

A CYLINDRICAL, PURE LEAD, LEAD-ACID CELL FOR FLOAT SERVICE*

R. V. BIAGETTI

Bell Laboratories, 600 Mountain Ave., Murray Hill, New Jersey 07974 (U.S.A.)

H. J. LUER

Bell Laboratories, Whippany Road, Whippany, New Jersey 07981 (U.S.A.)

Summary

A cylindrical, pure lead, lead-acid cell was designed specifically for float service applications. Unique design features, including concentric, pure lead, circular grids, provide long life, reduced maintenance and improved safety. In excess of 150 000 cells are currently in use in a variety of Bell System applications. The cylindrical cells are optimally installed in a fiber-glass-reinforced, modular battery stand.

Evolution of the new cell design from pilot plant to large scale production demonstrated sensitivity of field float behavior to subtle changes in manufacturing processes. Analysis of interrelated float behavior and PbO_2 morphologies are discussed.

Introduction

In 1970, Bell Laboratories formally announced the development of a cylindrical, pure lead, lead-acid cell which was designed specifically for Bell System float applications [1]. The new cell (Bellcell** battery) has been in commercial production since late 1972 at the C&D Battery Company, Leola, Pennsylvania and since late 1975 at Gould, Inc., Fort Smith, Arkansas. To date, approximately 150 000 Bellcells have been shipped from these manufacturing plants and installed in a variety of Bell System power plants. The following is a summary of the important design features of the new cell and experiences in installation and performance.

Design features

Since corrosion and growth of the positive plates is the major electrochemical failure mode of lead-acid batteries in Bell System float service, the

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new cell was designed to retard this mode of failure. Pure lead (99.99%) was selected for the grid material on the basis of extensive accelerated corrosion tests comparing pure Pb with Pb-Ca and Pb-Sb alloys [2]. The selection of pure lead for the grids essentially dictated a cylindrical, self-supporting structure since pure lead is too soft for grids to be suspended in the conventional vertical manner. The new design is illustrated in Fig. 1. The cell is assembled by alternately stacking positive and negative plates which are separated by conventional glass mats and microporous rubber separators. The negative plates are connected by casting a lead-antimony rod in the hollow core formed by the mating negative plate hubs. The positive plates are connected by a welding operation at the interfaces of the tabs. This operation is carried out using a continuous 3 kW CO₂ laser, and it is the only known application of such a laser in commercial production.

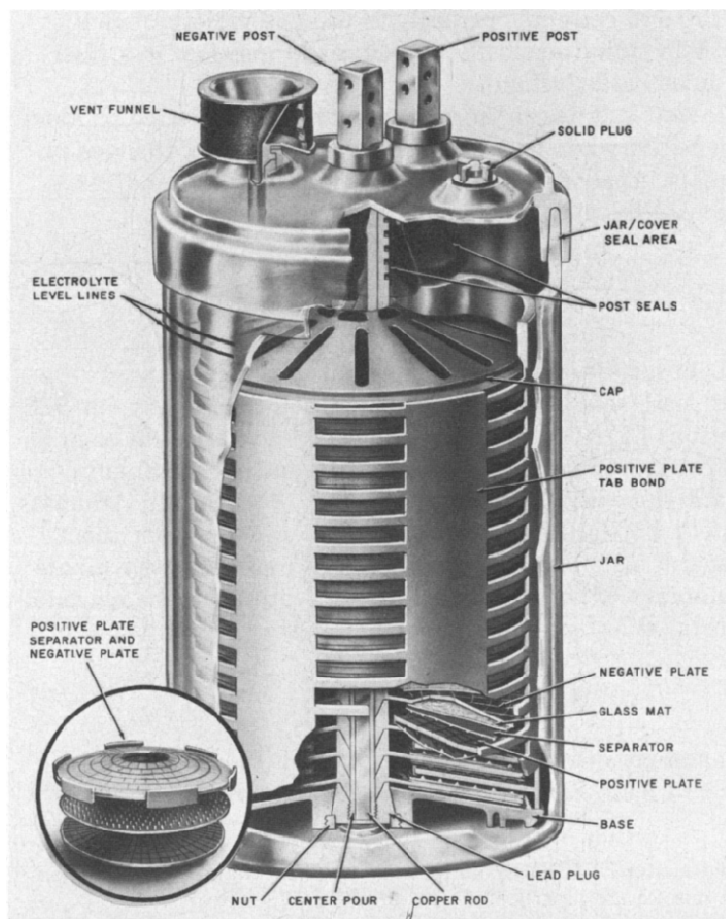


Fig. 1. Illustration of the pure-lead cylindrical cell.

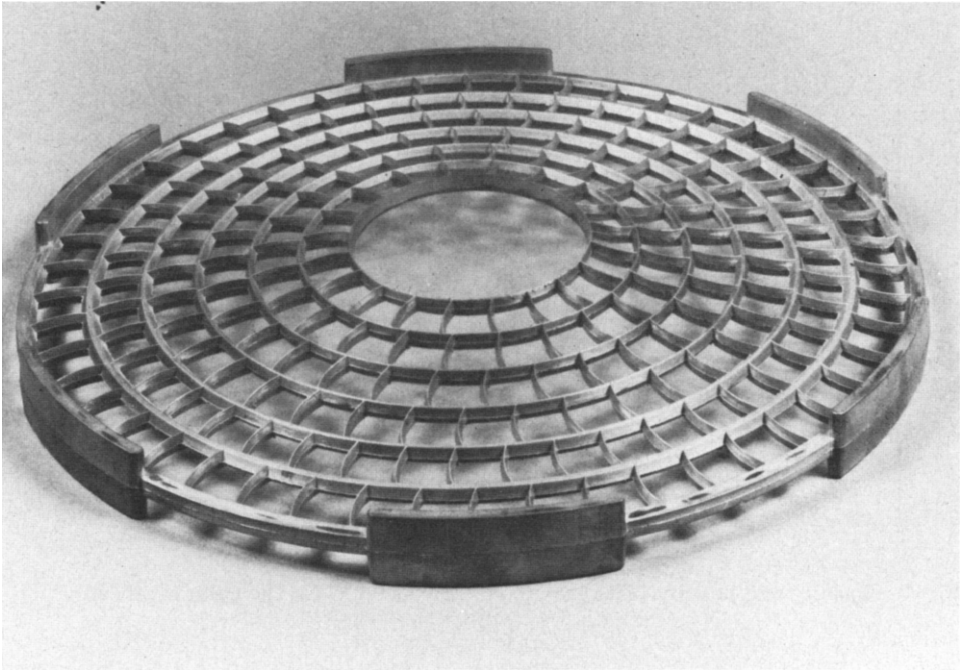


Fig. 2. Pure-lead positive grid.

Equally as important as the use of pure lead is the positive grid design shown in Fig. 2. The concentric rings are specifically designed such that, as corrosion occurs, each ring will grow at the same rate thereby maintaining continuous contact with the active material [3]. This results in a continuing increase in capacity as the cell ages. This effect is shown in Fig. 3 which shows the behavior of several cells under accelerated test at 93 °C for a time equivalent to 65 years at 25 °C. Based upon these results, as well as on similar tests at other temperatures, we confidently predict that corrosion and growth will not be life limiting for approximately a century at room temperature.

In addition to the grid design, the long life was made possible by the development of positive grid casting technology which produces very large grains, *i.e.*, $\sim 0.5 \text{ cm}^3$. It is also noteworthy that all other lead components are manufactured using low pressure die casting techniques.

Other important features of the new cell design include:

- (a) Jar and cover made of a transparent, flame-retardant, rigid poly-vinyl chloride material [3].
- (b) An infrared heat-sealing technique which provides a jar-cover seal with $>50\,000 \text{ lb}$ strength [4].
- (c) A post-seal system which incorporates a rigid epoxy sheath on the lead post which is flexibly coupled to the cover [5].

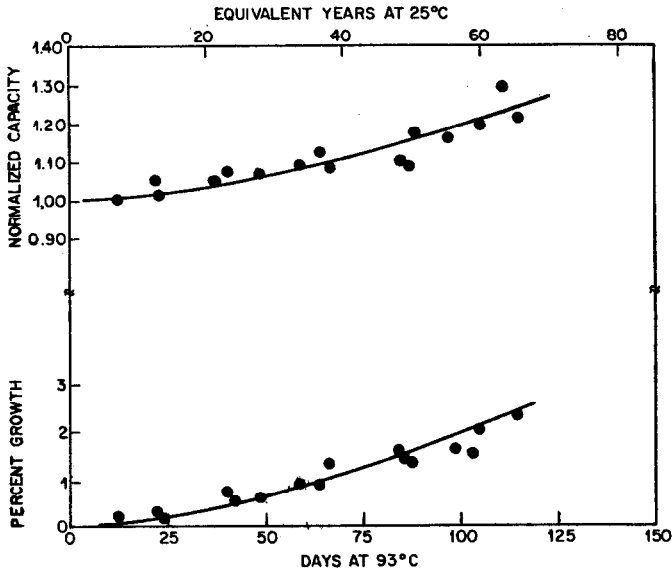


Fig. 3. Capacity and positive plate growth *vs.* time at 93 °C for the cylindrical cell.

Cell sizes and capacity

Four sizes of the Bellcell battery are manufactured. These are summarized in Table 1 and shown in Fig. 4. Components for all cell sizes are identical except for the jar which varies in height to accommodate the four sizes.

Battery stands

The two largest size Bellcells can be exchanged with equivalent capacity rectangular cells on a one-for-one basis on conventional metal battery stands. The smaller sizes presented a problem, however. Although they are shorter than their equivalent rectangular cells, their "footprints" are larger. Consequently, use of the smaller Bellcells on conventional stands would have required substantial increases in floor space. The solution was to provide a completely new stand design in which simplification and standardization

TABLE 1

| Ampere-hour capacity* | No. of positive plates | Height (in.) | Weight (lb) |
|-----------------------|------------------------|--------------|-------------|
| 1 600 | 18 | 24 7/8 | 346 |
| 864 | 9 | 17 | 198 |
| 488 | 5 | 13 1/2 | 133 |
| 296 | 3 | 11 5/8 | 100 |

*8 hour rate to 1.75 volts.

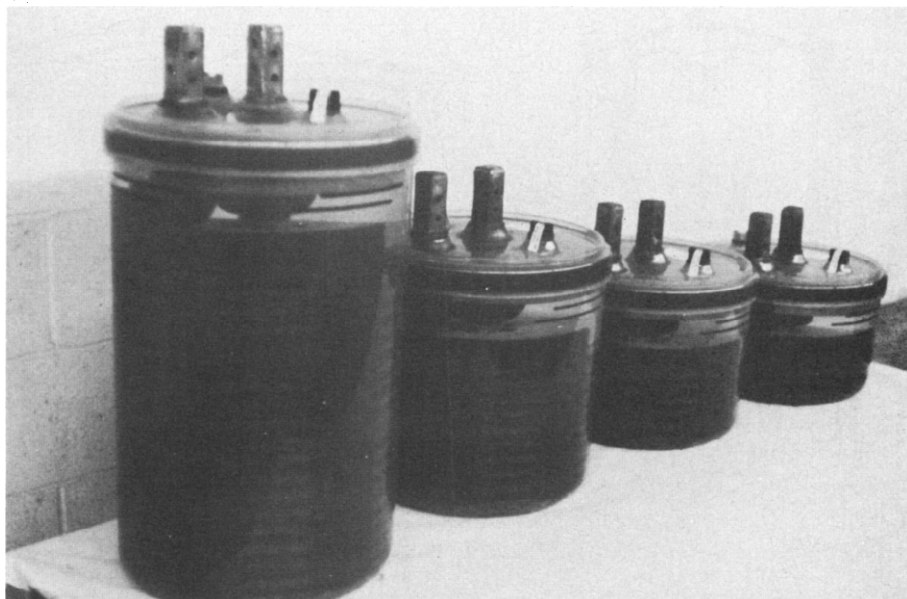


Fig. 4. Four cell sizes.

were the major objectives [6]. The new stand consists of two basic parts as shown in Fig. 5. The parts are made of nonconducting, flame retardant, glass-reinforced polyester. The basic module for the new stand consists of two bases and two backs, shown in Fig. 6. This module provides mounting space for four cells. These modules are further assembled to provide mounting positions for the total number of cells required. The modules are interlocked with dovetail keys.

Depending upon the cell size, several multitier arrangements are recommended, as shown in Fig. 7. These range from 3 tiers maximum for the largest cell to 4 tiers maximum for the three smaller cells.

Installation

Figure 8 shows a typical cylindrical cell battery plant in the process of being installed. This Figure shows the second tier of batteries being installed on a 2-row stand. The cell installation tool is a gantry which straddles the battery stand. The strength of the jar-cover seal allows the cell to be handled by the cover lip by an "ice-tong" clamp. Vertical movement of a cell is accomplished with an electrically driven chain hoist.

Applications

Applications of the Bellcell in the Bell System range from 12 volt to 140 volt plants to provide reserve for various switching and transmission

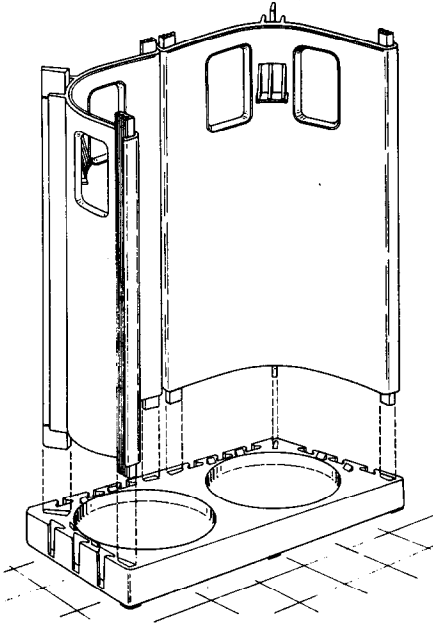


Fig. 5. Base and back for the polyester battery stand.

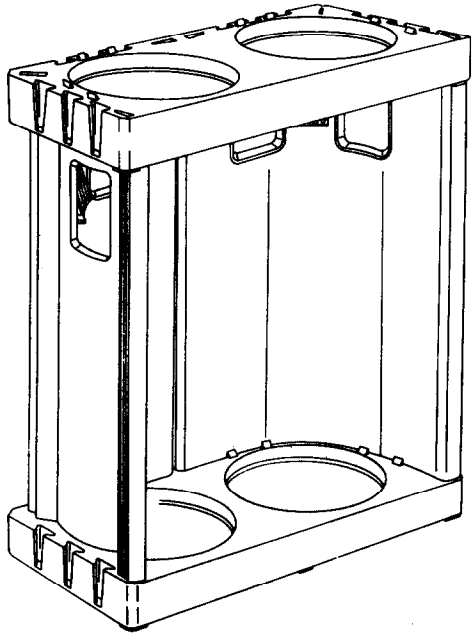


Fig. 6. Assembled battery stand module.

telecommunication facilities utilizing either electromechanical or newer electronic technologies. More recently (1977), the Bellcell has also been introduced into high rate discharge (~ 15 min) Uninterruptible Power Systems (UPS) designed to provide a.c. reserve for computer systems. Although the Bellcell battery design has not been optimized for high discharge rate UPS applications, its usage in these high voltage battery plants is based upon the safety features afforded by the leak-proof seals and the fire retardant jar and cover material. Figure 9 shows a portion of a 1368 cell battery plant partly consisting of 4 parallel 500 volt strings of batteries. This 3-tier battery plant provides reserve for a 2 000 kV A UPS.

Experience

As mentioned previously, one of the major design objectives of the new cell was to eliminate failure by corrosion and growth of the positive plates. To date, including early field trials, we have accumulated almost 9 years' experience in actual field use and, as expected, no corrosion and growth failures have occurred. Admittedly, 9 years' experience is too soon to verify our expectations of approximately a century of useful service, but growth data obtained on 10 year old room temperature laboratory test cells confirm the life expectations predicted from accelerated tests.

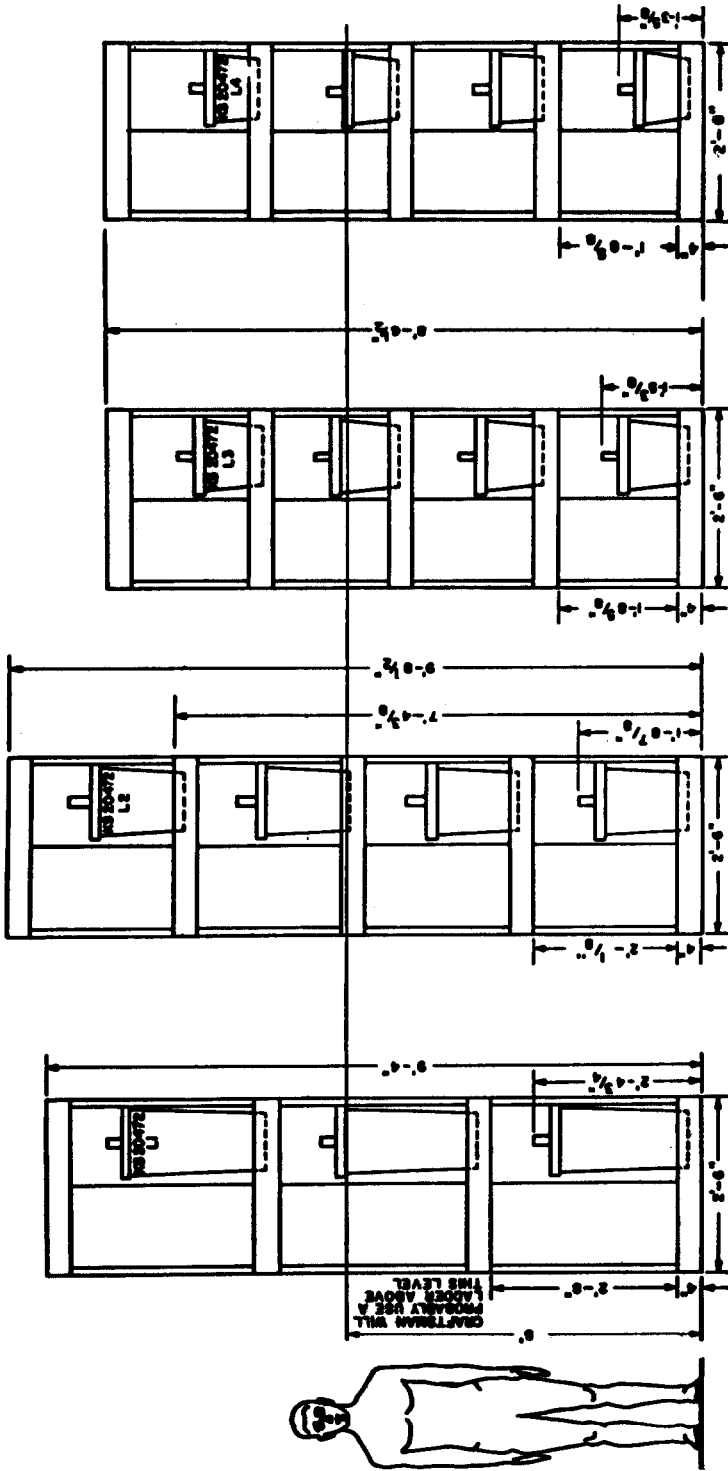


Fig. 7. Illustration of maximum multitier arrangements for various cell sizes.

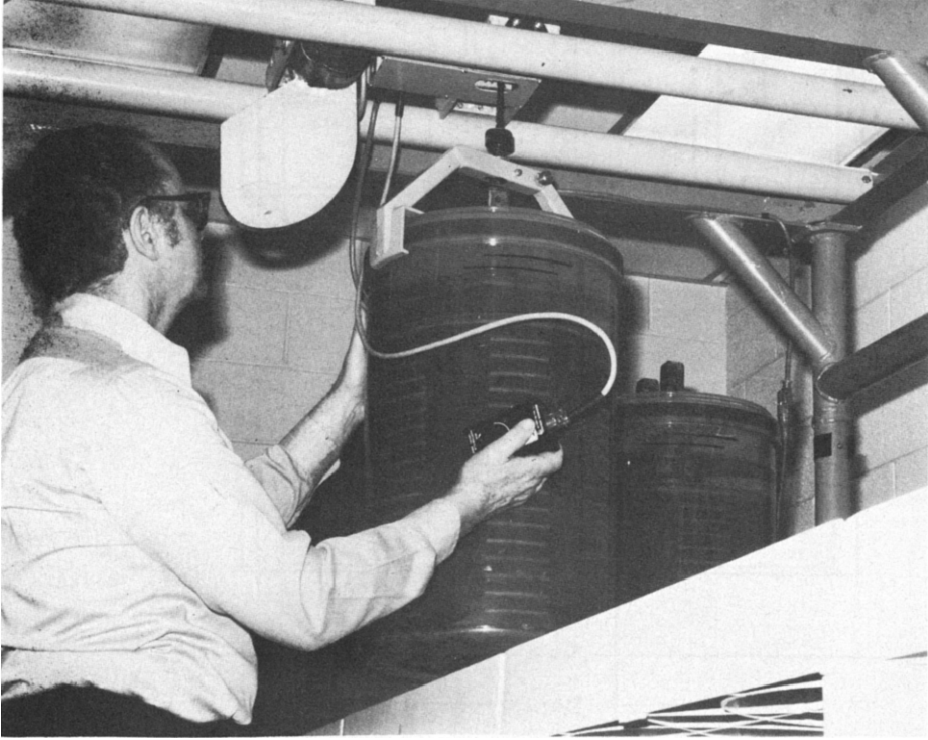


Fig. 8. Installation of a cylindrical cell battery plant.



Fig. 9. Portion of a 2 000 kV A battery plant.

Another design objective was to minimize maintenance by incorporating mechanically sound and corrosion resistant seals. Again, through our 9 years of experience, we have no known incidences of failure resulting from failure of the above seals. Also, no water additions have yet been required for the oldest (9 years) cells in the field. These experiences of low water consumption are consistent with very low corrosion rates.

Although our experience with the oldest cells has been excellent, we have experienced manufacturing scale-up problems that are typical of many new products evolving from development to large scale production. One such problem is described below.

Although the Bellcell represents a significant departure from conventional lead-acid cell designs, it remains fundamentally a lead-acid cell designed to utilize the energy available from the Pb/PbSO_4 and $\text{PbO}_2/\text{PbSO}_4$ couples. Accordingly, one particular performance problem that was encountered should be of general interest to both users and designers of lead-acid batteries. The following discussion focuses on that particular problem and the changes that were implemented to resolve the problem.

In Bell System service, lead-acid batteries are continuously trickle-charged (floated) at a battery voltage of 2.170 V per cell. The purpose of float is, of course, to maintain the battery in a full state-of-charge at all times, which requires that the float voltage selected be sufficient to maintain both electrodes above their thermodynamic reversible potentials. For 1.215 sp. gr. H_2SO_4 , the open circuit voltage of a lead-acid cell is 2.060 V. Therefore, at a float of 2.170 V/cell, 110 mV of overpotential (polarization) is provided in order to maintain the cells in a full state-of-charge. It must be emphasized that, in modern electronic switching systems, boost-charging of batteries is not possible. Accordingly, proper float operation requires a delicate balance of positive and negative plate characteristics such that the 110 mV overpotential is adequately distributed between positive and negative plates in order to maintain both electrodes in a full state-of-charge for the anticipated life of the battery. In 2.17 V/cell float service, positive plate and negative plate polarizations of ≥ 25 mV and ≥ 1 mV, respectively, are required [7].

After experiencing two years (1973 and 1974) of essentially trouble-free float operation, we became aware of a float problem with some cells manufactured starting in early 1975. This problem was recognized by the appearance of lead sulfate crystals on the positive element of the battery. These lead sulfate crystals are readily visible by inspecting the positive plate vertical lug columns (Fig. 1) with a flashlight. The presence of lead sulfate indicated that the positive plates were self-discharging even under float conditions and, as expected, $\text{Hg/Hg}_2\text{SO}_4$ reference electrode measurements showed 0 mV positive plate polarization for these cells. In order to analyze the problem, we made use of the well known Tafel relationship for the PbO_2 electrode,

$$\eta_1 = \eta_2 + 80 \log \frac{I_1}{I_2} \quad (1)$$

where η_1 and η_2 are the positive plate polarizations in millivolts at currents I_1 and I_2 , respectively. Battery strings were selected in the field that contained both satisfactory and unsatisfactory floating cells and, since the current required for float is typically <75 mA steady-state positive plate polarization measurements were made at higher currents (>1 amp). These measurements consistently gave characteristically different results that distinguished satisfactory and unsatisfactory floating cells. Typically, at 1.5 A satisfactory and unsatisfactory cells gave polarizations in the ranges of 165 - 175 mV and 140 - 150 mV, respectively. These two populations of positive plate polarizations explained precisely the phenomena observed on float. For example, 30 mA is a typical current that was obtained in measurements of cells on float. Using the 1.5 A values measured, eqn. (1) predicted the observed float polarizations of 30 - 40 mV* for the 165 - 175 mV (1.5 A) population and 5 - 15 mV for the 140 - 150 mV group. The latter range of polarizations is inadequate to maintain positive plates in a full state-of-charge and accounts for the sulfation observed on this group of cells.

Extensive investigations to ascertain the cause of the two populations of cells revealed that their behavior was related to the relative ratios of α - and β -PbO₂ in the positive plates. This relation was confirmed by first establishing a quantitative X-ray diffraction calibration curve for α/β -PbO₂ and then performing numerous analyses on plates from cells. Some of these results are shown in Table 2.

TABLE 2

| Cell | η_+ (mV) @ 1.5 A for cell | α -PbO ₂ (%) in 5th plate | η_+ (mV) @ 300 mA for 5th plate |
|------|-----------------------------------|--|---|
| 1 | 156 | 4.6 | 224 |
| 2 | 178 | 2.5 | 241 |
| 3 | 212 | ~0.5 | 250 |

The data show a correlation between the concentration of α -PbO₂ and the cell Tafel characteristics. In addition, individual plate polarizations also correlate with the quantity of α -PbO₂.

It is well known that the α/β -PbO₂ content of positive plates is very sensitive to the H₂SO₄ concentration used in formation [8, 9]. A retrospective analysis of manufacturing procedures revealed that changes that were made in the plate formation operation in order to optimize efficiency and manufacturing output would have favored increase of α -PbO₂ in positive plates. It is also known that α -PbO₂, when discharged, will convert to β -PbO₂

*The presence of unsatisfactory floating cells in the battery string, which minimizes the float current, causes the 30 - 40 mV positive plate polarizations of the satisfactory cells. Ordinarily, a battery string of only satisfactory cells would exhibit 50 - 70 mV positive plate polarizations.

on subsequent recharge [9, 10]. Therefore, rather than alter the forming operation, we chose to modify the cell processing procedures (discharge/recharge) in order to minimize the α -PbO₂ content. Specifically, the discharges were modified to yield ~2 200 ampere-hours capacity compared with 1 900 ampere-hours originally. Almost simultaneously, a 165 mV (1.5 A) minimum positive polarization requirement was introduced as a standard of cell acceptability. Implementation of these procedures has eliminated reoccurrence of the float problem previously defined.

As a direct result of the above float problem, we determined that the presence of PbSO₄ crystals on the positive plate element was an unambiguous indicator of the state-of-charge condition of Bellcell batteries on float. This led to the introduction of a simplified visual inspection maintenance routine which replaced relatively lengthy voltage and specific gravity measurements.

Conclusions

The usage experiences to date indicate that the design objectives for the cylindrical cell will be realized. No water additions have been necessary for up to 9 years' service.

A unique float problem was encountered which was caused by excessive α -PbO₂ in the positive plates. The problem was resolved in manufacture by modifying the cell processing procedures. Resolution of the problem led to the substitution of voltage and specific gravity measurements by simple visual inspection for PbSO₄ crystals as a regular maintenance routine.

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