(NASA-CR-157132) PRELIMINARY INVESTIGATION OF A SEALED, REMOTELY ACTIVATED SILVER-ZINC BATTERY Final Report (Eagle-Picher Industries, Inc., Joplin, Mo.) 33 p
HC A03/MF A01 CSCL 10C G3/44

N78-24647

Unclas
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PRELIMINARY INVESTIGATION OF A SEALED, REMOTELY ACTIVATED SILVER-ZINC BATTERY

FINAL REPORT

Report Number 1026-77-1

7 September 1977

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Contract Number 954768

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology sponsored by National Aeronautics and Space Administration under Contract NAS7-100.

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ABSTRACT

This effort involved the investigation into methods necessary to provide a remotely activated, silver-zinc battery capable of an extended activated stand while in a sealed condition. These requirements were to be accomplished in a battery package demonstrating an energy density of at least 35 watt hours per pound. Several methods of gas suppression were considered in view of the primary nature of this unit and utilizing the electroplated dendritic zinc electrode. Amalgamation of the electrode provided the greatest suppression of gas at the zinc electrode. The approach to extending the activated stand capability of the remotely activated battery was thorough evaluation of three basic methods of remote, milti-cell activation; 1) the electrolyte manifold, 2) the gas manifold and 3) the individual cell. All three methods of activation can be incorporated into units which will meet the minimum energy density requirement. The lightest weight unit was determined to be one utilizing the electrolyte manifold activation method and a single spherical electrolyte reservoir. This method of activation is also considered to be the most reliable to activate. The individual cell method is considered to be the most unreliable to activate but would have a high reliability to accomplish the activated stand without degradation. The gas manifold method is essentially a compromise of reliability but presents a greater developmental risk (and expense) to establish its capability.

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OF A
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SILVER ZINC BATTERY

FINAL REPORT

I. INTRODUCTION

This application for a silver-zinc battery is for outer planetary exploration. The battery would be activated upon reaching the vicinity of the target planet after completing an extended space travel period. The battery in a probe separates from the mother vehicle and continues the mission to the planet, providing electrical power along the way. The requirements of long unactivated and long activated life for the battery are necessary to complete the mission.

The probe mission represents a departure from currently designed remotely activated batteries. Activated stand time is normally expressed in hours with 90 hours being a possible maximum previously considered in design. For this application, 90 days is required creating a necessity for determining the limits of present designs and/or establishing other design possibilities. In addtion, the probe battery cannot vent any generated gases during its life and must be packaged at an energy density of at least 35 watt-hours per pound.

Three key design factors are considered to be essential for extended activated stand in a remotely activated unit. They are 1) adequate barrier separation between electrodes to prevent interplate shorting, 2) minimized electrolyte paths between cells to prevent intercell shorting and 3) complete, adequate activation of each cell. Separation material is available to provide the barrier for preventing interplate shorting. Factors 2 and 3 are functions of the remote activating and distributing system. This investigation considers three basic, related methods of activating multiple cells, 1) the electrolyte manifold, 2) the gas manifold and 3) the individual cell. Evaluation is made based upon stand capability, reliability and energy density.

This report begins by establishing the basic cell design and considering methods for gas evolution reduction. Subsequent to a discussion of the battery design including the various activation methods, a brief treatment is given to the impact of the radiation environment upon battery design. A relatively complete comparison of the different battery types is included within this report. The methods of activation are accomplished without incorporating any unique or exotic features. Since the effort was basically a feasibility evaluation, demonstration of the design concepts remains.

II. TECHNICAL DISCUSSION

.1) Cell Design

A basic cell configuration was established for the requirement. This cell contained certain features commensurate with high energy density design and requires processing in accordance with previously established procedures which enhance life/efficiency performance. Required electrical capacity is 12 ampere hours at 15 volts nominal. Maximum steady state discharge rate is 8 amperes.

To accommodate the ten-year dry life requirement at 25°C, a 10% additional active material loading is incorporated. With the dry storage allowance and an allowance for manufacturing variations, an initial (fresh) battery capacity requirement of 15 ampere hours was established. The resulting cell design elements are presented in Table I. A contingency amounting to 10% of the active zinc material was included for the recommended gas evolution treatment. Since amalgamation of the zinc appeared to provide the best control of gassing, the actual weight impact of the treatment would be less than 2 grams per cell.

TABLE I

CELL DESIGN

	GRAMS	
Silver Oxide	45.0	Electroformed Sintered Silver
Zinc	30.0	Electroplated Sponge Zinc
Positive Grid	2.2	0.20 g Expanded Silver
Negative Grid	3.2	0.22 g Expanded Copper
Asbestos Separation	2.7	0.005 Quinorgo 6000(2)
Cellophane Separation	2.9	0.001 193 Pudo(5)
Plate Connection	2.1	Grid Tab/Solder
Intercell Connection	0.9	Copper Wire
Contingency	3.0	Gas Evolution Treatment
Total	92.0 grams	

Active Surface Area	19.5 in^2
Current Density at 8 amps	0.41 A/in^2
Cell Volume	48 cc
Fresh Capacity Requirement	14.2 to 15.7 AH
Basic Electrolyte Volume	22.1 cc

1) Cell Design (Continued)

A typical discharge characteristic of the cell design is shown in Figure 1. A simplified discharge profile was used for this discharge at room ambient conditions. This characteristic is relatively unaffected at the required operating temperature of +5°C.

For the specified 90 day activated stand requirement, four layers of 1 mil cellophane are usually sufficient. Five layers are recommended here to provide a higher level of confidence in the stand accomplishment. The 5 mil layers of asbestos sheet also provide added protection against interplate shorting because of their bulk. And finally, the cell cavity is sized to accommodate the normal swelling of the cellophane material to prevent excessive pressure on the plate pack. This pressure increases the potential for developing interplate shorting. Each of the features mentioned in this paragraph are incorporated to insure that the cell, apart from the method of activation, will reliably perform after the activated stand period. These features are not conducive to high energy density but are considered necessary from a reliability standpoint.

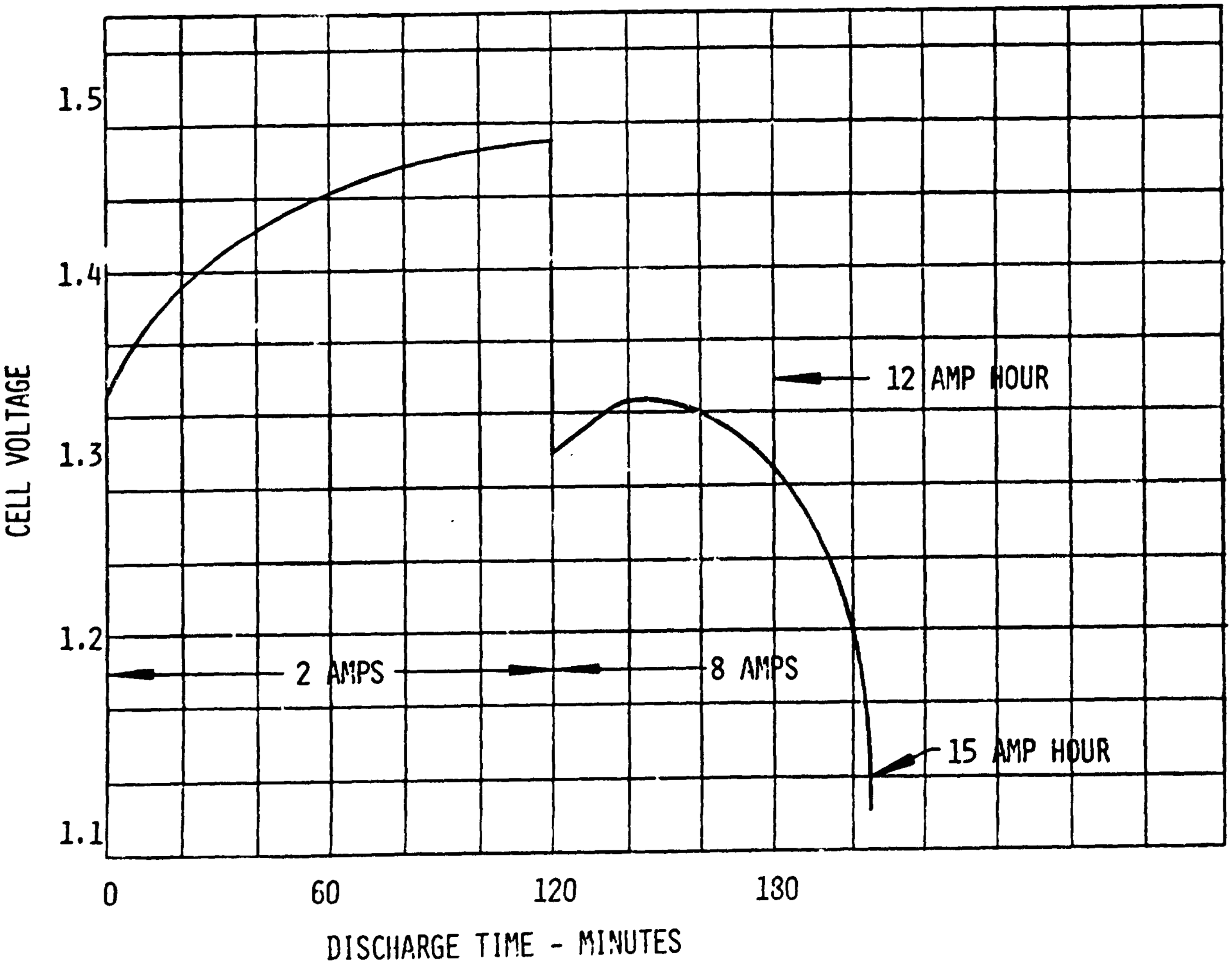
An additional consideration for stand reliability is the method of separation wrapping. Normally, short life primary and remotely activated cells use the simple "U" wrap method while longer life secondary cells use a tubular roll wrap. The roll wrap provides added protection of plate edges against shorting. The performance of the roll wrap in a remotely activated unit has not been demonstrated. Further evaluation of this cell should include the demonstration of roll wrap use since an added measure of stand reliability can be realized for a very small weight penalty.

2) Gas Evolution

To demonstrate the sealed operating capability of the basic cell, several tests were conducted using known methods for suppressing gas formation. These tests were limited to open circuit or stand in potassium hydroxide (KOH) electrolyte and were directed towards the zinc active material, the principal source of gas. Materials were immersed in KOH and gas collection was begun immediately to simulate the condition of the remotely activated cell. Collection was continued until a stabilized rate of gas evolution was established, usually in excess of 48 hours.

Hydrogen gas is evolved from the silver zinc cell during open circuit stand. This gas is the result of the dissolution of zinc in KOH electrolyte involving only the water of the solution. Gas production is inversely proportional to the concentration of the electrolyte. The reaction proceeds at a rate dependent upon temperature and solution saturation. During discharge, the gassing rate increases, partially due to the temperature increase resulting from discharge inefficiency. Also involved in the increase is possible mass transport/natural convection occurrences which make available to the zinc, unsaturated electrolyte.

FIGURE 1 - CELL DISCHARGE - ROOM TEMPERATURE



2) Gas Evolution (Continued)

The silver oxide active material also evolves gas during open circuit stand. The gas evolved is assumed to be loosely bound oxygen and the rate of evolution would be expected to decrease as a function of time. Discharge accelerates the rate of gas formation from the silver oxide due again to the temperature increase from discharge inefficiency. It would also be expected that the rate would decrease as the state of charge decreases due to the formation of the more stable monovalent silver oxide.

Methods to inhibit gas evolution have been developed in the past. The intent of the testing performed was to determine the most effective method considering energy density. The efficiency of the electroplated zinc electrode is considered to be superior to the efficiency of other electrodes. The electrode was established as the basic design and the prime target for the gas reduction effort. Because the plated zinc electrode is more efficient electrically, it also is more active in the production of hydrogen gas. Methods investigated were 1) amalgamation, 2) saturated electrolyte and 3) additive metal salts. The zinc amalgam is currently the most widely used method of gas suppression. And, as evident in Table II, the mercury treated zinc provides the greatest reduction in the gassing rate. Note that No. 122 Zinc is pure zinc powder as a reference. This powder is normally used in direct pasted zinc electrodes. Two different lots (1 and 2) of electroplated material are shown in Table II revealing the variation due to processing.

TABLE II

ZINC*

GAS EVOLUTION CC/HR
ROOM TEMPERAUTRE

	122	Lot 1 Plated	Lot 2 Plated
Untreated Zinc	2.0	8.3	3.4
Amalgamated Zinc	1.4	0.5	0.1
KOH Saturated w/ZnO		3.1	
KOH + PbO/Al_2O_3		8.8	2.2
KOH Saturated w/ZnO + Amalgamated Zinc		0.4	0.1

* 30 grams samples in 1.350 specific gravity KOH

The gassing rate differential between untreated No. 122 zinc and the plated material may be a function of active surface area. Surface area analysis resulted in a figure of 0.36 square meter per gram for No. 122 zinc and 2.98 m^2/g for the plated electrode material. The larger surface area in contact with the electrolyte would be expected to yield more gas, however, the difference in gassing rates recorded were not of the same magnitude as the difference in surface area. Processing also influences the plated material as evident in Lot 1 results. The higher rate of gassing from Lot 1

2) <u>Gas Evolution</u> (Continued)

is thought to be due to the presence of catalyzing impurities introduced during the plating process. Metals such as iron, nickel or platinum can serve as a catalyst to the hydrogen evolution reaction while in either electrolytic or electronic contact with zinc.[1]

The use of electrolyte saturated with zinc oxide does not appear to be as effective as amalgamation. The combined treatment of amalgamation and saturated electrolyte appears to yield the same result as amalgamation alone. Previous testing of this method of gas suppression has produced conflicting data as to the effects of the saturated electrolyte upon electrical performance. It is likely that in a primary application such as a remotely activated unit, some loss is experienced in the initial power capability. Since no long term storage history of ZnO saturated KOH in any type of reservoir is available, it would be desirable to avoid this method if possible. The results indicate that it is possible.

Another alternative to the previously mentioned methods of gas suppression would be to dissolve certain (foreign) metal salts in the electrolyte. While some metals are catalytic, other such as mercury, thallium, lead and tin are not and, in fact, impede the reaction by increasing the overvoltage for hydrogen evolution on zinc.[1] Small amounts of the metal salts may be added to the electrolyte to achieve the desired results. A previously isolated, presumably effective additive, lead oxide and aluminum oxide, was incorporated into the test evaluation. Although some reduction in gassing was indicated in Lot 2 material, Lot 1 was apparently uneffected. Possibly the supposed catalyzing impurities in Lot 1 material overcame any attempt to reduce gassing by using elements with a reverse action. In any event, the effect was not of a magnitude to provide competition with the amalgamation method.

Summarizing, in the matter of hydrogen evolution from the zinc electrode, amalgamating the electroplated zinc yields the greatest reduction in the gassing rate. Care must be exercised in the amalgamation process to prevent formation of undesirable side compounds which reduce the energy efficiency of the material. The addition of 2 to 3 percent mercury will maximize the effect. Power capability is relatively unaffected by the mercury content and under certain conditions may improve the performance. Gassing rates of less than 0.1 cc per hour from one cell's worth of zinc (30 grams) are necessary to prevent excessive pressure build-up in the battery. Limited testing at the +5°C operating temperature indicated that this rate could be achieved using the zinc amalgam. Coupled with possible use of a higher concentration of electrolyte, the gassing rate from the zinc electrode should be tolerable.

Control of gassing from the silver oxide electrode presents a different problem in that the dissolution of AgO in the electrolyte does not produce gas. The rate of evolution which is less than that experienced with the zinc still remains as a contributor to the pressure build-up in the

2) Gas Evolution (Continued)

activated cell. Limited testing has indicated that the form of silver oxide in the electrode causes evolution of oxygen. The basic design cell electrode is a charged, sintered silver material used extensively in silver zinc battery manufacture. Monovalent silver oxide (Ag_2O) is pasted, reduced to silver to form a porous, sintered silver plaque. The sintered plaque is charged to divalent silver oxide (AgO) in potassium hydroxide electrolyte.

Previous investigation of the formation process has concluded that no significant change or reduction in oxygen evolved from the sintered electrode can be attained by manipulating process variables within the range investigated.[2] One additional area was investigated during this effort. This area was the pasting of the monovalent silver oxide which uses tap water in the process. The intent was to remove impurities from the sintered plaque due to the use of tap water by using distilled water for oxide pasting. Subsequent gas collection from the material pasted resulted in recording a gassing rate at room temperature of 0.036 cc/hour from both samples regardless of the type of water used for pasting. The included impurities do not seem to influence the gassing rate. The gassing rate from both samples did appear to decrease with time as might be expected. Moving the collection apparatus to a +5°C chamber resulted in a rate drop to less than 0.01 cc/hour.

An electrode was formed by directly pasting chemically prepared AgO onto a silver grid. This electrode was observed in 1.350 sp. gr. KOH at room temperautre resulting in a recorded gassing rate of less than 0.003 cc/hour, decreasing. This suggests that the composition of the electrode itself is the main factor contributing to gas evolution. The sintered electrode is a mixture of silver species, i.e., silver, monovalent silver oxide and divalent silver oxide. The interaction of these elements which occurs during both activated and unactivated stand may produce the potential for oxygen evolution. In the case of the chemically prepared electrode, these interactions are not predominate because of the process and resulting electrode structure. The difference in the composition and structure of the two electrode processes is substantiated by the electrode performance which is significantly different.

Summarizing, the silver oxide gassing rate is basically tolerable at the expected operating temperature. No method of reducing this rate by process or composition changes is evident or necessary. The consistancy of the pasted AgO electrode has not been established sufficiently to warrant consideration in this design.

Cell separation material was immersed in 1.350 sp. gr. KOH to observe any individual gas evolution from these materials. The quantity used was equivalent to the amount required for the basic design cell. Material evaluated was cellophane, asbestos and Permion, the latter being considered as a substitute for cellophane. No gas was produced from any of these materials during a sixty-day observation period at room ambient conditions.

2) Gas Evolution (Continued)

Control of pressure build-up of the basic design cell during extended open circuit stand is best accomplished by amalgamation of the zinc electrode and maintaining a low temperature of exposure during the stand. Further reduction of gassing can be accomplished by increasing the concentration of the electrolyte at the expense of decreased energy density and increased internal impedance.

3) Battery Design

The approach to the battery design requires several basic established guidelines so that a fair appraisal of each type of activation method might be made. Of course, the basic cell configuration, i.e., quantity of materials, is maintained in each design considered. In addition, the volume that contains these cell materials was held constant through each design.

Required energy at minimum weight was the established philosophy of design, however, reliability was not sacrificed for small weight payoffs. Cell case material was set at 0.062 and 0.125 inch thick acrylic sheet. Relatively thick asbestos sheet was selected as the absorbent separator material and an extra allowance was provided for the swelling of cellophane separation These features are built into the volume of the cell cavity and enhance reliability of normal performance.

Where the coil tube was used as an electrolyte reservoir, 0.625 inch stainless steel tubing with 0.010 inch wall was selected. Apart from having good strength and being lightweight, this size tubing is considered to be the most efficient standard size when considering the weight, volume contained and the ability to empty efficiently. Each design incorporates an electrically initiated pyrotechnic device (gas generator) to provide the medium for moving the electrolyte from the storage reservoir to the cells.

Electrolyte is provided as 1.400 sp.gr. potassium hydroxide in quantities determined by the basic cell requirement and the efficiency of the emptying and distributing systems. In the coil tube system, for instance, an additional 10% is included to allow for emptying and 5% for distribution inequalities. In the single reservoir per cell systems, the 5% distribution factor can be omitted and in the systems which provide separation between the activating gas and the electrolyte, the emptying factor of 10% can be removed.

The weight analysis considers the use of 28 gauge stainless steel where necessary as a battery container. Additional weight reduction of up to 10% can be realized through the use of a suitable substitute material such as titanium alloy (AMS4910).

3) <u>Battery Design</u> (Continued)

With the guidelines of the preceeding paragraphs, three basic methods of remote, multicell activation were evaluated, 1) the electrolyte manifold, 2) the gas manifold and 3) the individual cell. Each of these methods will be discussed in the sections to follow. The methods are referred to as Type 1, Type 2 and Type 3 with variations within each type designated as A, B, or C. Table III summarizes the weight/volume results for each type and variation considered.

The remote activation system consists of a gas generator, electrolyte reservoir and a distribution arrangement to the multiple cells. Distribution of electrolyte to each cell must be configured to retard or eliminate intercell shorting through electrolyte paths between cells. In addition, the activation system must empty efficiently, distribute evenly and store electrolyte for a minimum period of ten years. Resulting from the consideration of all elements with emphasis given to minimizing component weight, Table IV is also included which presents a weight breakdown of each design. Table V lists the active volumes within each design used to develop the gas generator requirements based upon the electrolyte required and the void available.

TABLE III

ACTIVATION METHODS SUMMARY

	Type 1 Electrolyte Manifold			Type 2 Gas Manifold		Type 3 Individual Cell	
	A	B	C	A	B	A	B
Total Weight (gm)	2368	2028	1808	2164	2130	2386	2048
Energy Density (wh/lb)	34.5	40.3	45.1	37.7	38.3	34.2	39.9
Volume (in^3)	120	80	70	107	111	105	74
Energy Density (wh/in^3)	1.5	2.2	2.6	1.7	1.6	1.7	2.4

Design Goal less than 2332 grams

TABLE IV
WEIGHT BREAKDOWN
GRAMS

	Type 1			Type 2		Type 3	
	A	B	C	A	B	A	B
Cell Materials (10)	920	920	920	920	920	920	920
Cell Case	202	140	140	276	202	219	68
Manifold	56	70	70	105	63	63	54
Air Sump	63	0	0	90	39	36	0
Reservoir	146	146	47	48	75	129	129
GG Adapter	26	26	10	26	26	110	110
Manifold Adapter	35	28	10	11	50	108	108
Gas Generator	20	24	20	18	20	42	44
Electrolyte	365	365	328	310	310	346	346
Container	312	128	173	290	278	269	125
Connector	10	10	10	10	10	10	10
Conductors	15	15	15	15	15	20	15
Potting	198	156	65	45	122	114	119
TOTALS	2363	2028	1808	2164	2130	2386	2048

TABLE V

VOLUME BREAKDOWN

CUBIC CENTIMETERS

	Type 1			Type 2		Type 3	
	A	B	C	A	B	A	B
Cell Void	346	346	346	34.6	34.6	34.6	34.6
Manifold/Reservoir Void	22	16	14	1.7	2.9	2.4	2.0
Air Sump	73	0	0	33.5	9.6	10.2	0
Electrolyte	260	260	234	22.1	22.1	24.0	24.0
Gas Generator Minimum	785	1167	785	350	693	64(10)	100(10)
Compression Ratio	2.8	4.2	3.2	1.5	3.0	2.3	3.7

4) Electrolyte Manifold Activation (Type 1)

Electrolyte manifold activation is the method most commonly used in remotely activated, silver-zinc units. A single reservoir and gas generator discharges electrolyte into series connected cells via a common manifold which directs the flow to each cell. Since the manifold carries the electrolyte to the cells, an electrolyte connection between cells exists, a connection which results in internal discharging of active materials. The effects of this discharge is extremely variable depending upon the amount of electrolyte in the manifold, continuity of path, the potential difference and time. The last factor, time, separates this effort from commonly designed remote activated batteries. Normally, units have very short activated life and can tolerate internal discharge due to manifold electrolyte leakage currents. For the ninety-day stand requirement at relatively high energy density, the luxury of compensating active material cannot be afforded.

Aside from determining the tolerable level of internal discharge, certain steps can be taken to reduce the magnitude of the leakage. Since the Type 1 system has a large background of use, consideration was given to improved resistance to intercell discharge during stand. Figure 2 is a typical configuration of a Type 1 system with the exception of the distribution manifold. In the design of this manifold, it was attempted to achieve maximum path lengths and provide equal flow resistance to each cell. A laminated construction was devised which more than doubled the conventional length between cells, provides a parallel flow and provides equivalent length and shape paths to each cell. The weight impact of this arrangement was considered to be a good trade-off for the benefits in manifold characterisitics derived. Volumetrically, however, a greater penalty resulted.

Because of the extra volume projected by the laminated manifold, it was decided to incorporate extra cavities for each individual cell for expansion. These cavities are designated as "air sumps" and would provide a reduction in initial battery pressure resulting from the activation process. The laminated manifold also resulted in an additional unused volume normally taken up by the electrolyte coil reservoir. This is displaced by potting material of polyurethane foam (0.225 grams/cc) used to completely fill the remaining voids in the battery package.

The "conventional" prismatic packaging of the unit with a coiled tube reservoir is rather inefficient, resulting in a weight which is projected to slightly exceed the goal, 2368 versus 2332 grams. Volumetric efficiency is also poor. A portion of the unused volume could be used for containing the electrical connector and mounting provisions within the confines of the rectangular configuration shown which would result in a net decrease in unit weight.

The unit discussed in the previous paragraphs is more efficiently packaged in cylindrical form as shown in Figure 3. Designated a Type 1B system, the unusable volumes are eliminated. The manifold is modified from the configuration discussed previously incorporating a series-parallel flow arrangement. The parallel legs provide extra length while in the series section, wide separation can be maintained between cell entries of the highest potential difference. Because no conveniently usable volume is available in this design, the air sump sections for individual cells are eliminated.

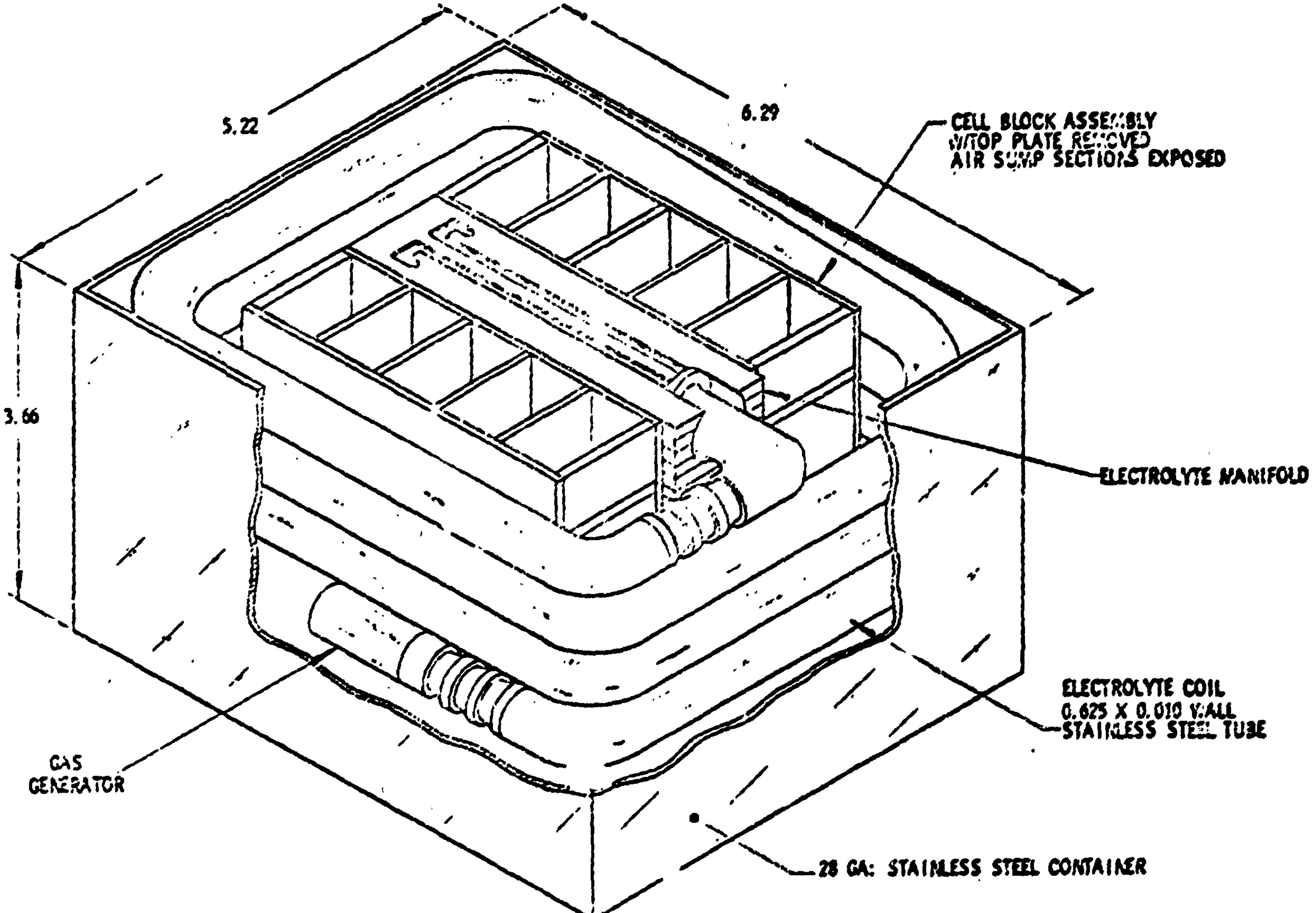


FIGURE 2

TYPE 1A SYSTEM
ELECTROLYTE MANIFOLD ACTIVATION

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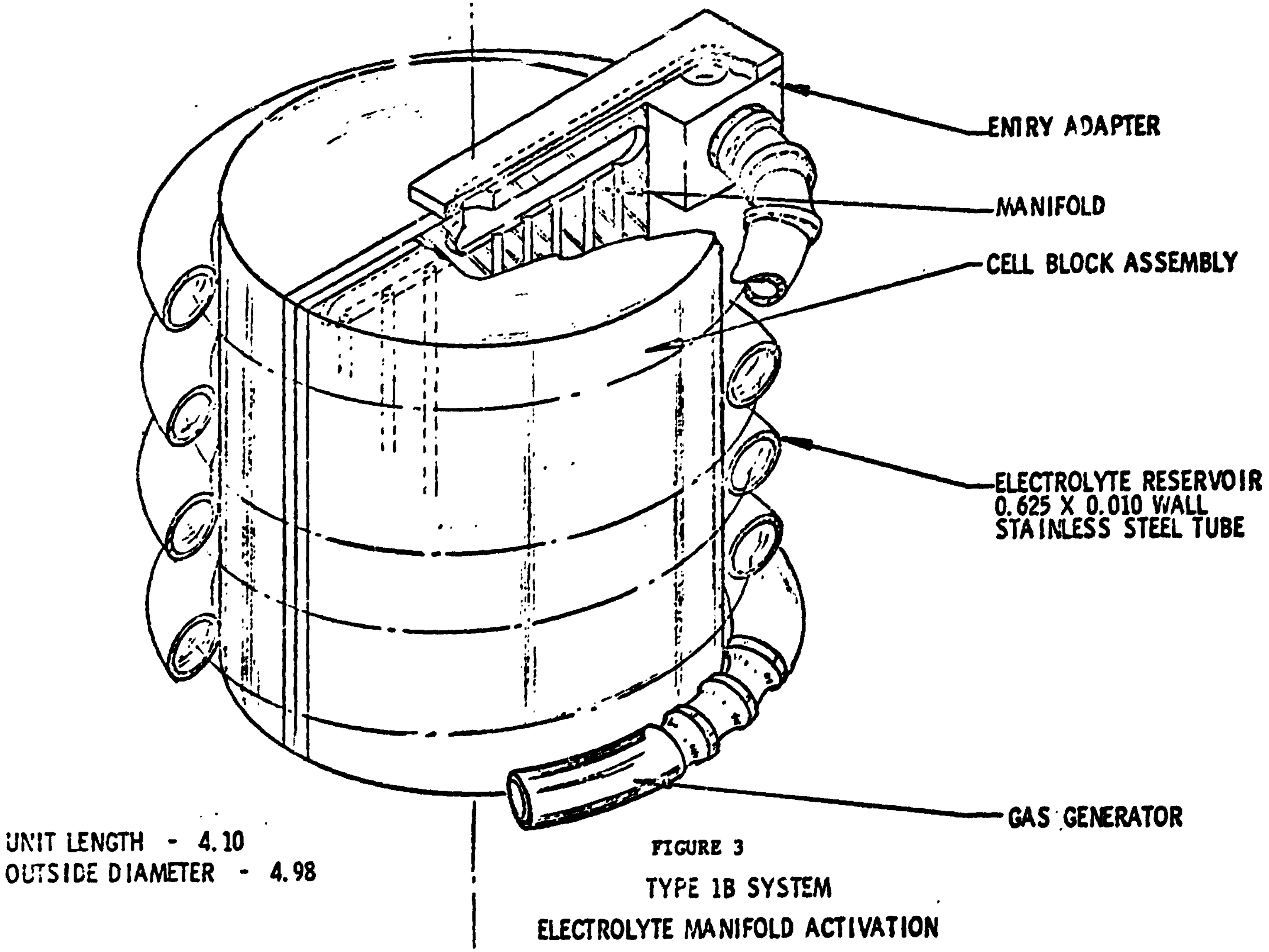
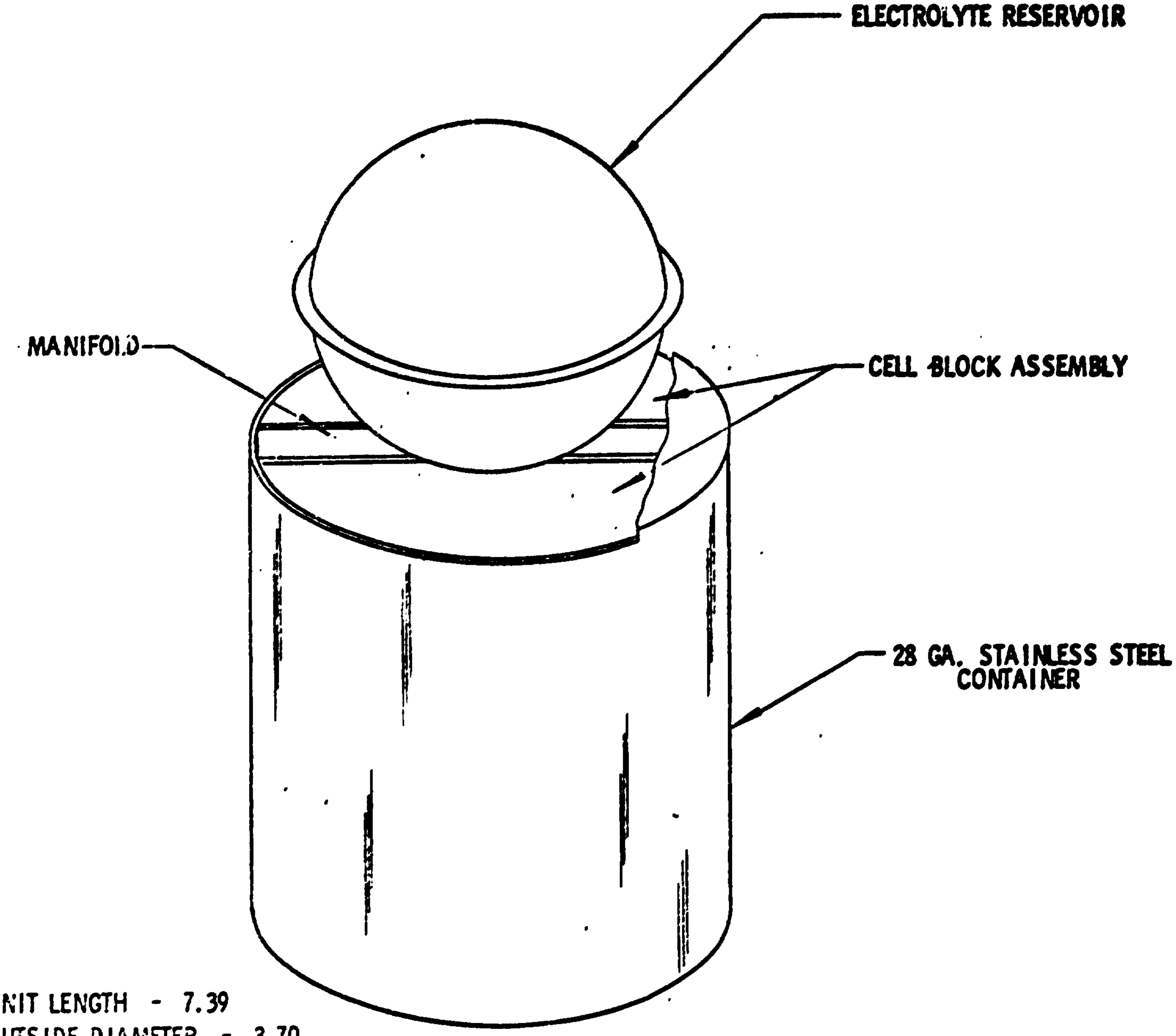


FIGURE 3

TYPE 1B SYSTEM

ELECTROLYTE MANIFOLD ACTIVATION



UNIT LENGTH - 7.39
OUTSIDE DIAMETER - 3.70
SPHERE DIAMETER - 3.01

FIGURE 4

TYPE 1C SYSTEM

4) Electrolyte Manifold Activation (Continued)

Packaging the unit cylindrically with the coil tube reservoir will also allow the the use of the coil tube as a battery cell block support or container. With the coil under block pressure and the load transmitted via the use of relatively dense potting material, the strength capability of the block becomes nearly equivalent to that of the coil. The end plates would require additional support and end caps of stainless steel are provided in the weight analysis (omitted in the drawing for clarity). The savings in weight in cell case, container and potting material amount to 14% over the rectangular form factor. A 33% reduction in volume is realized.

A third configuration is offered combining the cylindrical block and manifold system of the Type 1B design with a spherical electroltye reservoir. Designated Type 1C, the design is shown in Figure 4. The block and manifold are identical to the Type 1B but the block support is replaced by a steel container. The spherical reservoir was evaluated by a previous effort and was determined to have excellent characteristics as a storage/emptying device.[3] The sphere, constructed of 0.010 inch stainless steel, has a conforming internal hemispherical "diaphragm" of 0.005 inch stainless steel. A circumferential weld joint joins both halves of the sphere and the internal diaphragm. Application of pressure reversed the diaphragm within the sphere, emptying the contained electrolyte. Very efficient emptying was attained with the spherical device. The weight savings due to the use of the spherical container and a reduction of electrolyte required yielded the lightest weight configuration evaluated during this effort. The design features separation between the gas generator gas and the gas evolved from the cells. Separation allows some flexibility in gas generator output requirements and prevents gas generator combustion products from contaminating the electrolyte.

5) Gas Manifold Activation (Type 2)

A possible alternative to the electrolyte manifold is storage of electrolyte with each individual cell and manifolding the activating gas medium to each storage device. The single reservoir is replaced by multiple reservoirs, one for each cell. The use of a force transfer diaphragm or piston is necessary to seal the activating gas from the electrolyte. This method of activation would eliminate distribution problems and any electrolyte path between cells. Depending upon the activating mechanism, inefficiency of emptying would also be reduced or eliminated. Separation of activation gas is inherent in this design carrying within the possible advantages mentioned for the Type 1C design.

After considering other possible options and the problems associated with sealing, the individual electrolyte storage reservoir was selected to be a stainless steel sphere. The selection was based upon the ability to seal this reservoir satisfactorily for the required unactivated storage period and upon its competitive weight with other alternatives. The arrangement for this design is shown in Figure 5.

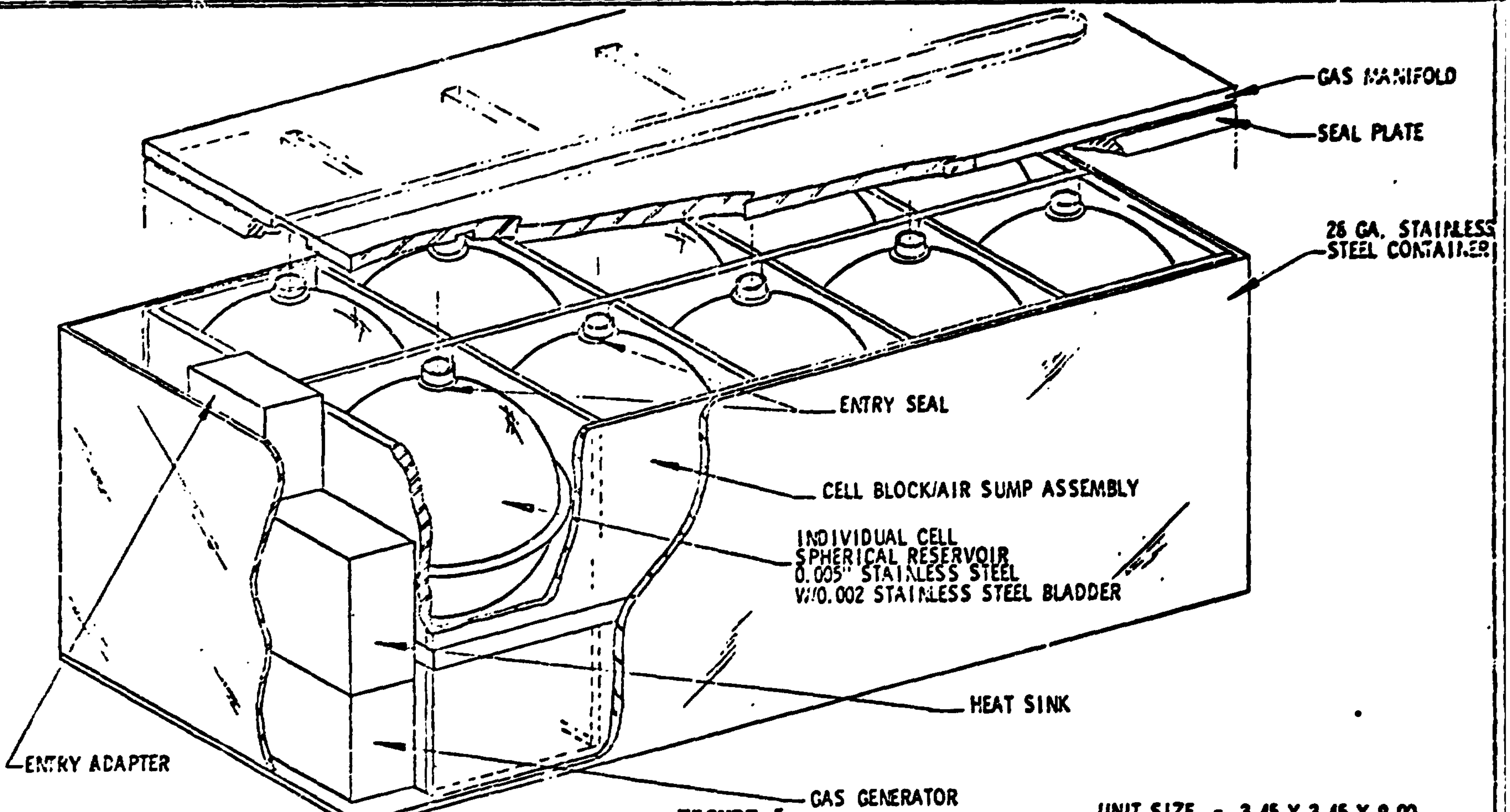


FIGURE 5
TYPE 2A SYSTEM
GAS MANIFOLD ACTIVATION

UNIT SIZE - 3.45 X 3.45 X 9.00

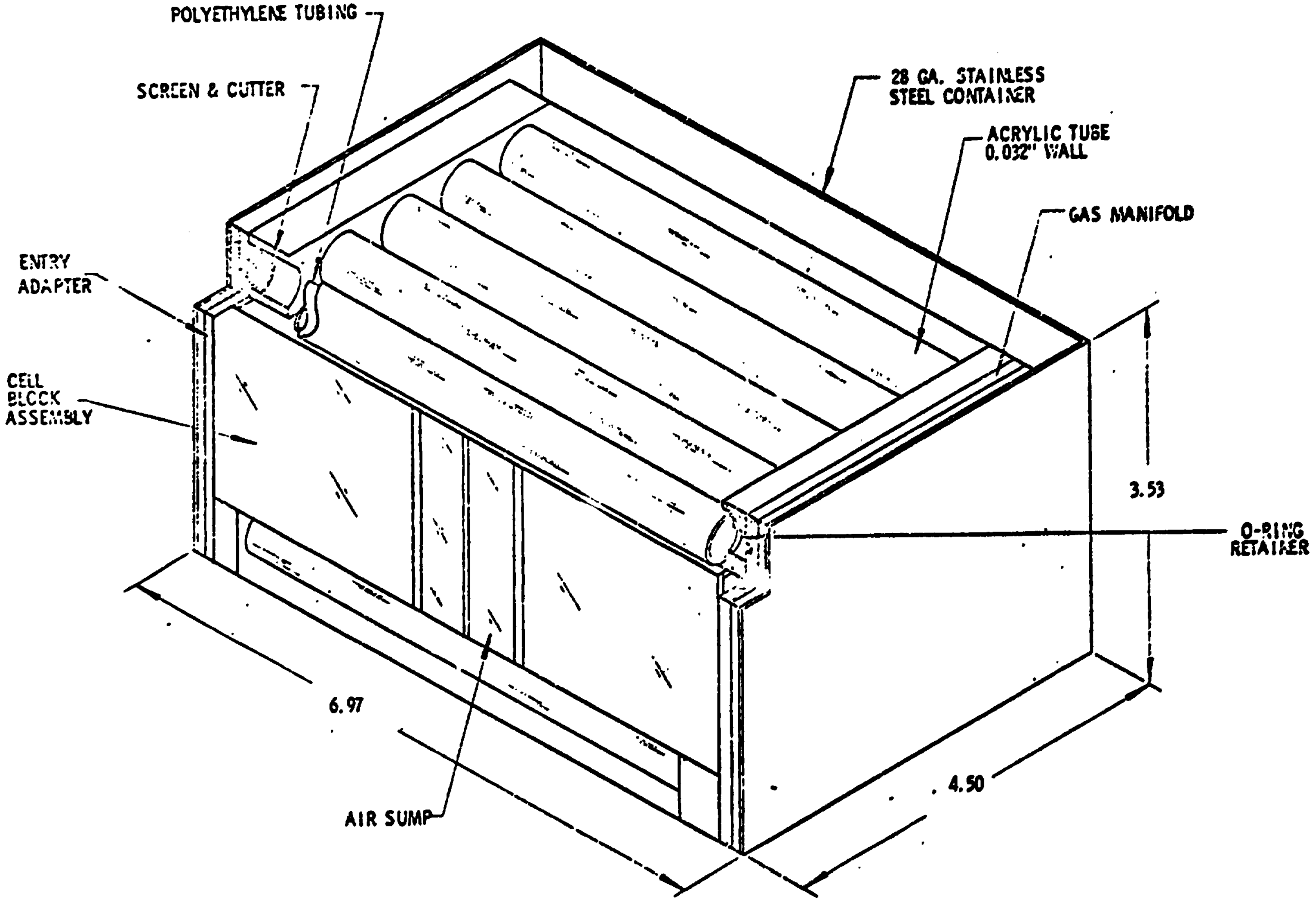


FIGURE 6
TYPE 2B SYSTEM
GAS MANIFOLD ACTIVATION

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5) Gas Manifold Activation (Continued)

Each cell would be activated by a spherical activation/reservoir device approximately 1.5 inch in diameter. The construction of the sphere would be of 0.005 inch steel with a 0.002 inch activation diaphragm. The design of both the activating diaphragm and the sealing diaphragm would be such as to reduce the deflecting resistance so that activating pressures might be minimized. The spherical reservoirs would be interconnected via a seal plate and manifold constructed from acrylic plastic sheet. To conform to the spherical reservoir, the cell cavity must be constructed in a cubical shape. This would require the use of more electrodes of smaller area than used in the cells of all other designs in this effort. Packaging the cell in this shape would tend to be awkward from a fabrication standpoint and slightly inefficient weightwise due to the need for additional interplate connections. Cell case packaging efficiency is improved.

The unused volume projected by the sphere is converted to individual cell "air sumps", as mentioned in the design of Type 1A. This volume, which is relatively large, could be used to further decrease the initial pressures resulting from activation. This arrangement of air sump and reservoir would also decrease the pressure differential across the entry seal providing additional confidence in maintaining this seal for the activated stand period. It does, however, increase the total cell case/air sump weight and decrease the overall volumetric efficiency.

Volume is provided for an entry adapter (entry to the gas manifold), heat sink and gas generator assembly. Provisions will be required for handling the heat from the gas generator to insure an adequately maintained entry seal. Since a gas manifold is being used, the heat could be shunted to the battery container without affecting electrical isolation. The entire assembly is placed in a closely fitting stainless steel container which would require very little potting material to insure proper support.

An all-plastic version of the gas manifold activation method is conceived as the Type 2B system shown in Figure 6. This design uses similar cell case cavities used in the Type 1A (and 3A) systems. The cell cavities are placed in a horizontally opposed positions and incorporate air sump sections which displace the unused volume. Each cell has an individual electrolyte storage reservoir which consists of a thin-walled acrylic tube supporting a polyethylene tubular "bag" filled with electrolyte. The bag is formed from a thin-walled (2 mil) polyethylene tube whose length is twice that required to fill the supporting acrylic tube. One end of the tube is heat sealed with a "piston" diaphragm of 6 mil polyethylene. The tubing is doubled back against itself over an o-ring and the piston diaphragm end. The piston diaphragm end is doubled back against itself internally resulting in a half length reduction of this section. In effect, a "rolling" diaphragm of polyethylene is formed from a single length of tubing. The bag can be placed in the supporting acrylic tube and then filled with electrolyte. A 2 mil sealing diaphragm is heat sealed to the open end of the tubing completing the seal of the reservoir. The o-ring acts as a retainer and seal for the tubing at the central fold. A filter screen and cutter assembly are required on the outlet end of the reservoir to insure diaphragm rupture and to prevent the ruptured diaphragm from blocking the cell entry passage. The entry adapter is formed from acrylic sheet with individual channels and passages machined as required for cell access (similar to Type 3A).

5) Gas Manifold Activation (Continued)

Not shown in the figure is the location of the gas generator/heat sink/entry adapter. A volume is provided for these elements in the package. The entry adapter would require a distribution channel arrangement to diagonally opposed corners of the block assembly to gain access to the gas manifold of each row of cells. A similar problem in handling the heat produced by the gas generator exists in this design as in the Type 2A system.

The gas generated is directed to the piston diaphragm end of each reservoir applying pressure to the electrolyte. The sealing diaphragm end deflects and ruptures causing the electrolyte to flow into the cells and the piston diaphragm end to return to its original, doubled-back position.

6) Individual Cell Activation (Type 3)

Combining individual electrolyte storage reservoirs of Type 2 design with individual cell gas sources results in a Type 3 system. The Type 3 system contains all the elements of the Type 1 design for each individual cell such that each cell could be activated independently of any other cell. The only common connection between cells is, of course, the series power circuit and the electrical circuit necessary to fire the individual gas generators.

A prismatic arrangement of the Type 3 system is shown in Figure 7. Containing cell cavities identical to those of the Type 1A system, the Type 3A system has close fitting, individual tubular steel reservoirs arranged in the nested configuration shown. The unused volume resulting from required reservoir length and radii is converted to an air sump section as discussed previously. Entry access to each cell is formed by machined channels and passages in a single acrylic sheet shown (the top plate has been removed for clarity).

This design resulted in the heaviest system evaluated although it is only 18 grams heavier than its comparable electrolyte manifold system, Type 1A. The weight is driven up by the necessity for having entry adapters, gas generator adapters, gas generator housings and sealing diaphragms for each cell reservoir rather than the single set of these items in the Type 1A design. Some of this weight is recouped in electrolyte weight since the distribution allowance of 5% is not necessary. Container weight is also saved due to the volumetric inefficiency of the Type 1A system.

The Type 3 system achieves positive separation between cell electrolyte since neither a gas nor an electrolyte manifold is used. Connection between cells can be made electrolytically via the firing circuit. Each leg of the firing circuit to each cell must be opened subsequent to activation to prevent this connection possibility. A multiple pyrotechnic switch could be used to accomplish the circuit break. Power from the battery itself would be used to fire the switch. In some instances, as with the probe application, paralleling of the individual cell initiators would be accomplished remotely from the battery and the circuit separation accomplished by simply disconnecting a multi-pin electrical connector.

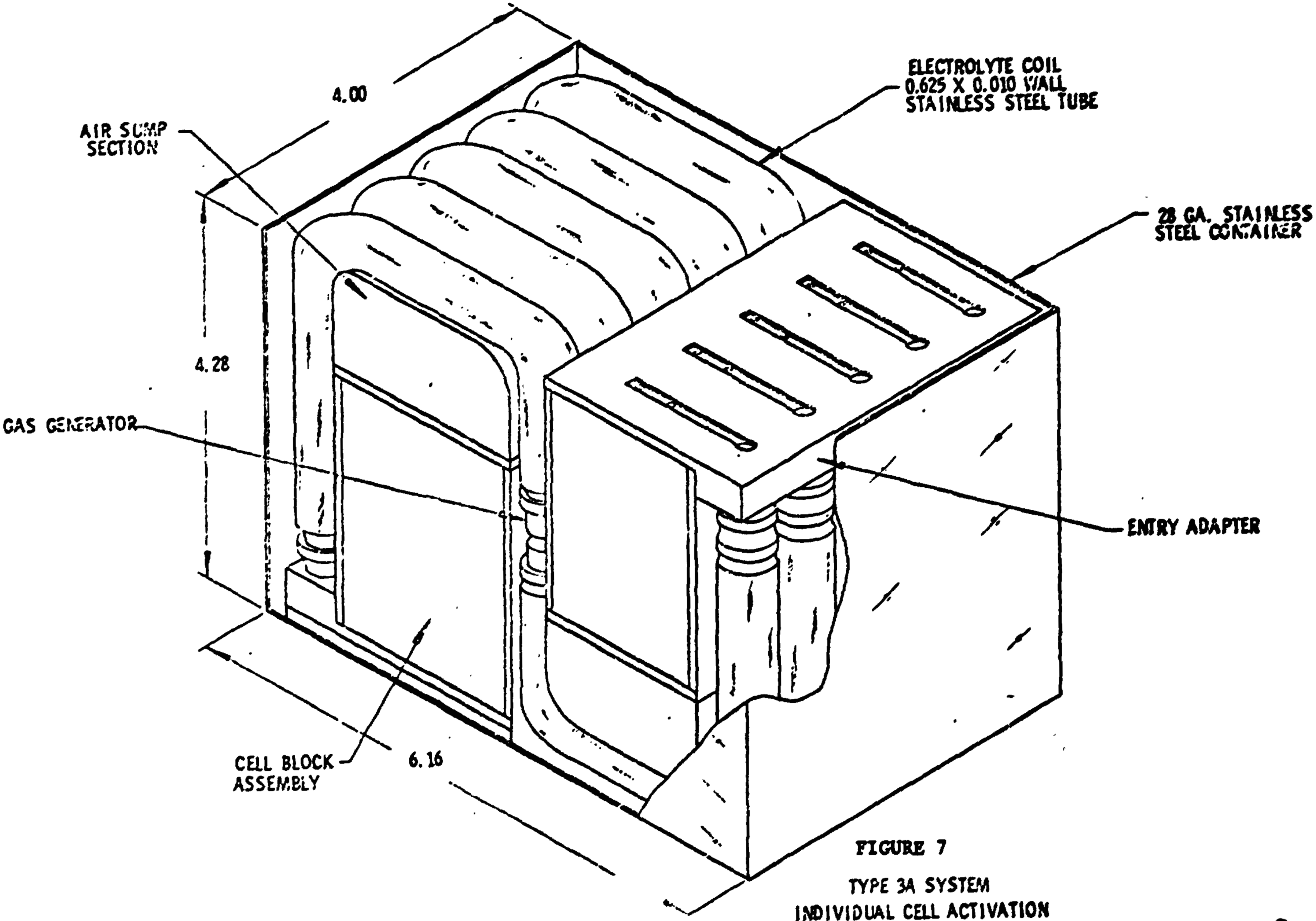

FIGURE 7

TYPE 3A SYSTEM
INDIVIDUAL CELL ACTIVATION

J. Bastin

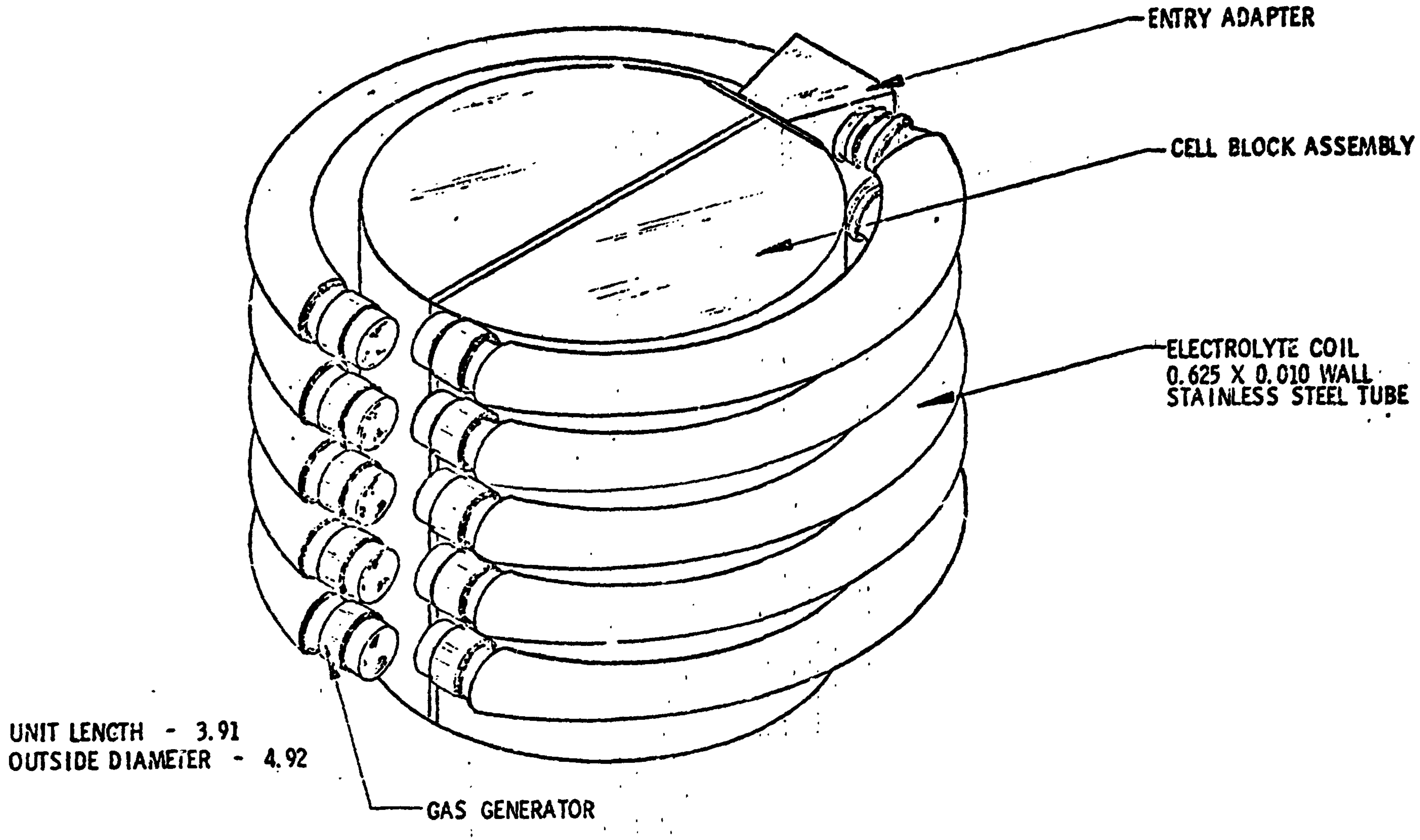

FIGURE 8
TYPE 3B SYSTEM
INDIVIDUAL CELL ACTIVATION

6) Individual Cell Activation (Continued)

The Type 3 system, as with the Type 1 system can be packaged more efficiently by using a cylindrical form factor. A reduction in material requirements for the cell case and manifold results. Also, as in the case of the Type 1B system, the electrolyte reservoir can be used to support the battery block, reducing the requirement for a container. Designated a Type 3B system, the concept is presented in Figure 8. Each individual cell has its own storage reservoir and gas generator. Disconnection of the gas generator firing circuit would be required as mentioned in the preceeding paragraph.

Both systems, Type 3A and Type 3B, would require an extra design effort in the area of the gas generator body and adapter to reduce the weight of these items. A stainless steel welded construction is recommended in this area. Consideration would be given to construction of the gas generator body (case) and electrolyte reservoir as a one-piece, inseparable assembly where the gas generator propellants could be loaded after the assembly.

7) Radiation Resistance

During the conduct of the probe mission, the battery is exposed to interplanetary radiation sources and radiation from on-board radioisotopes. Each of these sources combine to provide a total accumulated environment of protons, neutrons, electrons and gamma radiation fluence. Battery materials must be capable of resisting this exposure without degradation of performance or essential characteristics.

Previous efforts have been completed concerning the radiation vulnerability of the silver-zinc battery.[3] The primary agency for failure is dose and dose rate. The neutron exposure does not seem to be as effective. The neutron fluence threshold level for the silver-zinc battery is in excess of 1×10^{15} neutrons per square centimeter $(e > 0.1\text{Mev})$.

The most vulnerable material in the basic design is the cellophane separator material. In the gamma radiation environment, some polymers degrade while others crosslink. Cellophane unfortunately degrades with mild effects noted at 1×10^4 rad (Carbon). Cellophane is normally preferred in silver zinc design because of its low resistivity, however, in this application, a substitute material would be required.

A primary candidate material for substitution is 2291 40/20 Permion film. Permion is a trade name for a family of separators, 2291 being a film made from polyethylene subjected to radiation crosslinking and grafting. Polyethylene predominately crosslinks when exposed to radiation. The processing of the film in this manner is necessary to lower the resistivity (unprocessed film is impervious to ion flow). Polyethylene also is resistant to oxidation by silver species (a limitation of cellophane)providing long term stand capabilities in electrolyte. And since crosslinking occurs, further exposure to radiation serves to increase the degree of crosslinking.

7) <u>Radiation Resistance</u> (Continued)

Although the resistivity of the polyethylene film is significantly improved by the processing, a higher resistance than cellophane is the result. Further testing of this separator system would be required for this application to ascertain the performance capability especially at the operating temperature. For the absorbent separator material in the basic cell, asbestos sheet was selected because, being inorganic, it has a high resistance to the radiation environment and is used interchangeably with other absorbent materials in silver zinc cells.

Second on the vulnerability list is the acrylic sheet mentioned as the material to be used for the construction of cell cases, manifolds, sumps and adapters. The acrylic material, methyl methacrylate, exhibits mild physical change at 1 x 10^6 rad (Carbon). Acrylic sheet has been used extensively in the construction of remotely activated monoblocks because of its compatibility with the electrolyte, its transparency and its ease of fabrication and sealing. A suitable substitute material would be styrene-acrylonitrile (SAN) copolymer which is used extensively in molded cell cases for manually activated silver zinc batteries. SAN's vulnerability threshold would be similar to polystyrene which exceeds 1 x 10^8 rad (Carbon). Previous exposure of a silver-zinc battery to this level revealed no effects upon components other than a discoloration of the cell case material, SAN.[4] This battery also contained Permion (polyethylene) separator material and performed normally after the radiation exposure.

One additional area of concern which has not been thoroughly investigated is the radiolytic evolution of hydrogen and oxygen from the cell electrolyte. Since this unit is required to be sealed, this evolution would contribute to the gassing characteristic of the cell. This effect was noted in electrode testing at levels up to 9 x 10^8 rad (water).[5] During this testing, insignificant electrical performance changes were noted from both the positive and negative electrode. A material loss of less than 1.5% was noted from the silver oxide electrode. An organic type separator material was used during this testing in lieu of cellophane.

The remaining materials of the basic design and activation system options should be capable of withstanding the required exposure levels. Summarizing, the principal areas requiring further evaluation are the performance characteristics of Permion separation at the operating temperature and the fabricating/sealing characteristics of SAN. The long term sealing ability of SAN in electrolyte should be thoroughly investigated. These substitute materials or any other equivalent options are necessary to provide adequate confidence in the ability of the unit to provide required power subsequent to the long term activated stand and radiation exposure.

III. CONCLUSIONS AND RECOMMENDATIONS

A basic cell design was established containing features to enhance the reliability of activated stand. Performance of the cell was demonstrated yielding expected results at the operating temperature of +5°C. Combining high energy density with the requirement for extended activated stand resulted in a power characteristic which was lower than the required nominal but exceeded minimum requirements. This lower characteristic is due to the use of multilayers of cellophane separation for extended stand capabiltiy. Alteration of this basic cell design will be necessary to provide for radiation resistance. This will involve the use of a substitute separation material for cellophane. Permion 2291 40/20 is recommended for this purpose.

To control gas evolution from the basic cell, amalgamation of the negative electrode is the most effective means. The process can be effective with the electroplated zinc electrode as long as strict control is maintained over process parameters and an effort is made to prevent introduction of catalytic impurities into the final product. The electroplated zinc electrode is recommended because of its high power characterisic as opposed to other methods of formulation. High, primary power is the desired output from the zinc electrode. Present processing methods for the silver oxide electrode appear to be adequate for controlling gassing. No recommendations for changes for this electrode (formed sintered silver) resulted. There was also no evidence that the separation materials independently contribute to cell gassing. Asbestos, cellophane and Permion were included in that observation.

In combination with the basic cell design, the weight analysis of the three different methods of activation revealed that each type could be packaged with an energy density of at least 35 watt-hours per pound. From this and the work with the basic cell, the requirements of sealed operation and high energy density appear well within the capability of the designs. This depends upon the third and most important feature of the unit, the long activated stand capability.

With empahsis placed upon the long activated stand, the three activation methods provided a good cross-section of component arrangement possibilites. Coupled with several stated ground rules and a fixed cell design, a fair appraisal was conducted. Comparison of the three methods can best be made by referring to Table VI.

III. CONCLUSIONS AND RECOMMENDATIONS (Continued)

TABLE VI
DEVELOPMENTAL RISK ASSESSMENT

	TYPE 1 ELECTROLYTE MANIFOLD	TYPE 2 GAS MANIFOLD	TYPE 3 INDIVIDUAL CELL
Advantages	Conventional Design Inexpensive	Dry Manifold Single Gas Source KOH Efficient	Conventional Design No Manifold
Limitations	Wet Manifold KOH Inefficient	Expensive	Requires Switch Emptying Efficiency
Relative Risk	Medium	High	Low
Success Estimate	Good	Fair	Excellent
Development Problems	Manifold Spherical Activator (C)	Generator Heat Cell Form (A) Activator Functioning Seals	Generator Case/ Adapter Seals
Relative Reliability	High	Medium	Low

The Type 2 and Type 3 systems have an advantage over the conventional Type 1 electrolyte manifold activation in that both Types 2 and 3 have positive means for isolating individual cells from each other. Electrolytic paths between cells are thus eliminated, removing the principal limiting factor for activated stand.

The developmental risk is shown in the table as "Low" for the Type 3 method of activation which uses all the elements of conventional design. Developmental problems would be limited to improving the weight of the gas generator case and adapter components and to insuring that the seals of each reservoir-to-cell are adequate for preventing electrolyte link-up between cells. Type 2 is assessed as a high risk venture since the design represents the most radical departure from convention and presents the most development problems. Type 1 system is placed in between the other types because the actual wet stand capability of this system is unknown. By employing passive techniques such as the long path manifold and fine tuning of the electrolyte quantity, it is felt that the conventional Type 1 system would have a relatively good chance of success in demonstrating the long stand requirement. This chance of success is assessed as only fair for the Type 2 system because of its untried nature and problem potential. The Type 3 system gets an excellent rating of success because it combines convention with complete separation of cells electrolytically and presents relatively minor development problems.

This brings the discussion to the bottom line, the relative reliability. Because of the nature of the application, reliability was given high priority in governing design decisions. Reliability must also be a prime consideration in choosing the storage reservoir/activation system so essential to providing both unactivated and activated stand as well as activation upon demand. Assuming that the development risk has been accepted for each type, development problems have been solved and designs have been frozen, what is the relative reliability of the final products? It simply reduces to the reliability of the system to activate which is a function of the number of components in the activation system. The Type 1 system has a single reservoir and gas generator; the Type 2 system has multiple reservoirs and a single gas generator; and the Type 3 system has multiple reservoirs and gas generators. In the series connected power system of the battery, failure of any one of the components would result in an open battery or a complete failure to provide power. Depending upon the actual failure rates assigned to the components, a final reliability number would indicate the actual effects. Obviously, the Type 1 system would reflect the highest reliability while Type 3 would represent the lowest.

The requirements of this application could eventually be met with any one of the three activation types evaluated. The Type 1 system offers the best payoff in performance reliability from an ability to activate standpoint. Even if the final design of a Type 1 system is assessed a low reliability to stand activated, the total reliability figure would most likely exceed the other systems. Note that the failure to stand activated would likely result in a reduced energy capability and a partial success. Failure to activate would cause total failure.

It is recommended that future effort, if available, examine the functioning of the Type 2 system to observe merits of this method which may have been overlooked at this point. Comparing the Type 1 and Type 2 systems with results from actual component and hardware tests will provide the best relative characteristic evaluation. However, it is recommended that high priority be assigned to developing the manifold distribution system of the Type 1 method of activation because of its inherent reliability. Not thoroughly pursued in this effort are possible methods to close off manifold channels between cells once activation has been completed. This might be accomplished

III. CONCLUSIONS AND RECOMMENDATIONS (Continued)

mechanically, electromechanically or chemically and would eliminate the electrolytic paths established in the wet manifold. In addition, the Type 1 system is readily adaptable to a functioning single spherical reservoir which is considered to be the most energy efficient method of packaging. In this analysis, the spherical reservoir/Type 1 combination resulted in the lightest weight, lowest volume design.

IV. NEW TECHNOLOGY

Since this effort resulted in a recombination of conventional methods in a manner to provide desired characteristics, no reportable items of new technology have been generated. The gas manifold method of activating has been identified many years ago but has not been used extensively in hardware.