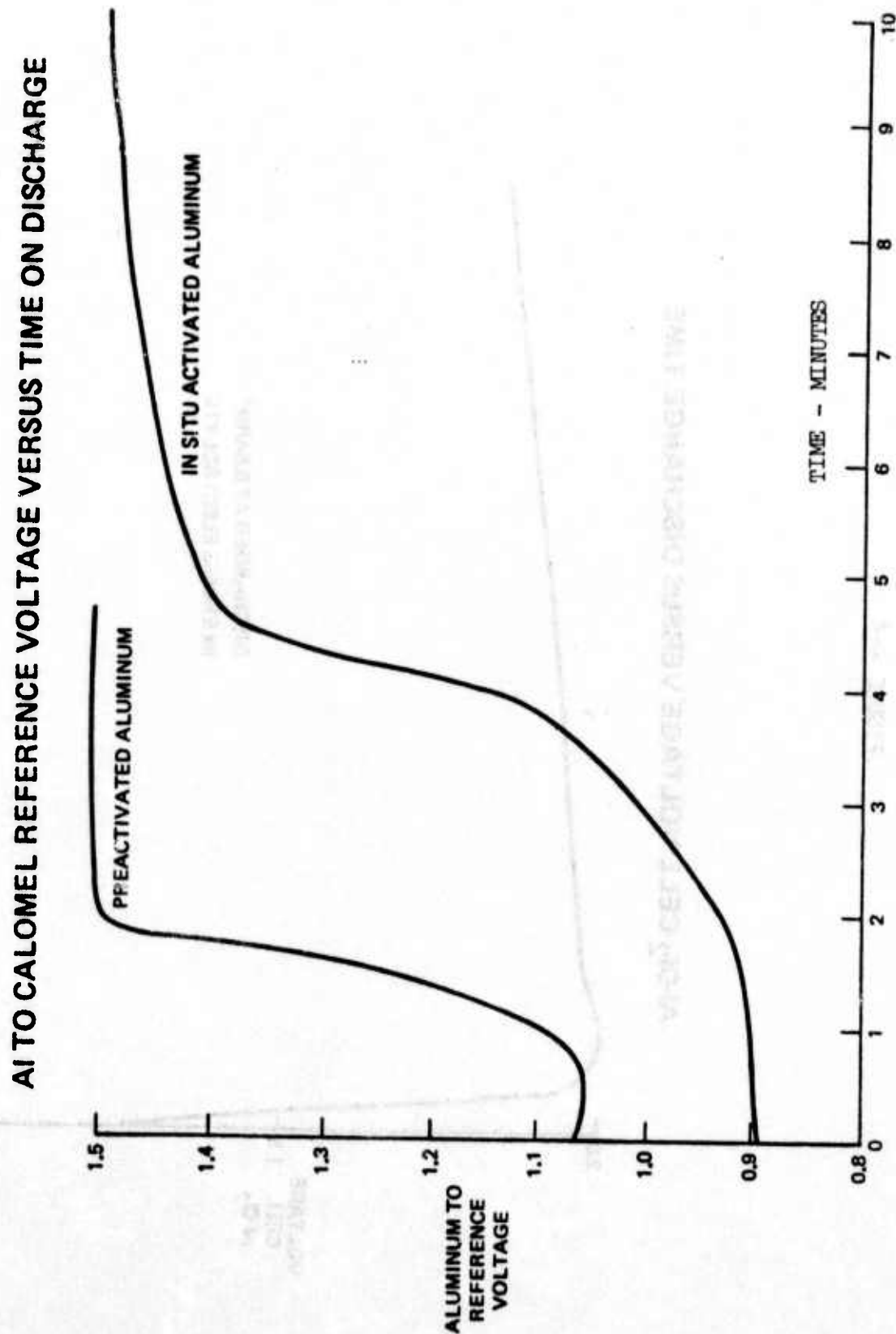
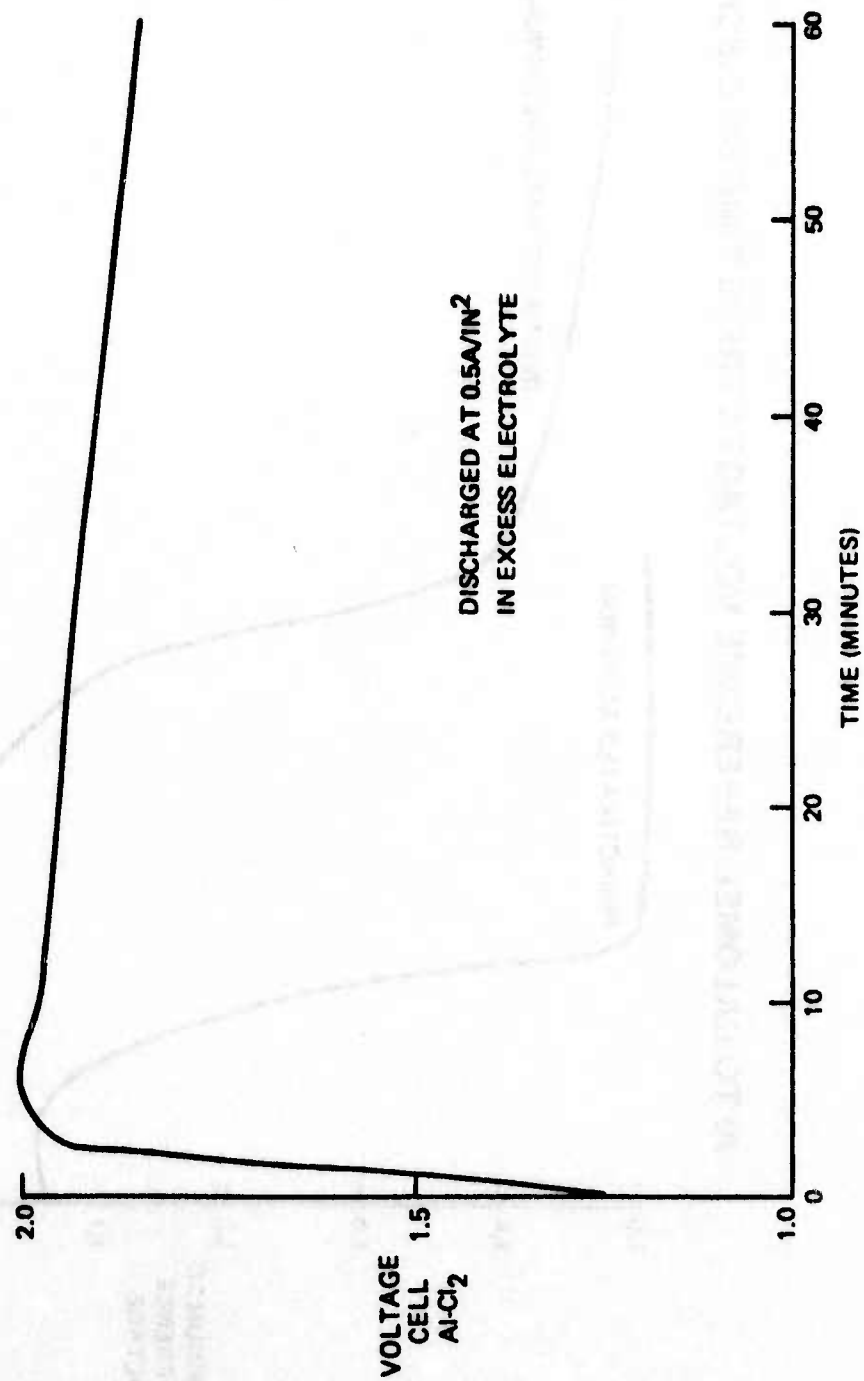


FIGURE A-8

Al-Cl₂ CELL VOLTAGE VERSUS DISCHARGE TIME



CELL REACTIONS

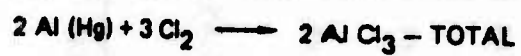
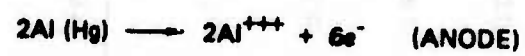


FIGURE A-9

CALCULATED WEIGHT AND VOLUME OF BATTERY COMPONENTS
(BATTERY TO OPERATE FOR 20 MINUTES AT 2.0A, 28.0V)

	WEIGHT PER CELL (GRAMS)	VOLUME PER CELL (CM ³)	WEIGHT BATTERY (GRAMS)	VOLUME BATTERY (CM ³)
CHLORINE GAS	0.66	0.60	9.90	9.00
COMPOSITE CHLORINE ELECTRODES	2.57	1.63	38.60	24.60
ALUMINUM ELECTRODES	0.45	0.17	6.75	2.50
30% CALCIUM CHLORIDE ELECTROLYTE	5.45	4.20	81.50	63.00
TOTAL	9.13	6.60	136.75	99.10

99.1 CM³ = 6.0 IN.³
136.75 G = 0.30 LBS

FIGURE A-10

CONCEPTUAL - DESIGN OF Al-Cl_2 CELL

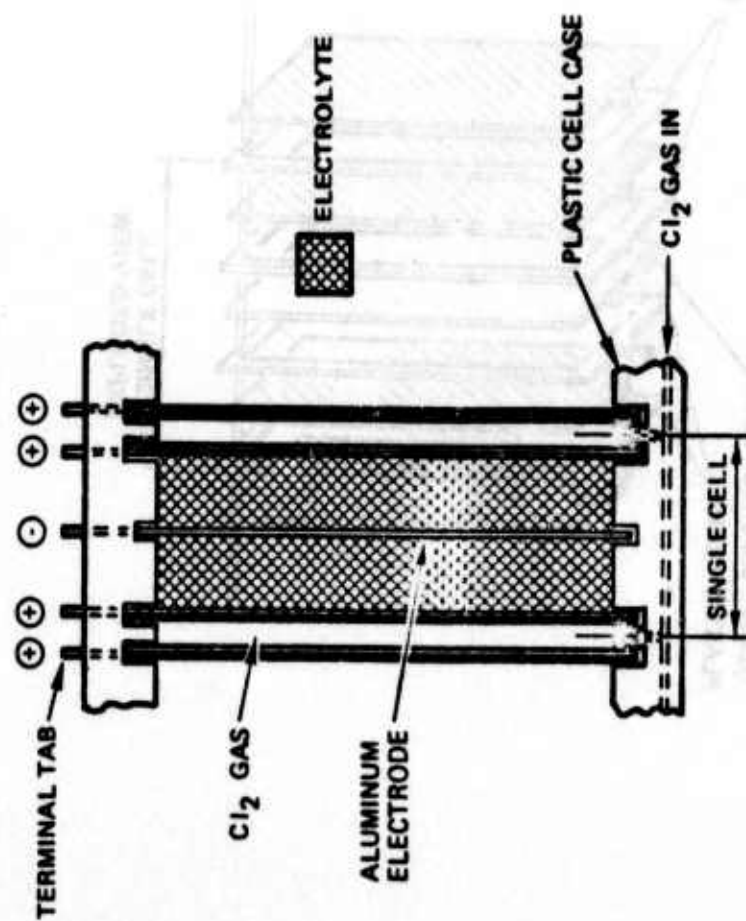


FIGURE A-11

SINGLE CELL EXPLODED VIEW

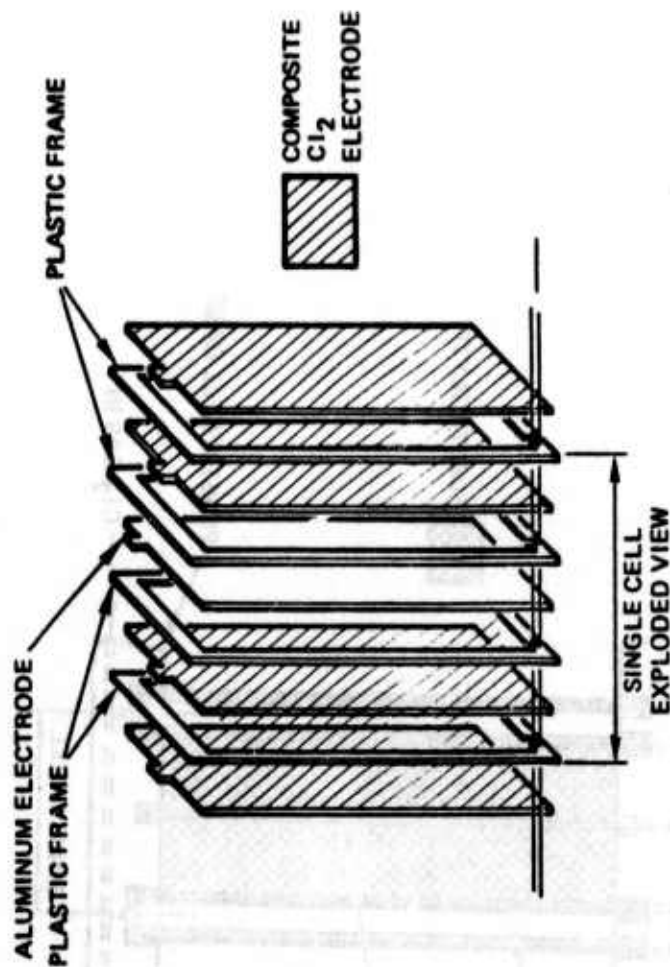


FIGURE A-12

Al-Cl₂ CELL VOLTAGE VERSUS DISCHARGE TIME

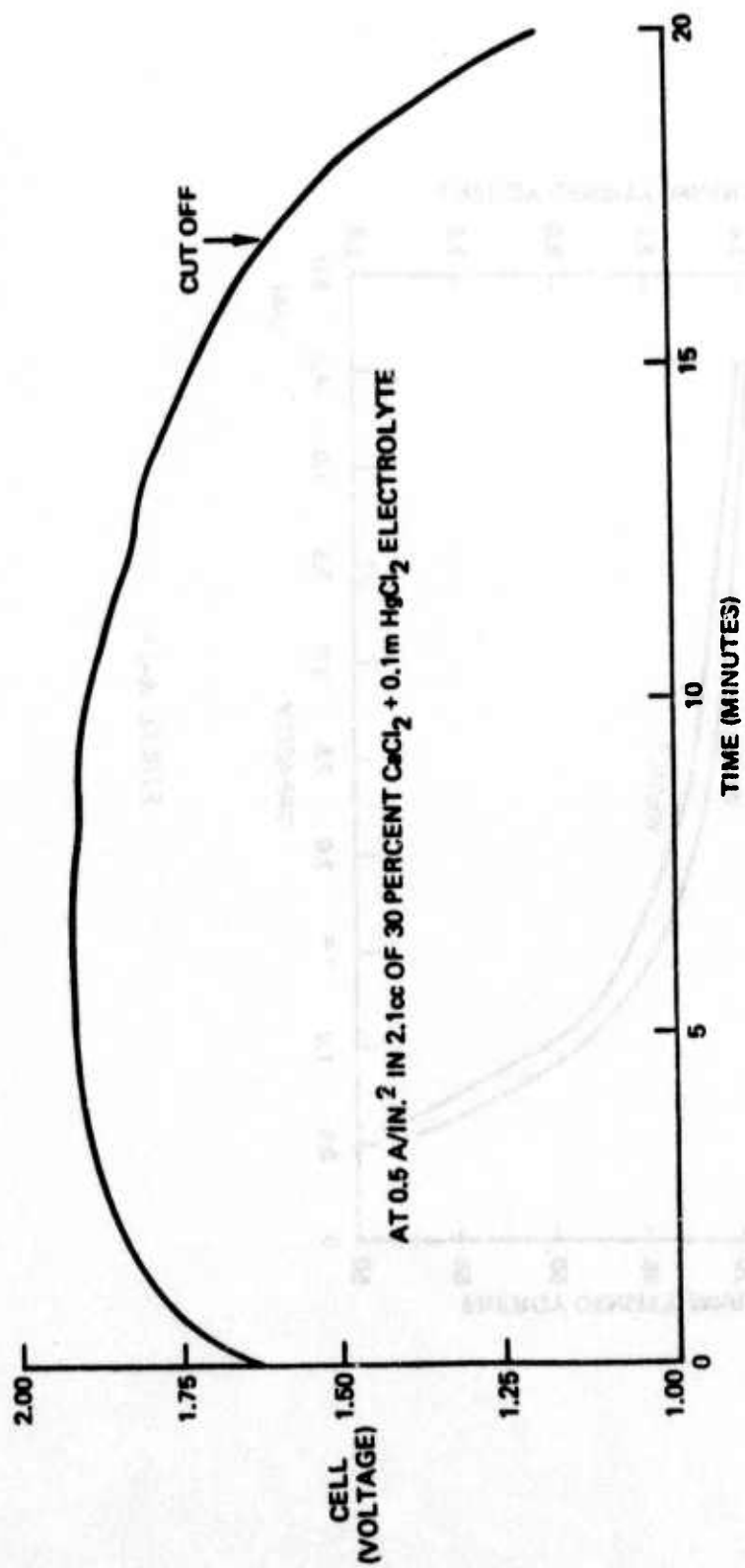


FIGURE A-13

ENERGY DENSITY VERSUS CAPACITY FOR 28V Al-Cl_2 BATTERY SYSTEM

DISCHARGED AT 2A

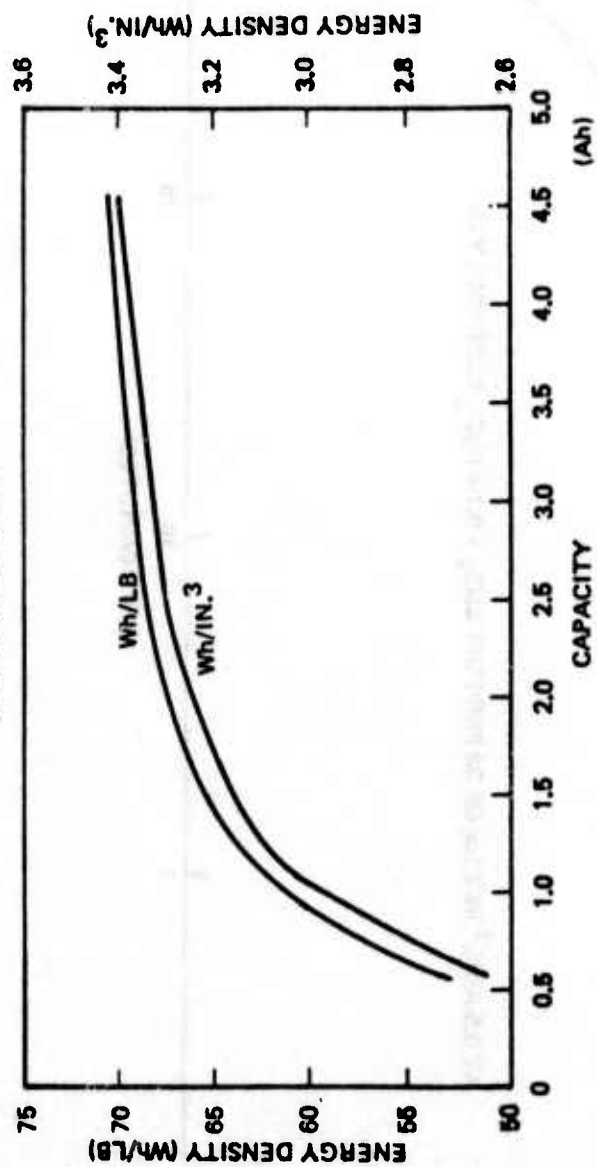


FIGURE A-14

SUPPLEMENTARY

INFORMATION

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The objective of this program was to provide advanced battery technology leading to the development of an improved primary power source, utilizing the activated aluminum anode, for expendable ECM jammers. This battery system, when fully developed, was expected to yield energy densitites of 60 Wh/lb and 6 Wh/in ³ at the 45 minute discharge rate.		

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