

CONFIDENTIAL

BIMONTHLY REPORT NO. 3

ON THE

WATER ACTIVATED BATTERY

Period: 22 October 1959 - 21 December 1959



25X1



25X1

ORIGINAL COPY 235979
 DECL EXT BY 02/04/2010
EXT BY SAME
REASON 3d(3)

CONFIDENTIAL

CONFIDENTIAL

TABLE OF CONTENTS

	<u>Page</u>
I. ABSTRACT.....	1
II. PURPOSE.....	1
III. FACTUAL DATA.....	2
A. Phase 2, Low Temperature Performance.....	2
1. Basic Approach.....	2
2. Exploratory Test.....	4
3. Small Scale Activation Tests.....	5
4. Evaluation of Results.....	8
B. Development of a New Cooling Method.....	9
1. Basic Approach.....	9
2. The Effect of Boiling on Electrical Output.....	10
3. The Effectiveness of External Vaporization.....	13
C. Phase 2, High Temperature Performance.....	15
IV. CONCLUSIONS.....	16
V. FUTURE PLANS.....	17
VI. PERSONNEL.....	17

CONFIDENTIAL

I. ABSTRACT

During the present period our efforts have been directed to phase 2 of the program. A new and practical battery cooling technique for improving high temperature performance has been developed. Exploratory and incomplete tests indicate the feasibility of operating the battery satisfactorily at both temperature extremes -40°C and $+40^{\circ}\text{C}$.

II. PURPOSE

Phase 1:

To demonstrate the feasibility of a large model, chemically rechargeable, magnesium-silver chloride battery, activated by three per cent salt solution at room temperature and delivering an average current of 3 A at 12 V for at least 60 minutes. The voltage regulation at a maximum load current of 5.3 A shall equal or surpass the stability obtained previously.

Phase 2:

To demonstrate reasonably satisfactory performance of this battery at environmental temperatures of -40°C and $+40^{\circ}\text{C}$, using a variety of electrolytes such as three per cent salt solution, tap water and others. It is recognized, however, that such performance cannot be expected to match that at room temperature.

Phase 3:

To fabricate and deliver six battery cases and 30 complete sets of chemical recharges for field testing purposes, including instructions on the proper handling, activation, deactivation, disposal and temperature control.

III. FACTUAL DATA

A. Phase 2, Low Temperature Performance

1. Basic Approach

Phase 1 being essentially completed, our attention shall now be directed towards phase 2, a study of environmental temperature and electrolytic variables. While satisfactory operation at room temperature or higher is mainly determined by the adequacy of heat dissipation, especially towards the end of the run, it is well-known that the low temperature operation of a water-activated battery is primarily determined by the activation process at the beginning of the run. Once activated, the successful completion of the discharge is virtually assured by the abundance of heat evolution, which is capable of maintaining the operating temperature of the battery at a level substantially above the environmental temperature. It has been found, for example, that a battery case, filled with water and surrounded by a 1 1/2" layer of cotton heat insulation, except for its open top surface, and with copper leads attached to its terminals to simulate actual operating conditions, could be maintained at

a battery temperature of 20°C with a supply of only 17 watts of heat, although the environmental temperature was kept at -59°C. In fact, it is questionable whether provisions for such good heat insulation should be made at all since standard operation releases about 250 watts, which is almost 15 times the minimum value required. Too much heat insulation may therefore lead again to excessive operating temperatures towards the end of the run.

It has also been found that adequate voltage regulation is difficult to maintain at operating temperatures substantially below 0°C. Since activation must cover a much lower temperature region, it is recommended that such activation be performed with the battery short-circuited until standard operation is feasible. Depending on conditions this may take from one to several minutes. During this shorted condition, the maximum possible internal heat is generated at the highest rate, resulting in a minimum sacrifice of battery capacity prior to standard operation. In all the following low temperature tests, activation has been accompanied by an initial period of shorting.

It is desirable to activate the battery by means of an electrolyte, which is essentially in the liquid state prior to activation with at least part of it remaining liquid at all times after activation. While it has been possible to activate a battery with tap water frozen solidly soon after adding it to the case, such activation is time consuming and it is therefore not recommended. Since the battery case may be much colder than the electrolyte, prior to activation, improved low temperature

activation can be attained by reducing the thermal capacity of the case to a minimum.

2. Exploratory Test

At the start of our low temperature studies it was our intention to perform a small number of tests, using the large model battery, described in Report No. 2. In implementing this, the paper heat insulated battery case, provided with a 4-cell chemical charge, was placed in a picnic cooler and its temperature was stabilized at -40°C by placing dry ice around it in the cooler. Ideally, activation should be initiated with a liquid electrolyte also precooled to -40°C . A 50 per cent alcohol solution is known to have its point of crystallization at about this temperature. Such a solution was therefore selected as our first low temperature electrolyte except for three per cent salt which was added to enhance its electrical conductivity.

With all ingredients precooled to -40°C and the battery terminals shorted by means of a 30 A DC ammeter, activation was initiated by adding half of the required amount of alcohol solution. During a 45 minute interval, the short-circuit current never exceeded 0.5 A, a value too low for adequate internal heat generation. Consequently, the battery temperature remained very low and no useful activation could be achieved. Only after warming up the battery to about 0°C and adding standard three per cent aqueous salt solution to fill the battery, did the short-circuit

current rise to 25 A. At this point a standard load was substituted for the short, whereupon discharge proceeded normally with the battery temperature rising very slowly.

This test leads one to conclude that the addition of alcohol to the electrolyte has no beneficial effect on low temperature activation, in spite of its lowering the freezing point substantially. It was also concluded that such successful activation may require a much larger number of tests than originally anticipated. Consequently it was decided to continue our exploratory testing on much smaller samples. This will be described in the next section.

3. Small Scale Activation Tests

In the interest of simplicity and speed it was decided to use for these exploratory low temperature tests, a single cell arrangement, developed during the previous contract and described on page 50 of the Annual Report. This small case, embedded in "vermiculite" heat insulation, is mounted inside a small beaker which, in turn, is surrounded by the low temperature environment of the cooler. The temperature of the cell is measured by thermocouples. Activation is said to be completed as soon as the short-circuit current reaches a value of $1 \frac{1}{4}$ A, which is about five times the equivalent maximum, standard load current (0.26 A) for this size. As stated previously, this usually occurs at a battery temperature of about 0°C. The sacrifice in battery capacity, resulting from this type of activation, is less than 10 per cent as measured by the reduction in thickness of the AgCl layer.

Our first activation tests with this cell were made, using brine (15 % NaCl) at its freezing point of -20°C . With the case at -43°C activation starts normally at a short-circuit current in excess of 0.5 A accompanied by a substantial increase in temperature. However, as a result of the large salt concentration, polarization sets in within one minute, preventing normal operation, even at room temperature. This run illustrates the importance of the study of the electrochemical behavior of any new system in addition to its low temperature performance.

Table I summarizes the results obtained with this type of low temperature activation. Only chloride salt solutions have been used so far. The magnesium chloride solutions in particular are part of the Mg/AgCl electrochemical system. Runs 7, 11 and 12 approximate the minimum freezing point conditions for the MgCl_2 and CaCl_2 electrolytes. Run 12, a duplicate of No. 11, has been added to illustrate the effect of CaCl_2 electrolyte aging on the activation time and on the polarization. Unfortunately we have had no opportunity as yet to verify this hypothesis on aging.

The list of potentially interesting low freezing point electrolytes tested so far (see Table I) is by no means complete and should be extended. Garrett and his co-workers* have suggested a variety of

* A.B. Garrett and co-authors: J. Phys. Chem., 53, 505 (1949).
"Some Fundamental Studies of Electrolytes and Electrochemical Couples Over the Temperature Range 25°C to -75°C ".
F. Rakowsky; A.B. Garrett, J. Electrochem. Soc., 101, 117 (1954),
"Low-Temperature Electrolytes".

TABLE I
 LOW TEMPERATURE ACTIVATION
 (Single Mg/AgCl Cell 1.2 inch²)

Run No.	Electrolyte	% Concentration	Initial Electrolyte Temp. °C	Initial Case Temp. °C	1/2 minute Short-Circuit Current Ampere	Activation Time	Remarks
3	NaCl	3	+23	-20	0.6	1 minute	-
4		3	+23	-38	0.85	1 1/2	-
5		3	-1.5	-40	0.35	2	-
15		11	-9	-40	0.8	1 1/2	Solution clear with low viscosity at -9°C; no polarization
9	MgCl ₂ .12H ₂ O	11	-15	-40	0.6	1 1/2	-
7		22	-31	-41	0.45	4 1/2	Solution cloudy and viscous at -31°C; some polarization
13	CaCl ₂ .6H ₂ O	15.5	-18	-40	0.55	2	No polarization
11		31	-42	-40	0.3	5	Solution is cloudy and viscous, not as bad as No. 7 however; some polarization
12		31	-42	-41	0.2	11	Solution 2 days old; polarization*

* Conceivably caused by carbon dioxide pickup from atmosphere.

additional systems that can be profitably investigated. Some of these are listed in Table II.

TABLE II
POTENTIAL LOW TEMPERATURE ELECTROLYTES

Aqueous Eutectic Solution	Minimum Freezing Point °C
CaCl ₂	-55
CaBr ₂	-83
CaI ₂	-77
Fe ₂ Cl ₆	ca. -55
LiBr - MgBr ₂	ca. -59
LiBr - CaBr ₂	Below -60

4. Evaluation of Results

Calcium chloride electrolytes of the type used in Run 11 (Table I) hold out considerable promise of fulfilling the low temperature requirements stated in Section II. In this instance, both the electrolyte and the case can be maintained at environmental temperatures of -40°C prior to activation. Since the storage of the chemical charges at low humidity probably requires the use of a dessicant and since calcium chloride performs this function very well, it is suggested that such a

dessicant can serve a dual purpose in case low electrolyte temperature activation is desired. The amount of dessicant packaged with the charge to be dissolved in 11 ounces of water prior to activation, can be determined by such activation requirements.

However, since only 11 ounces of electrolyte are required for activation, the initial temperature requirements for the electrolyte may not be as stringent as those applicable to the case. The other data listed in Table I become equally significant if a higher electrolyte temperature is permissible. In general, it can be seen that higher electrolyte temperatures permit the use of lower salt concentrations as well as substantially reduced activation times. Even run No. 5, using seawater at its freezing point, activates quite well.

In summary it can be said that the exploratory tests reported here and supplemented by others still to follow will be very helpful in narrowing down the choice for large battery testing, particularly if a clarification of the significance of the initial electrolyte temperature can be obtained from the sponsor.

B. Development of a New Cooling Method

1. Basic Approach

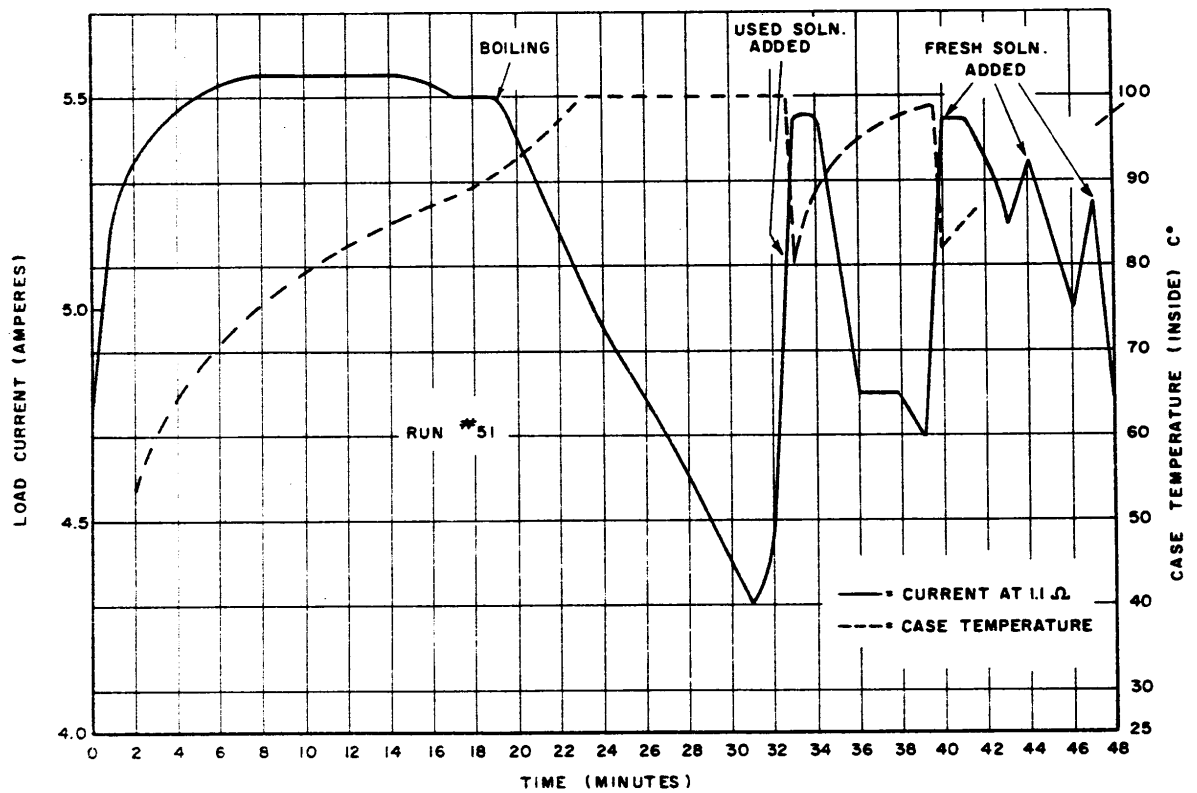
The reasons for the development of additional battery cooling, particularly in conjunction with high temperature operation, have been adequately described in Report No. 2. At a meeting with the

sponsor on 22 October 1959, it was stipulated that such additional cooling should preferably not require the use of accessories such as sand or a water bath. Neither should it lead to an increase in size or weight of the battery case. This requirement seems to rule out the use of cooling fins. In view of these new restrictions and remembering also that a high operating temperature of our special water-activated battery is not in itself detrimental to its functioning, it was felt that the additional evaporation of water might provide us with a satisfactory solution to our cooling problem. The cooling effect produced by the heating and vaporization of one gram of water added to the battery can be calculated to be equivalent to 41 watt minutes of heat. Thus the dissipation of 100 watts of heat by this process for a 20 minute period would require an additional supply of water of $2,000/41 = 49$ gms, which is only 15 per cent of the water required to fill the battery.

2. The Effect of Boiling on Electrical Output

Since the battery electrolyte contains more than 300 cm^3 of water the question naturally arises whether or not a boiling of the electrolyte has a detrimental effect on the satisfactory operation of the battery. Since such boiling has been observed to create foaming action, special provision was made for preventing such foam from spilling over the battery walls. In order to be able to study the effect of boiling for a longer period the battery case was pre-heated to 65°C by an oil bath. Figure 1 illustrates the results obtained on a 4-cell run No. 51.

11



EFFECT OF BOILING ON LOAD CURRENT

FIGURE 1

Assisted by the preheating, the battery temperature rises rapidly during the early part of the run. At 19 minutes after activation "boiling" becomes noticeable although the battery temperature is still below 100°C. This "premature boiling" is the result of the hydrogen formation, the bubbles of which begin to grow substantially in size already at a water vapor pressure slightly below atmospheric. As a result of the presence of these bubbles inside the cells the internal resistance of the battery increases and the load current drops. The foam formation, which extends beyond the cell boundaries, may also increase the internal leakage of the battery markedly, which in turn generates more heat. There may be a slight tendency for a chain reaction to develop. During boiling, electrolyte is removed from the battery. This excess electrolyte has a chance to cool down on the bench. At 33 minutes this liquid was returned to the battery; boiling stopped entirely for about one minute and normal output was resumed. At 34 minutes a second boiling cycle begins. Several such cycles have been identified in Figure 1.

Obviously the performance of a battery with a boiling electrolyte is very unsatisfactory, as can be seen from Figure 1, and it is therefore not recommended. The only other alternative, consistent with our basic approach, is the external vaporization of water.

3. The Effectiveness of External Vaporization

The necessary requirements for effective external vaporization are as follows:

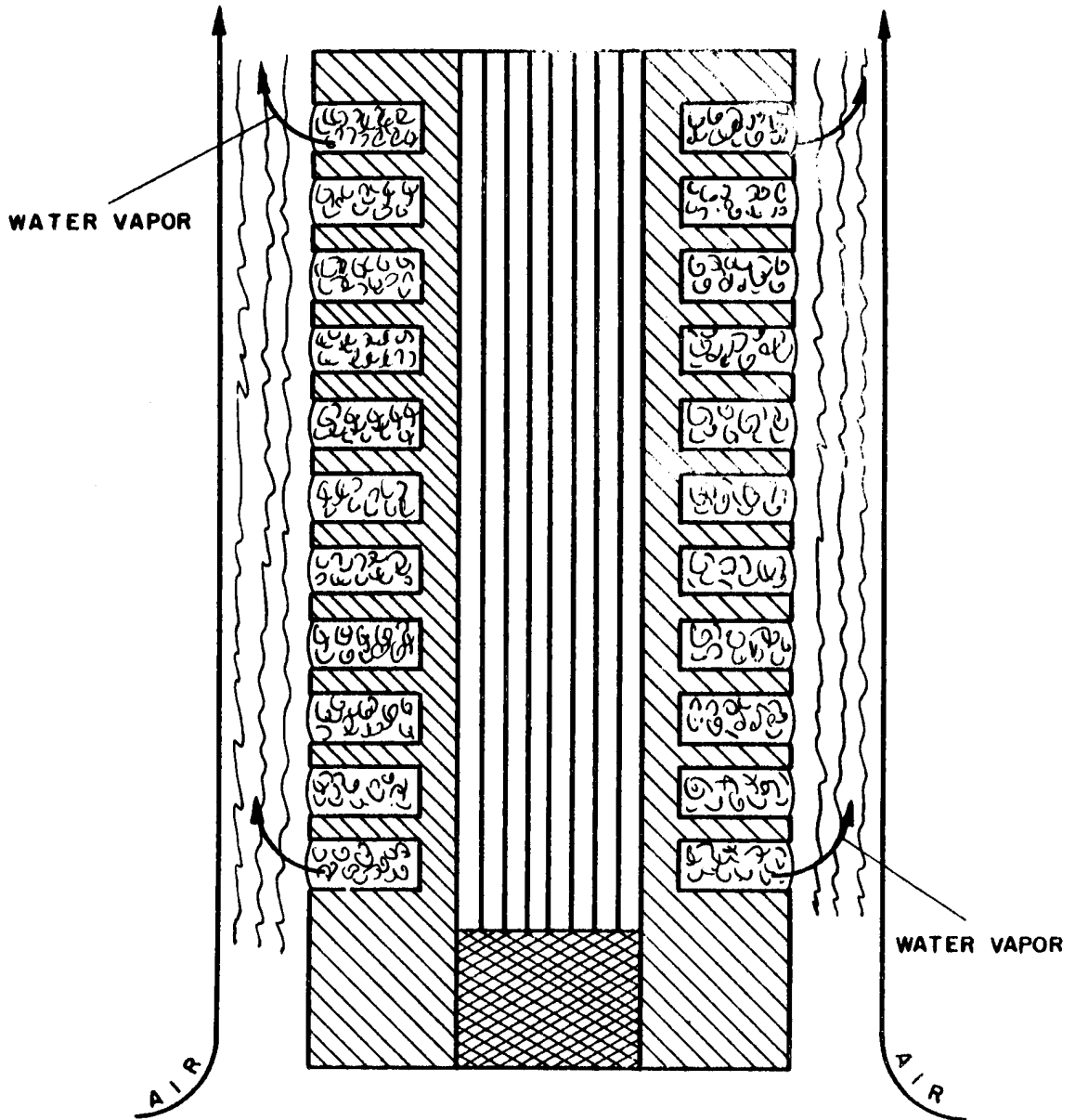
- a. The external water storage capacity must be adequate for this purpose to make it practical.
- b. The contact between water and circulating air must yield adequate vaporization.
- c. The conductance of heat from the battery to the site of vaporization must be excellent.

Figure 2 shows an enlarged cross-sectional view of the standard battery panels, each provided with 11 slots, which are filled with a highly porous, water absorbent substance such as cotton or wool. The outer surfaces of these water filled substances act as evaporators, while the ribs in between serve the following purposes:

1. They support the absorbers mechanically.
2. They prevent the absorbed water from draining downward.
3. They conduct the heat efficiently from the battery interior to the evaporating surfaces.

It was found that more than 100 grams of water could be stored externally with this arrangement.

The heat transfer measurements described in Report No. 2 are admirably suited to test the efficiency of this new cooling device. Examination of Figure 4 of that report shows that a battery temperature of 80°C is reached at a heating level of 80 W and 88°C at 120 W.



CROSS - SECTIONAL VIEW OF A BATTERY SHOWING
EXTERNAL VAPORIZATION

FIGURE 2

With the new external cooling feature added and with the laboratory air circulating freely along the two battery case panels by means of natural convection only, the same temperatures were reached at heating levels of 180 W and 250 W respectively. This corresponds to a substantial improvement in heat dissipation equivalent to 100 - 130 W at these temperatures. The water could no longer be made to boil at 250 W. At this heating level it was desirable to replenish the external water supply at 25 minute intervals.

C. Phase 2, High Temperature Performance

While to date no actual high temperature battery tests, incorporating this new external cooling feature, have been made, the heat transfer measurements, described previously, have been extended to include high temperature environments. By means of hot plates and infrared lamps a high temperature environment was simulated on the laboratory bench, creating an equilibrium temperature inside the battery case of about 47°C. At an internal heating rate of 250 W the water temperature inside the battery was viratually unchanged (87-88°C), although the external water supply required replenishment now at a rate of 16-19 minute intervals. Hence the cooling appears to be more efficient at higher temperatures.

To make sure that such excellent cooling performance is not influenced by our bench type arrangement, the equipment was moved into a steam tunnel. Cooling tests were repeated at tunnel temperatures of 38-39°C with the same results. Again the battery temperature could be stabilized at 87-88°C. Although no such tests have been made, it is felt

CONFIDENTIAL

that variations in the relative humidity of the air are not likely to affect the cooling efficiency to any appreciable extent.

IV. CONCLUSIONS

Incomplete information on the low temperature activation of the "water"-activated battery leads to the following tentative conclusions:

- a. The activating electrolyte must be a liquid.
- b. Calcium chloride solutions at -40°C do activate the battery.
- c. If it is permissible to use electrolytes at a higher activating temperature, much lower salt concentrations can be used and activation may be completed in 1 to 2 minutes.
- d. The sacrifice in capacity resulting from low temperature activation is small.
- e. Once activated, the discharge proceeds normally provided a reasonable load level can be maintained.

A new efficient cooling technique for improving the high temperature performance of the battery has been developed. It is based on the external vaporization of water and it does not require any accessories or increases in size or weight.

Although no full-scale battery tests on phase 2 have been made, it is felt that most technical problems encountered during this program have now been solved.

CONFIDENTIAL

CONFIDENTIAL

V. FUTURE PLANS

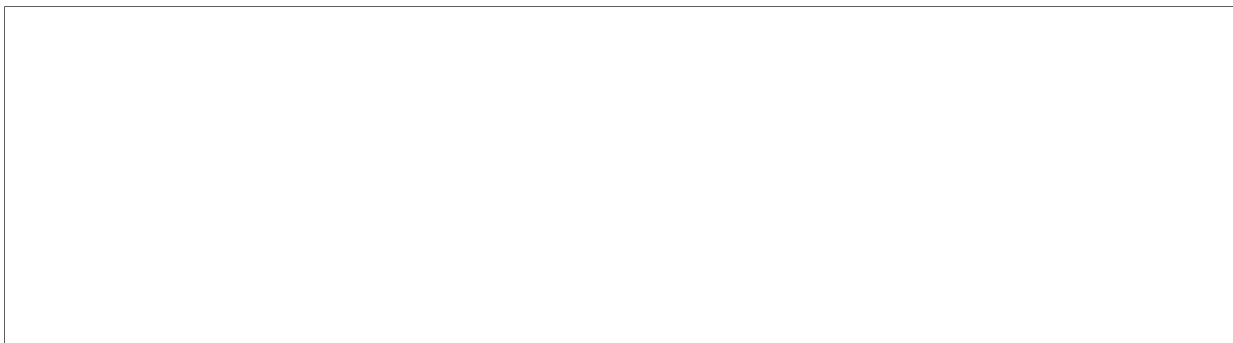
Proposals for the extension of the present contract are pending. Since they do affect the plans for the next reporting period, nothing definite can be said about them at this time.

In case no program changes are contemplated it is recommended that:

- a. The high temperature performance tests, including the new external cooling feature, be completed.
- b. The design of the battery case be finalized and work on phase 3 be initiated.
- c. Completion of the low temperature activation and performance program be postponed until the period after next.

VI. PERSONNEL

25X1



CONFIDENTIAL