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13 January 1954
Report No. 776
(Annual)
Copy No.

# RESEARCH ON ELECTROCHEMICAL FUEL CELLS

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*Contract N7 onr-46207*
*Task No. NR 359 272*

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13 January 1954

Report No. 776
(Annual)

# RESEARCH ON
# ELECTROCHEMICAL FUEL CELLS

Contract N7onr-46207
Task NR 359 272

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AEROJET-GENERAL CORPORATION

Azusa, California

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## CONTRACT FULFILLMENT STATEMENT

This report is submitted in partial fulfillment of Contract N7onr-46207, Task NR 359 272.

## I. OBJECTIVES

A. The basic aim of the work performed under this contract has been to investigate the feasibility of constructing continuous-feed primary batteries with high power-to-weight and energy-to-weight ratios for use in submarine and missile propulsion.

B. During the period covered by this report, the detailed objectives were as follows:

1. Investigate the utilization of chlorine as a cathode with metal anodes in primary cells with electrolyte based on sea water.
2. Determine dissolution rates of magnesium, aluminum, and their alloys as a function of current density and electrolyte concentration.
3. Determine the operating characteristics of magnesium and other electrochemically efficient metals and alloys as anodes under conditions that simulate cells with oxygen cathodes and sea-water electrolyte.
4. Study performance of oxygen cathodes using porous carbon of the air cell type, with electrolyte based on sea water, and attempt to develop cathodes suitable for use with both pure oxygen and air.
5. Investigate the possibility of indirectly increasing the voltage of the oxygen electrode by use of another appropriate oxidation-reduction couple as the working electrode.

## II. INTRODUCTION

A. Work under this contract has been concerned with the study of the feasibility of applying continuous-feed primary batteries to a submarine propulsion system. Such a system should provide a quiet, compact, efficient power source that would not require the vessel to surface at frequent intervals.

B. During the past three years the studies have resulted in development of the zinc-chlorine cell system in a form that is considered ready for prototype design. Other phases of the work have been concerned with feasibility studies of other electrodes and cell systems that are in principle capable of fulfilling the requirements of a submarine power source. The zinc-chlorine system compares favorably in realizable efficiency with any of the other systems investigated on a small scale. In addition, the other systems have severe practical limitations that make their development on a large scale unlikely in the near future. A large cell utilizing zinc and chlorine was constructed and tested during the latter part of this report period. Its performance indicated that development of the prototype power source would be straightforward.

C. Notable features of the exploratory work on other cell systems and electrodes are discussed briefly below. The major portion of this work was reported in detail in the previous two annual reports (References 1 and 2); the remainder is included in the body of this report.

## III. RESUME

A. Zinc-chlorine cells of potentially unlimited operating life have been developed in small laboratory size. Initial experiments with a large cell of near-operational size indicate that the advantageous performance of smaller cells can be duplicated readily.

B. A series of improvements in the technique of cathode fabrication has permitted the construction of zinc-chlorine cells with a service life under tests of at least seven days. During this time the decline in load voltage at a constant current drain of 0.25 amp/sq in. was only approximately 10%. Further, there are indications that, under normal operating conditions, the service life is many times greater than the arbitrarily chosen period of seven days. In addition, the cell has demonstrated a remarkable ability to perform stably at high current-drain rates (i.e., 2.5 amp/sq in.). Although convenience dictated the termination of such tests after relatively short periods (5 hours), there is every reason to believe that the cells could perform well at high current drains for extended periods.

C. Several experiments were performed on zinc-chlorine cells at pressures higher than atmospheric. Without exception, an increase in pressure was accompanied by an increase in the power output of the cell. In every instance, the magnitude of the voltage increase was larger than could be accounted for by electrochemical theory (i.e., the Nernst equation). This fact supports the belief that the rate-determining step in the mechanism of cathode depolarization is the dissolution of chlorine in the electrolyte within the mix-cake. It is doubtful, however, that the increase in power output with pressure will always be great enough to compensate for the increased weight of the system.

D. Exploratory experiments have been conducted on zinc-chlorine batteries with cells in series. Although these experiments revealed no loss in individual cell performance, several special problems associated specifically with details of battery construction were noted. Most important among these problems is the development of a very strong and highly conductive bond between the zinc anode of one cell and the cathode of the cell stacked next to it.

E. The majority of the tests were carried out with cells containing effective cathode surface areas of 8 sq in. In addition, a number of experiments were conducted on cells with effective surface areas of about 32 sq in. Toward the end of this annual report period, special equipment was designed and constructed which permitted the fabrication of cathodes with effective surface areas of 144 sq in. In the body of this report these three types of cathode are referred to as small, intermediate, and large respectively. A 24-hour discharge test of the first large cell indicated that performance equivalent to that of the smaller laboratory models can be expected.

F. Further work on oxygen-depolarized cells using Carbocell and Air-Cell carbon diffusers failed to eliminate the difficulties associated with high oxygen polarization and, in the case of magnesium anodes, metal hydroxide formation. The study of oxygen-depolarization cells as well as the study of cells using oxygen indirectly with another oxidation-reduction couple, was terminated early in the year in order to concentrate a full effort on the zinc-chlorine system, which showed great promise of rapid and successful development.

## IV. CONCLUSIONS AND RECOMMENDATIONS

A. The conclusions presented in Reference 2 remain unchanged, except that (1) the zinc-chlorine system has now been demonstrated to be capable of the performance required, and (2) further studies and considerations of magnesium-oxygen cells have reinforced the belief that neither magnesium nor oxygen is suitable for immediate use in cells for submarine power sources. It is recommended that intensive development of zinc-chlorine batteries be undertaken immediately, as these appear to be capable of development into operational units in a short time. Detailed recommendations for the cell development are presented below. It is further recommended that laboratory studies of an exploratory nature be continued in an effort to develop cell systems better than the proposed zinc-chlorine system.

B. It is recommended that the development program for zinc-chlorine batteries include substantially the subjects itemized below. Several of the subjects listed for study are included as precautions, inasmuch as changes are not expected to be necessary.

1. Design more effective means for maintaining cell clamping pressure in series-cell batteries.

2. Make preliminary designs of high-pressure containers and of light-weight, low pressure containers for batteries, in order to facilitate a choice between operation at low or high chlorine pressure.

3. Determine the limits and optimum values of electrolyte flow rate and zinc chloride concentration in electrolyte, from the standpoint of heat removal from the battery.

4. Determine the effect of the following operating procedures on battery performance over extended periods:

   a. Intermittent operation

   b. Extended shut-down

   c. Extended full-power operation

   d. Fluctuations in chlorine pressure

   e. Fluctuations in electrolyte flow

5. Determine whether optimum values have been selected for the following:

   a. Composition of mix-cake

   b. Thickness of mix-cake

   c. Amount and type of bonding agents

   d. Thickness of diffuser

   e. Pore size of diffuser

   f. Type and thickness of separator

## V. EXPERIMENTAL RESULTS

### A. SYSTEM CALCULATIONS

### 1. Introduction

a. There are two primary considerations in the choice of a chemical couple:

(1) The system must have a high theoretical energy output per unit weight of reactants, including electrolyte.

(2) A large percentage of this energy must be obtained in practice; i.e., the operating voltage must be large compared with the theoretical emf, and the battery itself must not be too large and must be capable of delivering its power at a reasonably high current density.

b. It is possible to characterize the performance of a battery by two parameters: the effective emf and the effective internal resistance of the cells.* The effective emf is a function of the chemical system and, in the case of a gas, the pressure. The internal resistance is a function of the components of the cell. Both are somewhat dependent on temperature. For a chemical couple having a given emf, research is directed toward a lower internal resistance and, of course, satisfactory voltage vs time characteristics.

c. Figures 1 to 7 represent the results of calculations of the weights of reactants and electrode structures for a number of possible battery systems. All are based upon an arbitrary requirement of 209 kw for seven days at 440 volts. The weights of the battery compartment, reactant container, and accessories have not been estimated, as it is considered that at this stage the present comparisons are sufficient to illustrate the relative merits of various systems. Assumptions regarding the effective emf as well as cathode and anode ampere efficiencies are given in the legends of the figures. A representative calculation for the curves presented is given in Reference 2 for the zinc-chlorine battery.

### 2. The Zinc-Chlorine System (Figure 1)

a. For a gas electrode, the current efficiency is a controlled variable. The cell voltage is usually a weak function of this efficiency; 90% current efficiency has been found (Reference 2) to be practical for chlorine.

b. The metal anode efficiency is a function of the electrolyte concentration and current density. Amalgamated zinc evolves practically no hydrogen from neutral or slightly acidic solutions. Because chlorine is soluble in water, excess chlorine will react directly with the zinc, so that in a zinc-chlorine cell the zinc efficiency is necessarily equal to the chlorine efficiency. (Very little chlorine is found in cell effluent solutions regardless of the chlorine current efficiency.)

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* See Appendix I for definitions.

## 3. The Magnesium-Oxygen System (Figures 2 to 5)

a. Oxygen efficiency is based on the reaction

$$O_2 + 4e^- + 2H_2O \longrightarrow 4OH^-$$

although the actual mechanism involves the reaction

$$O_2 + 2e^- + H^+ \longrightarrow HO_2^-$$

In any practical cell, the $HO_2^-$ will decompose rapidly to $O_2$ within the electrode, so that the overall reaction corresponds closely to the first equation. It has been found that almost all of the oxygen introduced can be utilized in gas electrodes, although, as expected, the potential attained is that of the reduction to peroxide.

b. The magnesium efficiency was found by experiment to be 67% over a wide range of electrolyte concentrations and current densities (Reference 2). The weights given for the system of Figure 2 are an absolute minimum for the magnesium-oxygen system, and it is likely that one of the heavier systems must be used.

c. Magnesium-oxygen systems are also penalized because of the precipitation of cell reaction products in a sea water electrolyte. Excessive hydrogen evolution also occurs. In order to produce a soluble reaction product, the sea water can be acidified with HCl. The study of the dissolution rate of magnesium as a function of current density and acid strength shows that the maximum 67% ampere efficiency is possible even in acid electrolytes if high enough current densities are used. In practice, the bulk acid concentration could be controlled as a function of current density so that a given current efficiency could be maintained (Reference 2). The voltage of a magnesium-oxygen cell is slightly higher in acid than in base owing primarily to the removal by the acid of the oxide film on the magnesium.

## 4. The Magnesium-Chlorine System (Figure 6)

a. Although little work has been done on magnesium-chlorine cells, work with chlorine cathodes in zinc-chlorine cells and with magnesium anodes in magnesium-oxygen cells in various electrolytes permits prediction of an effective emf of 2.64 volts for the system given in Figure 6.

b. As in zinc-chlorine cells, the chlorine current efficiency is a controlled variable. Because of the solubility of chlorine in the electrolyte, there will probably be greater local action on the magnesium than in neutral or hydrochloric acid electrolytes. A current efficiency of 50% for magnesium is probably a fair estimate.

## 5. The Zinc-Alkali-Free-Air System (Figure 7)

The assumptions noted in the legend of Figure 7 represent the absolute minimum weight requirements of a zinc-alkali-air cell. For any submerged operation, this battery would operate on either pure oxygen or on oxygen-enriched, recirculated air.

## 6. Summary

a. The system that offers most promise is zinc and chlorine. Although the magnesium-oxygen system has a much higher theoretical energy-to-weight ratio (2.61 kwh/lb) than the zinc-chlorine system (0.34 kwh/lb), this advantage disappears in the comparisons given for two reasons: (1) the zinc-chlorine system is more nearly reversible, i.e., it delivers current at a voltage close to the theoretical emf of the cell; and (2) the current efficiency is high, thus making the weight of reactants low.

b. For all the systems considered (Figures 1 to 7), fuel economy is most important for operation for periods even as short as seven days, so that low current densities, and hence high voltages, should be used. For any one system, the total weight of fuel and battery is not strongly dependent on the internal resistance of the cells; however, the weight of the battery alone depends on internal resistance. Further, a low internal resistance is imperative if the battery is to be capable of large emergency power output while the cruising power level remains at or near the optimum current density.

## B. ZINC-CHLORINE CELLS

## 1. Introduction

a. At the end of the last annual report period (Reference 2) the zinc-chlorine cell had undergone sufficient development to give, at a current density of 0.25 amp/sq in., an operating voltage which dropped from an initial value of 1.60 volts to a final value of 1.52 volts after 5 hours. Beyond this point failure of the cell was rapid. The primary reason for this improved performance was the use of the water-based mix-cake instead of plain porous carbon, leading to the fabrication of the Type IV cathode illustrated in the cell assembly of Figure 8. The performance of this cathode is discussed in detail in Section 2, below. As indicated in Figure 8, the general structural features of the cell were as follows:

(1) A cathode consisting of a water-based carbon mix-cake pressed against one face of a 0.5-in.-thick Grade 40 or 60 porous carbon diffuser element, into which gaseous chlorine is introduced.

(2) A sheet of zinc duplex whose carbon-coated side is bonded to the untreated face of the diffuser element; this represents the anode of the next cell in series.

(3) An anode consisting of a surface-amalgamated zinc plate of any desired thickness and an area slightly larger than that of the cathode.

(4) A fibrous, chemically inert material, generally glass wool (Pyrex Catalog No. 800), which functions as the separator.

b. The electrolyte was a simulated sea-water solution (see Table I) which was uniformly dripped on the separator of the vertically supported cell assembly during cell operation.

c. Although the general basic construction of the cathode remained unchanged during the year, important refinements in structural features were largely responsible for the tremendous improvement in cell performance.

d. The steady progress during the past year is presented in chronological order in the text of this report. Consequently, no general section on testing procedures and conditions to cover the entire period is included; however, information of this kind will be given in the appropriate sections on the individual electrode types.

## 2. Cells with Type IV Cathodes - Additional Experiments

### a. Development

(1) Because of the poor and inconsistent results obtained with Type III electrodes (Reference 2) which had been impregnated with waterproofing agents, another approach was made to the problem of obtaining good output voltage and long operating life.

(2) It was postulated that a molded carbon-black mix-cake pressed against the surface of the diffuser would allow any necessary waterproofing treatment of the diffuser without impairment of the electrical performance obtained from the active carbon. It was at first believed that such a mix would be washed out of the cell by the dripping electrolyte. However, when a cell incorporating a mix cake was tested it was found that no such washout occurred.

(3) The mix cake was made from Cabot No. 2047 battery carbon black, which has the desirable features of high conductivity and large specific surface area. The mix cake was made according to the following arbitrarily selected formula (basis 1 sq in. electrode area): 0.20 g Cabot No. 2047 battery black and 1 cc distilled water.

(4) To make the mix cake, dry carbon black was spread evenly in a hollow mold placed on the separator, and covered with a sheet of moist Munising paper. One-half of the required distilled water was added, the mold was removed, and the mix was pressed at 70 to 200 lb/sq in. The resulting mix cake was about 0.05 in. thick. The separator and cake were then removed from the press, and the remainder of the distilled water was added to the Munising paper to facilitate its removal.

(5) The molding of the mix cake on the separator, rather than on the porous carbon, prevented the possibility of premature wetting of the diffuser. The separator was initially cut to a size larger than the diffuser so that the molded mix cake could be trimmed to an appropriate size after it was placed on the porous carbon. This resulted in a much neater electrode and reduced the chance of an internal short circuit.

### b. Testing Procedure

The testing procedure for cells at atmospheric pressure included a preliminary conditioning cycle which consisted of placing the cell in a vacuum desiccator and evacuating the system for 16 to 48 hours. At the end of the evacuation, the desiccator was flooded with chlorine and then opened. The chlorine feed line was attached to the chlorine electrode while it was still surrounded by the chlorine atmosphere. The cell was then removed and placed on test. Previously, the chlorine electrodes had been thoroughly purged with chlorine immediately before testing. It was believed that this modified procedure reduced the possibility of gas blocks caused by nitrogen from the air, inasmuch as a large part of the adsorbed gas was removed from the porous carbon.

### c. Results - Small Cells

(1) The output, particularly the initial output, of the cell was dependent to a great extent on the pressure at which the mix-cake was molded. Previous electrodes had been constructed with mix-cakes molded at 30 psig. In evaluating the effect of mix-cake molding pressure on cell output, three 2 x 4-in. cells employing mix-cakes molded at 70 lb/sq in. were constructed. Three electrodes were used as a basis of comparison for the scaling-up tests. The curve for the small electrode in Figure 9 approximates the mean performance of the three. The specific internal resistance ranged from 0.90 to 1.10 ohm-sq in., with a common effective emf of 1.94 volts.

(2) A substantial increase in cell performance was obtained by molding the mix-cake at a pressure of 130 ± 10 lb/sq in. No further increase in cell performance was obtained when the mix-cake molding

pressure was increased to 200 lb/sq in. and above.

(3) The increase in mix-cake molding pressure from 30 ± 5 lb/in. to 130 ± 10 lb/sq in. resulted in an increase of the initial output voltage at atmospheric pressure from between 1.50 and 1.60 volts, to between 1.75 and 1.80 volts at a current density of 0.25 amp/sq in. The effective emf was raised from 1.80 to 2.02 volts.

(4) Two cells were constructed, each with a chlorine entry tube and a lattice of chlorine distribution channels drilled through the porous carbon diffuser parallel to the face. Previous small cells customarily had only the chlorine entry channel. The mix-cake was molded at 130 ± 10 lb/sq in. and the evacuation time was increased to two days. The initial output of these cells was outstanding; at the end of the first 10 min of operation at atmospheric pressure, the cells had an output voltage of 2.0 volts at a current of 0.25 amp/sq in. The cells had a low specific internal resistance of 0.45 ohm-sq in. and an effective emf of 2.09 volts. As the cell was discharged, there was a gradual decline in output voltage. After 5 hr of operation the specific internal resistance had increased to 0.79 ohm-sq in.

(5) One of these cells was continuously discharged at 0.25 amp/sq in. at atmospheric pressure for 20 hr to a cutoff voltage of 1.73 volts. The voltage drop over the 20-hr period was only 13.5%, despite the relatively high power output.

(6) The incorporation of the mix-cake resulted in an electrode which is much less susceptible to variations in chlorine flow rate. With the older type of electrode, a negative pressure, caused by a drop in chlorine flow rate below that required by the current drain, resulted in the prompt failure of the electrode. The mix-cake eliminated this difficulty so that, if negative pressures of short duration were developed, a simple adjustment of the flow rate returned the cell to its previous output level.

d. Results - Intermediate Cells

(1) In an attempt to duplicate the results obtained with the small cells in which the mix cake molding pressure was 70 lb/sq in., several tests were conducted on intermediate cells. These cells were as nearly as possible identical with the small cells in structural details, except that in some instances holes parallel with the face were drilled in the cathodes to ascertain whether better chlorine distribution would result in a significant increase in output.

(2) Figures 10 and 11 are representative of the results obtained with cells employing cathodes of the intermediate size. At the end of one hour of operation the effective emf and the specific internal resistance were calculated to be 2.02 volts and 1.50 ohm-sq in. respectively. In this cell it was necessary to replace the zinc anode at the end of 45 hours. After 62 hours of operation, the bond between the zinc duplex and the carbon electrode had failed at several points, and the test was terminated.

(3) A new mix-cake and piece of zinc duplex were bonded to the diffuser element salvaged from the experiment described in paragraph b. The performance of the cell fabricated from this reconstructed cathode is given in Figure 10. After 1 hr of operation the effective emf and specific internal resistance were 2.09 volts and 2.20 ohm-sq in. respectively; the latter value represents an increase of 47%. Furthermore, for the same chlorine flow the chlorine pressure differential had increased from approximately 1/2 in. of $H_2SO_4$ during the previous test to 3 in. of $H_2SO_4$ during this test.

(4) Another intermediate-size cell was continuously discharged for 87 hours. In this instance the mix-cake molding pressure was 130 psig. Between the first and eighty-seventh hour the specific internal resistance increased from 1.34 ohm-sq in. to 2.40 ohm-sq in. The terminal voltage decreased from 1.73 volts to a final value of 1.33 volts at a current density of 0.25 amp/sq in. Again the anode was changed once at 28 hours and again at 60 hours. During the changing of the zinc anode, cracks in the mix-cake and bare spots at the edges of the carbon diffuser were noted. Furthermore, the mix-cake had lost its original firm texture.

(5) Figure 9 contains three curves which show the average operating characteristics of one of the small cells described in Section c above, compared with two of the intermediate-size cells, all after operation for one hour. The tests were conducted under the same conditions, except that four holes had been drilled in one of the larger cells. The lowest specific internal resistance was obtained in the small electrode (1.04 ohm-sq in.) Curve B however, for current densities up to about 0.5 amp/sq in., higher operating voltages were obtained from the larger electrode containing the four chlorine channels (Curve A), although the specific internal resistance in this instance was 1.41 ohm-sq in. The effective voltages for these cells were 1.88 and 2.08, respectively. The other large cell exhibited poorer operating characteristics than either of the above cells (Curve C). In this instance, a specific internal resistance of 1.96 ohm-sq in. and an effective emf of 2.05 volts were obtained.

(6) Several other tests were made on intermediate cells with one or four chlorine channels. Better operating characteristics were obtained with the large number of channels. In the latter instance, the operating voltages at a current density of 0.25 amp/sq in. ranged from 1.61 to 1.73 volts after 1 hour of cell operation, compared with 1.54 to 1.56 volts when only one chlorine channel was used. The chlorine inlet pressure ranged from 4 to 12 mm of sulfuric acid for the former cells to 100 to 150 mm of sulfuric acid for the latter.

(7) For both the large and small cells, it appeared that one of the limiting factors in the performance of the Type IV electrode was the rate at which the chlorine diffuses to and through the mix-cake. This was evidenced by the fact that while the cell was being discharged, a large increase in chlorine gas flow resulted in a sharp rise in the power output of the cell. After the chlorine flow rate was reduced to the usual value,

corresponding to 90% material efficiency, the output of the cell returned to its former level. As indicated by the experiments with intermediate cells, the magnitude of this response to changes in gas flow decreased with an increase in the number of chlorine distribution channels.

## 3. Cells with Type V Cathodes

### a. Development of the Resin-Bonded Mix-Cake

(1) Cells in operation for long periods with a water-based mix-cake failed because of deterioration of the chlorine cathode. It was thought that the primary reason for this failure was the gradual swelling of the mix-cake, which caused a loss of electrical contact between the carbon particles in the mix-cake and resulted in an increase in the internal resistance of the cell.

(2) Another adverse effect that resulted from the use of a water-based mix-cake soon became apparent in the cells on which shelf-life tests had been conducted. As the mix-cake dried it shrank and cracked (see Figure 12).

(3) To prevent the swelling of the mix-cake during cell operation, and to reduce the possibility of cracking on dry storage, a mix-cake was made as described in Section 2,a except that a solution of Glyptal and thinner was substituted for the water. The mix-cake formula, on the basis of 1 sq in. electrode area, was as follows:

0.18 g Cabot No. 2047 battery carbon black

0.8 cc Glyptal bonding solution (1 volume G.E. No. 1202 Glyptal to 3 volumes G.E. No. 1500 thinner)

The mix-cake was molded at a pressure of 130 lb/sq in., assembled to the diffuser, clamped, and then baked for 24 hr at 70°C.

### b. Flushing-Type Electrode with Resin-Bonded Mix-Cake (Type V)

(1) It had been determined that gases which were insoluble or only slightly soluble, in the electrolyte, and not utilized at the electrode, became entrapped in the porous carbon diffuser and seriously interfered with the diffusion of the chlorine to the interface. Previously these inert gases were removed from the diffuser element by evacuating the cell just prior to testing. While evacuation of the cell effectively prevented gas blocks, the method appeared to be impractical for the final application of the battery. As a result, the electrode was redesigned so that the entrapped air could be removed by flushing.

(2) The porous carbon diffuser was provided with an exit channel at the bottom of the electrode and parallel with the chlorine entry tube (see Figure 13). By first adding the electrolyte to the assembled cell so that the separator and mix-cake surface were wet, air could be removed from the entire electrode by flushing with chlorine, because the capillary action of the electrolyte at the wet face effectively prevented the escape of gas through the porous face.

c. Testing Procedure and Conditions

The electrolyte was first added to the cell until the entire separator area was wet. The exit tube was opened and the electrode was flushed with chlorine for 5 minutes. At the end of this time the exit tube was closed, and the chlorine flow was reduced to that corresponding to 90% efficiency. In some tests the exit tube was left open and an excess of chlorine was permitted to flow through the electrode.

d. Results and Discussion - Small Cells

(1) A very significant advance in cell performance was obtained by the use of the resin-bonded mix-cake. The anticipated gain in voltage vs time performance was realized. Several cells were operated for periods of 78 hr with only moderate cathode deterioration. At a current drain of 0.25 amp/sq in., the voltage drop caused by cathode deterioration over the operating life was 0.12 volt, or 0.0015 volt/hr.

(2) During the long tests, the zinc anode was replaced at approximately 30-hr intervals. The zinc anode efficiency was found to be 92 ± 5%.

(3) Another cause of voltage drop with time, in addition to that caused by the deterioration of the cathode, was evident in cells which were in operation for extended periods. This additional voltage drop was found to be associated with a black deposit, initially thought to be zinc particles, which had flaked off the anode and accumulated on the glass wool separator; however, an analysis of a sample of this deposit revealed that it was primarily lead, which constituted the major impurity in the zinc used as anodes (see Table II). Further reference to this problem will be found in later sections of the text.

(4) Figures 14 to 16 show the voltage vs time characteristics at 0.25 amp/sq in., as well as the voltage vs current characteristics at various times during the discharge at 0.25 amp/sq in. The data of Figure 17, calculated from Figures 14, 15, and 16, summarize the changes in internal resistance with time.

(5) The frequent changes of the anode were necessitated by a combination of slight local action and non-uniform usage. The unevenness of use resulted in an uneven corrosion pattern on the anode, leading to an apparent increase in internal resistance. Of equal importance in the progressive increase in internal resistance was the formation of the black deposit on the separator heretofore mentioned. Thus, a change in both the separator and anode resulted in a substantial recovery in operating voltage. The irreversible deterioration of the cathode accounted for the remainder of the internal-resistance rise. The test was terminated after 78 hr because chlorine had corroded through the zinc duplex backing on the cathode.

(6) The test described above also showed that an additional advantage was gained by the use of the resin-bonded mix-cake, i.e., a decrease in the cell polarization at high current drains. Figure 18 shows a comparison of performance of the best cell made with a water-based mix-cake with that of a cell made with a resin-bonded mix-cake. After 5 hr the internal resistance of the cell with the water-based mix-cake was 0.78 ohm-sq in., while that of the cell employing the resin-bonded mix-cake was 0.46 ohm-sq in. After 15 hr the difference in internal resistance was even greater (1.08 ohm-sq in. for the water-based mix-cake, 0.66 ohm-sq in. for the resin-bonded mix-cake). The polarization of cells utilizing the resin-bonded mix-cake was so low that the electrolyte resistance constituted one of the principal iR drops in the cell. The use of recirculated electrolyte of high zinc chloride concentration resulted in cells with an internal resistance low enough to make possible current densities of nearly 2.00 amp/sq in. at a cell voltage in excess of 1.00 volt. Power densities of 1.80 watts/sq in. were obtained after 31 hr of operation. The fact that this power is available from the cell does not alter the optimum operating conditions of approximately 0.25 amp/sq in. (Reference 2). However, the extra power is important in that the cell can be called upon in emergencies to deliver high power.

(7) One test was made on a cell in which the mix-cake was molded on the diffuser. The performance of this cell was, within experimental error, the same as that of cells in which the mix was molded on the separator. The test was discontinued after 8 hr. This molding technique was avoided when water-based mixes were used, because of the probability that the excess water from the mix would penetrate the diffuser and cause early failure of the electrode. With the present mix formulation this difficulty would not arise, and the contact resistance between mix-cake and diffuser should be uniformly low.

### e. Results - Intermediate Cells

Several tests were conducted in which both water-bonded and resin-bonded mix-cakes were used. Figure 19 shows the best results obtained using the two mix-cakes. It may be noted that the best results obtained thus far using a water-based mix-cake were realized; however, even better results were obtained using the resin-bonded mix-cake. At a current density of 0.25

amp/sq in. the operating voltages were 1.73 and 1.82 volts, respectively, after 1 hr of cell operation. The corresponding specific internal resistances were 1.12 and 0.74 ohm-sq in., respectively. In addition, for the resin-based mix-cake an output voltage of 1.90 volts and a specific internal resistance of 0.45 ohm-sq in. were obtained after 15 min of cell operation at 0.25 amp/sq in.

### f. Series Cells

#### (1) Description of Battery and Testing Procedure

(a) A number of three-, four-, and five-cell batteries were made using small cells in which the cathodes were fed chlorine from a common manifold. An excess of chlorine was kept flowing through the cells and a common exhaust manifold was used. Carbon taps were built into each cathode so that the voltage of each cell could be determined. The order of chlorine feed from the manifold was staggered, so that if any variation occurred because of pressure drop in the manifold, this variation could be distinguished from that due to a position in the cell stack, i.e., due to heat effects or short circuiting. The entire unit was spring-loaded in a clamping device. The series connections were made by cementing a 1/8-in.-thick piece of zinc to the zinc face of a sheet of zinc duplex, and by cementing the back side of a diffuser element to the carbon face of the duplex. The cement was a mixture of Glyptal resin and the same carbon used for the mix-cake, except that the resin-carbon ratio was very much higher.

(b) The first test was performed on a five-cell battery in which electrolyte was dripped over the separator of each cell. No edge insulation was used. In succeeding tests, the edge of each duplex electrode was covered with asphalt and 1/2-in. polystyrene insulating fins were added. The electrolyte was then simply sprayed over the entire battery from a showerhead device.

#### (2) Results and Discussion

(a) All of the five cells of the first battery had initial output voltages, within experimental error, equal to the average output voltage of a single small cell. The rate of failure, or drop in voltage, was very much greater than for single cells. This was found to be due to short circuiting of cells through electrolyte paths that formed on the sides and edges of the battery.

(b) The asphalt and polystyrene insulation eliminated the short circuiting in the succeeding tests. In the No. 3 cell of the second five-cell battery, asphalt penetrated the separator and restricted the electrolyte entry. The output of this cell was definitely lower than the other four of the battery (see Figure 20). This one defective cell did not affect the performance of the other cells. The test was discontinued after 8 hr.

(c) Failure of one four-cell unit was caused by premature failure of the carbon-zinc bond. Another four-cell unit using recirculated electrolyte was discharged at a constant current drain of 0.12 amp/sq in. for 23 hr. This battery had initial and final output voltages of 7.7 and 7.5, respectively. After 5 hr, the internal resistance of the battery was 0.48 ohm-sq in; the internal resistance of the individual cells ranged from 0.46 to 0.51 ohm sq in. After 23 hr, the internal resistance of the battery had increased to 0.70 ohm-sq in., and the variation of the internal resistance between the individual cells was quite large (0.50 to 0.90 ohm-sq in.). Inspection of the various cells disclosed that in Cell No. 1, which had the highest internal resistance (0.90 ohm-sq in.), small amounts of electrolyte had penetrated at various spots in the cathode and led to uneven corrosion of the zinc anode. Cell No. 4 (internal resistance of 0.63 ohm-sq in.) also showed uneven corrosion of the anode. Cells No. 2 and 3 (internal resistances of 0.50 and 0.55 ohm-sq in.) exhibited fairly even corrosion of the anodes.

(d) A three-cell unit which operated for 8 hr failed because a high spot, resulting from uneven corrosion of the zinc, punctured the separator and shorted the center cell.

### 4. Cells with Type VI (Diffusion-Feed) Cathodes

#### a. Introduction

Experiments were made with diffusion-feed electrodes in the hope that they would prove practical; their use would have resulted in a simplified cell construction. It was demonstrated, however, that there was a limitation to the maximum current as a result of the inability to remove air from the diffuser by flushing. In addition, wetting of the exposed diffuser edges by electrolyte was a major difficulty in long-term operation.

#### b. Description

(1) The Type VI diffusion-feed cathode is shown in Figure 21. There were no entry tubes or exit tubes in the diffuser element. Chlorine entered by diffusion through the open edges and bottom. The top of the electrode was covered with Carboline, and fins were provided to protect the sides of the electrode from wetting by the dripping electrolyte.

(2) Because the assembled cell was placed in a vessel filled with gaseous chlorine, the back of the zinc anode was coated with Glyptal in order to prevent chlorine attack during cell operation.

#### c. Preparation of the Mix-Cake -- Small Cells

(1) The substitution of a resin in place of water as the mix-cake binder eliminated the danger of premature wetting of the diffuser element. Thus, techniques involving the molding of the mix-cake directly on the diffuser element became acceptable. With this in mind, attention was turned

to the development of a mix-cake fabrication technique which would result in a uniform and firmly bonded mix-cake. The initial procedure evolved is as follows:

(a) A stainless steel mold was placed around the diffuser element; the height of the mold was such that the resulting cavity contained 0.18 gram of Cabot No. 2047 battery carbon black per sq in. of diffuser surface.

(b) The carbon black was added in excess by means of a flour sifter.

(c) A straight-edge leveling bar was then moved across the mold surface to remove the excess carbon.

(d) The carbon black in the mold was then covered with a piece of Munising paper (or Whatman No. 1 filter paper) to facilitate the removal of a porous carbon block which was saturated with bonding solution (see Section 3,a,(3)) and placed on the paper.

(e) The whole assembly was then pressed at 190 psi; and transfer of the bonding solution from the carbon block into the mix-cake occurred readily.

(f) The electrode assembly was then pressure-clamped and baked for 24 hr at 70°C.

(g) After bonding was completed, the paper was removed from the top of the mix-cake and the diffuser element was cemented to the zinc duplex.

(2) In order to minimize any edge effects, the dimensions of the carbon diffuser and its associated mix-cake were increased to 2 1/4 x 4 1/4 in. Henceforth, all references to "small" cells involve cathodes of these revised dimensions.

### d. Preparation of Mix-Cake - Intermediate Cells

Because molds of the type described in Section 4,f were unavailable, the mix-cakes used in the intermediate-size cells were molded directly on the separator as described previously.

### e. Results - Small Cells

Figure 22 illustrates the effect of prior evacuation on cell performance. At low chlorine pressures (15 psig), the cells tested without prior evacuation operated satisfactorily at current drains below

0.5 amp/sq in. However, as shown in Figure 22, at higher current drains there was a marked increase in cell polarization. Without prior evacuation, at low chlorine pressure, the residual air in the vessel contributes appreciably to the total gas concentration (50 mole% at 15 psig), and the rate of diffusion of chlorine through the diffuser to the interface is reduced. This results in increased polarization at higher current drains. As expected, at higher chlorine pressures (80 psig) where the residual air becomes a small portion of the total amount of gas, the cell operated satisfactorily even at higher current drains.

### f. Results and Discussion - Intermediate Cells

(1) Tests employing these cells were conducted to determine the effect of chlorine pressure on cell performance. Both Type V and Type VI electrodes were used at the desired pressures. It should be noted that a positive chlorine flow was maintained during tests with the Type V electrode. The effect of prior evacuation on Type VI electrodes was also studied.

(2) Typical results of the tests employing Type V electrodes may be found in Figure 23. The cell was initially operated at atmospheric pressure for 1 hr, after which the effective emf and specific internal resistance were determined. The cell was then sealed in the test vessel, the chlorine pressure was increased to 80 psig, and another set of polarization characteristics was determined. An effective emf of 2.02 volts and a specific internal resistance of 0.52 ohm-sq in. were obtained at atmospheric pressure, as compared with 2.10 volts and 0.50 ohm-sq in. at 80 psig. It may be noted from Figure 23 that although the internal resistance of the cell was relatively unaffected by the increased chlorine pressure, the cell operating voltages were increased by about 0.09 volt for comparable current drains. For instance, at a current density of 0.26 amp/sq in., operating voltages of 1.87 and 1.95 volts, respectively, were obtained.

(3) Figure 24 illustrates typical results obtained employing the Type VI electrode. In this test the cell was initially sealed in the test vessel and, after evacuation, chlorine was admitted until a pressure of 10 psig was attained. The cell was operated for 1 hr at a current density of approximately 0.25 amp/sq in., after which the polarization characteristics were determined. The chlorine pressure was then increased to 25 psig, and changes in the polarization characteristics were noted. At 10 psig the effective emf and specific internal resistance of the cell were 2.02 volts and 0.52 ohm-sq in., respectively, as compared with 2.06 volts and 0.53 ohm-sq in. at 25 psig. Although the internal resistance of the cell was not affected by the increased pressure, the operating voltages at comparable current drains were raised by about 0.025 volt. At a current density of about 0.25 amp/sq in. the cell voltages were 1.88 and 1.90, respectively.

(4) Figure 25 gives the results of a test utilizing a Type VI electrode without initial evacuation of the pressure vessel. Chlorine pressures were 10, 30, and 80 psig. The mole fractions of chlorine in the test vessel under these conditions were 0.405, 0.670, and 0.845, respectively. At 10 psig pressure, good cell performance was obtained up to current densities of about 0.5 amp/sq in. (i.e., 1.88 volts at 0.25 amp/sq in.); however, at higher current drains there was a marked increase in cell polarization. At current densities of 0.5 amp/sq in. and less, the effective cell emf was 2.03 volts and the specific internal resistance was 0.54 ohm-sq in. At 30 and 80 psig pressure, the voltage vs current density plots were linear up to the maximum current density utilized (approximately 1.0 amp/sq in.). At a current density of 0.25 amp/sq in., an operating voltage of 1.95 volts was obtained at 30 psig, as compared with 1.99 volts at 80 psig. The effective emf's were 2.07 and 2.11 at these pressures, and the specific internal resistances remained relatively constant at 0.43 and 0.41 ohm-sq in.

g. Although the Type VI cathodes appeared to perform as well or better than the flushing type of cathode previously described at moderate current densities, a major difficulty in the long-term operation of the cathodes was soon apparent. Cells of this type showed wetting around the edges as a result of the moist atmosphere to which they were exposed. It is conceivable that this wetting could become sufficiently serious to prevent or hinder adequate chlorine entry into the diffuser element. In addition, for operation at low pressures and relatively high current densities, this type of electrode requires evacuation before use. These observations led to the termination of experiments employing the Type VI electrodes in favor of Type VII, described in the following section.

### 5. Cells with Type VII Cathodes

#### a. Description

The structural features of the Type VII cathode are identical with those of Type V, illustrated in Figure 13. The fundamental difference lies in the fabrication of the mix-cake. The Type VII electrode (2-1/4 in. x 4-1/4 in. x 0.5 in.) employed a resin-bonded mix-cake molded directly onto the diffuser element by the technique described for the Type VI electrode.

#### b. Results and Discussion

The Type VII cathode as well as the Type VI cathode was employed in experiments especially designed to ascertain the cause or causes of non-uniform utilization of the zinc anodes. These results are given in Section 7, below.

### 6. Improved Diffuser to Zinc Duplex Bond

a. Introduction

Prior to this point in the program, the agent used to bond the diffuser element to the zinc duplex (i.e., to the anode of the next cell in a series battery) consisted of a thick paste of Glyptal and Cabot carbon black. After setting, this mixture formed a highly conductive but structurally weak bond.

b. Development

(1) In order to obtain a highly conductive, yet strong bond, Carbo-Fix liquid and Carbo-Fix powder (Carboline Co., St. Louis, Mo.) were substituted for Glyptal. The optimum proportions of Carbo-Fix liquid, Carbo-Fix powder, and Cabot No. 2047 carbon black were determined by preparing a mixture of 20 g of Cabot No. 2047 carbon black and 110 ml of Carbo-Fix liquid and adding various amounts of Carbo-Fix powder. Bonds of zinc duplex to diffuser element and zinc metal to diffuser element were then made.

(2) The samples were baked 4 hr at 140°C under a clamping pressure of 190 psi.

c. Results

Table III shows the resistivities of the resultant bonds. The bond strengths between zinc metal and diffuser elements were poor. On the other hand, the bond strengths between zinc duplex and diffuser elements were excellent. As anticipated, the higher the proportion of Carbo-Fix powder, the stronger was the bond. In the case of 20 and 30 wt.% Carbo-Fix powder, the resulting bond strengths were such that structural failure of the diffuser element occurred before that of the bond when the bonded pair was subjected to mechanical shock. Furthermore, attempts to strip the zinc duplex from the diffuser element resulted in the removal of the carbon backing of the zinc duplex.

### 7. Uneven Zinc Corrosion

a. Introduction

(1) At this stage in the program the problem of uneven zinc corrosion appeared to be the remaining obstacle in obtaining long service life. This uneven corrosion resulted in unused or little-used high spots on the zinc anode which had the effect of increasing the electrode spacing and hence the internal resistance of the cells. Furthermore, there were instances in which the unused portions of the zinc were sufficiently sharp to puncture the separator and short-circuit the cell.

(2) The experiments described in the following paragraphs were carried out to determine the cause of uneven zinc corrosion.

b. Results and Discussion

(1) Experiment No. 1

(a) A series of three experiments, performed under widely varying conditions, gave rise to zinc corrosion patterns of striking similarity. In each case there were wrinkle patterns on the mix-cake which were mirror images of the zinc corrosion pattern. The zinc corrosion pattern in all three instances consisted of a well-used center portion bounded by a slightly used border. The only feature common to the three cells was the fabrication of the mix-cakes at the same time, using the technique described for Type VI electrodes.

(b) The experimental conditions for the three tests were as follows:

Cell 1 - Type VII cathode, immersed, spacer (no separator), atmospheric pressure

Cell 2 - Type VII cathode, non-immersed, glass wool separator, atmospheric pressure

Cell 3 - Type VI cathode, non-immersed, Dynel separator, 15 psig chlorine pressure

All cells were discharged at high drain rates (1.0 to 2.0 amp/sq in.). After the first 10 to 15 minutes, all cells exhibited a gradual drop in load voltage. When the cathodes were sectioned, a darkened area was observed around the perimeter of the diffuser element of each of the three electrodes. The darkened area comprised approximately 1/2-in. lateral penetration. This closely matched the unused border of the zinc anodes. At that time it was believed that the darkened areas were due to excess Glyptal which had entered the diffusers during the mix-cake fabrication, in which case it was conceivable that the Glyptal-impregnated portion of the diffusers acted as a block to chlorine diffusion. In order to determine whether this was actually the case, Experiment No. 2 was performed.

(2) Experiment No. 2

Several Type VII electrodes were made in which 2 to 10 drops of pure Glyptal were placed on the center of the diffuser face prior to mix-cake fabrication. The cells utilizing these electrodes were discharged for 15 minutes at high currents and then disassembled. The tests made with the center-impregnated electrodes failed to disclose any corresponding non-uniformity at the zinc anode. However, the mix-cake surface continued to develop wrinkles at random spots which, as in previous cases, showed corresponding irregularities on the zinc surface. Close inspection of the wrinkled areas indicated that these were regions in which the mix-cake and diffuser were out of contact, causing high internal resistance at these points and resulting in decreased utilization of the corresponding zinc area.

### (3) Experiment No. 3

This experiment showed conclusively that poor bonding between the mix-cake and the diffuser element was responsible for irregularities in the zinc corrosion pattern. A Type VII cathode was constructed using a clamping device in which the clamping plate next to the mix-cake contained a small hole in its center. The cell was discharged under the same conditions as previously noted and, on disassembly of the cell, the anode exhibited a reproduction of this hole as an upraised portion on its surface.

### (4) Conclusions

The above experiments proved that good bonding between the mix-cake and diffuser was of primary importance in obtaining uniform utilization of the zinc anode. As a result, a revised method of mix-cake fabrication was developed.

## 8. Cells with Type VIII Cathodes

### a. Development

(1) In order to insure good bonding between the mix-cake and diffuser element over the entire electrode surface, the method of preparation of the mix-cake, as described previously for Type VI and VII cathodes, was modified.

(2) Since the tests with center-impregnated electrodes showed no detectable interference by the Glyptal spot to chlorine diffusion, there seemed no valid objection to impregnation of the entire diffuser with Glyptal during the preparation of the mix-cake.

(3) The new procedure for making the resin-bonded mix-cake is as follows: A piece of Whatman No. 1 filter paper is placed on a surface-ground steel plate. On top of the filter paper is placed a flat steel mold 2-1/4 x 4-1/4 in. in internal area and 3/32 in. deep. The depth of the mold is such that the resulting cavity will contain 0.18 g of Cabot No. 2047 battery carbon black per square inch of diffuser surface. The carbon black is added in excess by means of a flour sifter. A straight-edge leveling bar is then moved across the mold surface to remove the excess carbon. Another steel frame, 2-1/4 x 4-1/4 in. in internal area and 1/4 in. deep, is positioned over the mold by means of a series of guide pins. This frame serves as a guide when the diffuser element is placed on the carbon black. The diffuser element (Grade 40 or 60 as specified in each experiment), prior to being placed on the carbon black, is saturated with the bonding agent, a

mixture of Glyptal and thinner in the volume ratio, unless otherwise specified, of 1:3. After the diffuser is positioned in the guide, another surface-ground steel plate is placed on the diffuser element and the entire assembly is pressed at 190 psi for several minutes, the higher pressure ensuring better contact between the faces. The mold and guide are then removed, and the electrode is clamped at a pressure of 190 psi and baked for 24 hours at 70°C. After bonding is completed, any filter paper adhering to the mix-cake surface is removed by means of fine emery paper.

b. Testing Procedure and Conditions

(1) The physical assembly of the cells was identical with that used for cells employing the Type VII electrode.

(2) The tests were conducted at an accelerated rate, i.e., the cells were externally short-circuited in order to maintain the maximum current drain possible for a period of 5 hours.

c. Results and Discussion

(1) The results of the first test (using a Grade 60 porous carbon block are shown in Figure 26. The cell was discharged at a constant current density of 2.25 amp/sq in. for 5 hours. The specific internal resistance at the end of this period was 0.33 ohm-sq in. The load voltage at the drain of 2.25 amp/sq in. was 1.03 volts and remained relatively constant over the entire 5-hour period. At the conclusion of the test the cell was disassembled. The surface uniformity of the zinc was excellent. The surface of the mix-cake was free of wrinkles or any other indication of change.

(2) A test was conducted using a thinner-to-Glyptal ratio of 2 to 1 rather than 3 to 1. This cell was discharged at an average current drain of 1.5 amp/sq in. for 5 hr. The specific internal resistance of the cell was 0.50 ohm-sq in., and the load voltage dropped from 1.18 to 0.95 volts during the test. The zinc anode used in this test was only 1/8 in. thick, and substantial portions around the perimeter of the zinc had been completely used, resulting in a progressive voltage drop near the end of the test (see Figure 27). Once again the surface uniformity of the zinc was good, and the mix-cake was free of any visible, physical change. However, because of the lower power output of this cell, compared with that discussed in the previous paragraph, all subsequent mix-cakes were made using a thinner to Glyptal ratio of 5 to 1.

## 9. Additional Experiments

a. Effect of Temperature

(1) To measure the effect of temperature on cell performance, a cell employing a Type V cathode was discharged at a chlorine

pressure of one atmosphere inside a heated chamber. The electrolyte feed line was passed through the heating bath to preheat the electrolyte. The temperature recorded as that of the system was the temperature of the effluent electrolyte at the bottom of the chamber.

(2) The cell was discharged for one hour at room temperature (22°C) and then heated to 76°C in 20 minutes. The voltage rose from 1.92 to 1.95 at a drain of 2.00 amp (0.25 amp/sq in). The voltage returned to 1.92 when the system was cooled. This gain was approximately that expected on the basis of increased conductivity of the electrolyte. The opposite effect, caused by the decreasing solubility of chlorine with increasing temperature, was apparently negligible.

### b. Silicone-Bonded Mix-Cake

(1) A Type VIII cathode was fabricated in which Dow-Corning XR-807 silicone resin was used as the bonding agent. The XR-807 is an alkyd-silicone resin containing 25% silicone. The bonding mixture used was one part resin to four parts thinner. The cell employing this cathode was discharged for 3 hours at 2.0 amp/sq in. (see Figure 28). The specific internal resistance of the cell was 0.29 ohm-sq in. The corrosion of the zinc was very uniform, and the mix-cake surface showed no detectable change.

(2) As the above experiment indicates, there are other resins which can be used in place of Glyptal. The choice of Glyptal was dictated by convenience, and it is quite conceivable that an active search could reveal a bonding agent whose chemical inertness is equivalent to that of Glyptal but whose use might result in a cell with a lower internal resistance. Furthermore, the curing of Glyptal 1202 (a thermosetting resin) involves an oxidation process as well as heat conversion. It would be a distinct advantage to substitute a non-oxidizing, heat-convertible thermosetting resin.

### c. Effect of Increased Electrolyte Path

(1) A cell employing a Type V electrode whose dimensions were 2 in. x 8 in. x 0.5 in. was constructed. The method of electrolyte feed (i. e., with the electrolyte added at the top of the cell through a multiple dropper) was the same as in the normal-sized cells. Thus, the electrolyte path through the cell was effectively doubled.

(2) After 2 hours discharge at 1.5 amp/sq in., which is sufficient to give an interpretable anode corrosion pattern, the cell was disassembled and inspected. No detectable difference in corrosion occurred between the upper and lower portions of the electrode. This indicated that the present method of electrolyte entry was adequate for long cell configurations.

### d. Studies on Separator Materials

(1) The poor mechanical strength, as well as the difficulties in handling of glass wool, led to the search for a new separator material. The following materials were investigated:

(a) Webril, impregnated with Polyblend (Kendall Mills)

(b) Webril, impregnated with GRS latex (Kendall Mills)

(c) Glass-fiber paper (Hurlbut Paper Company)

(d) Non-woven Dynel mats (Kendall Mills)

(2) The impregnated Webril materials suffered progressive chemical deterioration during cell operation. No such failure occurred with Dynel or glass-fiber paper. However, after initial saturation of these two separators by electrolyte, there was little, if any, evidence of free passage of fresh electrolyte through the separators. As a result, concentration polarization caused rapid cell failure.

(3) The search for a new separator material is still in progress.

### e. Self-Leveling Ability of Anodes

(1) The anode in a cell system such as that under consideration is in principle self-leveling. Any raised portions of the anode surface would have a higher-than-average local current density and utilization rate because of the smaller electrode spacing and consequently smaller iR drop through the electrolyte. However, in practice, self-leveling of the anode does not occur if the cathode exhibits gross variations in properties. Cathodes embodying the improvements in mix-cake molding discussed in this report and so uniform that even relatively large variations in the anode surface are self-leveling, as the following experiment shows.

(2) A cell was discharged at high drain for 18.2 ampere-hours, using a smooth zinc anode, and then disassembled. Examination of the anode revealed a uniform corrosion pattern, indicating that the cathode had been properly fabricated.

(3) The same cathode was assembled into a cell with an anode which had an irregular corrosion pattern as the result of a previous cell failure. This cell was discharged at high drain for 1.4 ampere-hours and then disassembled. Examination of the zinc revealed that the corrosion pattern had become almost completely uniform, thus confirming the anticipated self-leveling capability of the present zinc-chlorine cells.

## 10. Cells with Type IX Cathodes

### a. Development

(1) As described, the mix-cake for Type VIII cathode was made on the surface of a piece of Whatman No. 1 filter paper. Presumably, almost any grade of filter paper would have been equally acceptable. After the Glyptal-bonded mix-cake was baked, the filter paper was removed from the mix-cake surface by means of fine emery paper. Generally, the latter operation resulted in variations in thickness and uniformity in any one mix-cake and between different mix-cakes.

(2) This undesirable variable was eliminated by substitution of 0.002-in.-thick aluminum foil for the filter paper. After baking, the foil was easily stripped off, leaving a clean, uniform mix-cake surface which required no further treatment.

(3) In many instances, at the conclusion of a test, a projection of unused zinc was found on a lower corner of the anode (Figure 29A). The projection appeared on the corner of the zinc directly opposite the sealed end of the chlorine exit hole. In such cases, the projection caused increasing separation between anode and cathode during operation, with a resultant increase in internal resistance. Frequently, this projection punctured the separator and short-circuited the cell, causing failure.

(4) In an attempt to eliminate this difficulty, the sealed end of the chlorine exit hole was opened and an exit tube was provided from each side of the cathode. This procedure resulted in the appearance of smaller projections, one on each lower corner of the anode (Figure 29B).

(5) It became apparent that the preliminary flushing of the porous cathode with chlorine did not remove residual air from the pores of the diffuser in the region immediately above the chlorine exit hole. Uniform utilization of zinc at the lower corners was achieved (Figure 29C) by extending the lower cathode at least 1/4 in. below the zinc anode, so that the region of the diffuser opposite the exit holes need not be cathodically active. In large cells it will be possible to effect this arrangement without significantly increasing the waste volume of the cell, although in the laboratory cells it results in a rather large ratio of total volume to active volume.

(6) Figure 30 is a sketch of the cathode currently used and represents what is considered the final design.

### b. Testing Procedure and Conditions

(1) All tests were conducted at atmospheric pressure using glass wool (Pyrex Catalogue No. 800) as the separator.

(2) The Glyptal-to-thinner ratio used for mix-cake fabrication was 1:3 in every instance.

(3) The general procedure for extended discharge tests was to subject the cell to a short (0.5 to 1.0 hr), high-drain (2.0 to 3.0 amp/sq in.) discharge. At the end of this period, if the cell showed no signs of failure (i.e., voltage drop), the circuit load was decreased to maintain a discharge rate of 0.25 amp.sq in. for the remainder of the test period.

### c. Results and Discussion - Extended Discharge Test No. 1

(1) This cell operated for a total of 170 hr, the last two-thirds of the period with a cracked diffuser. This successful operation with a broken cathode demonstrated the ability of the present design to perform under adverse conditions.

(2) Details of the construction and operation of the cell are given in Table IV and Figure 31. The diffuser was made of Grade 60 porous carbon. The zinc anodes, with an effective area of 7.3 sq in., were 1/4 in. thick (equivalent to 25 amp-hr/sq in.). The cell was operated at 0.275 amp/sq in., and each anode therefore had a theoretical operating life of 91 hr. New anodes and separators were installed approximately every 50 hr. The glass-wool separator was 0.045 in. thick and there was no initial high-drain discharge.

(3) When the first anode was changed after 49.3% of the theoretical life, examination showed that the zinc surface was rough, but uniformly used. However, there was evidence that the roughness of the zinc surface caused mechanical abrasion of the glass-wool separator, with the result that some of the sharper portions of the zinc surface penetrated the separator. This resulted in short-circuiting of the cell and, of course, declining cell voltage. Identical results were obtained with each anode used in the test; i.e., uniform zinc surface usage accompanied by roughening of the surface.

(4) Examination of the separators during each cell disassembly revealed the presence of the black, flaky deposit (principally lead) mentioned earlier in the report. Although surface amalgamation of the anodes had not entirely prevented formation of the deposit, it was eliminated in succeeding tests by the addition of a small amount of mercuric chloride to the electrolyte. It is believed that in the future, utilization of zinc of high purity (99.96 wt %) will eliminate the necessity of adding mercuric chloride to the electrolyte.

(5) It is of interest to note that each change of the anode resulted in an initial operating voltage which was higher than the initial operating voltage of the preceding electrode pair. Table IV shows that no significant decrease in initial internal resistance occurred with each

zinc change. No completely satisfactory explanation of this phenomenon has yet been advanced.

(6) At some time between 70 and 85 hours, the cathode was cracked across the center as a result of momentary excessive clamping pressure, but no immediate change in performance resulted. During succeeding cell disassemblies, electrolyte was prevented from penetrating through the crack by careful manipulation. There was, however, some evidence of local action on the anode, thus leading to a decrease in zinc utilization efficiency. However, the test was carried to conclusion.

(7) At the end of seven days of continuous operation the anode and separator were changed again, and the cell was operated at the high average current of 1.96 amp/sq in. for 3 hours. Cell performance is illustrated in Figure 32. The specific internal resistances at the beginning and end of the high-drain period were 0.39 ohm-sq in. and 0.54 ohm-sq in., respectively. This performance indicated that despite the crack, the cathode had not become substantially wet during the seven-day period.

(8) The effect on cell performance of electrolyte penetration through the crack was illustrated by the following experiment: Immediately after the high-drain operation of the cell (Paragraph 7, above), the current drain was re-established at 0.275 amp/sq in. and maintained for 11 hours. The cell voltage after 11 hours was 1.73 volts. At this point, chlorine feed was interrupted for 3.5 hours. When the chlorine feed was resumed, the initial cell voltage was down to 1.56 volts at 0.275 amp/sq in. Within 5 hours, the cell voltage had dropped to 0.82 volt, although the open-circuit voltage was still 2.11 volts. At this point, a new zinc anode was substituted, with no improvement in cell performance. After 1.3 amp hr, disassembly of the cell revealed almost no utilization of the lower half of the zinc anode. Large quantities of electrolyte could be blown from the exit tubes of the cathode. This experiment showed that deliberate interruption of chlorine supply to a defective cathode could cause failure, although by proper handling the cathode could be made to perform satisfactorily for an extended time.

(9) The completion of this test represented the first successful use of a single cathode for an extended period. The need for a separator with greater mechanical strength as well as the need for the elimination of the separator surface deposit was emphasized by this extended discharge test. Despite these defects, the test showed conclusively that a cathode constructed by the technique described herein is capable of operating for at least seven days without change or degeneration. Furthermore, utilization of the zinc surface has been shown to be uniform over extended periods of low-drain operation as well as over short periods of high-drain operation.

### d. Results and Discussion - Extended Discharge Test No. 2

(1) The cell used in this test was similar to that used in the first test except that the diffuser was of Grade 40 instead of Grade 60 porous carbon, and the separator was only 0.030 in. thick.

(2) An initial high-drain discharge of 8.8 amp-hr at 2.6 amp/sq in. established that the cathode was serviceable. During the test a current density of 0.25 amp/sq in. was maintained. The electrolyte used in this test contained 5g $HgCl_2$(in 100 ml 12N HCl) in 5 gal of simulated sea water. Further details of the construction and operation are given with the results in Table V and Figure 33.

(3) Operating voltages of this cell were higher than those of the previous cell. Furthermore, during the first 50 hours, the voltage dropped far less. The first anode was replaced after 55% of its theoretical operating life. A small leak developed in the cathode surface after approximately 80 hours, resulting in diminished cell efficiency (both chlorine and zinc) and necessitating increasingly frequent anode changes. These changes are indicated in Figure 33. Attempts to repair the leak permanently did not prove successful.

(4) Several points may be noted regarding the behavior of the cell after each anode change. First, the initial operating voltage became lower after the leak had developed. Second, the decline in cell voltage became increasingly rapid with each zinc change. Furthermore, each succeeding anode revealed a poorer corrosion pattern. Obviously, in this case, the leak not only permitted chlorine to escape through the mix-cake but also permitted electrolyte to penetrate into the cathode. This led to improper chlorine distribution within the diffuser and, as a result, to poorer and poorer corrosion patterns.

(5) At the conclusion of the seven-day period, the cathode surface appeared unchanged. It was apparent that Grade 40 carbon could be successfully used as a diffuser. The sudden decline in performance of the cell after 80 hours was due to the development of a chlorine leak near the edge of the cathode, rather than to an inherent inability of the cathode to perform for the required period.

### e. Results and Discussion - Extended Discharge Test No. 3

(1) In this test, the cell, which contained a Grade 40 porous-carbon diffuser, was assembled with a single zinc anode 3/4-in. thick, sufficient for cell operation during the entire test period. The anode was made by clamping together six 1/8-in.-thick surface-amalgamated zinc pieces for 1 hr.

(2) Separator thicknesses of 0.030 in. during the first 96 hr and 0.045 in. for the last 72 hr were used. The electrolyte contained $HgCl_2$ as in Test No. 2. The preliminary high-drain discharge at 2.5 amp/sq in. was for 9.0 amp-hr; the rate during the test was 0.25 amp/sq in. Further details of the test are given in Table VI and Figure 34.

(3) Figure 34 indicates a remarkable improvement in extended operation. The initial drop from 1.77 volts to 1.65 volts represents normal cell performance when cell operation is changed to low-drain discharge after a period of high-drain discharge. Visual observation showed that the second drop, from 1.65 volts to 1.61 volts, occurred as the first interface was reached. At and beyond this point, the cell maintained remarkable stability at 1.61 volts for a continuous period up to 136 hours (96 hours at 1.61 volts). At 136 hours, a 2-hour interruption in chlorine feed effected a sufficient increase in internal resistance to cause a voltage drop to approximately 1.51 volts, where it remained until the end of the seven-day period.

(4) At 96 hours, a decrease in the open-circuit voltage indicated that cell disassembly was advisable. It was discovered that conditions at the anode and cathode surface were excellent, but that mechanical abrasion had caused enough tearing of the separator to produce some contact between anode and cathode. Figure 35 is a picture of the separator. A new 0.045-in. thick separator was installed, and the test was resumed with no change in operating voltage. The mechanical abrasion was probably caused by relative movement of anode and cathode as the cell clamp is tightened; a more efficient clamping device now being designed will eliminate this trouble.

(5) The interruption of chlorine flow resulted in some electrolyte penetration into the cathode, with a subsequent increase in internal resistance. The operating voltage of the cell remained at approximately 1.50 volts from 168 hours until about 175 hours, after which a steady decline began. At 190 hours, the cell voltage was down to 1.15. Disassembly of the cell at this point revealed that much less of the upper half of the zinc had been utilized than the lower half, indicating that the upper portion of the cathode had become wet with electrolyte during chlorine interruption. The cathode surface condition appeared excellent after 190 hours, and the corrosion pattern of the zinc surface, although higher in the upper portion, was free from gross surface irregularities. Judging from the performance of the cell during the first 136 hours, and the condition of the anode and cathode at the conclusion of the test, it appears highly probable that stable cell operation can be obtained for extended periods.

### f. Conclusions

The successful completion of extended discharge test No. 3 indicated that the final design of the cathode was intrinsically sound. Its ability to operate for extended periods has been demonstrated. Consequently it was believed that the time had arrived to attempt a scaling up of the small cell to a size which might be considered as a small operational unit. The results of such efforts are described in the following section.

## 11. Large Cells - Type IX Cathodes

### a. Introduction

(1) One-foot-square cells were constructed using as nearly as possible the preparative technique developed for the small cells. A cell this size is large enough to be considered a small operational unit, inasmuch as a 440-v battery of such cells would deliver approximately 15,000 watts at the most economical drain of 0.25 amp/sq in. At maximum power, such a battery would deliver close to 50,000 watts, at approximately 240 v.

(2) The first of these large cells tested gave outstanding performance during the initial 24 hr. Performance thereafter was impaired by wetting of the electrode, a result of an imperfection in the electrode surface that would not be present in a production cell.

(3) A special set of molds and an associated clamping device were designed and fabricated in order to prepare the mix-cake by the technique developed for the Type IX cathode. An additional refinement in the clamping device provided for the removal of thinner vapors from, and the drawing of air through, the diffuser element during the baking period.

### b. Testing Procedures and Conditions

The diffuser element was of Grade 40 Carbocell and the separator thickness was 0.030 in. The electrolyte, which contained $HgCl_2$ as described in the previous section, was re-circulated during the test. No preliminary high-drain discharge was made, the current being adjusted immediately to 0.25 amp/sq in., where it was maintained throughout the test period.

### c. Results and Discussion

#### (1) Results

(a) Figure 36 illustrates the results of the initial test of a large cell. The performance of the cell during the first 24 hr operating period was very good, being comparable with that of small cells. The terminal voltage varied from an initial value of 1.68 volts to a final value of 1.72 volts. The specific internal resistance at 1 and 5 hr was found to be 0.65 ohm-sq in.

(b) Figure 36 compares the 24-hr performance of the large cell and the small cell in extended discharge test No. 3. It is apparent that the scaling-up process was accomplished with no loss in performance at moderate current drains, demonstrating the feasibility of fabricating operational-unit size cells.

(c) Shortly after the 24-hr period, a 3-hr interruption of chlorine flow during the night resulted in sufficient wetting of the cathode to cause gradual cell failure. However, in order to develop a definite corrosion pattern, the discharge of the cell was continued at 0.25 amp/sq in. until a total of 56 hr had passed, at which time the voltage was still 1.28. The test was then terminated.

### (2) Discussion

It has been demonstrated that large cells can be made that almost duplicate the performance of small cells. It is important that such good performance was obtained with the first large cell tested, after a 20-fold scale-up from the small size. The experience gained in the fabrication of this cell will enable succeeding cells to give performance equal to or better than that of small cells.

## C. MAGNESIUM-OXYGEN CELLS

### 1. Introduction

Early in the year efforts were made to develop a magnesium-oxygen cell in which the difficulties associated with basic deposits on the anode could be overcome. An investigation was made of the feasibility of using a recirculating, chlorine-free electrolyte in the cell in addition to the adaptability of Air-Cell carbon cathodes to the magnesium-oxygen system. Because the results obtained contrasted so unfavorably with the then known characteristics of the zinc-chlorine system, further work on magnesium-oxygen cells did not appear warranted.

### 2. Results and Discussion

#### a. Magnesium-Oxygen Cells with Air-Cell Carbon Cathodes

(1) When an Air-Cell carbon cathode with forced air flow (Section A,3,(b),(5)) was used with a magnesium anode in a saturated ammonium chloride electrolyte, an initial performance of 1.18 volts at 0.15 amp/sq in. was obtained, but the voltage fell rapidly. Examination revealed that the electrolyte had penetrated approximately 0.25 in. into the carbon in an hour.

(2) Acid electrolyte (0.5N hydrochloric acid) penetrated the Air-Cell carbon even more rapidly, and within an hour a steady 0.89 volt at 0.15 amp/sq in. was reached, owing entirely to hydrogen evolution on the cathode; i.e., the output of the cell remained constant long after the air supply was cut off.

(3) It must be assumed, therefore, that the Air-Cell carbon developed for use in an alkaline cell is probably unsuitable for long-term use in neutral or acid electrolytes.

### b. Magnesium Hydroxide Precipitate

(1) In order to determine the feasibility of using a recirculating, chloride-free electrolyte in the cell, with magnesium hydroxide removed from the cell effluent by filtration, the following test was made. The object was to find the amount of electrolyte that would be removed from the circulating system with the magnesium hydroxide and hence would have to be supplied as makeup.

(2) A piece of magnesium was completely anodized in sodium sulfate solution and the precipitate was filtered and weighed. The cathode was pure silver sheet. An external emf was applied. The current density varied from 0 to 0.4 amp/sq in. for 24 hr; the magnesium current efficiency was found to be 59%.

(3) It was found that, for 38.4 g of magnesium used, 452.3 g of precipitate was formed as a wet filter cake. This corresponds to 20 moles of water per mole of magnesium hydroxide. Thus, the use of magnesium anodes appears to be ruled out, as it is not feasible to carry or produce enough chloride-free water to make up for that lost in the filter cake.

## REFERENCES

1. Aerojet Report No. 575, 11 January 1952 (Confidential)
2. Aerojet Report No. 665, 6 January 1953 (Confidential)

## TABLE I

### COMPOSITION OF SIMULATED SEA WATER*

| Salt | g/kg |
|---|---|
| NaCl | 26.518 |
| $MgCl_2$ | 2.447 |
| $MgSO_4$ | 3.305 |
| $CaCl_2$ | 1.141 |
| KCl | 0.725 |
| $NaHCO_3$ | 0.202 |
| NaBr | 0.083 |
| | 34.421 |
| | water to 1000.00 |

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* Sverdrup et al., The Oceans, Prentice-Hall, Inc., New York, 1942, p. 186.

## TABLE II

## ANALYSIS OF SEPARATOR DEPOSIT AND ZINC

| Element | % Composition<br>Zinc Anode | <br>Separator Deposit |
|---|---|---|
| Aluminum | | 0.0063 |
| Bismuth | | 0.023 |
| Boron | | 0.028 |
| Cadmium | 0.05 | 0.11 |
| Calcium | | 0.18 |
| Chromium | | 0.00068 |
| Copper | | 0.15 |
| Gallium | | 0.067 |
| Iron | 0.03 | 0.27 |
| Lead | 0.30 | 80.00 |
| Magnesium | | 0.21 |
| Manganese | | 0.0015 |
| Mercury | | 5.00* |
| Silicon | | 0.059 |
| Silver | | 0.0046 |
| Tin | | 0.042 |
| Zinc | 99.62 | 2.40 |
| Chloride | | 6.10** |

* Most, if not all, the mercury comes from the amalgamation of the anode.

** Chloride comes from the electrolyte.

## TABLE III

### RESISTIVITIES OF CARBO-FIX BONDS

Basic Mixture: 20 g Cabot No. 2047 battery carbon black
110 ml Carbo-Fix liquid

| Wt% Carbo-Fix Powder | Type of Bonded Element | Resistance ohm-sq in. |
|---|---|---|
| 0 | Zinc duplex-diffuser | 0.725 |
| 10 | ↓ | 0.712 |
| 20 | ↓ | 0.029 |
| 30 | ↓ | 0.016 |
| 0 | Zinc metal-diffuser | Bond failure |
| 10 | ↓ | 0.336 |
| 20 | ↓ | 0.322 |
| 30 | ↓ | 0.420 |

## TABLE IV

## EXTENDED DISCHARGE TEST NO. 1

Cell Behavior With Time (see Figure 31)

| Time (hr) | Cell voltage | Effective specific internal resistance, $R_i$ (ohm - sq in.) |
|---|---|---|
| 0.5 | 1.71 | --- |
| 2 | ---- | 0.39 |
| 8 | 1.67 | ---- |
| 16 | 1.65 | ---- |
| 22 | ---- | 0.66 |
| 24 | 1.58 | ---- |
| 32 | 1.48 | ---- |
| 40 | 1.29 | ---- |
| 45 | 1.31 | 0.85 |
| 45* | 1.74 | 0.40 |
| 48 | 1.75 | ---- |
| 56 | 1.74 | ---- |
| 64 | 1.65 | ---- |
| 68 | ---- | 0.70 |
| 72 | 1.55 | ---- |
| 80 | 1.47 | ---- |
| 88 | 1.40 | ---- |
| 90 | 1.34 | 0.87 |
| 90* | 1.73 | 0.42 |
| 92 | ---- | 0.39 |
| 96 | 1.75 | 0.39 |
| 100 | ---- | 0.40 |
| 104 | 1.76 | ---- |
| 112 | 1.69 | ---- |
| 117 | ---- | 0.85 |
| 120 | 1.56 | ---- |
| 124 | ---- | 1.27 |
| 128 | 1.42 | ---- |
| 136 | 1.42 | ---- |
| 141 | 1.28 | 1.40 |
| 141* | 1.76 | 0.39 |
| 143 | ---- | 0.41 |
| 144 | 1.82 | ---- |
| 147 | ---- | 0.41 |
| 149 | ---- | 0.41 |
| 152 | 1.80 | ---- |
| 160 | 1.71 | 0.52 |
| 170 | 1.68 | 0.65 |

---

* Zinc anode and separator were changed.

## TABLE V

### EXTENDED DISCHARGE TEST NO. 2

Cell Behavior With Time (see Figure 33)

| Time (hr) | Cell voltage | Effective specific internal resistance, $R_i$ (ohm - sq in.) |
|---|---|---|
| 0.5 | 1.78 | 0.30 |
| 8 | 1.77 | ---- |
| 16 | 1.80 | 0.42 |
| 24 | 1.80 | ---- |
| 32 | 1.75 | ---- |
| 40 | 1.71 | 0.57 |
| 48 | 1.72 | ---- |
| 52 | 1.62 | 0.84 |
| 52[*] | 1.86 | 0.33 |
| 56 | 1.83 | ---- |
| 64 | 1.84 | ---- |
| 72 | 1.82 | 0.43 |
| 80 | 1.83 | ---- |
| 88 | 1.75 | ---- |
| 92 | 1.53 | 0.85 |
| 92[*] | 1.73 | 0.48 |
| 96 | 1.70 | ---- |
| 104 | 1.59 | ---- |
| 112 | 1.32 | 0.99 |
| 112[*] | 1.72 | 0.50 |
| 120 | 1.68 | ---- |
| 128 | 1.58 | ---- |
| 136 | 1.50 | ---- |
| 139 | ---- | 1.19 |
| 144 | 1.46 | ---- |
| 152 | 1.44 | ---- |
| 160 | 1.32 | ---- |
| 166 | ---- | 1.38 |
| 170 | 1.20 | 1.45 |

---

[*] Zinc anode and separator were changed.

## TABLE VI

### EXTENDED DISCHARGE TEST NO. 3

### Cell Behavior With Time (see Figure 34)

| Time (hr) | Cell voltage | Effective specific internal resistance, $R_i$ (ohm - sq in.) |
|---|---|---|
| 0.5 | 1.77 | 0.30 |
| 8 | 1.75 | ---- |
| 16 | 1.65 | ---- |
| 24 | 1.66 | 0.40 |
| 32 | 1.66 | ---- |
| 40 | 1.61 | ---- |
| 48 | 1.61 | 0.43 |
| 56 | 1.62 | ---- |
| 64 | 1.61 | ---- |
| 72 | 1.62 | 0.43 |
| 80 | 1.61 | ---- |
| 88 | 1.59 | ---- |
| 96* | 1.58 | 0.50 |
| 104 | 1.62 | ---- |
| 112 | 1.59 | ---- |
| 118 | ---- | 0.66 |
| 120 | 1.61 | ---- |
| 128 | 1.59 | ---- |
| 136 | 1.60 | ---- |
| 144 | 1.52 | 1.39 |
| 152 | 1.53 | ---- |
| 160 | 1.50 | ---- |
| 168 | 1.48 | 1.49 |

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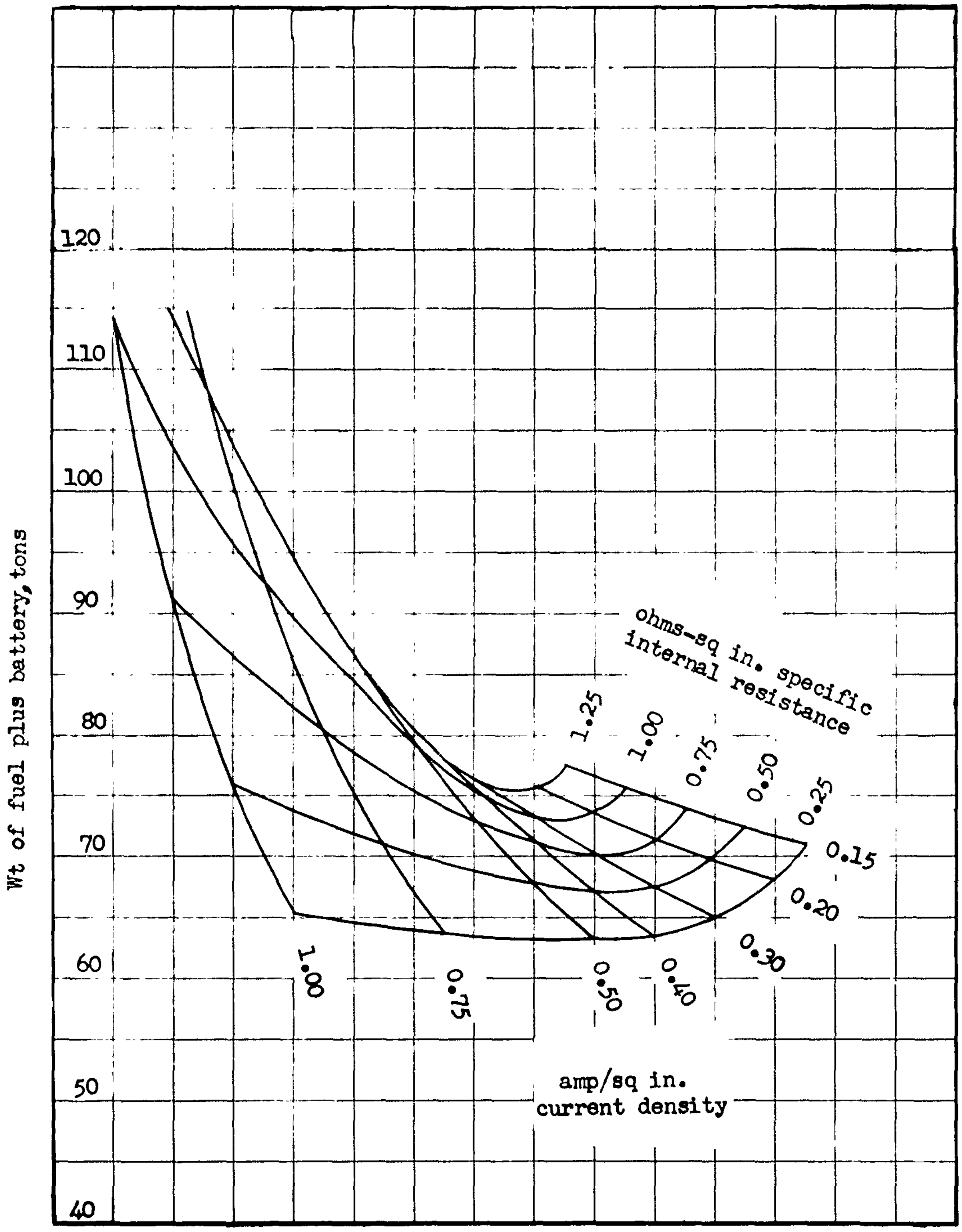
* Separator replaced.

C-3277 LJE:JDM/em 11-11-52

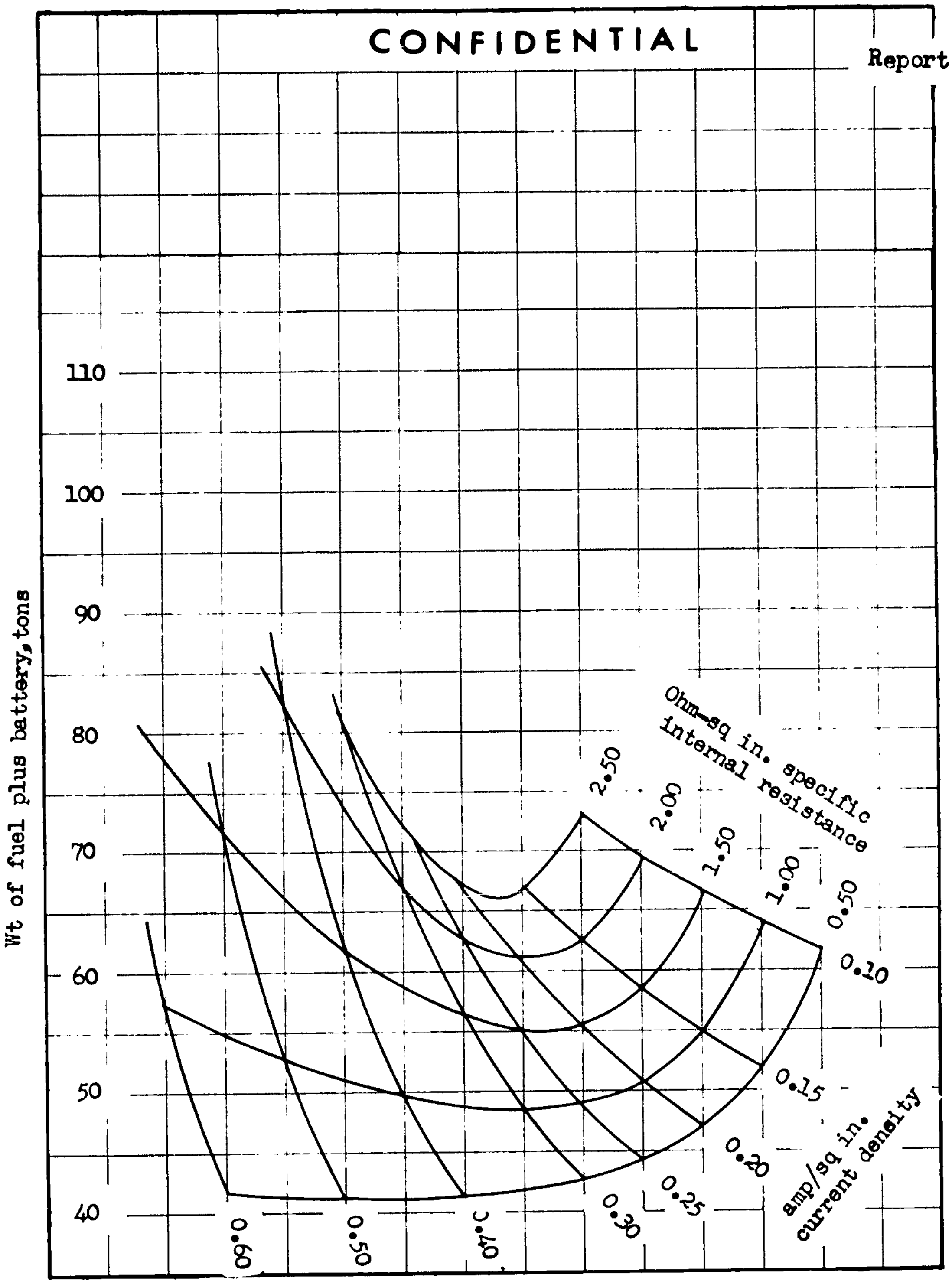


WEIGHT OF ZINC—CHLORINE SYSTEM

Reactant and electrode weight needed for 7 day operation at 209 kw and 440 volts.
Effective emf, 2.00 volts
Zinc efficiency, 90%
Chlorine efficiency, 90%

Figure 1

C-3280 LJG*JDM/em 11-11-52



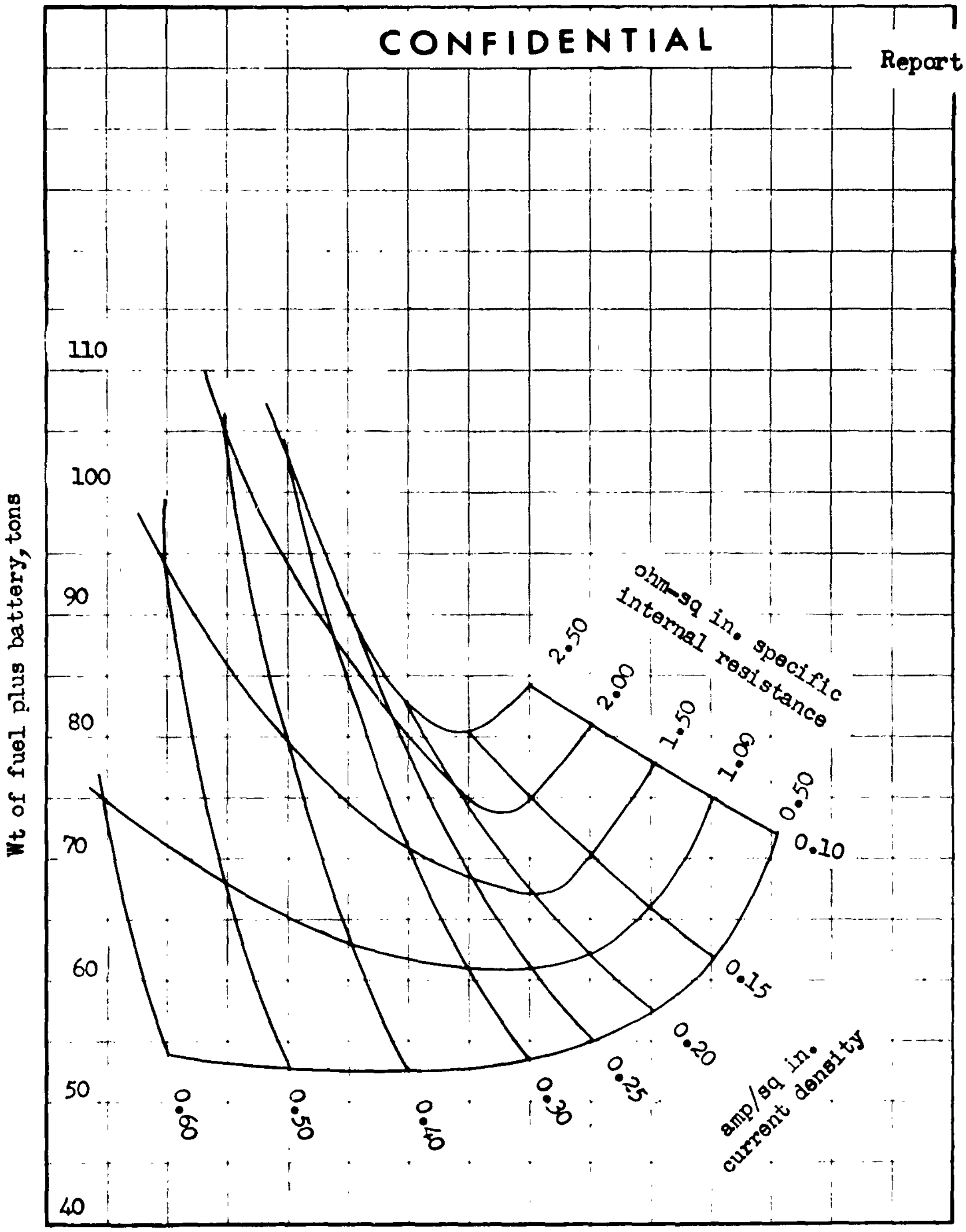
WEIGHT OF MAGNESIUM—OXYGEN SYSTEM

Reactant and electrode weight needed for 7 day operation at 209 kw and 440 volts.
Effective emf, 1.40 volts

Magnesium efficiency, 67%
Oxygen efficiency, 95%

Figure 2

C-3278 LJG*JDM/em 11-11-52

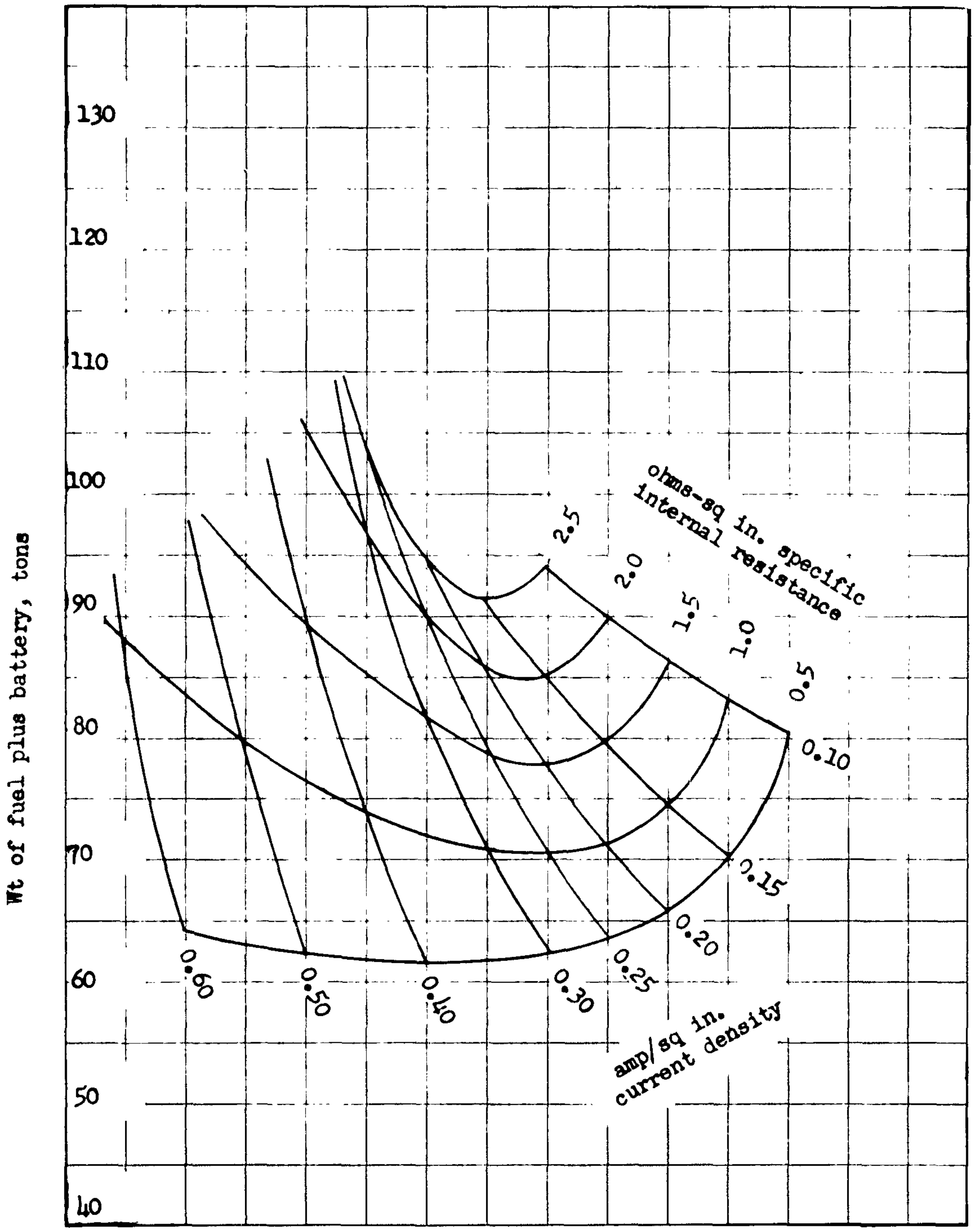


WEIGHT OF MAGNESIUM—OXYGEN SYSTEM
Oxidizer carried as $H_2O_2$

Reactant and electrode weight needed for
7 day operation at 209 kw and 440 volts.
Effective emf, 1.40 volts
Magnesium efficiency, 67%
Oxygen efficiency, 95%

Figure 3

C-3341 JDM:em 12-30-52



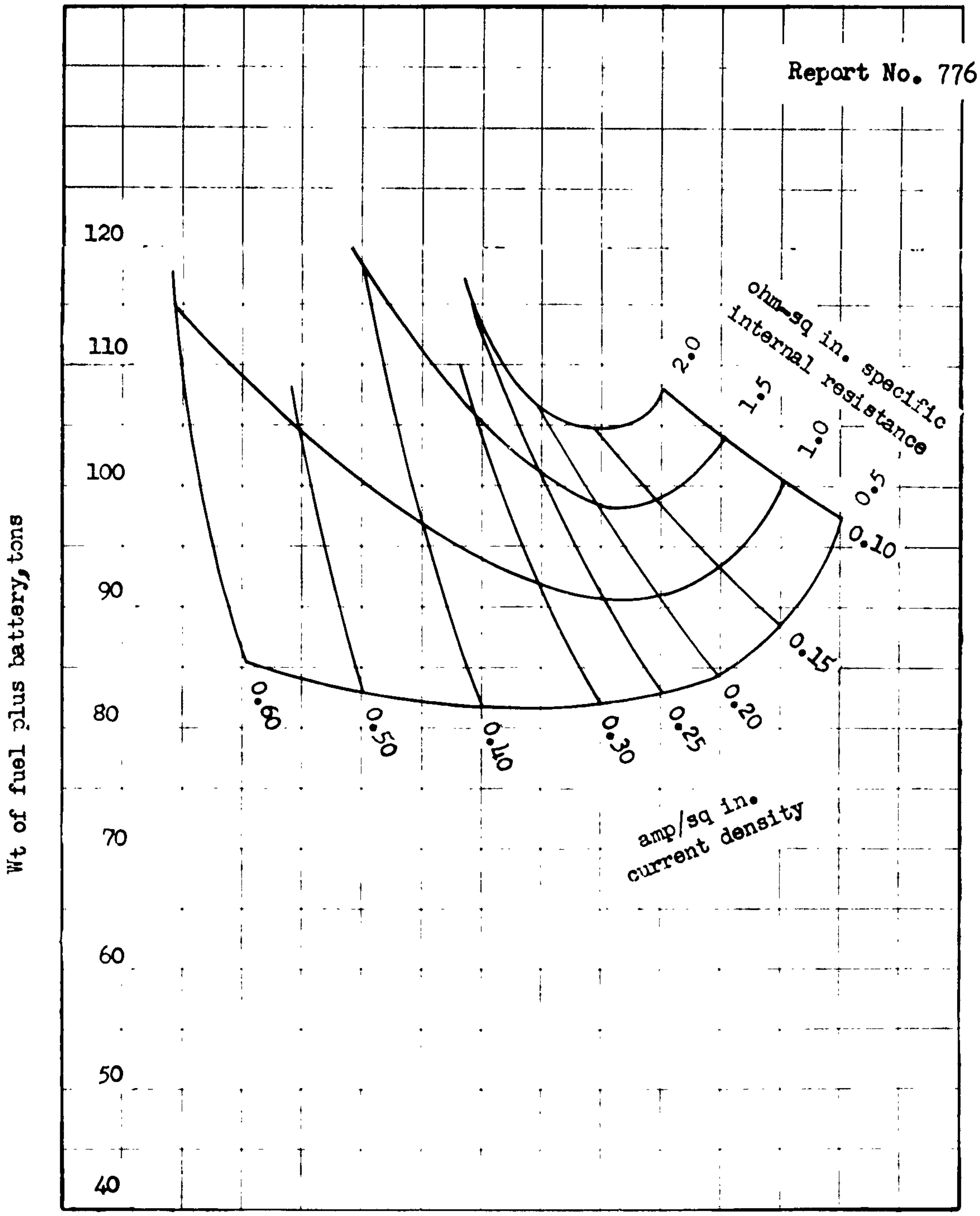
WEIGHT OF MAGNESIUM---OXYGEN SYSTEM
Oxidizer carried as $H_2O_2$

Reactant and electrode weight needed for
7 day operation at 209 kw and 440 volts.
Effective emf, 1.40 volts
Magnesium efficiency, 67%
Oxygen efficiency, 67%

Figure 4

Report No. 776

C-3279 LJG*JDM/em 11-11-52



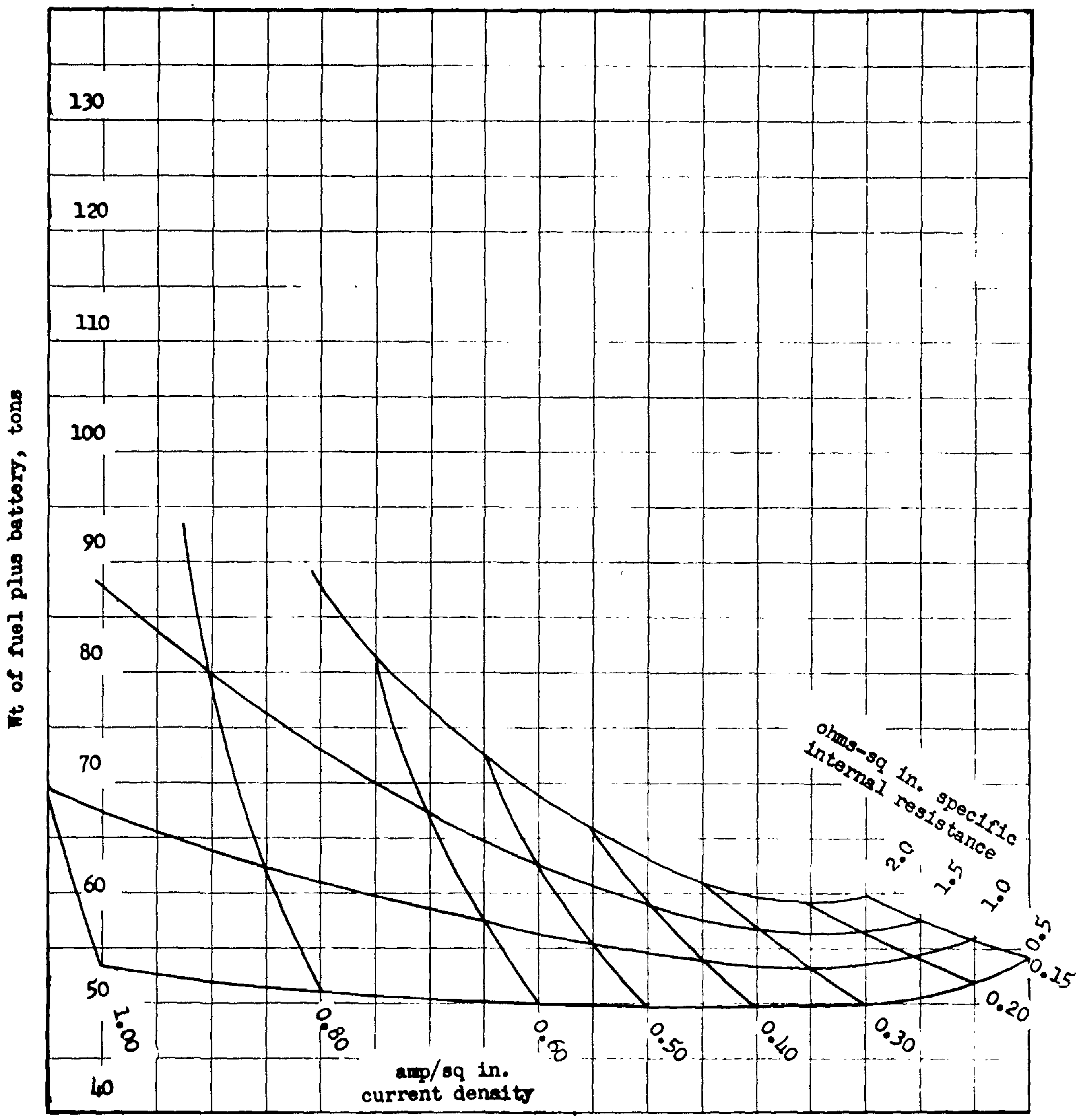
WEIGHT OF MAGNESIUM—OXYGEN SYSTEM
HCl Carried for Electrolyte

Reactant and electrode weight needed for 7 day operation at 209 kw and 440 volts. Effective emf, 1.50 volts

Magnesium efficiency, 67%
Oxygen efficiency, 95%

Figure 5

C-3342 JDM:em 12-30-52

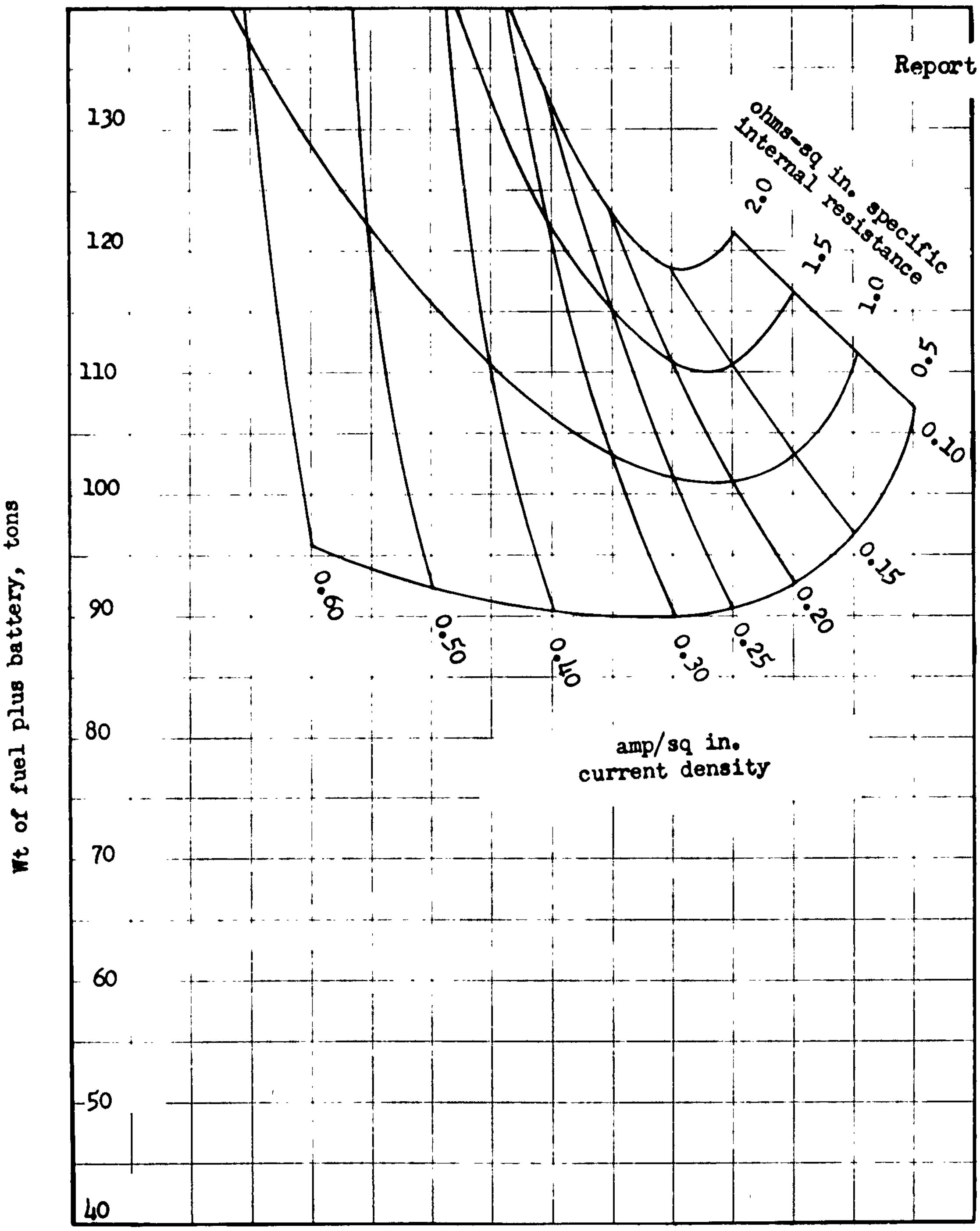


WEIGHT OF MAGNESIUM-CHLORINE SYSTEM

Reactant and electrode weight
needed for 7 day operation at
209 kw and 440 volts
Effective emf, 2.64 volts
Magnesium efficiency, 50%
Chlorine efficiency, 90%

Figure 6

C-3340 JDM:em 12-30-52

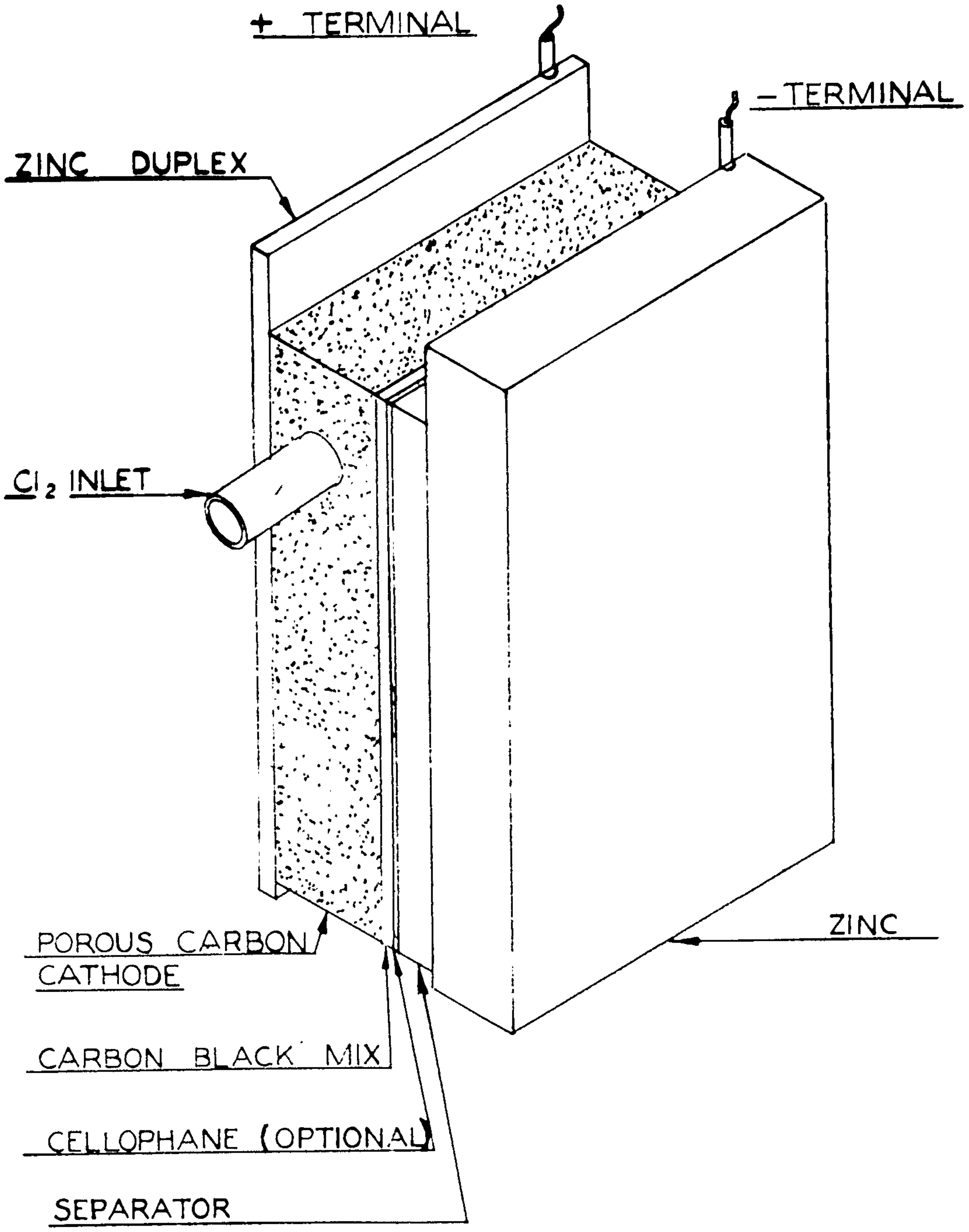


WEIGHT OF ZINC—LITHIUM OXIDE—
FREE AIR SYSTEM

Reactant and electrode weight
needed for 7 day operation at
209 kw and 440 volts.
Effective emf, 1.30 volts
Zinc efficiency, 90%

Figure 7

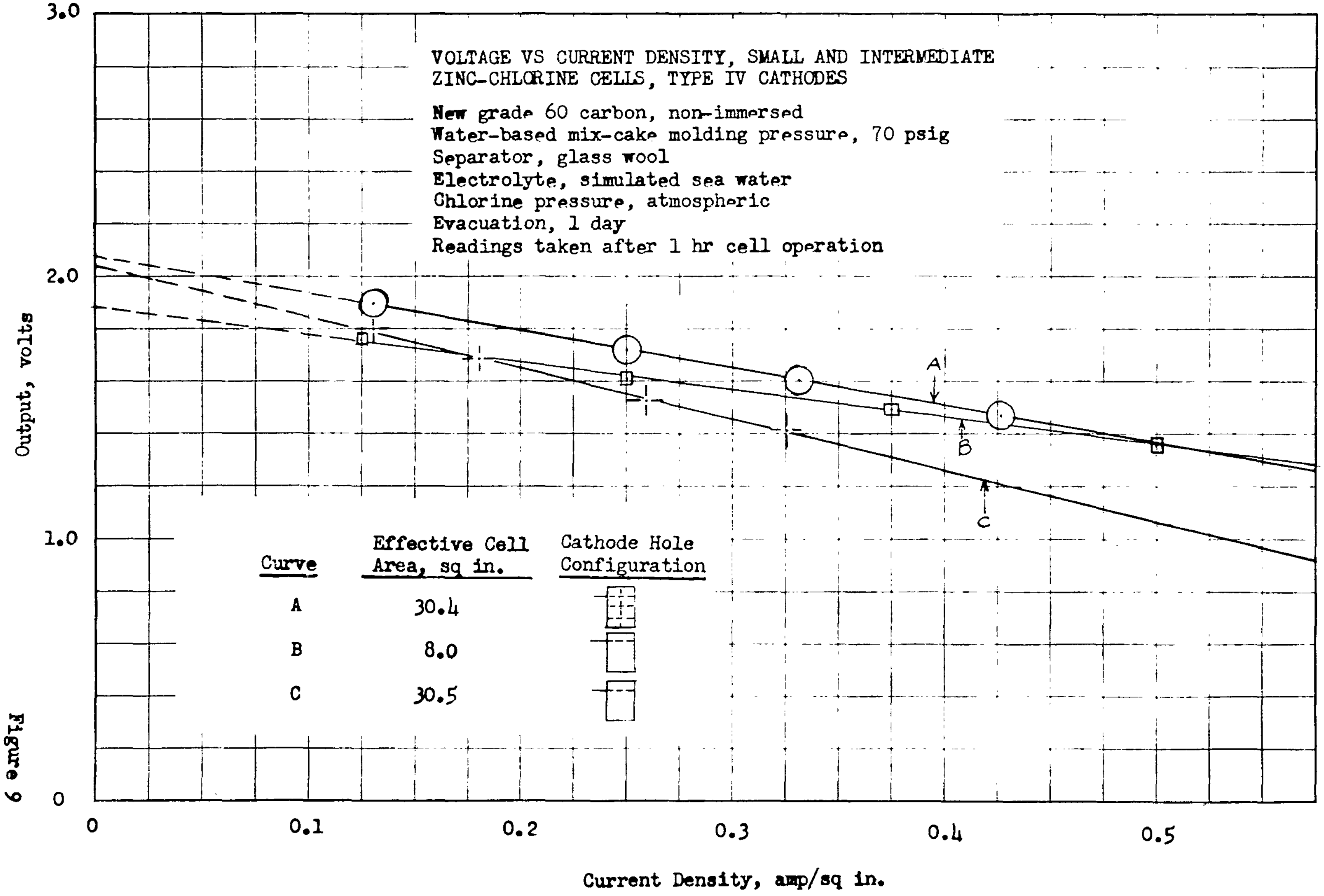
C-3282 LJC 11-12-52



TYPE IV CHLORINE CATHODE IN A ZINC-CHLORINE CELL

Figure 8

C-3344 EPD:em 1-12-53

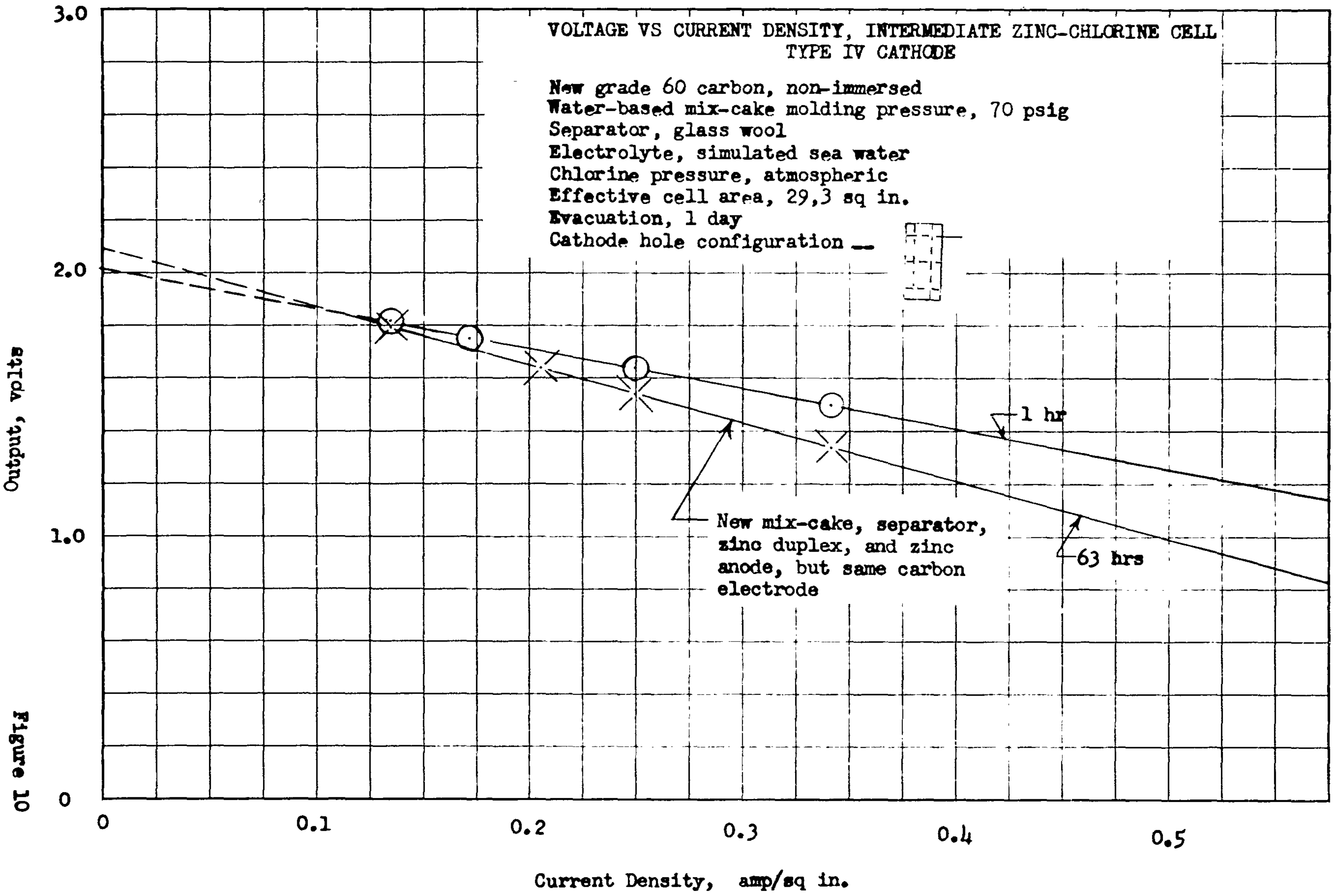


VOLTAGE VS CURRENT DENSITY, SMALL AND INTERMEDIATE ZINC-CHLORINE CELLS, TYPE IV CATHODES

New grade 60 carbon, non-immersed
Water-based mix-cake molding pressure, 70 psig
Separator, glass wool
Electrolyte, simulated sea water
Chlorine pressure, atmospheric
Evacuation, 1 day
Readings taken after 1 hr cell operation

Figure 9

C-3345 EPD:em 1-12-53

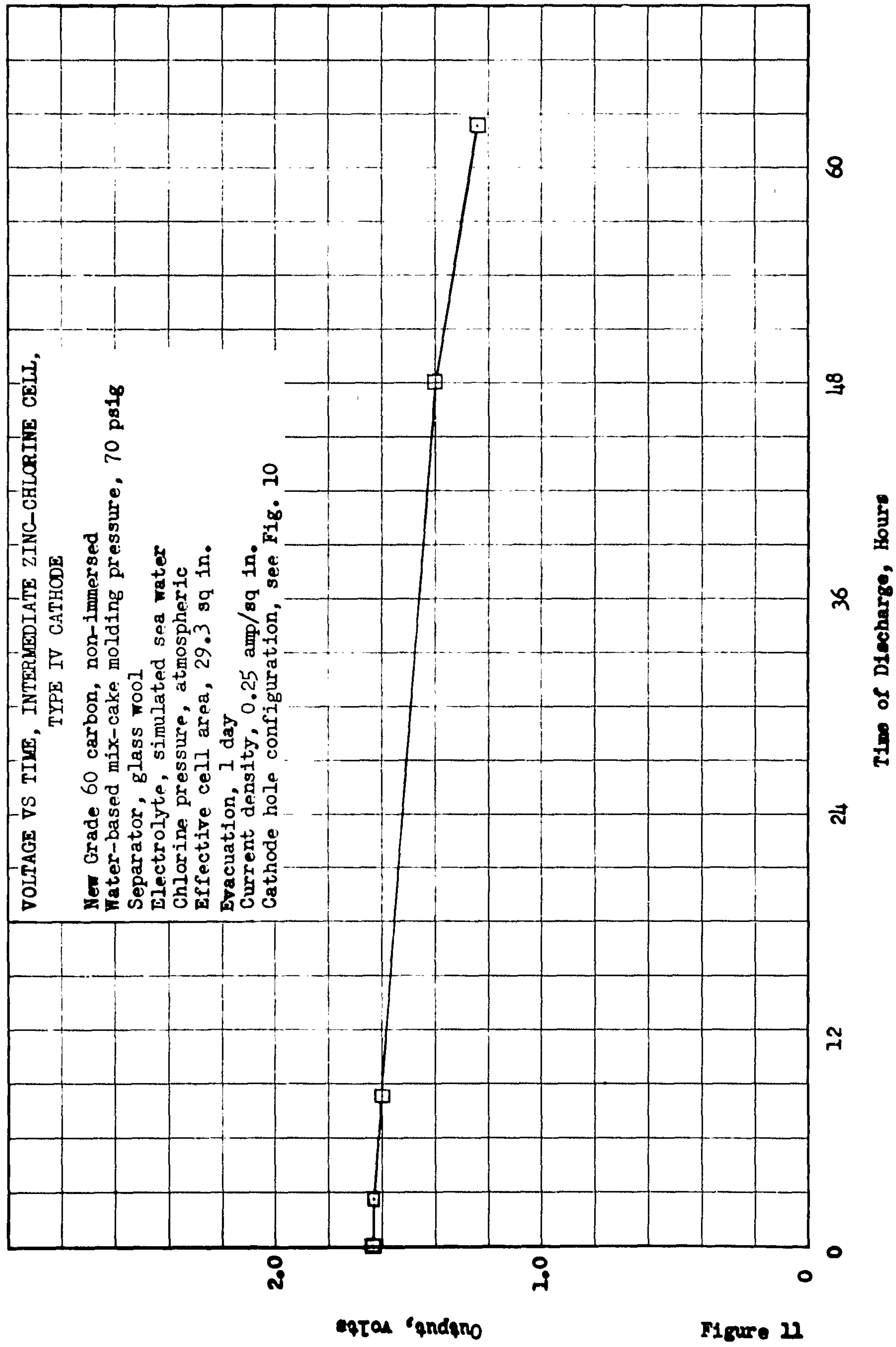


VOLTAGE VS CURRENT DENSITY, INTERMEDIATE ZINC-CHLORINE CELL
TYPE IV CATHODE

New grade 60 carbon, non-immersed
Water-based mix-cake molding pressure, 70 psig
Separator, glass wool
Electrolyte, simulated sea water
Chlorine pressure, atmospheric
Effective cell area, 29,3 sq in.
Evacuation, 1 day
Cathode hole configuration

Figure 10

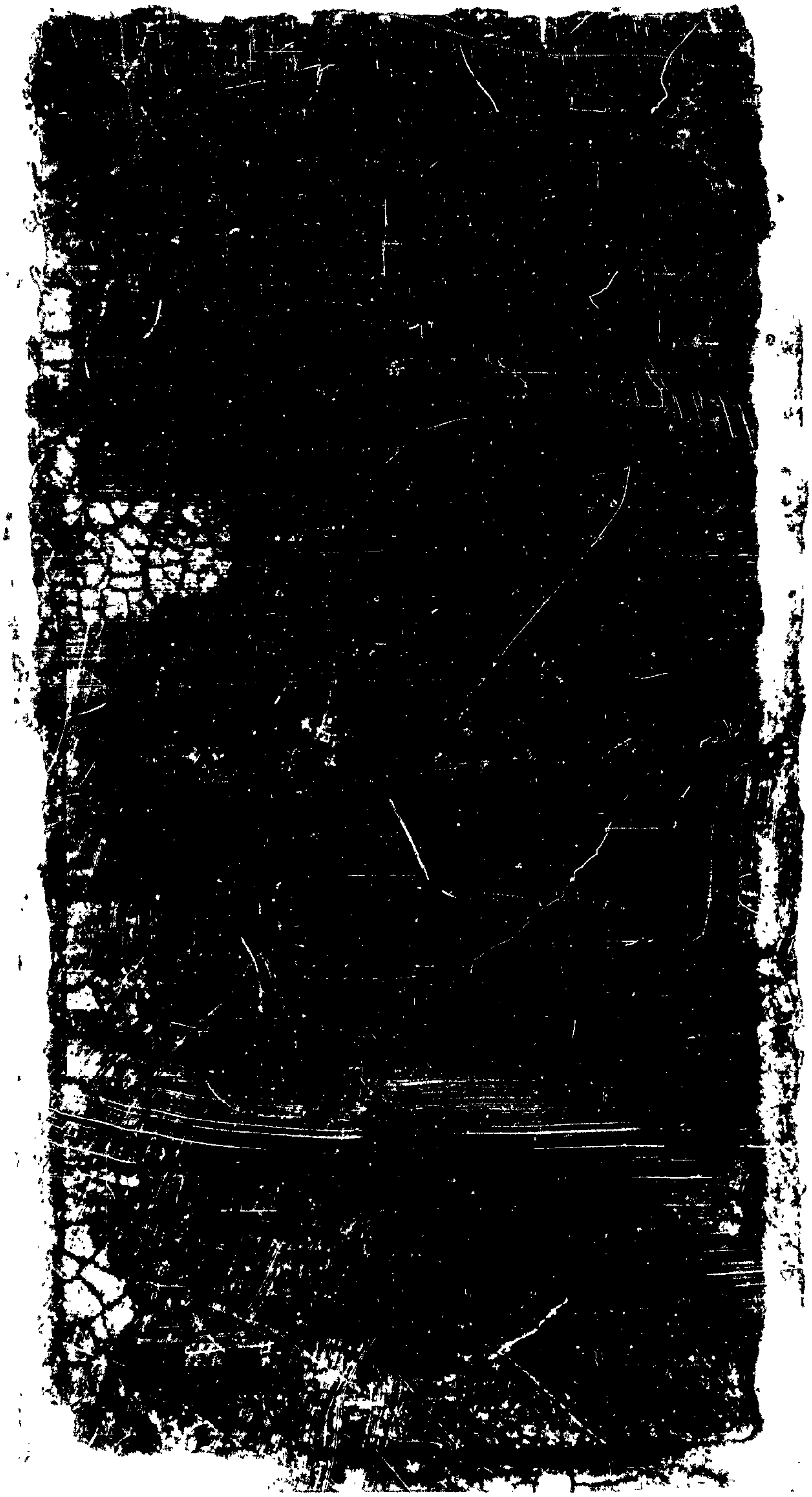
C-3346 EPD:em 1-12-53



VOLTAGE VS TIME, INTERMEDIATE ZINC-CHLORINE CELL,
TYPE IV CATHODE

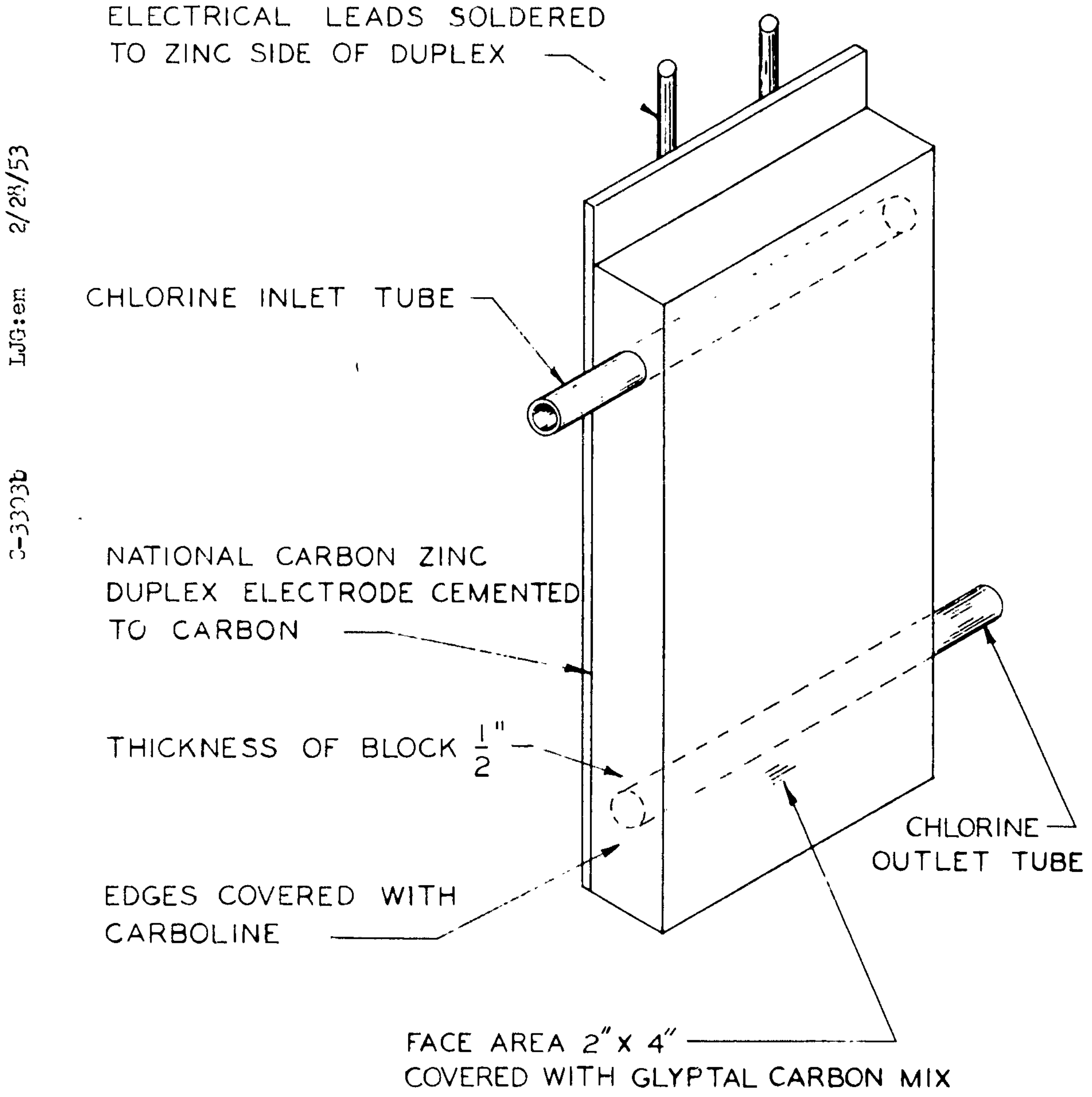
New Grade 60 carbon, non-immersed
Water-based mix-cake molding pressure, 70 psig
Separator, glass wool
Electrolyte, simulated sea water
Chlorine pressure, atmospheric
Effective cell area, 29.3 sq in.
Evacuation, 1 day
Current density, 0.25 amp/sq in.
Cathode hole configuration, see Fig. 10

**Figure 11**



WATER-BASED MIX-CAKE AFTER DRYING IN ASSEMBLED CELL

Figure 12

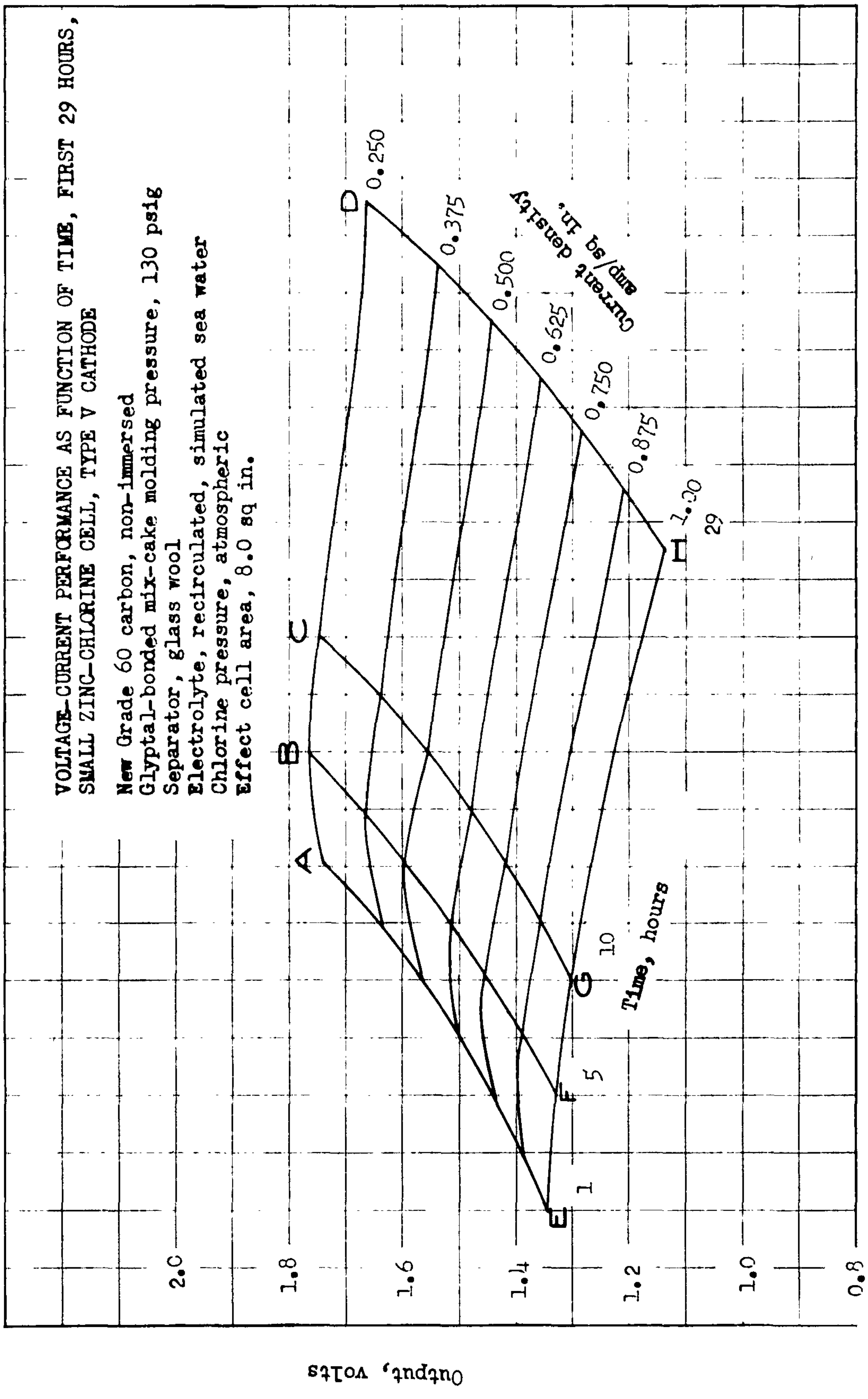


CHLORINE ELECTRODE

TYPE V

Figure 13

C-3370 JDM:em 3-3-53

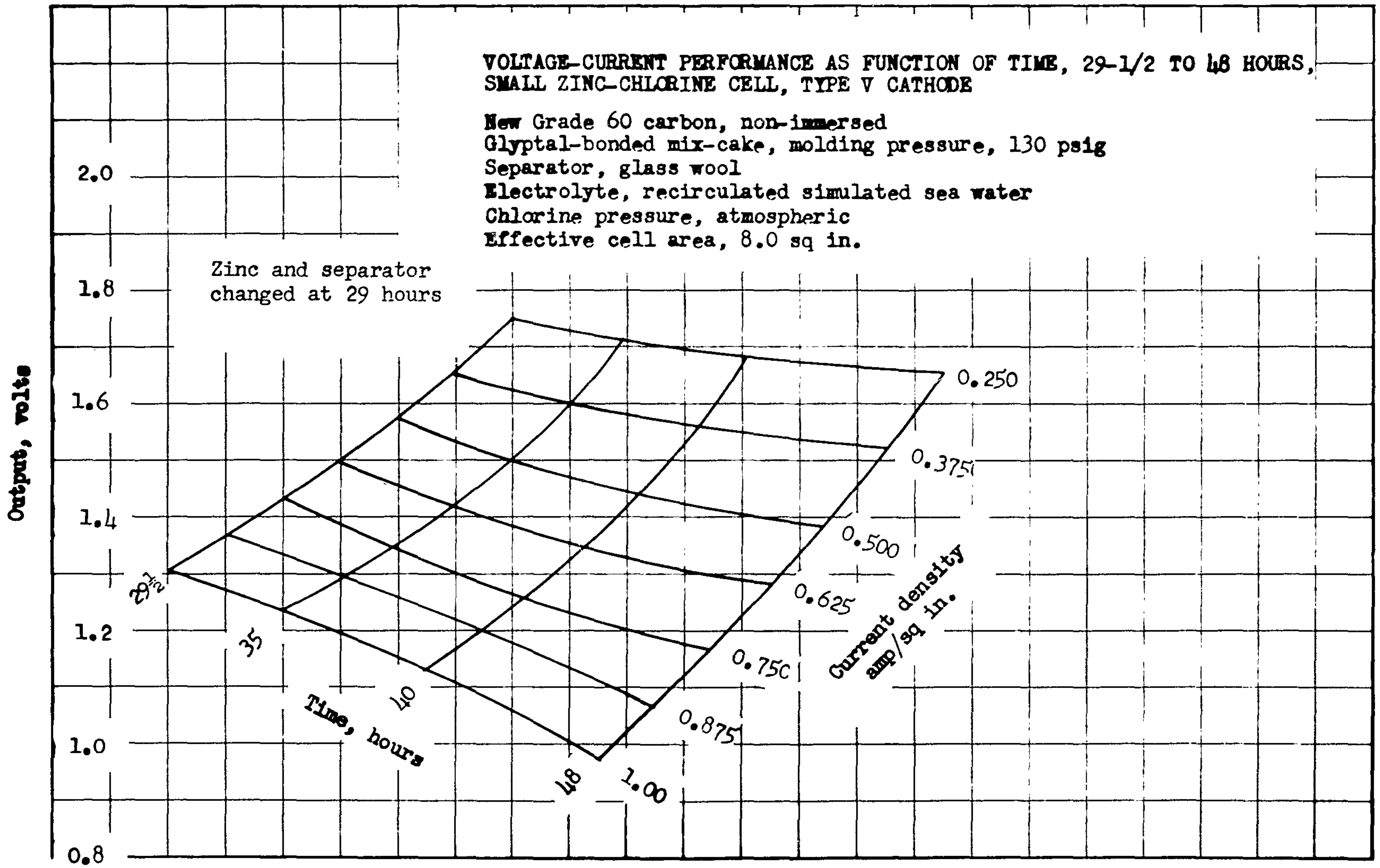


VOLTAGE-CURRENT PERFORMANCE AS FUNCTION OF TIME, FIRST 29 HOURS, SMALL ZINC-CHLORINE CELL, TYPE V CATHODE

New Grade 60 carbon, non-immersed
Glyptal-bonded mix-cake molding pressure, 130 psig
Separator, glass wool
Electrolyte, recirculated, simulated sea water
Chlorine pressure, atmospheric
Effect cell area, 8.0 sq in.

Figure 14

C-3371 JDM:em 3-3-53

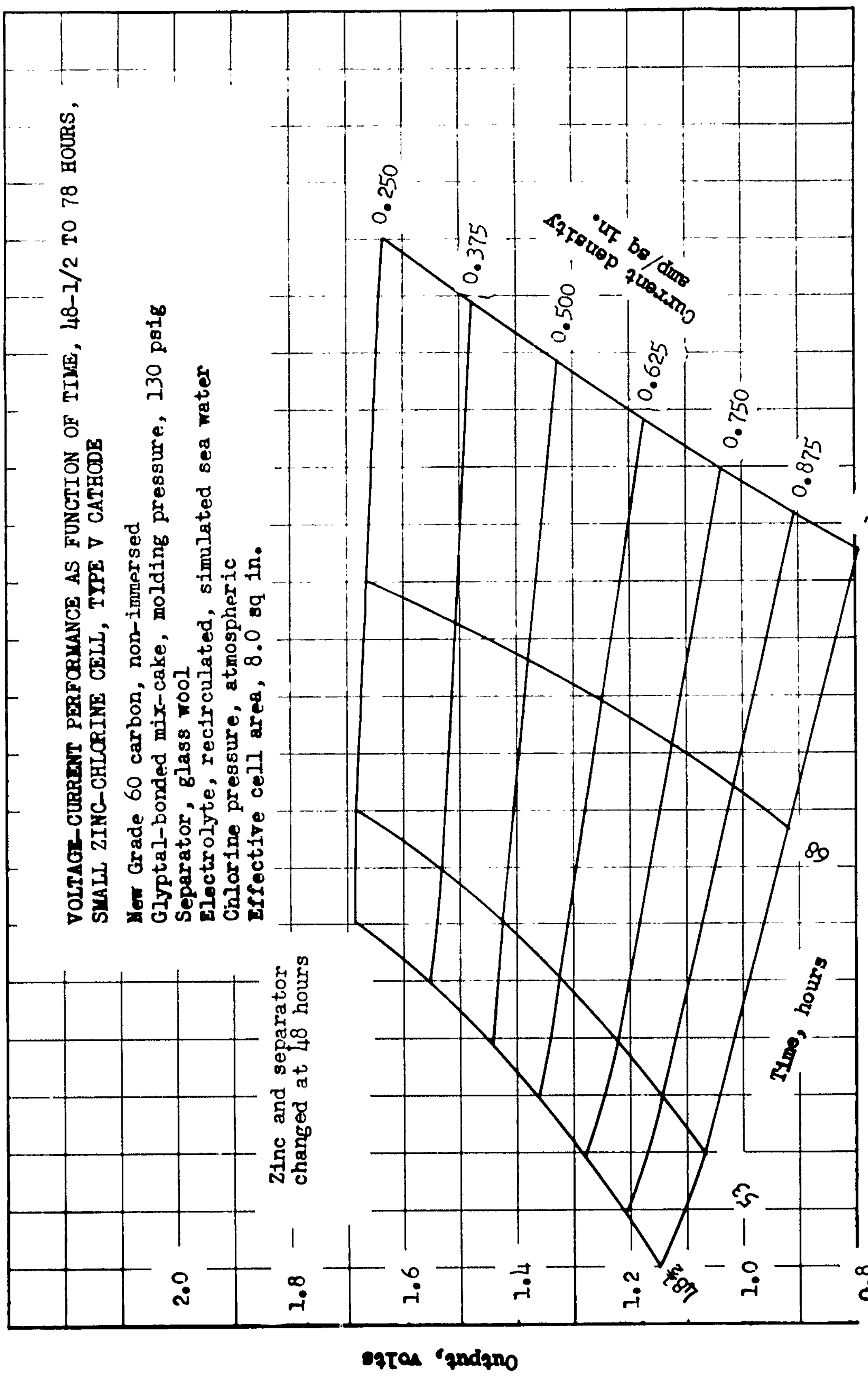


**VOLTAGE-CURRENT PERFORMANCE AS FUNCTION OF TIME, 29-1/2 TO 48 HOURS, SMALL ZINC-CHLORINE CELL, TYPE V CATHODE**

**New** Grade 60 carbon, non-immersed
Glyptal-bonded mix-cake, molding pressure, 130 psig
Separator, glass wool
**Electrolyte**, recirculated simulated sea water
Chlorine pressure, atmospheric
**Effective** cell area, 8.0 sq in.

Zinc and separator changed at 29 hours

C-3372 JDM:EM 3-3-53



VOLTAGE-CURRENT PERFORMANCE AS FUNCTION OF TIME, 48-1/2 TO 78 HOURS, SMALL ZINC-CHLORINE CELL, TYPE V CATHODE

New Grade 60 carbon, non-immersed
Glyptal-bonded mix-cake, molding pressure, 130 psig
Separator, glass wool
Electrolyte, recirculated, simulated sea water
Chlorine pressure, atmospheric
Effective cell area, 8.0 sq in.

Zinc and separator changed at 48 hours

Figure 16

C-3375 JDM:em 3-3-53

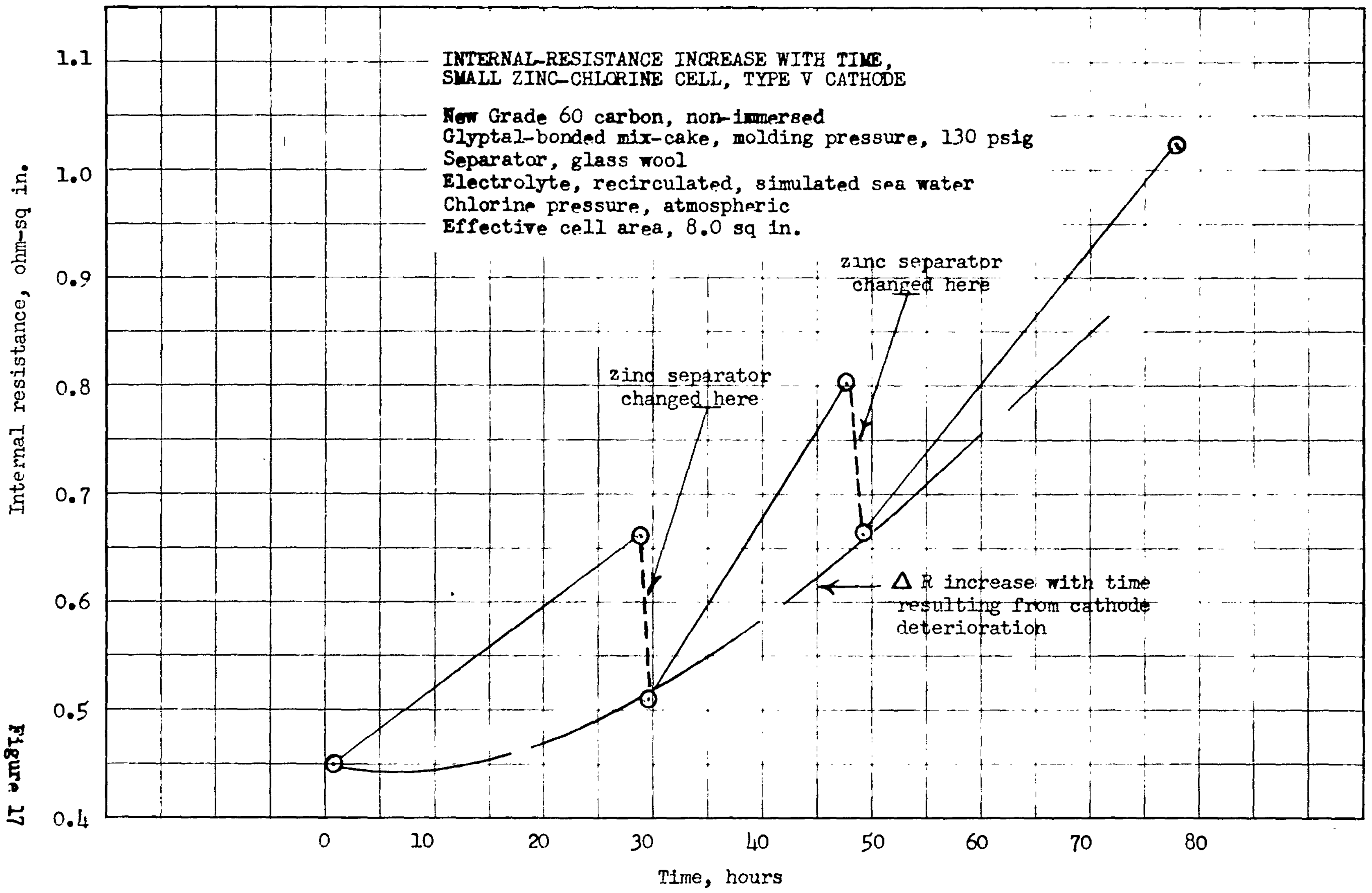
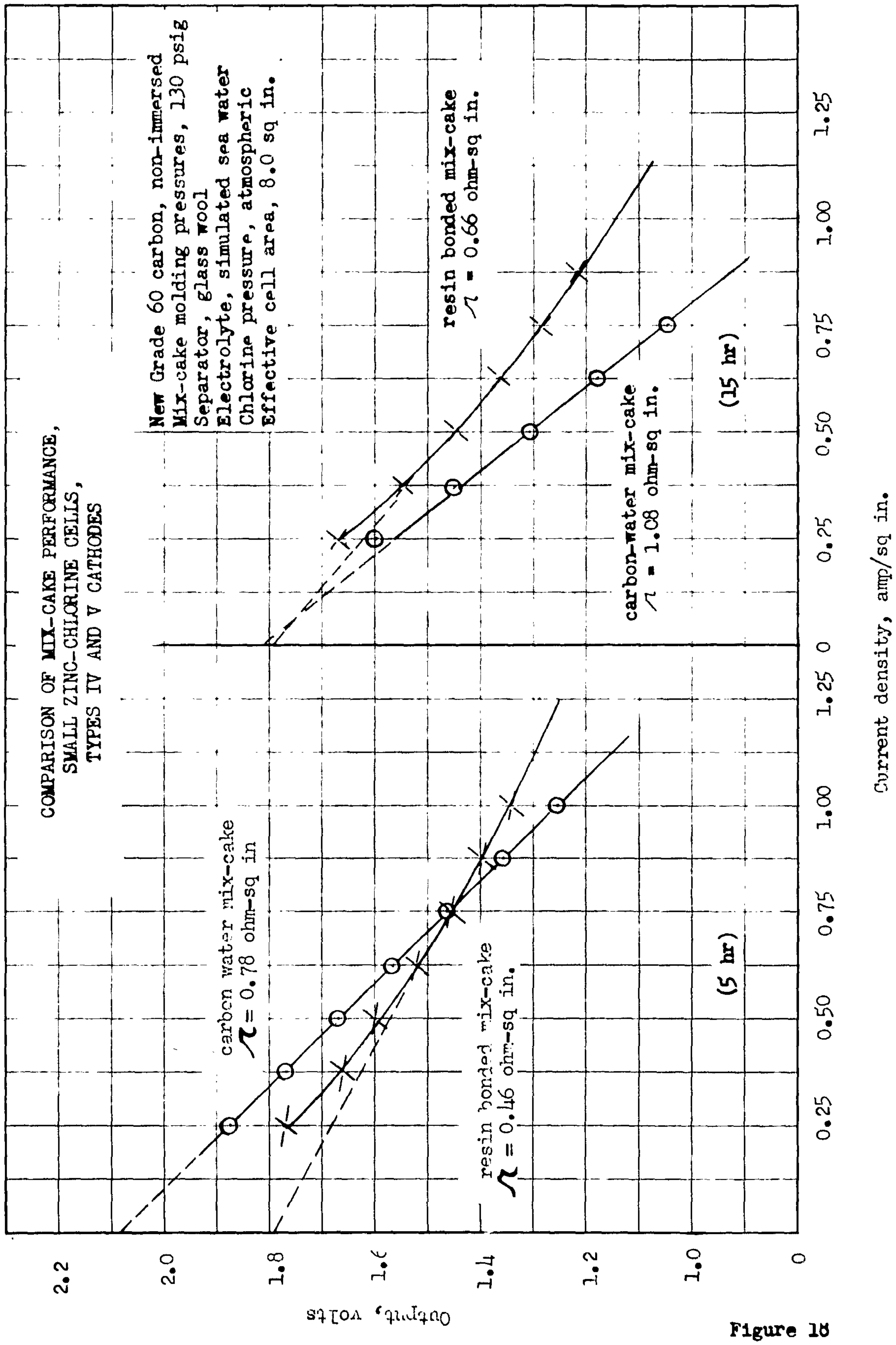


Figure 17

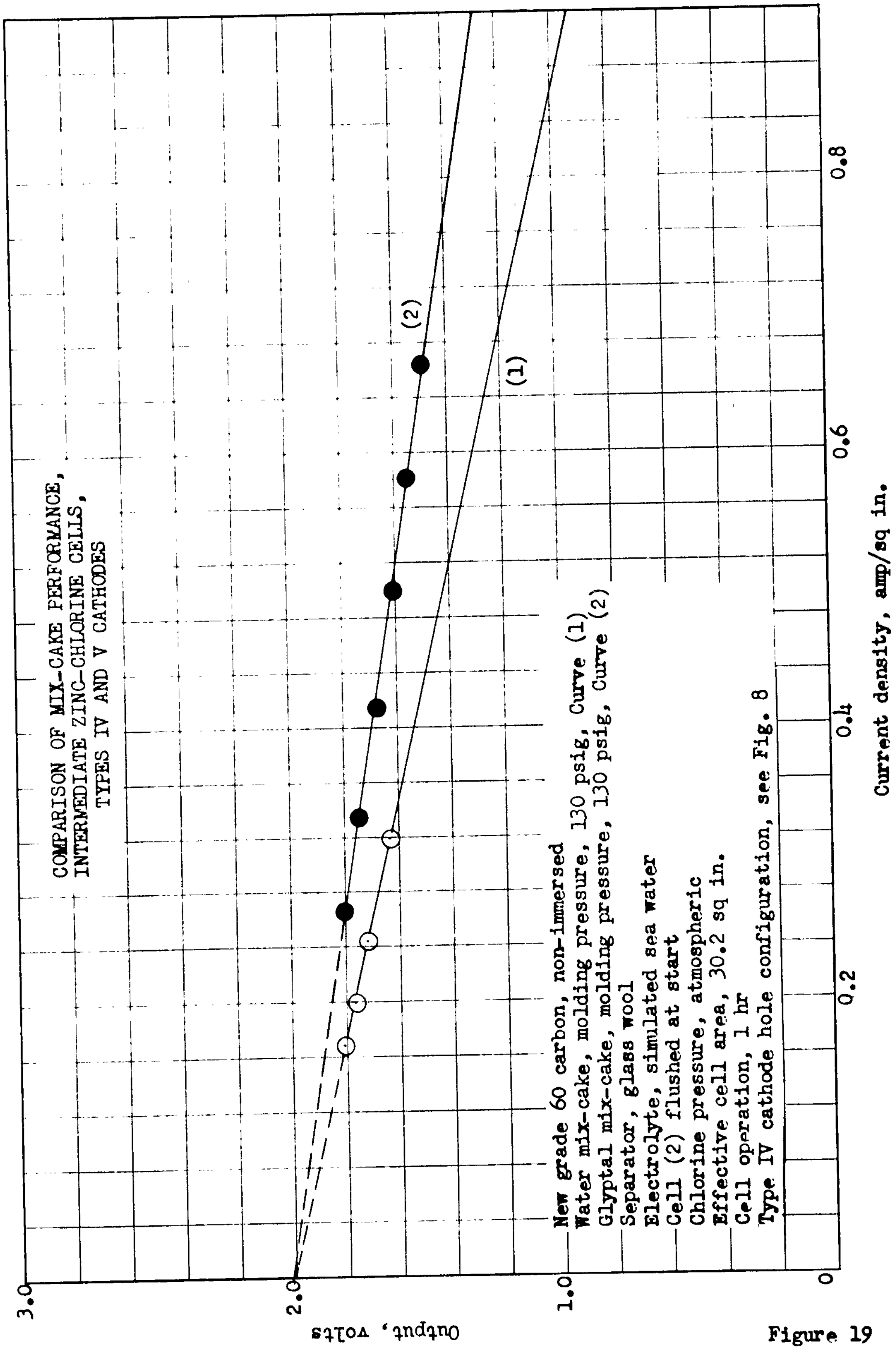
C-3373 JDM:em 3-3-53


COMPARISON OF MIX-CAKE PERFORMANCE, SMALL ZINC-CHLORINE CELLS, TYPES IV AND V CATHODES

New Grade 60 carbon, non-immersed
Mix-cake molding pressures, 130 psig
Separator, glass wool
Electrolyte, simulated sea water
Chlorine pressure, atmospheric
Effective cell area, 8.0 sq in.

Figure 18

C-3378 EPD:em 3-3-53

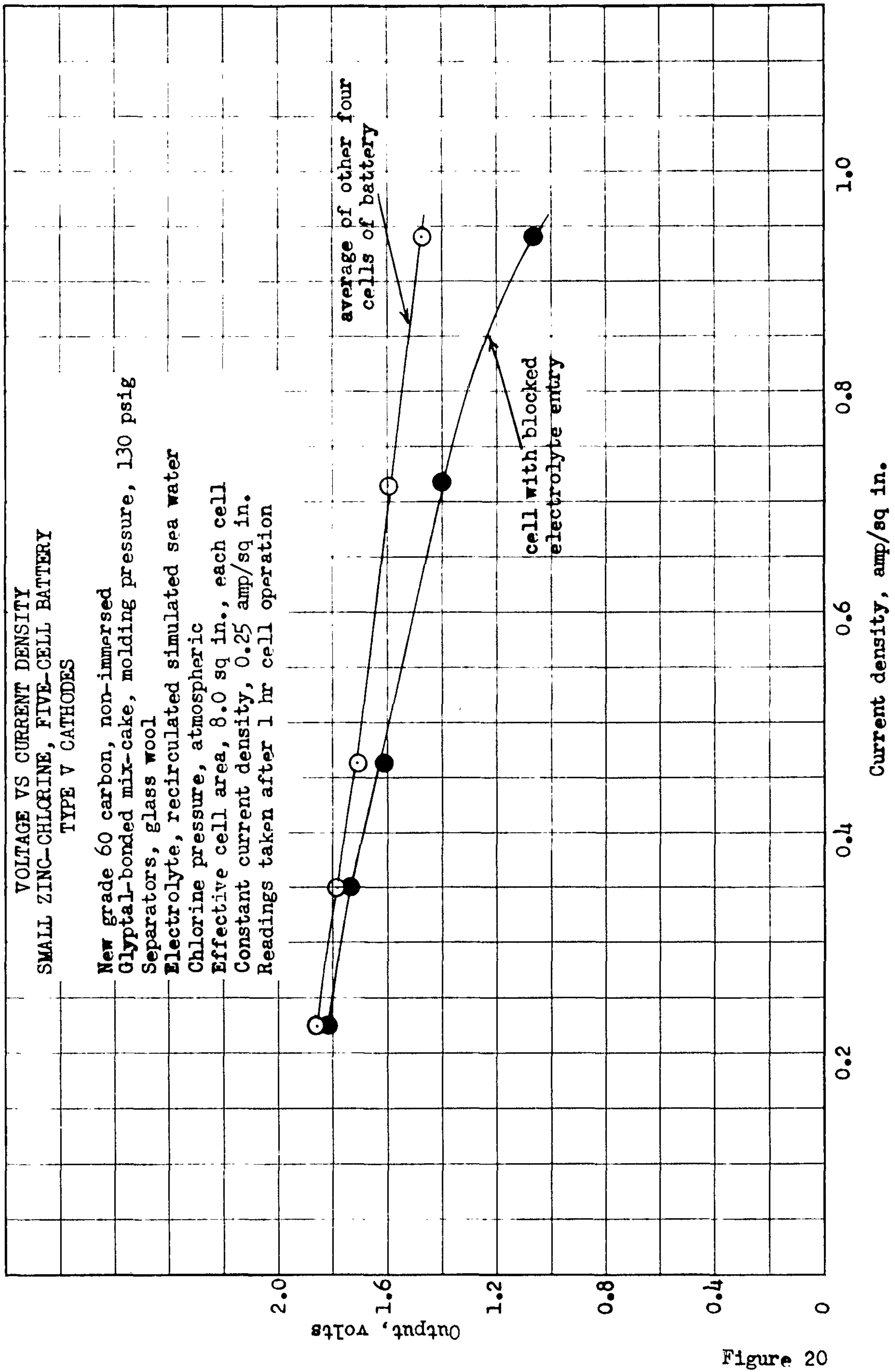


COMPARISON OF MIX-CAKE PERFORMANCE,
INTERMEDIATE ZINC-CHLORINE CELLS,
TYPES IV AND V CATHODES

New grade 60 carbon, non-immersed
Water mix-cake, molding pressure, 130 psig, Curve (1)
Glyptal mix-cake, molding pressure, 130 psig, Curve (2)
Separator, glass wool
Electrolyte, simulated sea water
Cell (2) flushed at start
Chlorine pressure, atmospheric
Effective cell area, 30.2 sq in.
Cell operation, 1 hr
Type IV cathode hole configuration, see Fig. 8

Figure 19

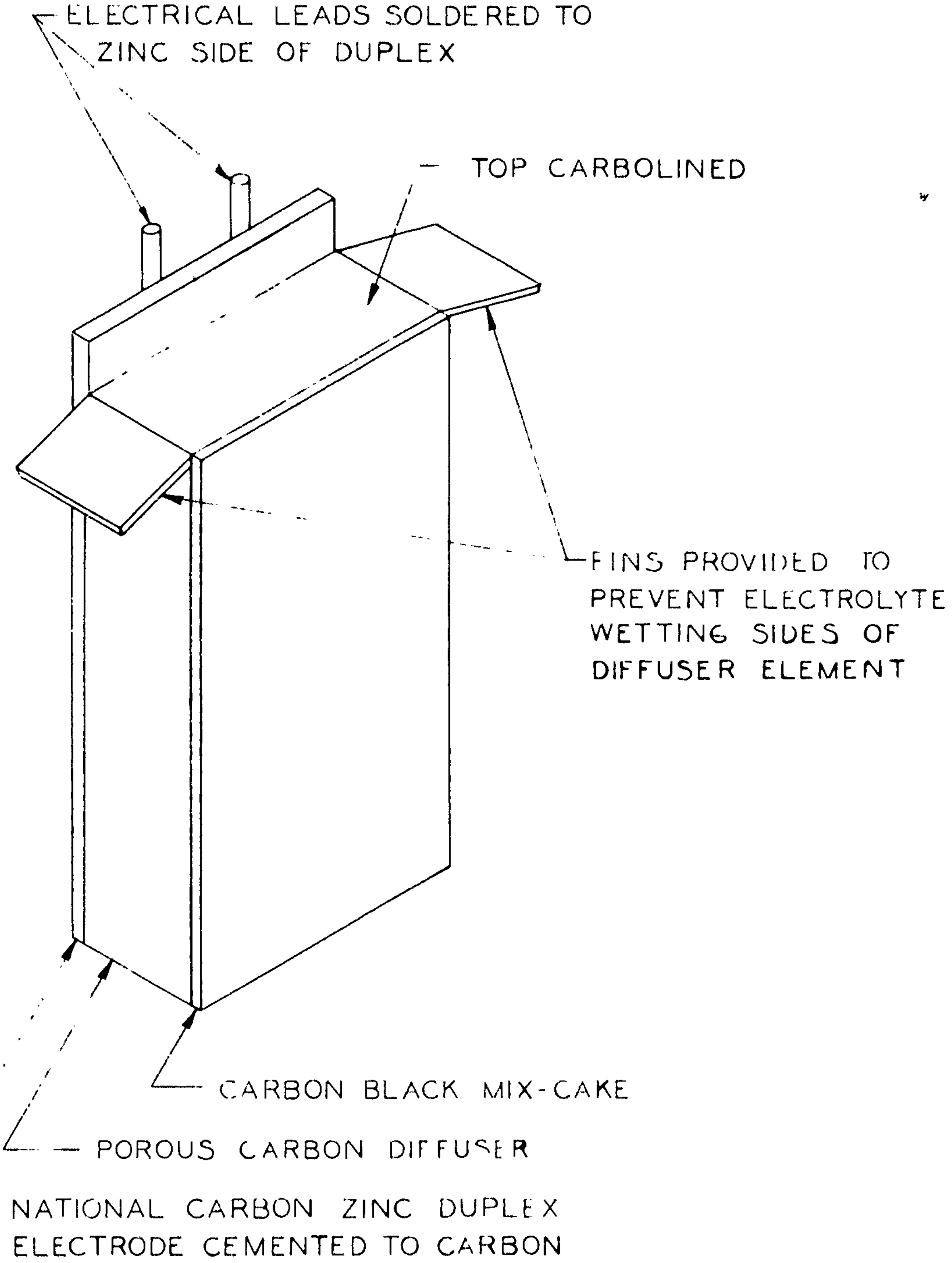
C-3380 LJG:em 3/3/53



VOLTAGE VS CURRENT DENSITY
SMALL ZINC-CHLORINE, FIVE-CELL BATTERY
TYPE V CATHODES

New grade 60 carbon, non-immersed
Glyptal-bonded mix-cake, molding pressure, 130 psig
Separators, glass wool
Electrolyte, recirculated simulated sea water
Chlorine pressure, atmospheric
Effective cell area, 8.0 sq in., each cell
Constant current density, 0.25 amp/sq in.
Readings taken after 1 hr cell operation

Figure 20

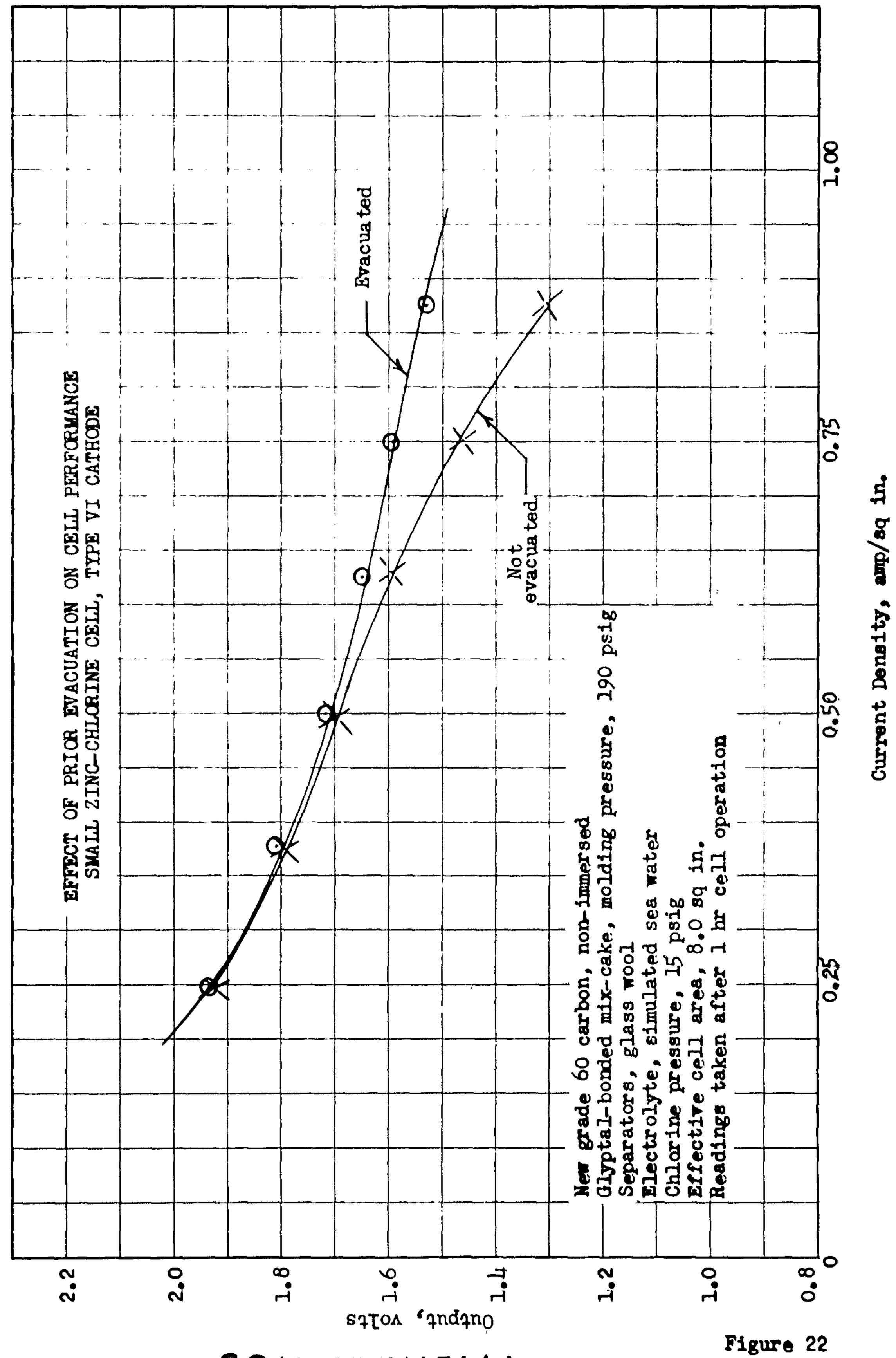


C-3389

DIFFUSION-FEED CHLORINE ELECTRODE
TYPE VI

Figure 21

C-3391 EFD:mg 5-14-53

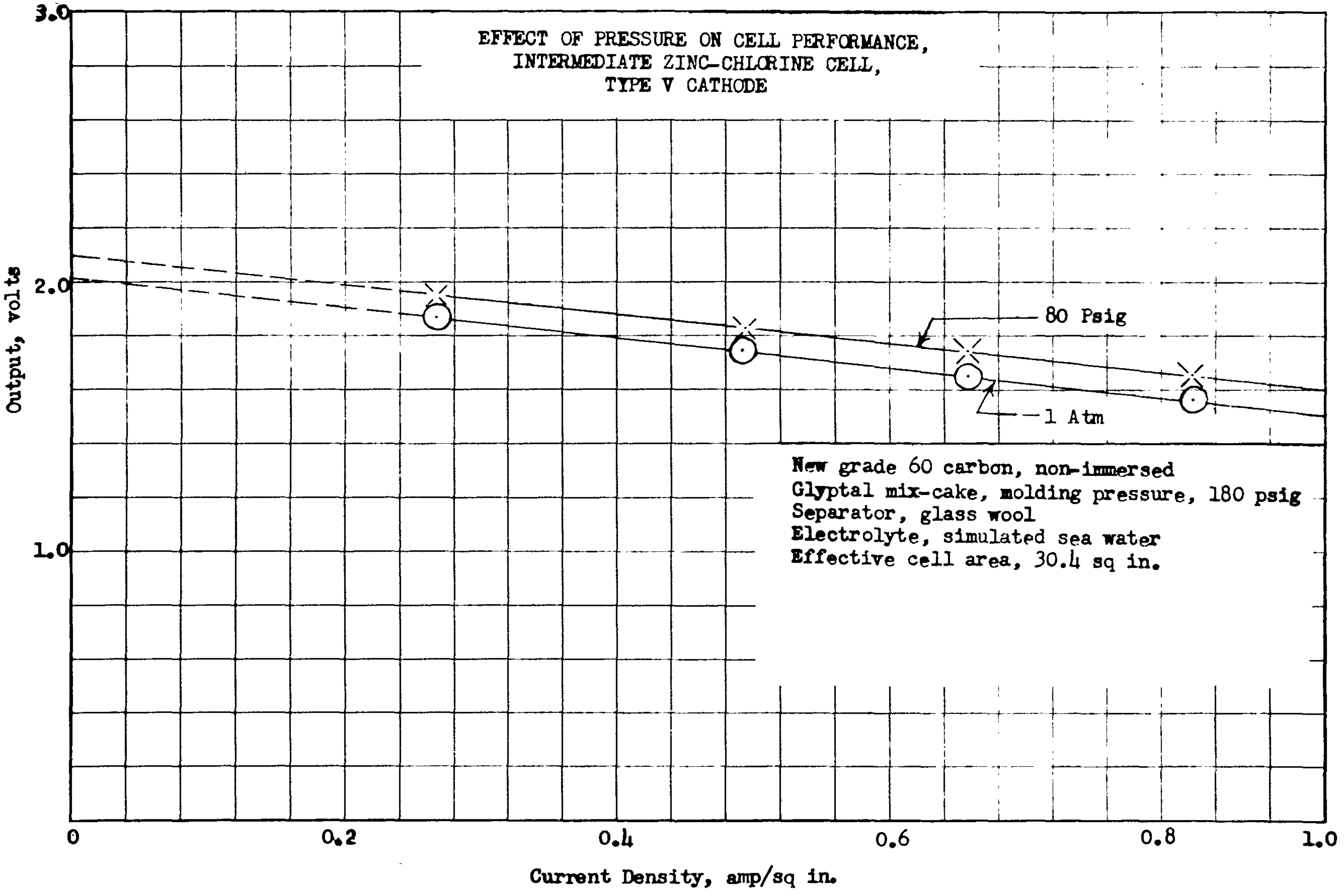


EFFECT OF PRIOR EVACUATION ON CELL PERFORMANCE
SMALL ZINC-CHLORINE CELL, TYPE VI CATHODE

New grade 60 carbon, non-immersed
Glyptal-bonded mix-cake, molding pressure, 190 psig
Separators, glass wool
Electrolyte, simulated sea water
Chlorine pressure, 15 psig
Effective cell area, 8.0 sq in.
Readings taken after 1 hr cell operation

Figure 22

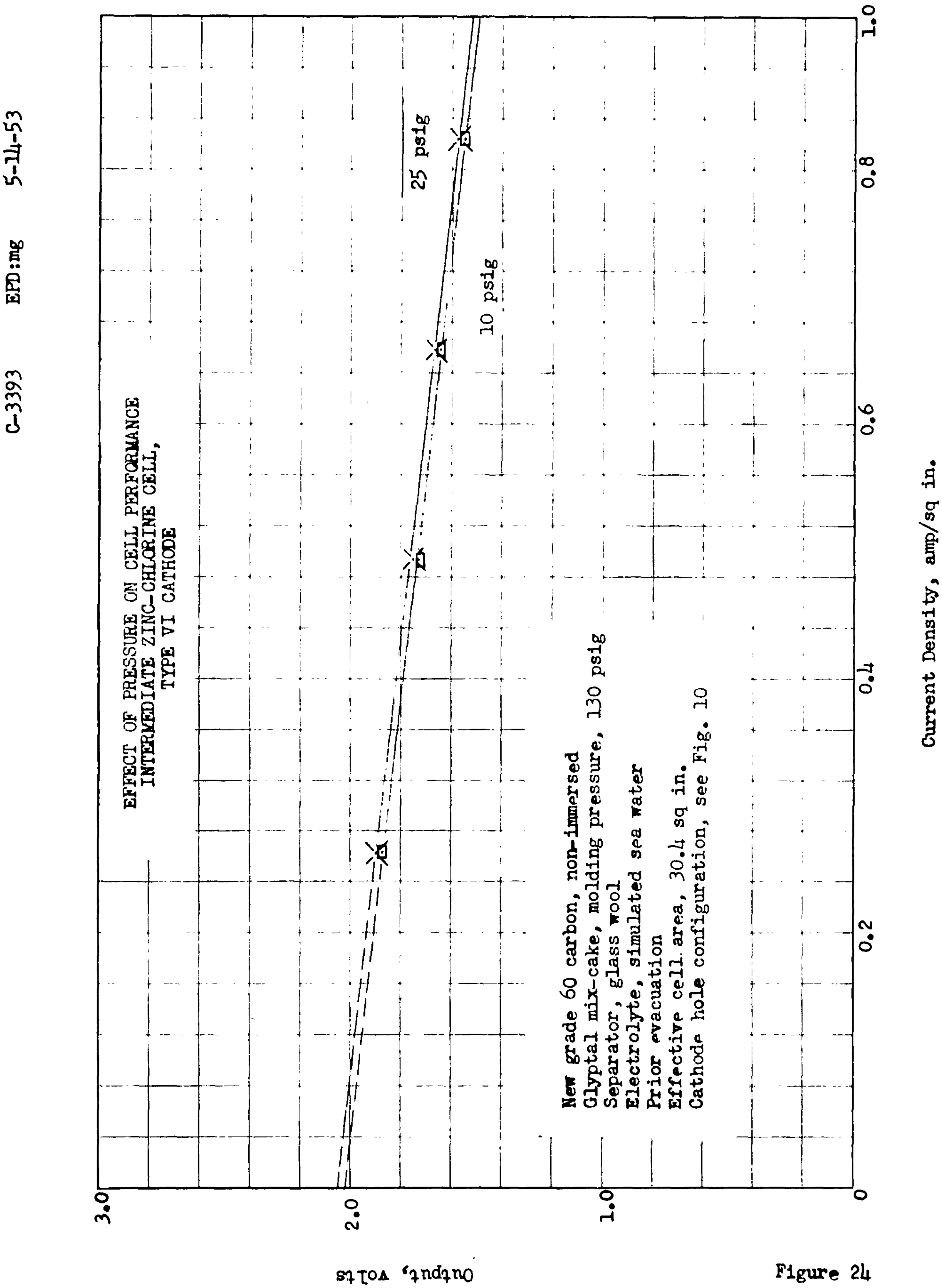
C-3392 EPD:mg 5-14-53



EFFECT OF PRESSURE ON CELL PERFORMANCE,
INTERMEDIATE ZINC-CHLORINE CELL,
TYPE V CATHODE

New grade 60 carbon, non-immersed
Glyptal mix-cake, molding pressure, 180 psig
Separator, glass wool
Electrolyte, simulated sea water
Effective cell area, 30.4 sq in.

Figure 23

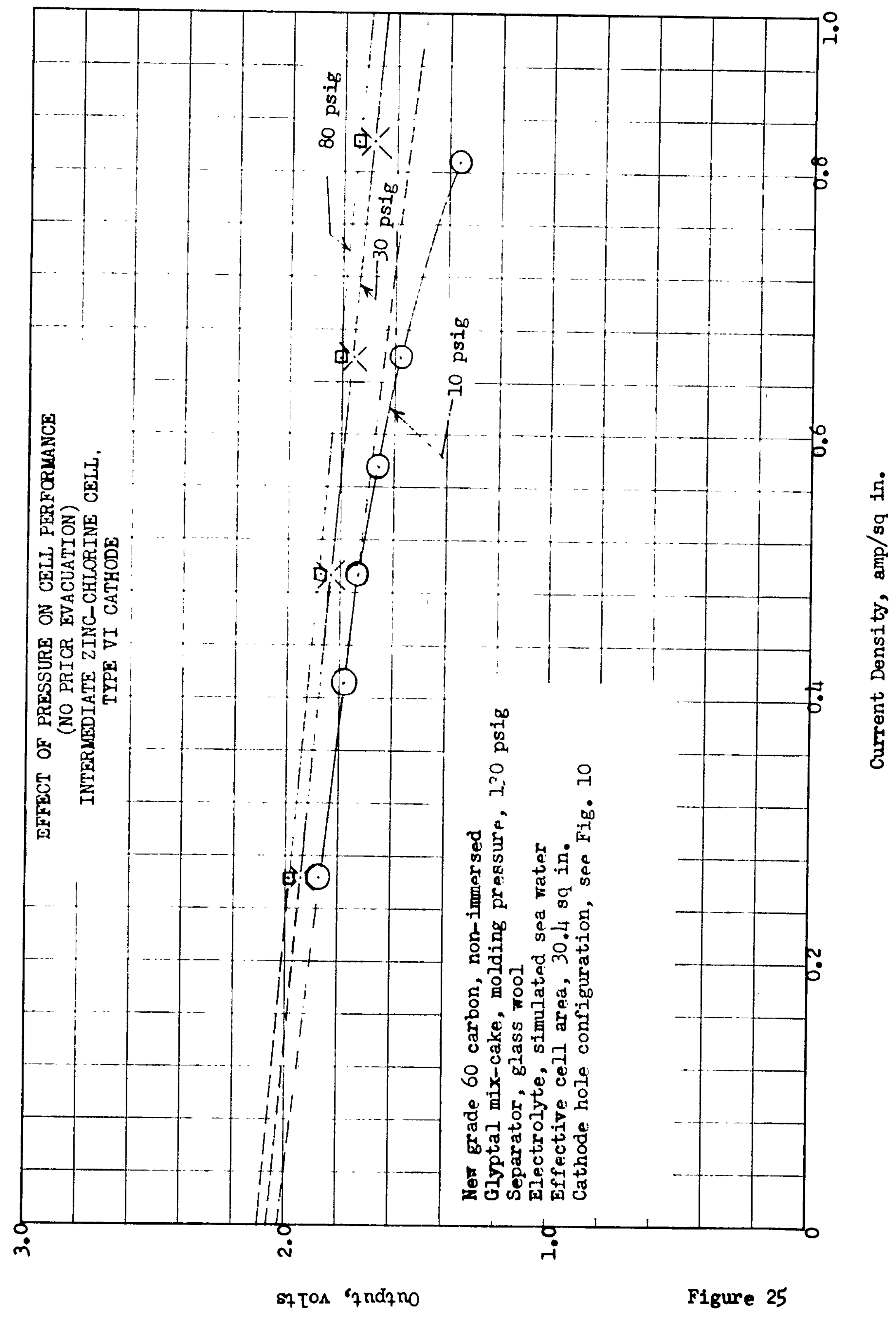


EFFECT OF PRESSURE ON CELL PERFORMANCE
INTERMEDIATE ZINC-CHLORINE CELL,
TYPE VI CATHODE

New grade 60 carbon, non-immersed
Glyptal mix-cake, molding pressure, 130 psig
Separator, glass wool
Electrolyte, simulated sea water
Prior evacuation
Effective cell area, 30.4 sq in.
Cathode hole configuration, see Fig. 10

Figure 24

C-3394 EPD:mg 5-14-53



EFFECT OF PRESSURE ON CELL PERFORMANCE
(NO PRIOR EVACUATION)
INTERMEDIATE ZINC-CHLORINE CELL,
TYPE VI CATHODE

New grade 60 carbon, non-immersed
Glyptal mix-cake, molding pressure, 120 psig
Separator, glass wool
Electrolyte, simulated sea water
Effective cell area, 30.4 sq in.
Cathode hole configuration, see Fig. 10

Figure 25

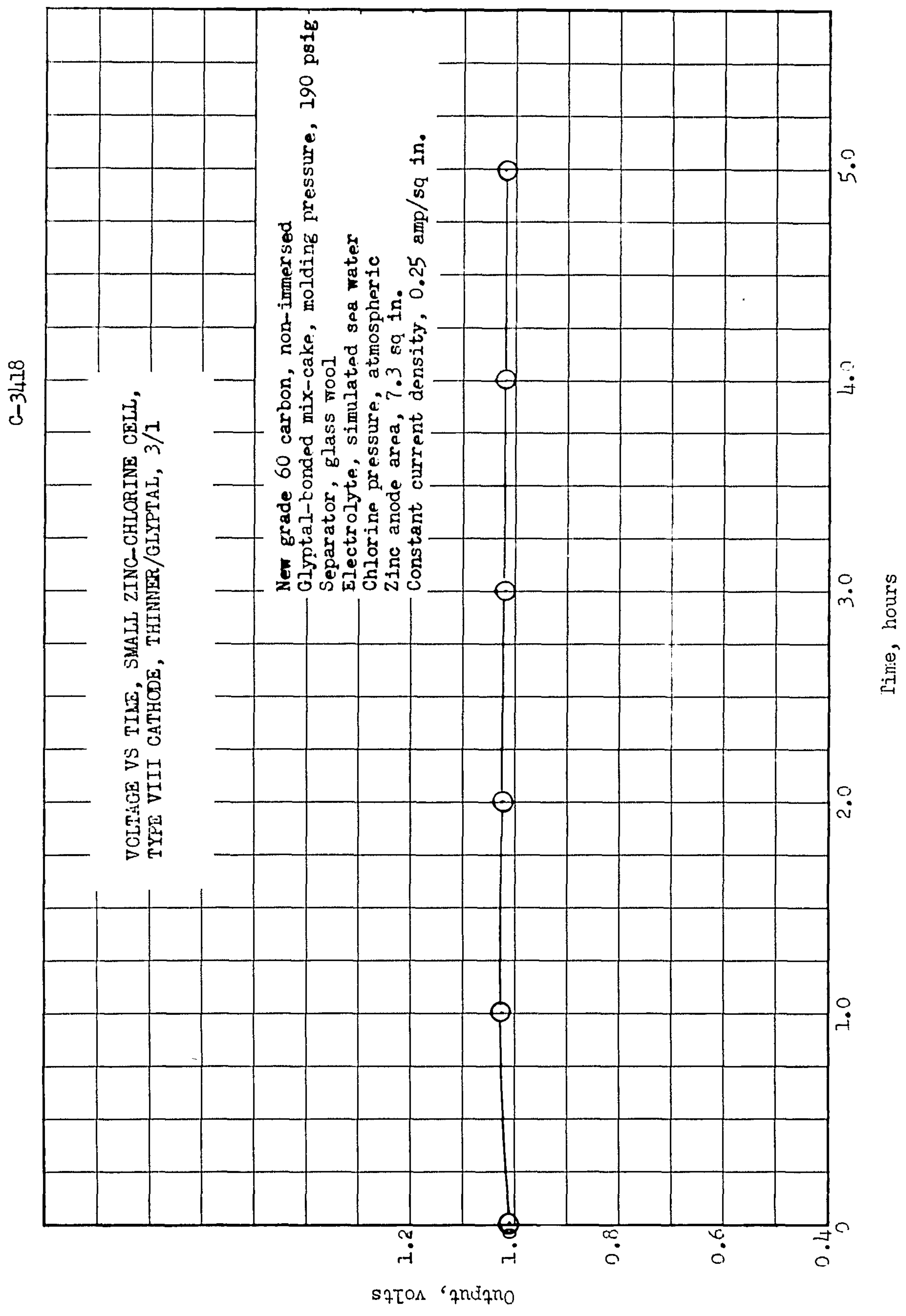
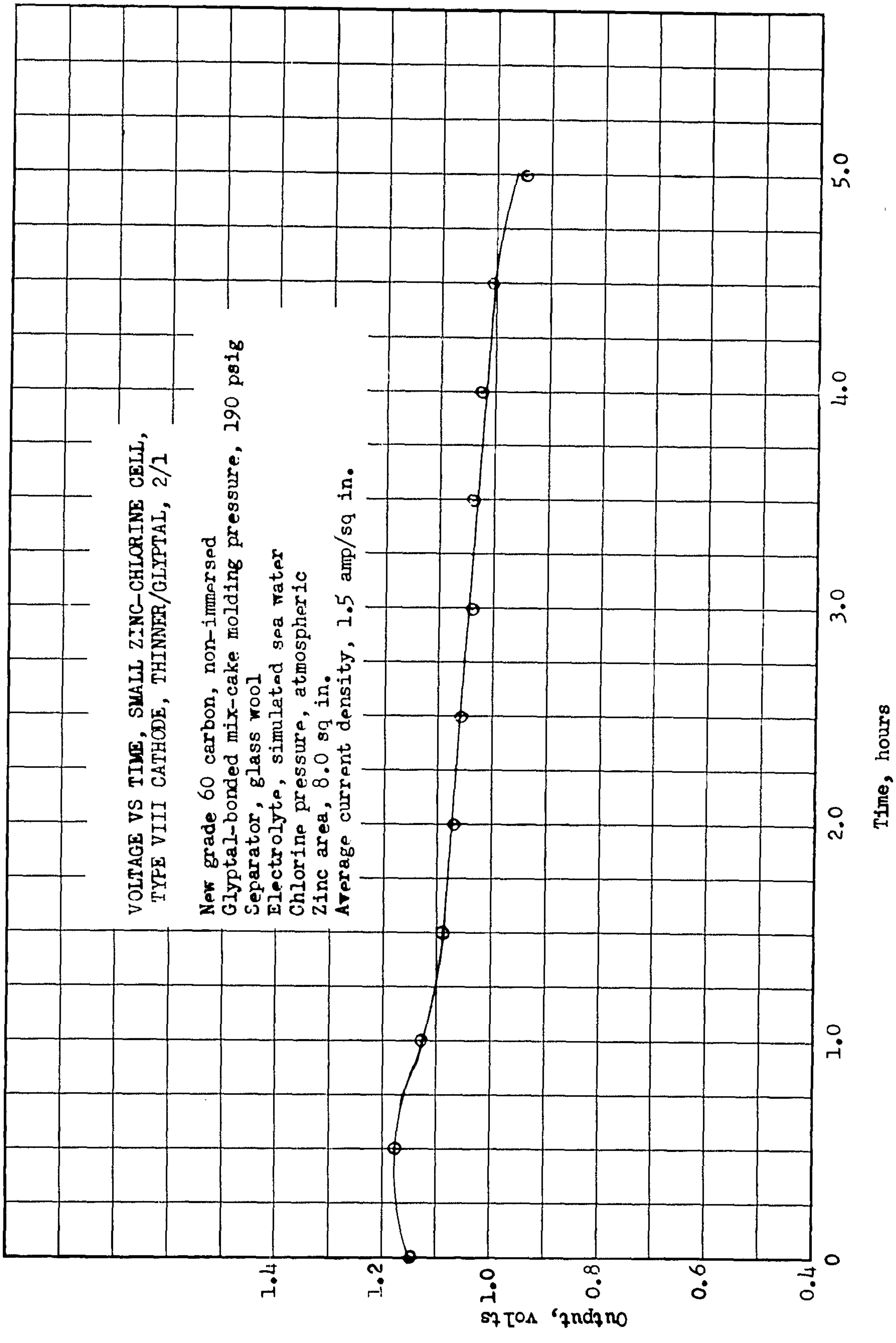

C-3418
VOLTAGE VS TIME, SMALL ZINC-CHLORINE CELL,
TYPE VIII CATHODE, THINNER/GLYPTAL, 3/1
New grade 60 carbon, non-immersed
Glyptal-bonded mix-cake, molding pressure, 190 psig
Separator, glass wool
Electrolyte, simulated sea water
Chlorine pressure, atmospheric
Zinc anode area, 7.3 sq in.
Constant current density, 0.25 amp/sq in.
1.2
1.0
0.8
0.6
0.4
Output, volts
0
1.0
2.0
3.0
4.0
5.0
Time, hours

Figure 26

C-3420

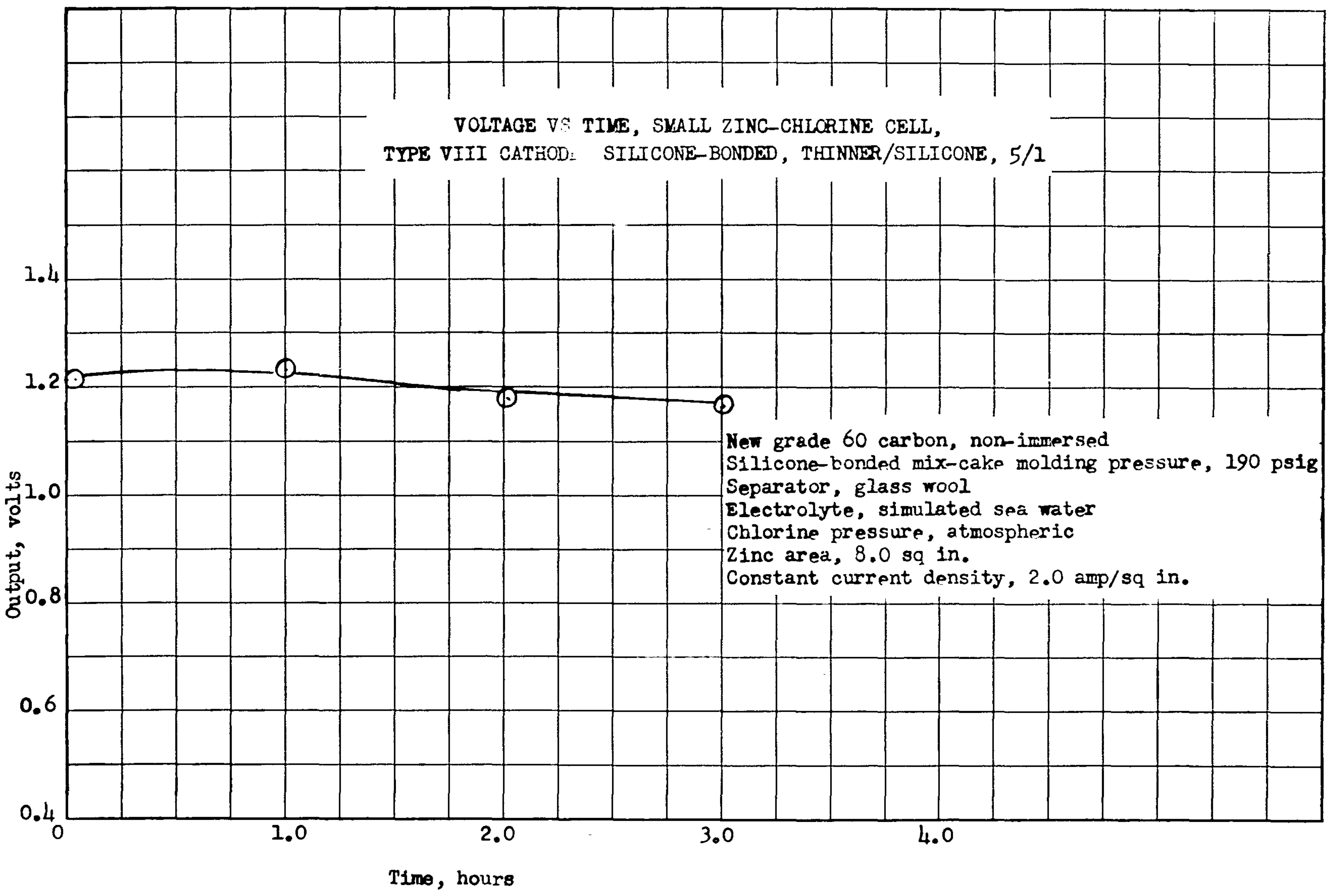


VOLTAGE VS TIME, SMALL ZINC-CHLORINE CELL,
TYPE VIII CATHODE, THINNER/GLYPTAL, 2/1

New grade 60 carbon, non-immersed
Glyptal-bonded mix-cake molding pressure, 190 psig
Separator, glass wool
Electrolyte, simulated sea water
Chlorine pressure, atmospheric
Zinc area, 8.0 sq in.
Average current density, 1.5 amp/sq in.

Figure 27

C-3423



VOLTAGE VS TIME, SMALL ZINC-CHLORINE CELL,
TYPE VIII CATHODE SILICONE-BONDED, THINNER/SILICONE, 5/1

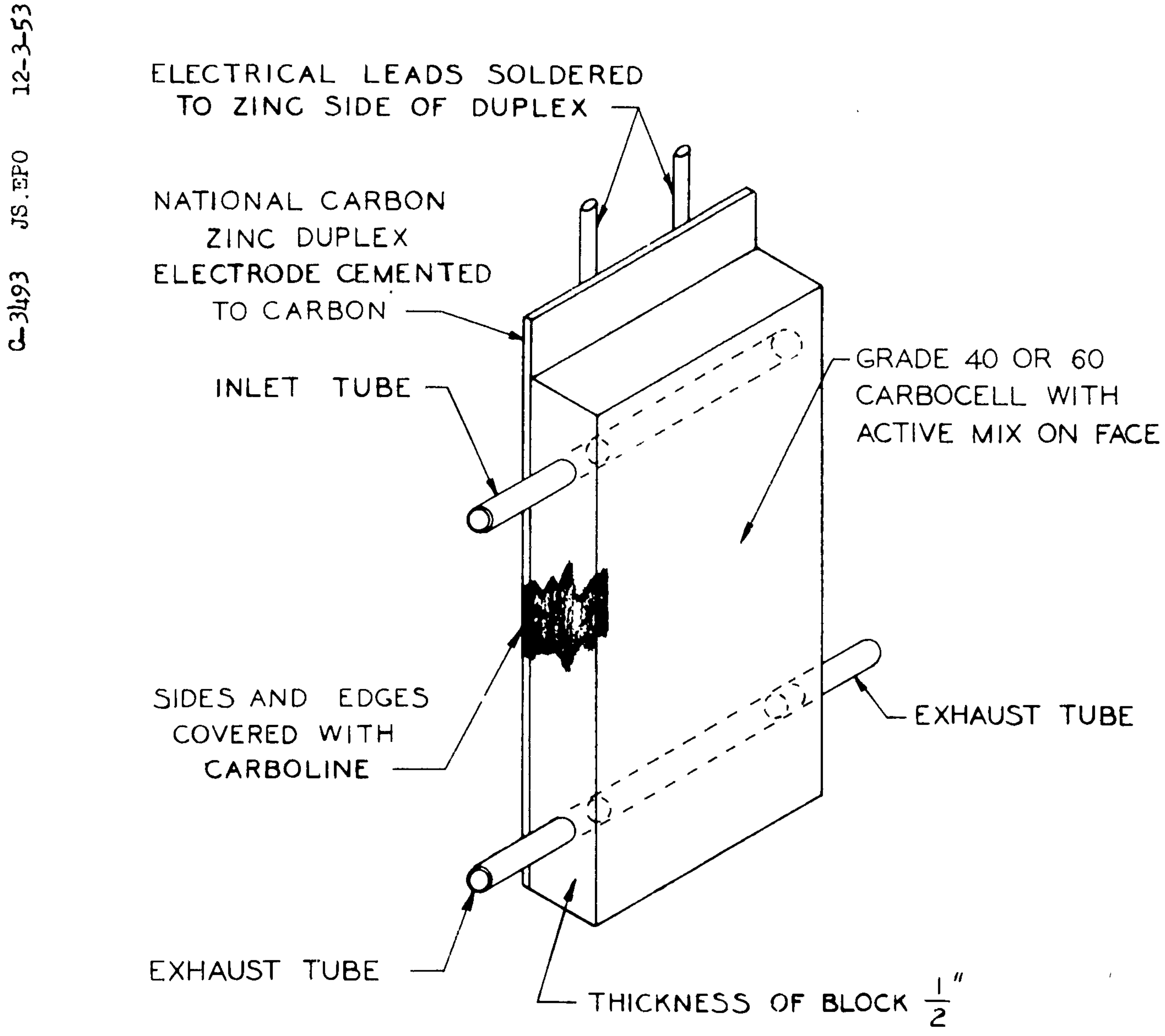
New grade 60 carbon, non-immersed
Silicone-bonded mix-cake molding pressure, 190 psig
Separator, glass wool
Electrolyte, simulated sea water
Chlorine pressure, atmospheric
Zinc area, 8.0 sq in.
Constant current density, 2.0 amp/sq in.

Figure 28

0953-233

ELIMINATION OF CORNER IN SECTION ON RING
(END VIEW)

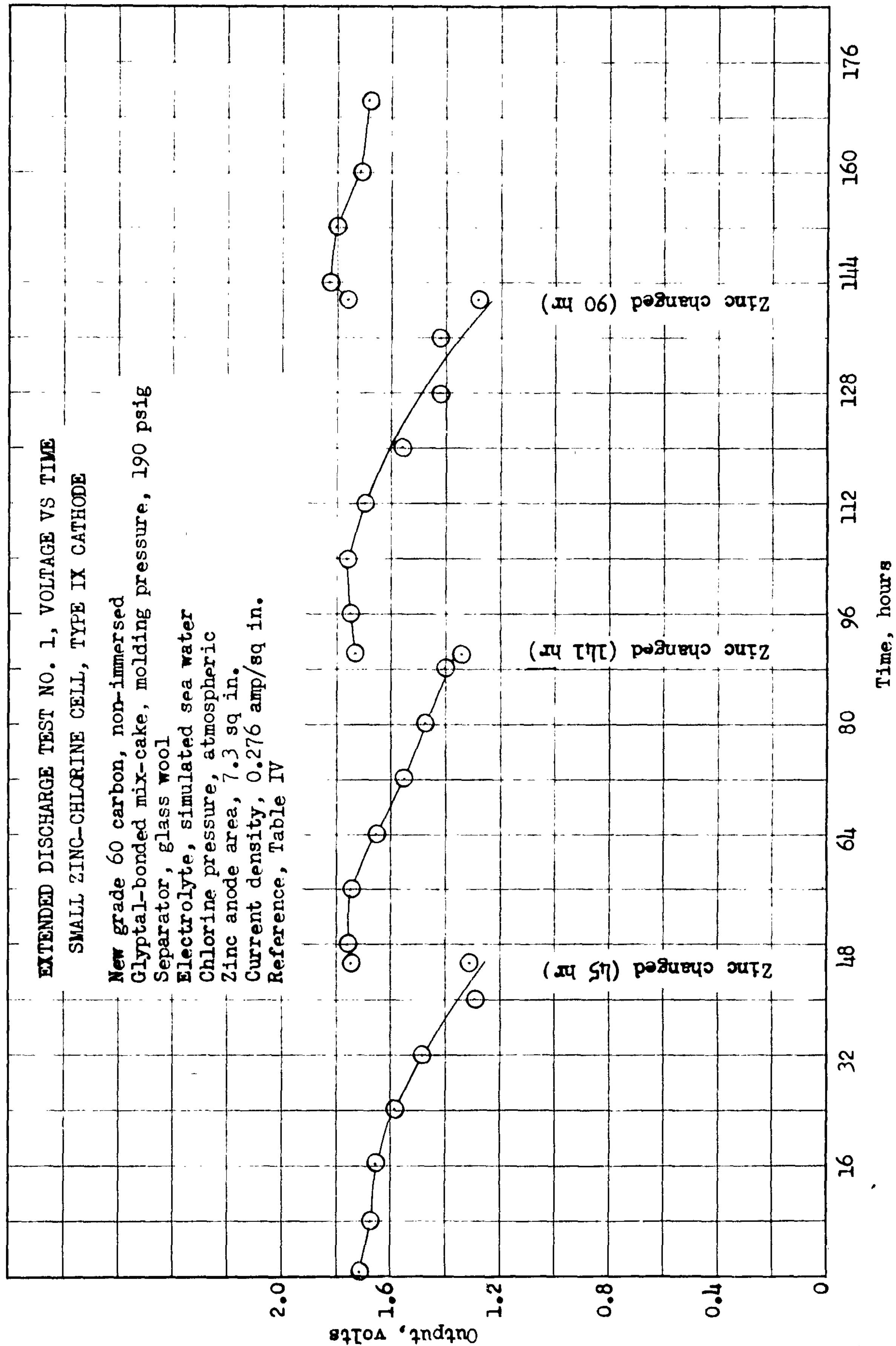
Figure 29



TYPE IX CATHODE

Figure 30

C-3442 EPD JS:em 9-10-53

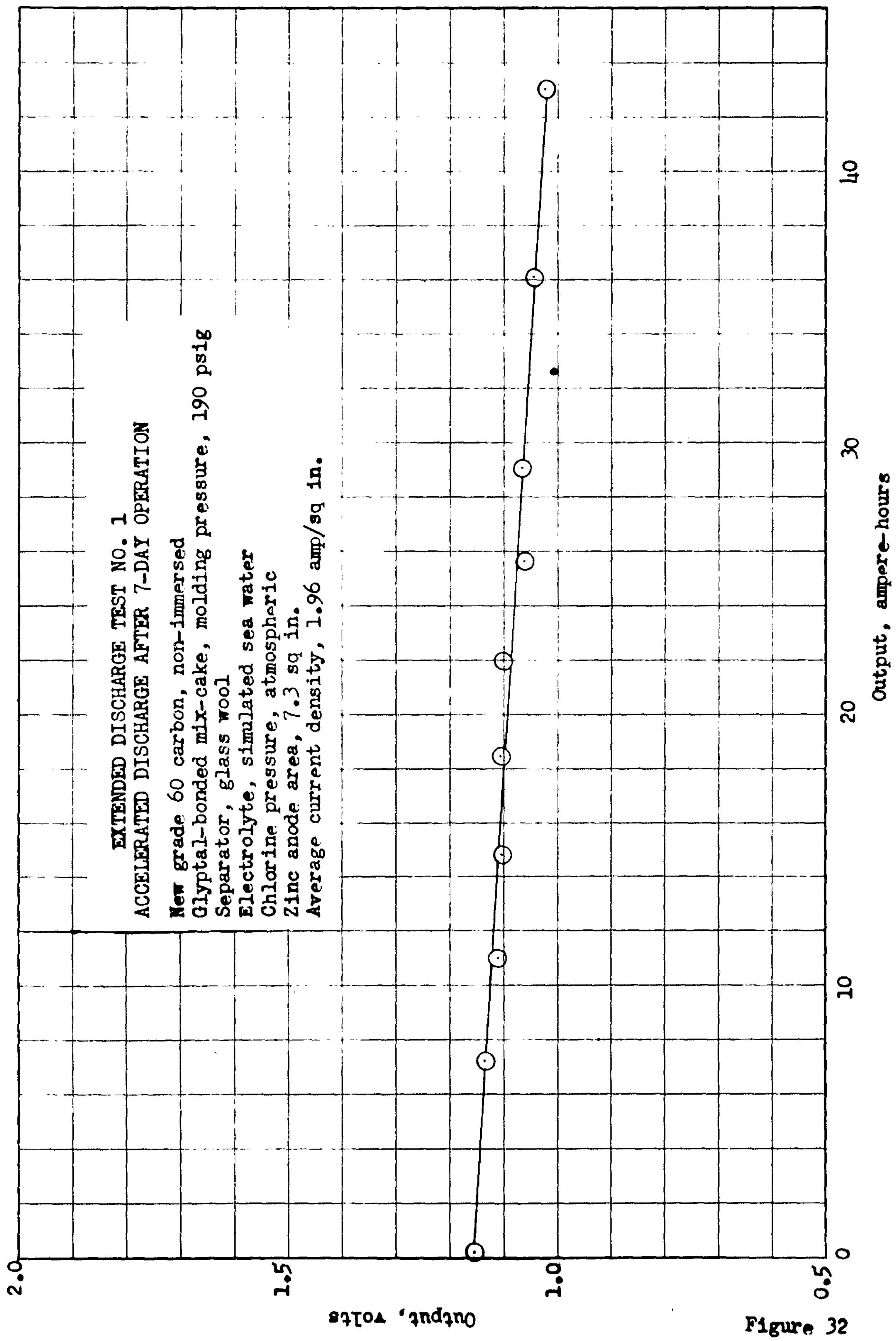


EXTENDED DISCHARGE TEST NO. 1, VOLTAGE VS TIME
SMALL ZINC-CHLORINE CELL, TYPE IX CATHODE

New grade 60 carbon, non-immersed
Glyptal-bonded mix-cake, molding pressure, 190 psig
Separator, glass wool
Electrolyte, simulated sea water
Chlorine pressure, atmospheric
Zinc anode area, 7.3 sq in.
Current density, 0.276 amp/sq in.
Reference, Table IV

Figure 31

C-3443 EPD,JS:em 9-10-53

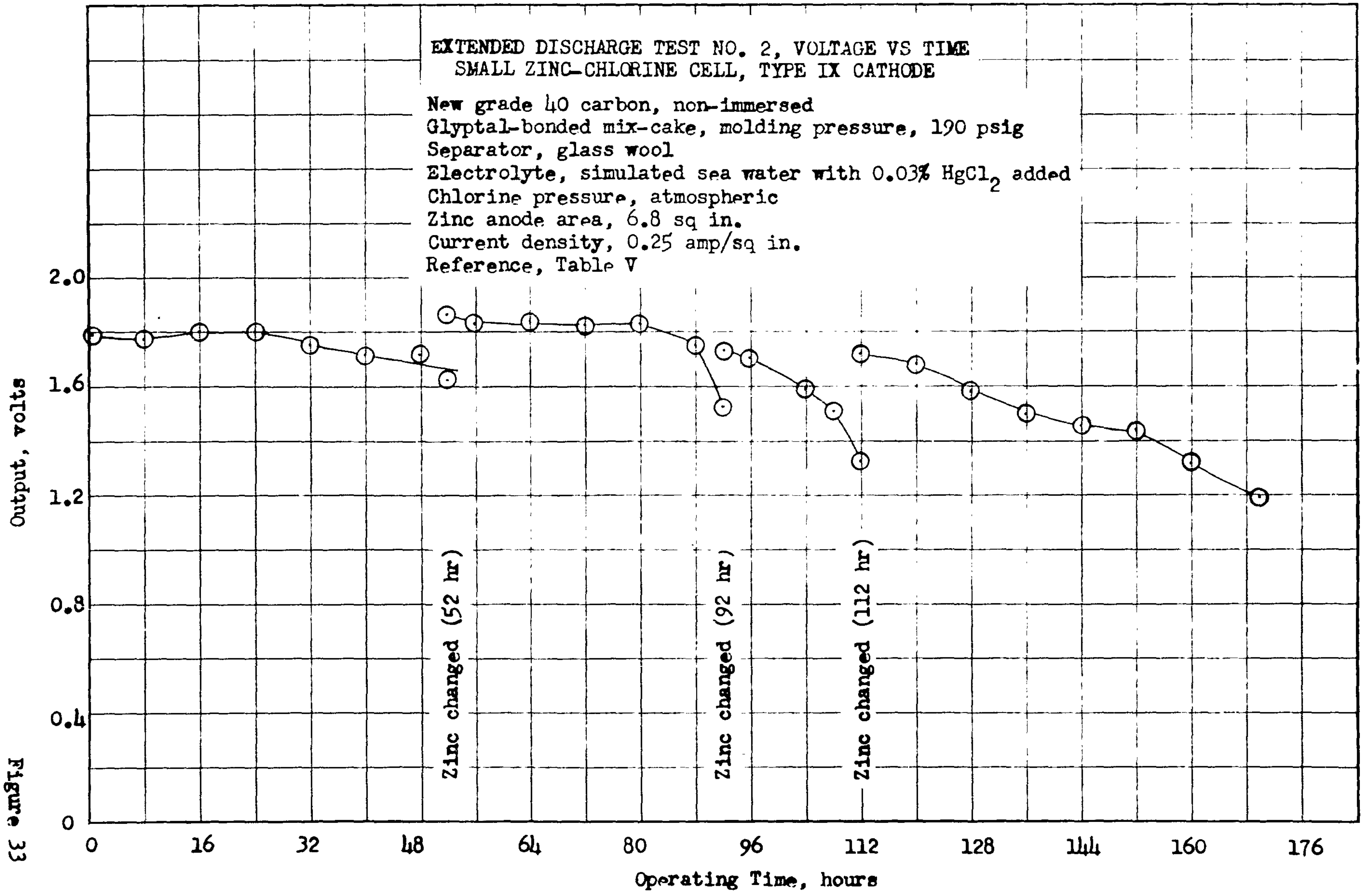


**EXTENDED DISCHARGE TEST NO. 1**
ACCELERATED DISCHARGE AFTER 7-DAY OPERATION

**New** grade 60 carbon, non-immersed
Glyptal-bonded mix-cake, molding pressure, 190 psig
Separator, glass wool
Electrolyte, simulated sea water
Chlorine pressure, atmospheric
Zinc anode area, 7.3 sq in.
Average current density, 1.96 amp/sq in.

Figure 32

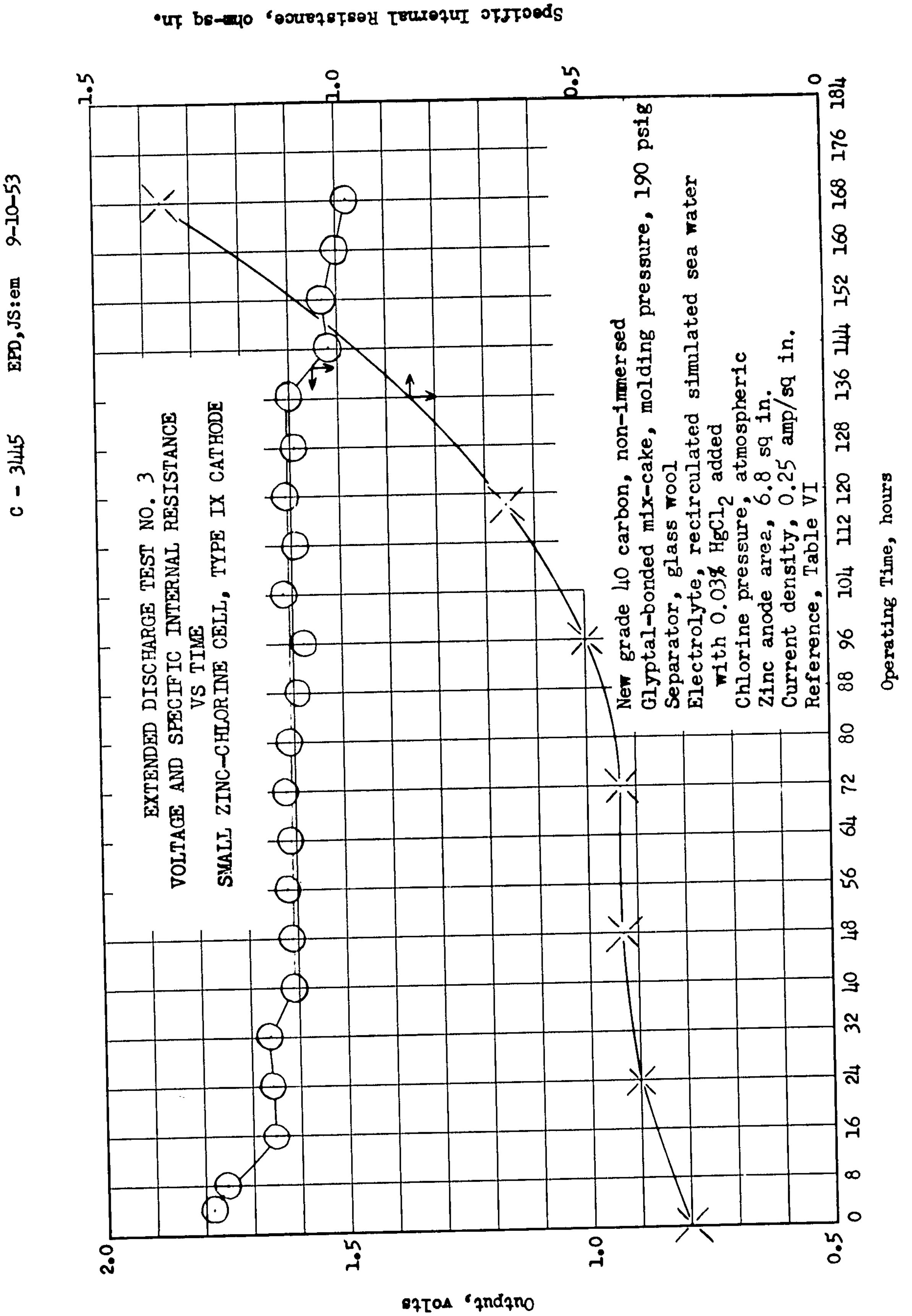
C-3444 EPD,JS:em 9-11-53



EXTENDED DISCHARGE TEST NO. 2, VOLTAGE VS TIME
SMALL ZINC-CHLORINE CELL, TYPE IX CATHODE

New grade 40 carbon, non-immersed
Glyptal-bonded mix-cake, molding pressure, 190 psig
Separator, glass wool
Electrolyte, simulated sea water with 0.03% $HgCl_2$ added
Chlorine pressure, atmospheric
Zinc anode area, 6.8 sq in.
Current density, 0.25 amp/sq in.
Reference, Table V

Figure 33



C - 3445 EPD,JS:em 9-10-53

EXTENDED DISCHARGE TEST NO. 3
VOLTAGE AND SPECIFIC INTERNAL RESISTANCE
VS TIME
SMALL ZINC-CHLORINE CELL, TYPE IX CATHODE

New grade 40 carbon, non-immersed
Glyptal-bonded mix-cake, molding pressure, 190 psig
Separator, glass wool
Electrolyte, recirculated simulated sea water
with 0.03% $HgCl_2$ added
Chlorine pressure, atmospheric
Zinc anode area, 6.8 sq in.
Current density, 0.25 amp/sq in.
Reference, Table VI

Figure 34

GLASS-WOOL SEPARATOR AFTER 96 HOURS OF SERVICE
IN EXTENDED DISCHARGE TEST NO. 3

Figure 35

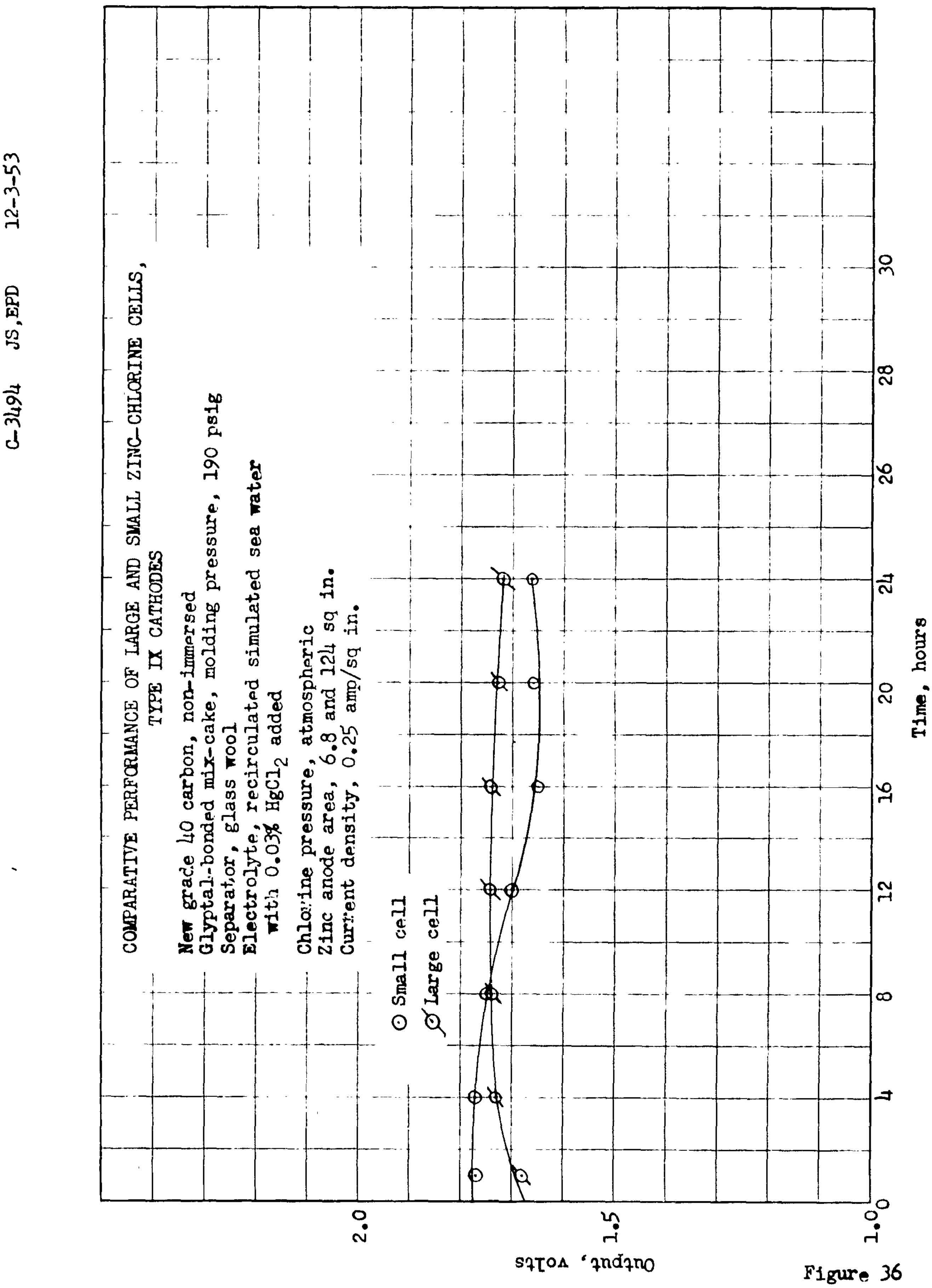

G-3494 JS,EPD 12-3-53
COMPARATIVE PERFORMANCE OF LARGE AND SMALL ZINC-CHLORINE CELLS, TYPE IX CATHODES
New grade 40 carbon, non-immersed
Glyptal-bonded mix-cake, molding pressure, 190 psig
Separator, glass wool
Electrolyte, recirculated simulated sea water with 0.03% HgCl2 added
Chlorine pressure, atmospheric
Zinc anode area, 6.8 and 124 sq in.
Current density, 0.25 amp/sq in.
⊙ Small cell
⊘ Large cell
Output, volts
2.0
1.5
1.0
Time, hours
0
4
8
12
16
20
24
26
28
30

Figure 36

## APPENDIX

### ELECTROCHEMICAL DEFINITIONS

In general, for a galvanic cell

$$V = E - IR_i$$

where

$E$ = emf of cell, volts

$V$ = terminal voltage

$I$ = current, amperes

$R_i$ = internal resistance, ohms

When $E$ and $R_i$ are constant

$$\frac{dV}{dI} = -R_i$$

That is, the negative slope of the linear portion of the curve of output voltage vs current is the internal resistance of the cell. Although $E$ and $R_i$ are not always constant because of various types of polarization, heat effects, changes in electrolyte composition, etc., the plot of $V$ vs $I$ often remains linear over a large range of $I$. It is therefore convenient to define, for the linear portion of the curve, the effective internal resistance of the cell as

$$R_i = -\frac{dV}{dI}$$

and to define the voltage at the zero-current intercept of the straight line as the effective emf of the cell. The effective voltage is in general lower than the observed open-circuit voltage of the cell; i.e., the $V$ vs $I$ curve exhibits positive curvature at low currents. The open-circuit voltage is frequently much lower than the reversible emf of the cell (e.g., in cells with magnesium anodes). The open-circuit voltage is of little interest in cells intended for high-drain applications. The standard emf of the cell may be used for determining power efficiency based on the theoretical input to the cell, but the effective voltage must be used in calculations of operating characteristics at different power levels.