THE AEROSPACE CORPORATION

Electrolyte Loss Tendencies
of
Primary Silver-Zinc Cells

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- CHEMISTRY ISSUES
- TRENDS IN CELL DESIGN
- FLIGHT USAGE
- STATIC VOLUME-BASED MODEL
- APPLICATION TO EXISTING DESIGNS
- CONCLUSIONS

BACKGROUND

- SILVER ZINC CELLS WIDELY USED
- RECENT TRENDS EMPHASIZE LONGER WET STAND TIMES
- DESIGN MODS TREND TOWARD WETTER CELLS
- WETTER CELLS INCREASE THE PROBABILITY OF EXPELLED ELECTROLYTE
- THERE HAVE BEEN SEVERAL INSTANCES OF ELECTROLYTE LOSS PROBLEMS WITH FLIGHT ARTICLES
- ELECTROLYTE LOSS CAN RESULT FROM SEVERAL DIFFERENT PROBLEMS
- A TASK WAS CARRIED OUT TO INVESTIGATE A CELL'S TENDENCY TO LOSE ELECTROLYTE

Silver-zinc batteries are used in applications where high energy density and high discharge rates are required. These batteries are mostly used in the primary mode where they are not required to be recharged. All launch vehicles use silver-zinc batteries in sizes ranging from about one ampere hour (Ah) to 250 Ah. For the launch vehicle applications addressed here, batteries are assembled except for the introduction of electrolyte and carefully stored until they are called up for use. At that time, electrolyte is added as part of the overall activation process prior to installation on the vehicle. Once the cells are filled, reactions take place that can result in small amounts of electrolyte being expelled from them. There have been several recorded instances where electrolyte expulsion has resulted in the rejection of either that particular battery or the entire production lot of batteries that were felt to have a generic problem. An in-flight failure of a battery suggested that the problem resulted from the effects of small amounts of electrolyte forming an ionic conduction path inside the battery box. This presentation will review the causes for the different kinds of problems within a cell that can result in the expulsion of small amounts of electrolyte. It will also present a static volume based model that was found to be useful in estimating the tendencies for different silver-zinc cell designs to expel electrolyte after they are activated and what precautions and remedies are available to minimize or preclude this problem. In applying this model to four different cell designs, it accurately predicted a problem with a cell design that was felt to be responsible for an inflight battery failure due to the expulsion of electrolyte from the cells.

CHEMISTRY ISSUES

- CELL PERFORMANCE DEPENDS ON ELECTROLYTE CONCENTRATION AND AMOUNT
- GASSING RATE DEPENDS ON AMALGAMATION
- OXALATE PROBLEM DEPENDS ON AMOUNT OF ELECTROLYTE

The amount of electrolyte and the concentration of potassium hydroxide required for the cell's intended application is determined by the mass transport and the super saturation limits of the zincate ion under the conditions the cell is being discharged and the duration over which the discharge is required. Foundation studies carried out at Naval Research Laboratory in the late 1940s were instrumental in helping manufacturers establish their own design codes in terms of surface area, porosity, and electrolyte quantities.

Zinc is an amphoteric metal, and thus is thermodynamically unstable in aqueous potassium hydroxide. The reaction of the zinc with aqueous potassium hydroxide solution results in hydrogen evolution. In practice, the rate of hydrogen evolution is reduced by amalgamation of the zinc electrodes and by stringent quality control measures. The addition of mercury to the zinc electrodes (amalgamation) raises the hydrogen overvoltage and effectively inhibits the evolution of hydrogen by "local action", which is essentially corrosion of the zinc. Normally, the mercury constitutes about 1% to 2% by weight of the finished anode. Increasing the mercury content from 1% to 2% decreases the rate of evolution of hydrogen by a factor of ten.

Besides the electrolyte requirements being dictated by current density (milliamperes per square centimeter) and capacity (milliampere-hours per square centimeter) there are other factors to be considered as well. The amount of electrolyte affects the rate of growth of potassium oxalate crystals that form within the layers of cellulosic separator material. These crystals, which result from the interaction of potassium hydroxide with cellophane, can lead to tears in the separator during the rigors of launch. Very often this results in potentially dangerous short circuits within the cell. The concentration of electrolyte affects the rate of formation of potassium oxalate as well as the gassing rate at the zinc electrodes.

TRENDS IN CELL DESIGN

- ● LONGER WET STAND TIMES
  - – From 15 days towards 90 days
  - – More electrolyte
  - – More separator
- ● WETTER CELLS MORE PRONE TO EXPEL ELECTROLYTE
- ● ABSORBENT PADS CAN BE USED

Cells are of course designed so that excessive amounts of electrolyte will not be expelled. However, many of the current cell types were originally designed twenty or thirty years ago. Since that time, there has been an effort to extend the wet stand time from 15 days (for the very short wet stand limits associated with batteries using cells with only a few layers of separator) to up to 90 days for some requalified cell types. It is well known that extra layers of cellophane separator material can increase the wet stand time, but at the expense of an increased internal resistance. The addition of more electrolyte is another method used to increase the wet stand time since it retards the growth of oxalate crystals mentioned above. For these reasons, the net free volumes within some of these designs have gotten smaller.

CAUSES OF ELECTROLYTE LOSS

- POOR AMALGAMATION STEP
- NORMAL VENTING OF CELLS
- IMPROPER PRESSURE ON "O" RING SEAL
- EXCESS ELECTROLYTE DURING FILLING
- DISPLACEMENT OF ELECTROLYTE BY HYDROGEN IN ZINC ELECTRODES
- INADEQUATE HEAD SPACE

This chart lists the major factors that have caused electrolyte to be expelled from silver zinc cells. Different manufacturers use different methods of amalgamating their zinc plates. From time to time the amalgamation levels or quality are ineffective or the surface of the zinc plates are unusually high. Either of these situations can result in excessive gassing when the cells are first filled. Following the addition of electrolyte, gassing will take place, but the vent valve will allow the hydrogen gas to be vented as the pressure builds up. As the gas escapes, small droplets of electrolyte can also be expelled as well. If the vent valve has been improperly seated against the "O" ring, hydrogen gas along with small amounts of liquid can be lost from the interior of the cell via this path. Another problem that is seen occasionally is caused by excess amounts of electrolyte being added to the cell as a consequence of incorrect amounts contained in the filling bottles that are assigned to each cell. However, cell designs that have an inadequate amount of free volume will be the main issue to be addressed in this presentation. Much of the electrolyte is designed to be held within the pore structure of the electrodes and separators. Zinc electrodes are typically 65% porous. The hydrogen gas forming at the zinc surfaces within the pore structure of these electrodes can push electrolyte out into the free volume of the cell. If there is an inadequate amount of head space within the cell, the electrolyte can be pushed out through the vent valve and onto the top of the cell.

CELL FILLING PRIOR TO FLIGHT

- REMOVE VENT VALVE
- ATTACH FILL TUBE
- VACUUM BACK FILL CELL
- LET STAND "N" DAYS
- APPLY VACUUM "Y" TIMES
- INSTALL VENT VALVE
- MONITOR CELL/BATTERY VOLTAGE
- INSTALL ON SPACECRAFT

A general list of steps that are followed during the normal processing of a silver zinc battery at the launch site. These procedures are specific to the contractor, but the major elements are the same. Batteries are stored refrigerated and without electrolyte. The cells are filled with a prescribed amount of electrolyte that is contained with a fill bottle (one for each cell) by a vacuum back filling process and then allowed to stand for a period of time during which the open circuit voltages are monitored and the battery voltage under a test load is measured for compliance to specifications. Depending on the contractor, one or more reapplications of vacuum are applied to redistribute the electrolyte within the porous elements within the cell and at the same time disengage and remove the hydrogen gas trapped within the zinc electrodes. The cell vents are then installed and tightened to the proper torque and finally the battery installed on the spacecraft.

CELL BACKFILLING SETUP

To Vacuum

Bell Jar

Electrolyte Resevoir
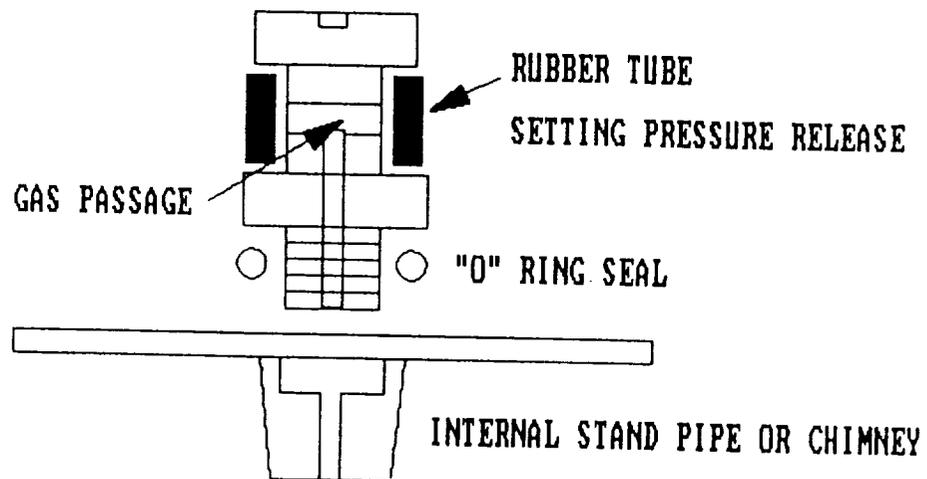
Bubbles

Empty Cell
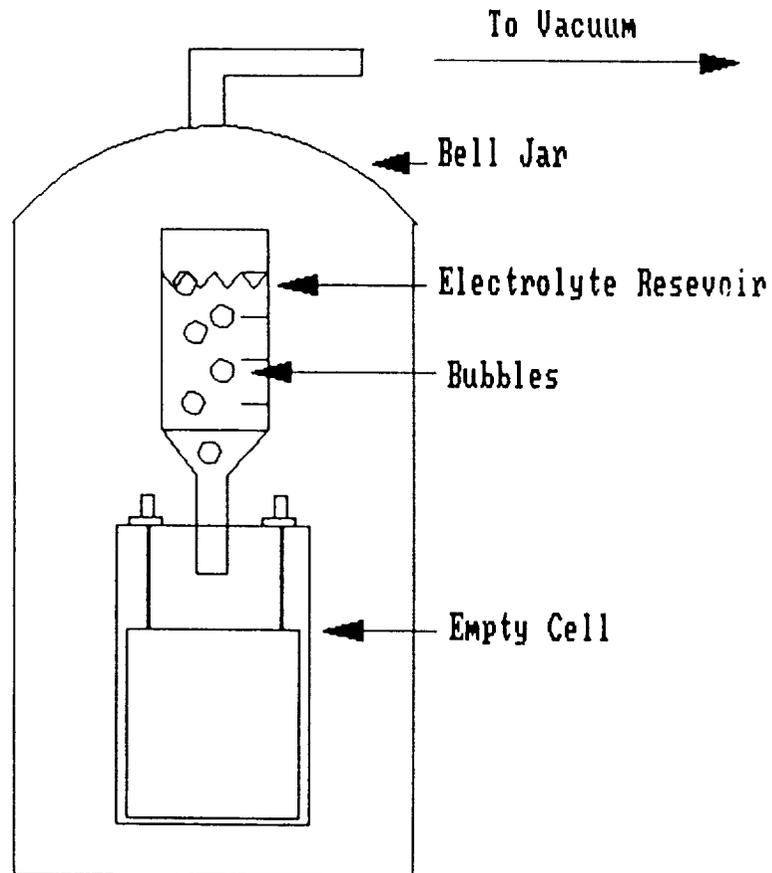
A schematic of a vacuum filling fixture. In actual practice, all the cells of the battery are filled at one time. In one arrangement, plastic tubes which are connected at one end to the individual reservoirs are threaded into the opening at the cell top at the other end. This threaded opening is later used for the insertion of the vent valve.

FLIGHT USAGE

- CELL VENT VALVE OPENS IN THE RANGE OF 3-5 PSI DIFFERENTIAL

- BATTERY HOUSING VENTS AT ABOUT 11 PSI DIFFERENTIAL

- WHEN VEHICLE REACHES ALTITUDE, BATTERY VENTS TO SPACE

- VEHICLES GOING TO GEO CAN VENT SEVERAL TIMES

- LOSS OF 1.5 VOLTS DUE TO SHORTED CELL DOES NOT CREATE A PROBLEM

- LOSS OF A FULL BATTERY DOES

This chart lists a short description of the pressure environment the battery will see during its short useful life in space. To be noted is the fact that a battery will be expected to vent at an altitude when the outside pressure drops below about 1 psia. At this point the individual cells will also vent as they adjust to the lower pressures inside the battery box. This coupled with the slow or not so slow reaction of the zinc with the electrolyte will produce a small amount of hydrogen gas that will vent first to the battery box and then to space given the proper levels of differential pressure.

CELL TOP AND VENT VALVE

RUBBER TUBE

SETTING PRESSURE RELEASE

GAS PASSAGE

"O" RING SEAL

INTERNAL STAND PIPE OR CHIMNEY

A close up view of the vent valve that is placed on each cell. The short piece of rubber tubing stretched around the gas passage within the valve allows pressure to be relieved as the rubber band is stretched away from the opening and then will reseal as the pressure is released.

STATIC CELL MODEL

- DISASSEMBLE AN UNACTIVATED CELL

- MEASURE THICKNESS, WEIGHT, POROSITY, ETC.

- DETERMINE VOLUME OF ALL INTERNAL COMPONENTS AND THAT OF THE CELL

- CALCULATE NET INTERIOR FREE VOLUME

- DETERMINE VOLUME OF ELECTROLYTE IN ZINC ELECTRODES

- DETERMINE WHETHER CELL CAN EXPEL ELECTROLYTE

This chart outlines the steps in developing a static volume-based model of a silver zinc cell. It starts with an unactivated cell that will be completely disassembled. Each component is weighed and measured. For the electrodes, the active material must be removed so the substrates can be weighed as well. Knowing the density of the materials used, the volumes of each part can be determined. As a double check on all these volume calculations, a cell's internal volume is also determined prior to disassembley by using standard gas expansion techniques. This requires a cell to be connected to a standard volume and allowing the gas to expand into the cell that has been taken to a known pressure. The two values for net internal volume as defined in the next charts agreed to within 2%.
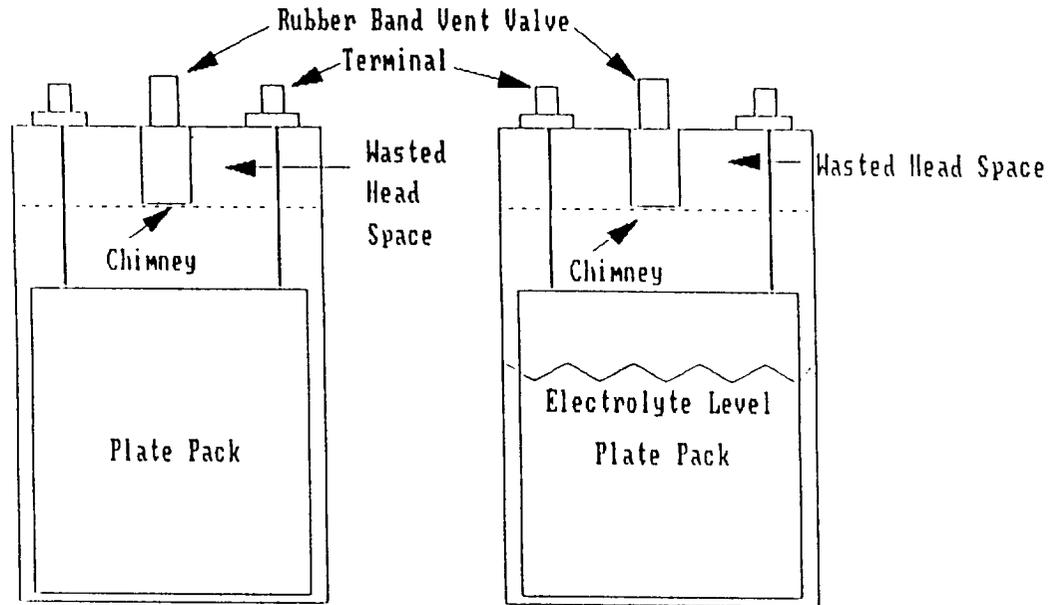
CELL VOLUME DEFINITIONS
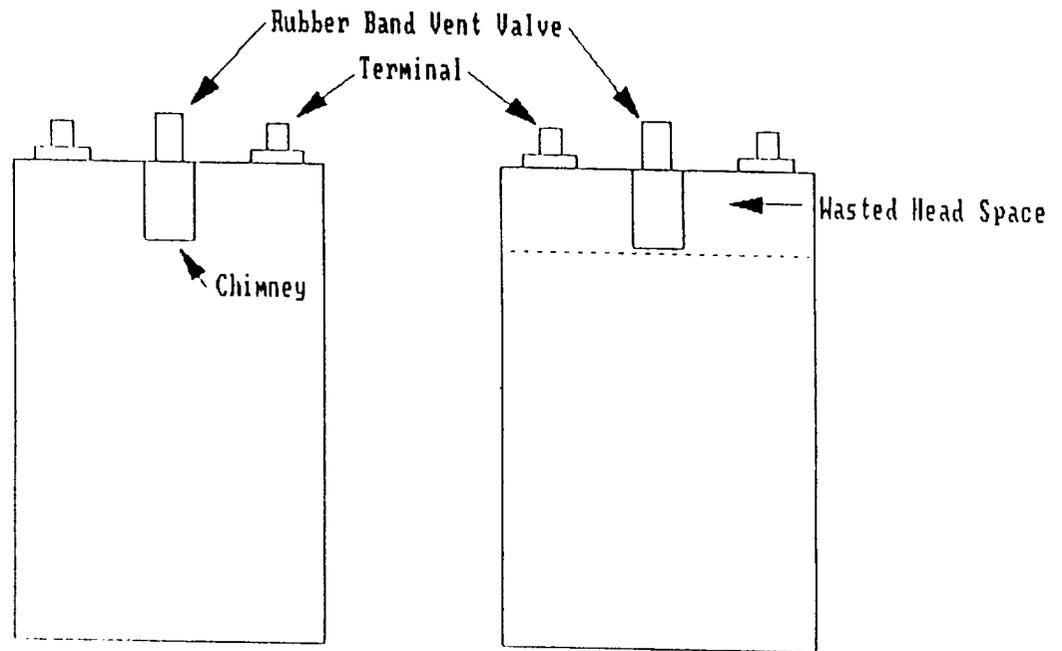
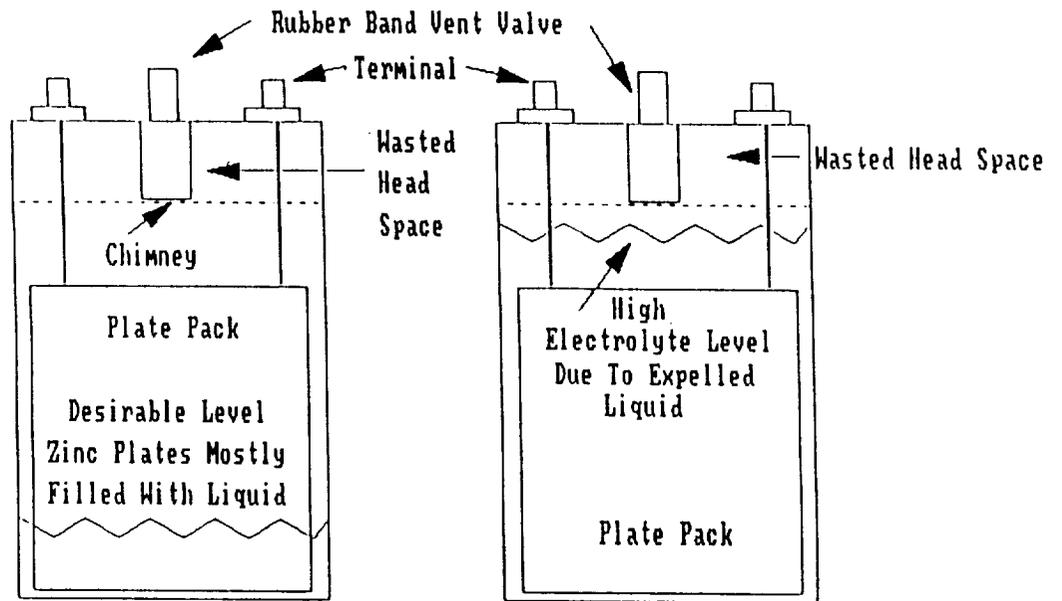*Gross Interior Cell Volume* *Net Interior Cell Volume*

These three charts describe how the different cell volumes that are within a cell are defined. The chimney that sticks down into the cell in effect wastes some of the head space but is needed to prevent electrolyte loss in case a cell is inverted. From the Net Interior Cell Volume, the pieces and parts of the plates and separators are accounted for and then subtracted. Finally after the electrolyte is added, the Net Interior Free Volume can be determined. However, depending on the amount of hydrogen gas trapped within the pores of the zinc plate material, different amounts of free electrolyte will be inside the cell.

CELL VOLUME DEFINITIONS

Rubber Band Vent Valve

Terminal

Wasted Head Space

Wasted Head Space

Chimney

Chimney

Plate Pack

Electrolyte Level

Plate Pack

Gross Interior Free Volume   *Net Interior Free Volume*

CELL VOLUME DEFINITION

Desirable electrolyte distribution   *Undesirable electrolyte distribution*

RESULTS FROM FOUR TYPICAL CELLS

Cell Parameter	145 Ah	13.5 Ah	10 Ah	4.5 Ah
Zinc Porosity	68.7 %	66.5 %	62.7%	57.5 %
Net Cell Interior Volume	359 cc	77 cc	57 cc	19 cc
Gross Free Vol	218 cc	47 cc	39 cc	11 cc
Net Free Vol	44 cc	12 cc	16 cc	2.8 cc
Minimum Free Electrolyte Vol	1.1 cc	-0.7 cc*	-4.1 cc	2.0 cc
Permissible Loss from Zn	41 %	80 %	163 %**	114 %

* Pore volume greater than electrolyte fill   ** No gross expulsion possible

By applying the model to four different cell designs, the different cell volumes were determined. Cell designs where the porous volume within the zinc electrodes is large compared to the Net Free Volume are subject to electrolyte being forced from them during the course of cell standing or during discharge. When the permissible loss is greater than 100%, it means that all of the electrolyte contained with the zinc plates could be displaced by hydrogen gas and there would be no danger for electrolyte loss from the problem being addressed here. If electrolyte loss is asssociated with this type of cell design the problems may be related to surfactants in the electrolyte or or separator, or to vent valves that were improperly tightened during final battery processing.

CONCLUSIONS

- SILVER ZINC CELLS ARE NOT HERMETICALLY SEALED
- VARIOUS FLIGHT PROGRAMS HAVE EXPERIENCED ELECTROLYTE LOSS PROBLEMS
- SEVERAL DIFFERENT CAUSES FOR EXCESSIVE ELECTROLYTE LOSS HAVE BEEN SEEN
  - Some related to quality issues
  - Some related to inappropriate cell designs
- STATIC MODELING CAN BE HELPFUL FOR ESTIMATING ELECTROLYTE LOSS TENDENCIES

Since silver zinc cells are not hermetically sealed, care must be taken to prevent the loss of electrolyte which can result in shorting paths within the battery box. Prelaunch battery processing is important in being able to minimize any problems with expelled electrolyte. Just as important are the quality issues related to amalgamation, soponifiable impurities, and the electrolyte quantities contained in the individual filling bottles. Static modeling of the cell design can be useed to determine the electrolyte loss tendencies of that individual cell design.