COMPARISON OF POSITIVE GRID ALLOYS FOR FLOODED INDUSTRIAL LEAD ACID BATTERIES

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ABSTRACT

There are two families of alloys generally employed in the manufacture of industrial lead-acid batteries. This paper discusses the significant performance and maintenance characteristics and life implications of each alloy.

INTRODUCTION

Alloys currently used in the lead-acid battery industry fall into two main classifications: antimony and calcium. For the purposes of this paper the following alloy types were tested: 5% lead antimony, 1.6% lead antimony selenium, 0.03% lead calcium and 0.05% lead calcium tin aluminum.

Use of antimony in the positive grid, in the range of 2 to 5 %, dates back to 1881 and was originally added to the positive grid melt to achieve rigidity (1) despite concerns about dissolved antimony in the form of Sb_2O_3, being re-deposited at the negative plate thus increasing local action (2). Concentrations as high as 11% have been observed in tubular batteries used in Standby applications. It was also recognized that antimony had a lower hydrogen overvoltage than lead, which would promote increased gassing and water loss in service (3). Typical applications now utilize between 4 – 12 % antimony (4) with a growing trend toward low antimony, <3%, alloys. Cycle testing has shown a beneficial effect of antimony because of its cohesive influence on the structure of the positive active material.

Low antimony selenium alloys are considered a subset of the antimonial group. This alloy came into usage in the early 1980's and has achieved popularity in Europe. Product offerings typically include either 2.8% or 1.6 % antimony. Binary low antimony alloys are difficult to cast and produce a large grain structure with resultant cracking and increased corrosion hence the addition of 0.02% selenium to act as a grain refiner. Ostensible benefits include low self-discharge, low float currents and good ability to cycle.

The need for improved maintenance characteristics promoted the development of the lead calcium alloy by Haring and Thomas in 1935 (5). These alloys feature a low self-discharge rate, low float currents, low gassing rate and longer life. These cell types first saw operation in the Bell system in the early 1950's. Passivation at the active material to grid interface in binary calcium alloys may result in premature capacity loss (PCL) in cyclic operations.

Pb-Ca-Sn-Al alloys are a subset of the lead calcium alloy. The aluminum is added to prevent oxidation of the alloying elements during the casting process. In addition to superior corrosion characteristics, the use of tin improves the ability to cycle calcium alloys. By improving the conductivity of the active material/grid interface and reducing the thickness of the semi-conducting layer of PbO, tin thus virtually eliminates premature capacity failure (PCL) (6).

EXPERIMENTAL

The test routine consists of the following variables: open circuit stand loss testing, Tafel testing and accelerated life testing

Open Circuit Stand Test

An open circuit stand test to determine the rate of stand loss on open circuit of the PbCa, PbSb and PbSbSe cells was performed. Stand testing was not run on the PbCaSnAl alloy because its self-discharge rate was considered to be similar to binary calcium alloy cells. Following the recharge from a baseline measured capacity discharge; the cells are brought to a full state of charge and placed on open circuit. After a suitable period without any charge return, the measured capacity discharge is then repeated with the difference in capacity attributed to self-discharge. The self-discharge is then calculated from the capacity loss and time on stand and expressed as self-discharge rate/month.

Tafel Testing

A Tafel line from the as built condition was run on the PbCa, PbSb and PbSbSe cells. The Tafel line will be repeated at the conclusion of accelerated life testing to denote any change in the float characteristics.

As with the open circuit stand test, the PbCaSnAl batteries were not Tafel tested for identical reasons.

Accelerated Life Testing

Following baseline capacity testing four cells each of PbCa, PbSb and PbSbSe, were placed on float charge per the manufacturer's recommendations and life tested at 140° F (60°C). During the aging procedure cell voltage and float current are collected on a daily basis. The cells are removed from the hotroom at 84 day intervals, or approximately every 3 years at ambient per Telcordia acceleration factors, and the measured capacity discharge is repeated. Discharge testing methodology follows IEEE-450-2002 guidelines.

In addition, prototype cells designed for UPS service and utilizing a proprietary PbCaSnAl grid alloy were life tested at 160°F. While the test methodology for aging remained the same, the scheduled pulls from the hotroom were shortened to 30 day interval to accommodate the shorter time required for aging. These results will be reported also.

RESULTS AND DISCUSSION

The main prerequisites and generally accepted requirements of modern industrial standby batteries are:

- Self discharge characteristics
- Stable float characteristics
- Longevity - the ability to deliver design life and capacity retention

Self-Discharge

Self-discharge is defined as the ability of a cell to retain some portion of its capacity under specified conditions of temperature, usually 77°F, after it has been stored for a period of time without being charged (normally expressed as a percentage of rated capacity). On new batteries it is usually ascribed to the local action occurring at the plates, between the active material and grid metal. Table 1 shows the results of the fully charged capacity tests, capacity after stand loss testing, time on test and the rate of self-discharge per month. The self-discharge rate is graphically displayed in Figure 1.

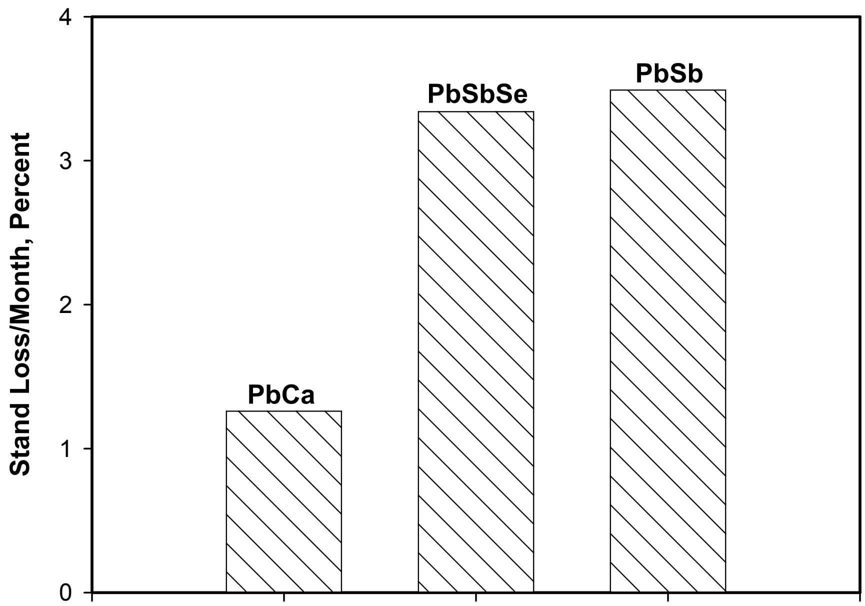
The tested stand loss rate for the lead-calcium cells was 1.26%, which is in good agreement with the commonly accepted rate of 1% self-discharge rate per month. The results for the antimonial alloys are nearly identical and somewhat surprising as conventional wisdom states that the self-discharge rate should increase with increasing antimony content. The stand test on the PbSb cells will be repeated for confirmation and validation of these results and will also be reported in a later paper.

Table 1

	PbCa	PbSbSe	PbSb
Initial Capacity	108.9%	110.6%	104.3%
Capacity after Stand Test	104.7%	95.9%	97.9%
Percent Difference	4.2%	14.7%	6.4%
Days on Test	100	132	55
Self-discharge Rate/Month	1.26%	3.34%	3.49%

The entire open circuit stand test will be repeated at the conclusion of accelerated life testing to determine stand losses as a function of battery age and to ascertain the effect of antimony transfer.

Figure 1: As Built Self-Discharge Rate of Various Alloys



Float Characteristics

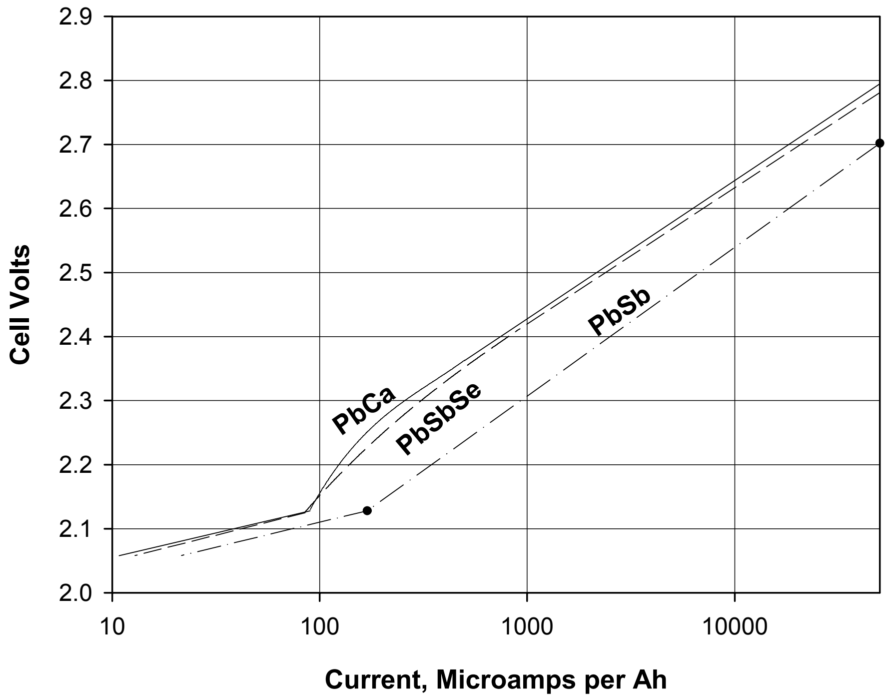
The purpose of float is to maintain the cell in a fully charged state by offsetting any internal losses that occur as a result of self-discharge and to maintain the positive plate polarization voltage at a level that minimizes growth and corrosion characteristics. As such, the grid alloying elements play a major role in determining the float current drawn by any particular cell type.

Tafel testing on the cells shows the float current for the lead calcium batteries to be the lowest of the three alloys tested, followed somewhat closely by the lead antimony selenium cells and lastly by the antimony alloy. Float current values are summarized in Table 2 and graphically depicted in Figure 2.

Table 2

Cell Type	**Float Current, μAmps/Ah**
Lead Calcium	130
Lead Antimony/Selenium	175
Lead Antimony	225

Figure 2: Comparison of Cell Voltage vs Charging Current

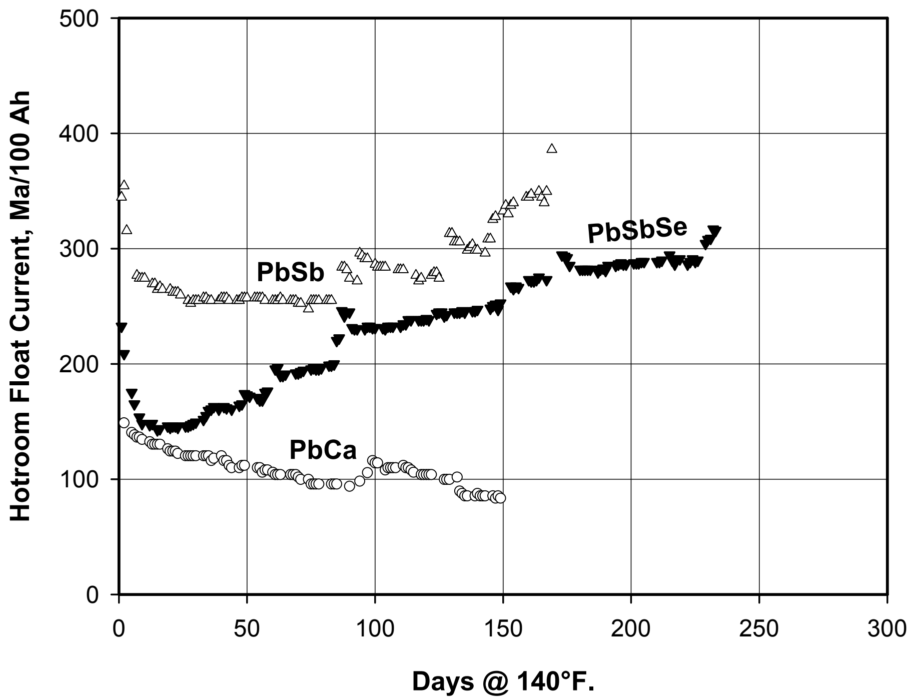


The relatively low as built float current of the lead antimony selenium alloy often invites proponents to claim the float characteristics of lead calcium alloy. As we shall see from examination of the float currents recorded during accelerated life testing that comparison is overstated.

During accelerated life testing at 140°F cell voltages and float current on all cell types was monitored on a continuous basis as presented in Figure 3. The calcium cells exhibit the lowest float current, which is still decreasing after almost 150 days on test, the result of the lessening effect of platinum depolarizer additive. Since there is no poisoning of the negative plate from antimony transfer, the float current for the lead calcium cells is expected to remain low for the remainder of the test period (7).

Both the antimony and low antimony selenium cells show symptoms of antimony transfer. After an initial dip, the float current on the low antimony selenium cells continually rises and after 230 days (~ 8 years) is double its lowest value seen at the beginning of the life test, over 300 ma/100 Ah or over 3 times greater than the value for an equivalent lead-calcium cell for the same period on float. This type of float behavior, strongly mimicking a traditional lead-antimony cell makes it difficult to understand how acceleration factors for lead-calcium alloy can be used for computing life at 77°F on lead antimony selenium alloy during an accelerated life test (8). The antimony cells had the highest initial float current, 250 ma/100 Ah, which remained stable for three years. The current then increases to 350 ma/100 Ah after six years equivalent time at ambient temperature

Figure 3: Hotroom Float Currents @ 140°F.



Longevity

Accelerated life testing at 140°F. (60°C) was started on cells built with PbCa, PbSb and PbSbSe alloy. Life testing is still in its infancy and thus it is premature to draw any firm conclusions. All cell types show stable capacity at this juncture. Testing of these samples is still ongoing and will be updated in a future paper. Capacity results to date at the 8 hour rate of discharge are included in Figure 4.

The accelerated life test was used to collect float current data for reporting on the float characteristics of the various cell types.

An additional accelerated life test has been recently started for the purpose of determining water consumption characteristics. Results will be reported in a future paper.

Figure 5 shows the capacity retention of a new cell design built with the proprietary PbCaSnAl alloy versus the old UPS cell design. After 150 days on life test, equivalent per IEEE-535 acceleration factors to 15 years at ambient, the capacity of the old design has fallen below 12 minutes while the newer design still has a runtime of about 14.5 minutes.

Figure 4: Capacity Retention During Accelerated Life Testing

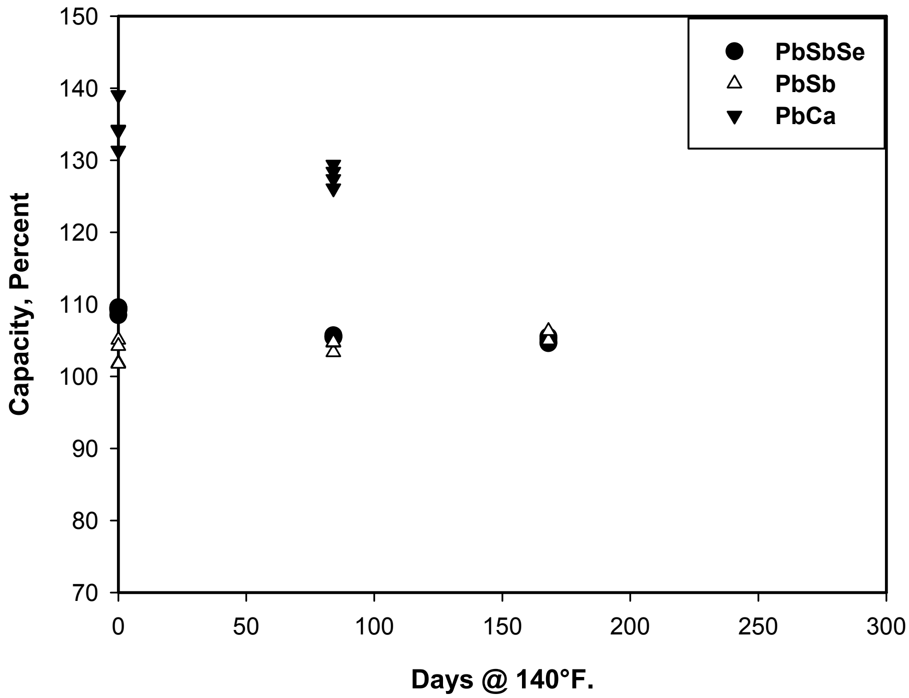
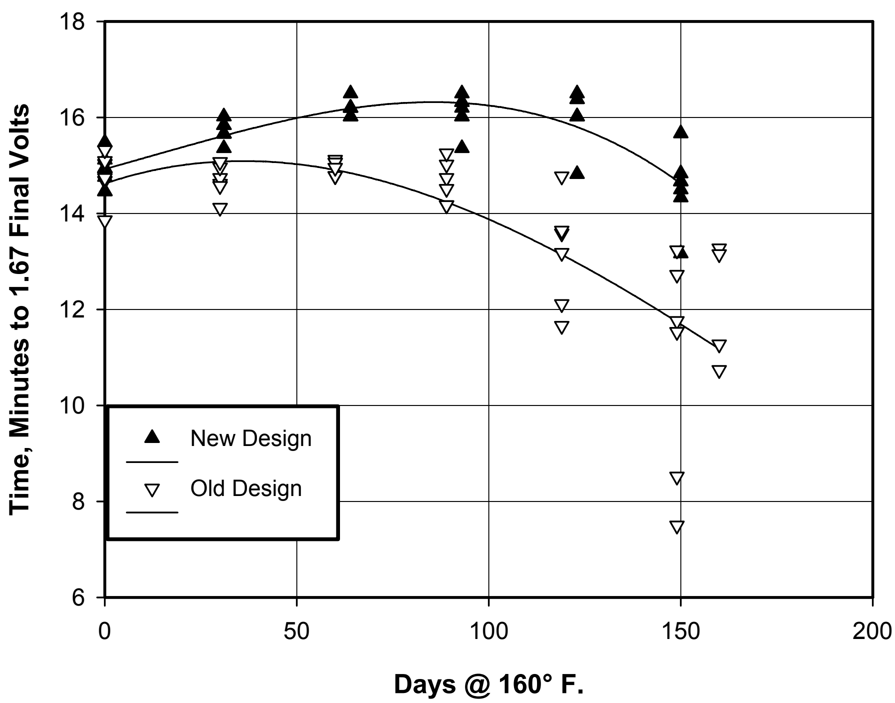


Figure 5: Old Vs Improved Design Life Testing



CONCLUSION

Data from Stand testing and float current monitored during accelerated life testing suggest there are no fundamental performance differences between PbSbSe and PbSb.

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