鉛電池の50年――米国テレコム用据置鉛蓄電池の経験と課題

1950-THE YEAR IT ALL BEGAN
50 YEARS OF LEARNING HOW TO LIVE WITH EACH NEW GENERATION OF LEAD ACID STANDBY BATTERIES

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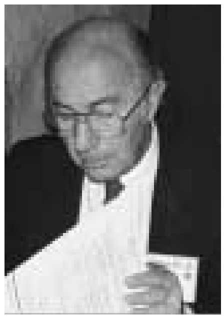

著者のDr.David.O.Federは60年代からAT&T（現Lucent Technologies）社ベル研究所で鉛電池開発に関わり，その後EESS社の社長として現在もこの分野の指導的立場にある。著者の経験を中心にテレコム用電池の発展の経緯と技術課題を総括している。この論文の要旨は以下の通りである。

1. 1950年は，Pb-Ca合金がPb-Sb合金に代わり本格採用された年である。現在の制御弁式電池（VRLA）の前史である液式電池を含めて，この50年間に起こった重要な技術革新が米国ベルシステムで定着するには大規模に組織されたフィールドスタディーやメーカーとの共同作業と共に試行錯誤を伴う基礎的技術解明が不可欠であった。
2. Pb-Ca合金の導入（電槽のプラスチック化なども同時進行）に伴う大混乱を解消し，長寿命の信頼性を確立するのには20余年の歳月を要した。この間に得られたPb合金の腐食やグロスの知見は今も有用であり，また今日では周知のTafelプロットの電池電極反応への適応もこの時が始まりと言う。ベル研究所設計の傘型格子円筒セルは30年以上たった現在も稼動しており，鉛電池の信頼性の高さを物語っている。
3. 据置電源の理想であるシール電池の代案としてVRLAが登場したのは，Pb-Caの液式電池が落ち着いた80年前後である。電解液はガラスファイバーマットに吸収させて固定化した。たとえ100%酸素再結合反応したとしても，正極腐食とバランスした負極の水素発生は不可避であり，逆止弁付きのVRLAとなった。
4. 液枯れ，弁故障，熱逸走，負極ストラップ腐食などの新たな故障モードと共に，フロート充電運転のままで電池容量を計れないことが現場の問題であった。コンダクタンス/インピーダンス法を用いた数万個電池規模のフィールドスタディーが90年代に行われた。同様の調査は欧州でも行われた。コンダクタンス/インピーダンス法と放電法の高い相関性が確認され，容量低下と共に内部抵抗は増加した。但し，これらの調査を通じて明らかになったことは，非常に高い確率で3年位の短期間から容量不足が起ると言うショッキングな事実であった。
5. VRLAの早期容量低下の原因究明が本格化して未だ数年である。負極からの水素発生の精密測定などが始まり，「水素バランス」（正極腐食と負極自己放電）の重要性とVRLAの核心についての理解が進んだ。
6. 今日，材料技術の進歩と上記の知見に基づく長寿命化技術が複数開発されている。また，屋外使用の普及は本格的なモニタリング技術の開発動因ともなっている。IT時代を支えるインフラの1つとして据置電池の長寿命高信頼性技術は益々重要となっている。

・著者略歴：米国コロンビア大学化学工学科卒業後，1954年AT&T社入社，ベル研究所で各種電池の設計開発に従事。1984年，Electrochemical Energy Storage Systems, Inc. を設立し社長として米国内外技術指導の傍ら，INTELECなどの学会や各種の電池及びテレコム関連標準化委員会に，また特に最近は，VRLAの「Ballanced Cell」の理論と応用，ベル系テレコム会社（複数）のリチウム据置電池検討委員会などに従事。

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Abstract : This paper traces the Bell System's 50 year adventure with the problems and solutions resulting from each new standby battery technology introduced into widespread System use. It describes the change from Pb-Sb to Pb-Ca in 1950, and the 20-30 years of problems, tests, research and development leading finally to a well understood, reliable, long life flooded cell technology. Then, VRLA technology was introduced.

The promises and realities of VRLA performance and life are described. The search for a non-invasive technique to characterize the "State of Health" of VRLA cells led to a massive capacity/conductance correlation study. The study involving >24,000 cells has validated the correlation between conductance and other ohmic techniques and VRLA capacity, as measured directly off float. It also led to the realization that premature capacity aging was common in the 2 US studies of > 40,000 cells and a Swedish study of > 35,000 cells.

Again, problems have led to research and most recent studies have developed a new "Balanced Cell" concept, which appeared to explain some of the failures and led to both simple, immediate solutions as well as more complex, elegant solutions involving a new level of material purity to prevent cell inbalance.

SO, IT WAS IN 1950 THAT THIS NEW ADVENTURE BEGAN !

Background :

For more than half a century, prior to 1950, the Reserve Battery Plant of the Bell System in the USA and Canada consisted almost entirely of lead antimony flooded stationary batteries. For the user, Pb-Sb batteries had the advantage that simple measurement of cell voltage or specific gravity could indicate "State of Charge" and often "State of Health". These also provided one of the main disadvantages, since these measurements required maintenance work, often to be followed by additional work for boost charges. The boost charge, besides requiring maintenance effort, placed extra requirements on the power supply system, in order to accommodate the higher voltage of the boost mode and severe requirements on the ventilation system, to insure the safe removal of the explosive hydrogen as well as safe exhaust of the toxic arsine and stibine evolved.

What happened in 1950 ?

In the USA and Canada, in 1950, the Bell System introduced lead calcium technology into their Central Office standby reserve battery plants. After 30-40 years experience with lead antimony batteries, this new lead calcium technology was expected to significantly simplify battery maintenance, provide a quantum jump in battery life expectancy, reduce ventilation requirements and remove potentially toxic gases from the battery rooms.

With no antimony, self discharge was reduced and with it the need for boost charging. This significantly reduced the rate of water loss, ventilation requirements and there were no toxic gases evolved. Further, since the Bell Labs tests indicated that, with proper control of calcium content, positive grid corrosion could be significantly reduced, battery life must be longer. These first Pb-Ca cells were sold as "25 Year Guaranteed Life", with the end of life criterion increased from the 75% of rated capacity specified for Pb-Sb, to 90% of rated capacity for Pb-Ca technology.

Surprises-1950 TO 1960 :

With any new technology, one must expect some surprises. The first surprise came as the cells were first introduced. Voltage variations went far beyond the limits expected. In keeping with the maintenance requirements for Pb-Sb, whole strings of batteries were removed, the high and low voltage cells were each segregated and matched and reinstalled as "matched strings" (this practice was continued for at least 6 years). But the voltage variations remained as wide as before the matching. Manufacturing specifications were rewritten to insure that trace amounts of antimony were not introduced into the Pb-Ca cells and to require several weeks float, in the factory, for cell matching, before acceptance. But it made no difference. **It took literally 20 years** before the float characteristics of the positive and negative plates of Pb-Ca cells were sufficiently understood to allow proper remedial action. The technology which evolved, the introduction of reference electrode measurements; the understanding of the Tafel curve; the understanding of when the consequences of voltage variations were significant and when they were not, along with the techniques to make the proper measurements are described in several of the references cited [1,2,3].

Surprises-1960-1970:

In 1963, 13 years after the introduction of Pb-Ca batteries into the Bell System, the author was placed in charge of a department responsible for Bell System Lead Acid Battery Development, Application and Use. In less than two months, the **first surprise** came literally with a "flash", in the form of a **rash of battery fires**, at a frequency and extensiveness previously unknown. We quickly learned that a "new" element had crept into the Bell System Battery Plants…. **transparent plastic battery jars replacing the older hard rubber jars**. The advantage of plastic jar transparency was compromised by their stress sensitivity, causing cracks and leaks, which led directly to battery fires fed by the jar composition (with ingredients chemically similar to Napalm!).

Fortunately, the key factors; positive grid and plate growth stressing the brittle, flammable plastic, causing cracks and acid leaks to a **grounded metal rack or shelf and the significance of voltage differential** were rapidly understood and emergency steps taken to eliminate the possibilities, while the more difficult task to qualify new flame retardant materials. proceeded at a more deliberate pace. We also realized that while the old hard rubber jars could ignite and burn slowly, they rarely cracked since they were far more flexible than the plastic, but merely bulged from the stress of plate growth [4].

The **second surprise** arrived almost simultaneously with the fires, but was fundamentally far more serious. A series of actual capacity tests on about a dozen strings of Pb-Ca batteries, by one of the Bell Companies, showed poor capacity, well before the 25 year life expectancy. The test results were confirmed by my engineers, resulting in immediate action jointly among Bell Labs, AT&T all the Bell Companies and Western Electric Organizations. This collaboration produced a System-wide capacity testing program, apportioned among the 21 Regional Bell Companies. Both Pb-Ca and Pb-Sb cells, older than 5 years and from 180 to 1680 Ah were discharge capacity tested, directly off float, at the 5 hour discharge rate. The numbers of cells to be tested were allocated on the basis of the size of each of the Regional Bell companies. In all, capacity data on more than 5000 cells were obtained, with visual inspection conditions noted on approximately 100,000 cells. The capacity data are shown in Figure 1 and Table 1, below[5]:

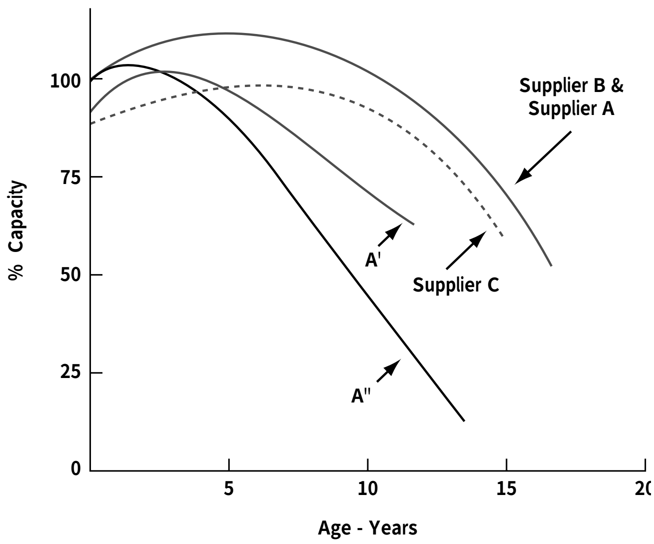


Fig. 1　Aging Characteristics of 180-1680 Ah Pb-Ca Batteries

Table 1 shows the capacity measured for 3146 cells rated at 1680 Ah, after 5 to 15 years of service. It indicated significant capacity failures. It also showed that all vendors were not equal! Results also showed that adherence to the newly introduced end of life failure

Vendor	No. of cells tested	Percent of cells with capacities less than		
		90%	85%	75%
A	1063	51	46	37
B	1053	36	24	6
C	1030	15	6	3

Table 1 Result of 1965 surver of Pb-Ca cells in the Bell system.

criterion of 90% would require a massive replacement program. Bell Labs and AT&T immediately re-introduced the 75% end of life criterion, which had been the traditional value for Pb-Sb cells! (This was subsequently adjusted to 80%)

Fig. 1 showed graphically how the cells aged. It clearly shows that the "Marketing Claim" of 25 year life would not be achieved by any of the designs tested. A 15 year projected life was far more realistic for the designs of vendors A,B and C.

The **third surprise** is shown in Figure 1 by the catastrophic premature failures of the products A' and A", each introduced by vendor A as **presumed improvements to their original A design**. Figure 2 highlights the differing aging behavior of the designs.

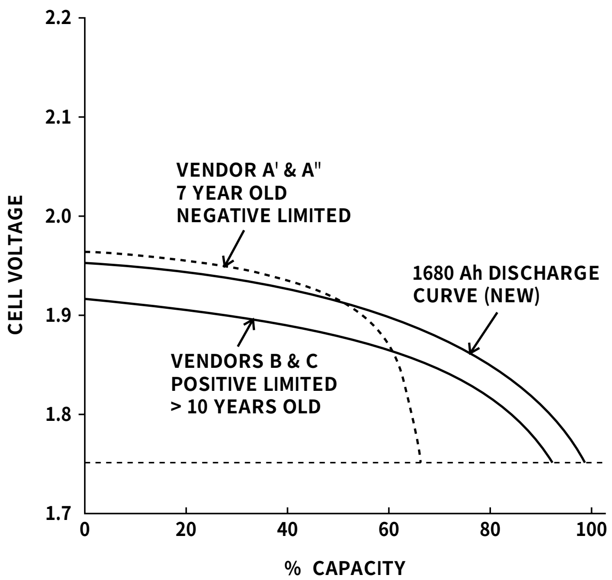


Fig. 2 Discharge Characteristics of 1680 Ah Pb-Ca Batteries After Aging

Fig. 2 shows typical discharge curves after some aging, compared to the new cells. Note the lowered discharge plateaus of vendor B &C's products after 10 years aging. By contrast, designs A' & A" show excellent initial discharge plateaus, followed by precipitous drops. It was determined that this was caused by negative plate premature capacity failure, resulting from "improvements" made to the negative expander systems.

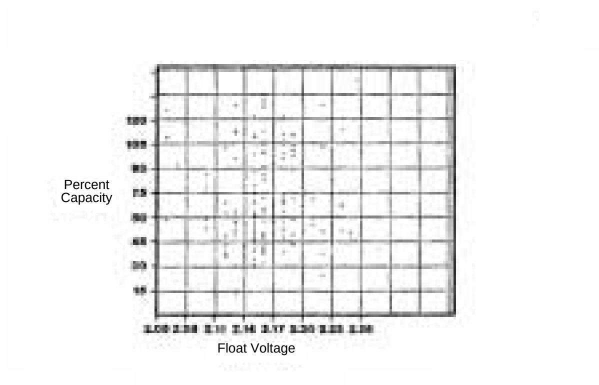


Fig. 3: PERCENT CAPACITY VS. FLOAT VOLTAGE

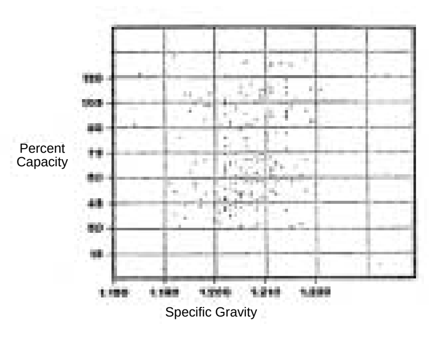


Fig. 4: CAPACITY VS. SPECIFIC GRAVITY

Fig. 3 and 4 show the next surprise!

Fig. 3 and 4 represented a serious "culture shock" to both vendors and the telephone company users. Unlike the Pb-Sb technology, with which they were so familiar, those figures show clearly that there was no correlation between actual measured discharge capacity and either cell voltage or specific gravity for the Pb-Ca technology [6].

The nicest surprise-support for battery research!

By 1964, the combined effects of the fires, the capacity failures, the new information about the inadequacy of cell voltage and specific gravity, and the increased incidence of post seal and jar/cover seal leakage made it clear that the overall Pb-Ca battery “system” was not properly understood, either by the manufacturers or by their largest user, the Bell System. This stimulated a major program effort to understand these problems and develop suitable correctives.

The “war” was fought on two fronts.

At the C&D Battery Company, a major supplier, Dr. Eugene Willihnganz concentrated on understanding the float behavior of Pb-Ca batteries and (other antimony-free flooded systems). His work formed the basis of much of today’s knowledge of Pb-Ca float characteristics, and is directly applicable to an understanding of a large portion of the float behavior of valve-regulated lead acid (VRLA)batteries. He developed the Tafel Curve as a practical measurement tool to understand and control the float characteristics of both the positive and negative plates. This insured that the positive plate received its ideal polarization to minimize corrosion and growth, while the negative remained at least minimally polarized to prevent self discharge(3,4). Other workers have followed his lead and contributed to understanding the effect of oxygen recombination in flooded cells, shifting the negative Tafel curve to insure proper positive polarization, etc.[1,2,3,7,8].

The work at Bell Labs concentrated on understanding the material, design, manufacture and performance variables affecting the corrosion and growth of the life-limiting positive grid; material studies to allow use of fire retardant (oxygen index >28, ASTM V-0) battery jar and cover materials and leak- free post seal designs.

The results of all these efforts are fully documented in the 1970 “Cylindrical Cell” Issue of the Bell System Technical Journal and were also shared with the entire Battery Industry, worldwide, in a Symposium held at our Murray Hill, N.J. Laboratories in 1969. Industry attendees came from Asia, Europe, Canada and the USA [2,9].

These studies developed a quantitative understanding of the physical and metallurgical design variables affecting positive grid growth, allowing the design of a novel circular grid of concentric rings. The design of the rings were such as to allow continued corrosion and growth without any change in the ring spacing. This allow the grid to maintain continued contact with the positive active material, not only retaining its original capacity, but actually increasing as the PbO_2 corrosion produst added to the active material capacity. First produced commercially in 1972, the design is still a major product, purchased with increasing demand by the expanding telecommunication industry in the USA [9].

Of even greater significance was the development and validation of elevated temperature, Arrhenius-based accelerated testing techniques to determine and predict grid growth, post-seal leakage, jar/cover/element stress interaction and other long term phenomena. These techniques, as well as many of the cylindrical cell design features and material choices were adopted and modified by our vendors to enhance their own product designs and performance [9,10,11,12].

The result for the Battery Industry is the ability to choose designs and materials to achieve any desired float life from less than 10 years to greater than 40 years for flooded antimony-free lead acid cells.

In the subsequent discussion of VRLA cells, **it should be remembered that it required more than 25-30 years, from the 1950 introduction of Pb-Ca cells** to achieve this level of understanding in design, manufacture and use, for flooded, antimony-free cells in telephone float standby service! **SO, JUST WHEN WE UNDERSTOOD FLOODED CELLS, VRLA DESIGNS APPEARED!**

WHAT ABOUT VRLA----ANY SUPRISES??

PERIOD I- The simplistic period :

As initially introduced, VRLA batteries appeared to provide an ideal solution for backup power for the rapidly evolving Telecom revolution. The initial simplistic techno-marketing description of its design, properties and behavior advertised that by making “minor” modifications to the conventional lead acid, flooded/vented long life central office design, a new, superior long life design had evolved, with the following properties:

1. Sealed
2. No gas
3. No water addition
4. No specific gravity measurement
5. Maintenance-free
6. Operable in any position
7. 20 Year design life

To achieve these desirable properties, the battery designers had simply changed from a micro-porous separator system to a non-woven fiberglass separator, which then was partially filled with electrolyte, absorbed and thus immobilized in the fiberglass. The amount of electrolyte was reduced to allow direct gas phase transport of oxygen from the positive to the negative at rates 10,000 times faster than in the liquid phase of conventional flooded designs.

Simple in concept, seemingly simple in execution, these modifications allowed for essentially 100% of the oxygen generated at the positive electrode on float (overcharge) to be rapidly transported to the negative, where it would be recombined back to water, thus eliminating any gaseous evolution:

Oxygen evolution at the positive: $2H_20 \rightarrow 4H^+ + 4e^- + O_2$

Oxygen reduction at the negative: $4H^+ + 4e^- + 0_2 \rightarrow 2H_20$

If the recombination process were 100% efficient, then no gas would be evolved and all of the above characteristics could be claimed, including the 20 year design life, since it was assumed that the ultimate failure would be capacity loss resulting from positive grid corrosion and growth, as in the proven 20 year designs of flooded/vented, antimony-free grid alloy systems used in telecom central offices.

However, if all of the stated claims were true, none of the conventional maintenance measurements would be relevant to this technology. This prompted the author to note [13,14]: **“… However, they (VRLA batteries) also contain a designed-in penalty of ignorance, or inability to determine the condition of the battery on float and knowledge of its ability to provide the reserve needed, if called upon to perform”.**

The significance of this “penalty” became apparent, as more detailed understanding of the performance characteristics of the technology was developed and as actual field performance results began to become available.

PERIOD II-Reality sets in:

In a short time, certain fundamental electrochemical realities became evident, which indicated significant complexity of the technology and undercut some of those initial claims:

On float, in addition to the evolution of oxygen at the positive PbO_2 electrode, positive grid corrosion occurs:

$$Pb + 2H_2O \rightarrow PbO_2 + 4H^+ + 4e^-$$

This reaction consumes oxygen from the water in the electrolyte. In order to maintain electrochemical and electronic balance in the cell, an electrochemical equivalent of hydrogen is required

to be evolved at the negative:

$$4H^+ + 4e^- \rightarrow 2H_2$$

Thus, in their simplest form, these secondary reactions reduce oxygen recombination efficiency below 100% and must result in the emission of gaseous hydrogen, loss of oxygen to positive grid corrosion and, hence, permanent loss of water from the limited electrolyte within the cell. The emission of gaseous hydrogen means that the cell cannot be sealed, but must contain a re-sealable valve, hence the term Valve Regulated, which is contained in the VRLA acronym. Further, this valve must both open and close reliably, at predetermined pressures, which insure that jar bulging won't occur and on resealing, insure that no air re-enters the cell to cause so called "chemical" negative self-discharge.

$$2Pb + O_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$$

In addition, need for reduction in the loss of water from an electrolyte limited design, placed additional stringent requirements on the integrity and life of the jar/cover seals and post seals and dictated selection of plastics for jar and cover which were least permeable to hydrogen and water loss.

Even in the early stages of product introduction, it was clearly recognized that at or near 100% recombination, virtually all of the current flowing through the cell on float was performing no net chemical reaction, but was essentially only creating heat. The significance of this heating effect was not appreciated, possibly because most of the initial installations were charged at constant current. However, with the rapid expansion of the technology into conventional constant voltage telecom installations, a new term "Thermal Runaway" appeared, describing catastrophic heating effects. This heating increased cell temperatures, which in turn increased float currents, causing further increase in cell temperatures, etc., until the temperature literally "ran away" in working plants. These caused cell heating, jar bulging, jar meltdown and in many cases, cell explosions and fires. While it had long been known that another recombinant technology, sealed Ni-Cd cells, should never be charged at constant voltage, due to possible thermal runaway, this phenomenon was overlooked in most early VRLA installations, its reality actually denied by many of the manufacturers, until the catastrophic results became too obvious to ignore [15,16].

At this point, it is instructive to examine the original claims for VRLA technology and compare them with the actualities which were understood by the early 1990's:

Sealed-This was not possible, due to continuous hydrogen evolution as the by-product of positive grid corrosion. This could also result from overly aggressive overcharge, liberating gaseous oxygen and hydrogen. A resealable valve was required and the nomenclature changed to "Valve Regulated" on all national and international standards, **but only on some manufacturer's literature.**

No gas-This was obviously not accurate, as indicated above.

No water addition-This was unfortunately true, hence no way to compensate for premature dry-out.

No specific gravity measurement-Specific gravity measurement was theoretically possible by measuring a stable open circuit voltage and subtracting 0.840. However, this required taking the cells off-line for extended periods sufficient to allow voltages to stabilize and thus losing their ability to provide standby power during that period.

Maintenance-free-A more appropriate term was **Maintenance-Proof**, since conventional maintenance techniques were ineffective in detecting any problem except perhaps cells with internal shorts and on-line technology was not yet available to detect thermal runaway until after meltdown.

Operable in any position-This was generally true, but doubts had already begun as to capacity problems resulting from electrolyte stratification effects as related to specific cell design and orientation.

20 Year design life-There were early rumors of premature failures, coupled with the need for a technique to detect cell condition and protect against catastrophic failures. These created the next period, which will be called:

PERIOD III- Discovery:

As indicated above, early in the 1990's, it became obvious that a need existed for a technique which could characterize the condition of a VRLA cell/battery, without resorting to a complete discharge to determine actual cell/battery capacity. So-called "OHMIC" techniques were being considered, either as low frequency conductance or impedance measurements or as some sort of DC resistance technique.

The obvious need was for a study of these techniques, coupled with actual capacity discharge tests, in order to determine the degree of correlation, if any. In the spring of 1991, this author made a presentation to the Battery Council International (BCI), in which he compared the possible techniques of voltage, current, temperature, shallow discharges, etc and ohmic techniques against the possible aging and failure mechanisms, known at that time for VRLA technology [17] as listed below:

1. Positive grid corrosion and growth
   - Loss of contact to the grid results in capacity loss
   - Grid corrosion consumes water and leads to dry-out
   - Higher specific gravity causes increased grid corrosion
   - Dry-out causes further increase in specific gravity
   - Higher positive polarization (compared to flooded cells) causes faster grid corrosion

2. Dry-out is a new failure mode
   - Gas evolution may be greater than expected
   - Temperatures are higher
   - Grid corrosion is greater
   - Post seal leaks are fatal
   - Jar/cover leaks are fatal
   - Water diffusion through plastic jar/cover may be significant

3. Valve operation is critical
   - If valve sticks open-dry-out and negative self-discharge will occur
   - If valve sticks closed-jar bulge and possible explosion

4. Inadequate cooling
   - Thermal runaway
   - Explosion

5. Internal failures
   - Negative post/strap/lug internal corrosion results in "open cell"
   - Shorts cause voltage decay, paste shedding and separator breakdown
   - Full discharge = very low specific gravity = possible "lead through"

He concluded that ohmic techniques were the most promising but the necessary data for correlation were not available.

Fortuitously, Midtronics, a manufacturer of conductance measuring equipment was interested in participating in such a program. Together, over a period from 1992 until 1996, a cooperative program was carried out among

Midtronics, several telecom and UPS users, in which this author was privileged to be able to present the results in a series of papers at INTELEC, ILZRO, VARNA and other technical conferences [18,19,20,21,22,23,24].

PERIOD IV-Conductance Study leads to study of capacity aging characteristics:

It must be noted that **this study began as an attempt to correlate conductance measurements with cell capacity.** In order to carry out the study, actual discharge capacity test results were needed. At that time, while it was understood that the correlation would be challenged, there was no indication that the actual capacity results would become the major outcome of the program, indicating premature capacity failures of products of all manufacturers tested, without regard to size or specific design. These results will be presented first and the capacity/conductance/impedance correlation results treated in a subsequent section of the paper.

At the 1995 INTELEC, this author presented detailed information regarding the field performance of approximately 24,000 VRLA cells, as measured **by actual off float discharge capacity testing, while still in service** [25]. The cells in that study ranged from one to nine years in age and represented the products of nine different battery manufacturers, from the USA, UK and the Pacific Rim countries. Results are shown in Table 2. In that study, >15,000 cells failed to meet their 80% capacity requirement, out of a total test population of >23,000, for a 68% overall failure percentage (conductance and Impedance results will be discussed in a later section).

Failure rates among the nine manufacturers, ranged from 27% to 86% for cells 3-7 years old, as shown in Table 3. Of greatest concern was the startling increase in failure rates with age, at only 25-50% of the cells' design life.

In data shown in Fig. 5, cells 1-2 years old had low failure rates, but by the third year the failure rate had

Table 2

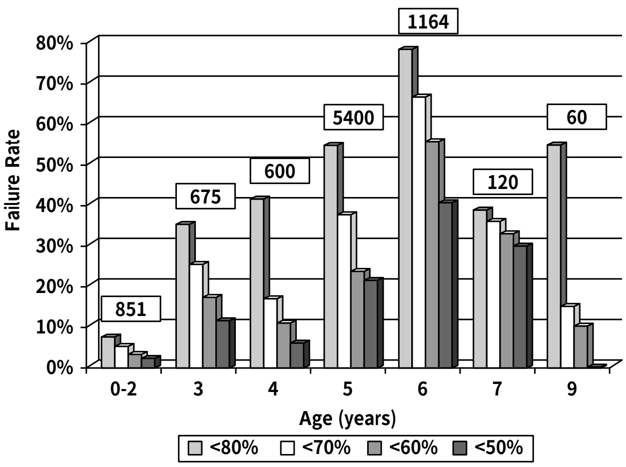
PUBLISHED VRLA CAPACITY TEST RESULTS: 1991-1995
WITH ASSOCIATED CONDUCTANCE/IMPEDANCE RESULTS

DATE PUBLISHED	# CELLS TESTED	# CELLS FAILED	% FAILED	CELL FAILURES CORRECTLY INDENTIFIED BY CONDUCTANCE/IMPEDANCE	
				# FAILURES CORRECTLY INDENTIFIED	% FAILURES CORRECTLY INDENTIFIED
3/91	12	0	0	-	-
5/92	442	337	76%	324	96%
6/93	633	502	79%	483	96%
9/93	1494	907	61%	849	94%
4/94	2496	1246	50%	1172	94%
5/94	6891	4410	64%	4336	98%
5/95	23176	15813	68%	15086	95%

Table 3

CAPACITY TEST RESOLTS
CELLS 3-7 YEARS OLD

MANUFACTURER	# TESTED	# FAILED	% FAILED < 80%
MFR A	15627	10747	69%
MFR B	4791	2568	54%
MFR C	712	338	47%
MFR D	288	171	75%
MFR E	1509	1298	86%
MFR F	1265	519	41%
MFR G	472	293	62%
MFR H	66	18	27%
MFR I	192	102	53%
TOTAL	24922	16054	64.4%

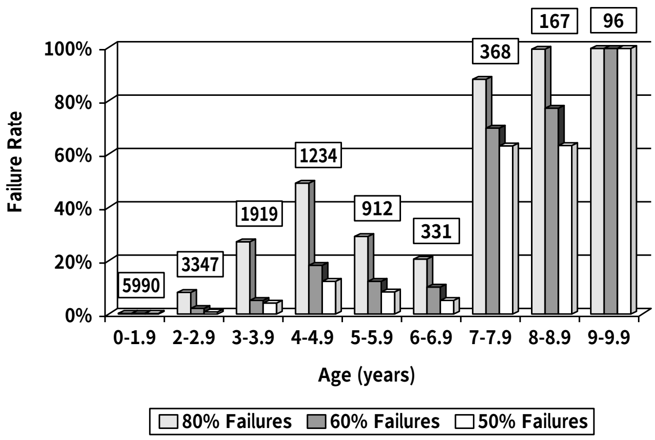


#Cells in Sample Shown Above Bars TOTAL 8,870
Fig. 5: Cell Failures by Age-All Manufacturers-1995 Data [25]

increased to 35% and then grew rapidly to 79% at 6 years.

In a paper presented at the 1998 INTELEC, the authors examined capacity test results from approximately 15,000 VRLA cells which were not included in the earlier study. This study includes a significant percentage of cells whose designs were too new to be included in the earlier tests. In addition, cells of some of the earlier designs, with either design or manufacturing improvements were included in the test results [14].

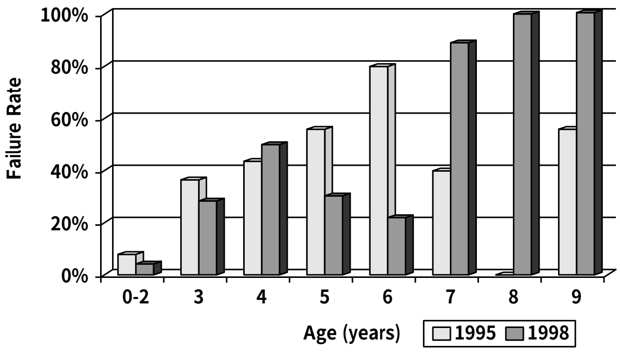
Overall, capacity tests were performed on more than 14,000 cells, of the AGM design representing products of five manufacturers and cell sizes from 50 Ah to 4,800 Ah. The combined overall results are depicted graphically in Fig. 6.



#Cells in Sample Shown above Bars TOTAL 14,364

Fig. 6: Cell Failures by Age?All Manufacturers 1998 Data [14]

These results are similar to the overall data taken from the 1995 paper and are compared directly in Fig. 7. In each case, the failure rates show acceptably low values in the first 2 years, but then increase rapidly in subsequent years.



TOTAL CELLS
1995… 8,870
1998…14,364

Fig. 7: Cell Failure Data-1995 Versus 1998 Results [14]

The data shown in the previous tables and figures represent only a small fraction of the detailed capacity aging information contained in the two referenced INTELEC papers [14,25].

Further, in a paper also presented at the 1995 INTELEC, Selanger and his co-authors from Sweden, report on a study of the capacity/age/failure rates of some 35,000 VRLA cells, in Telecom, Utility and Defense usage [26]. Fig. 8 shows their results, taken from Fig. 1 of their paper.

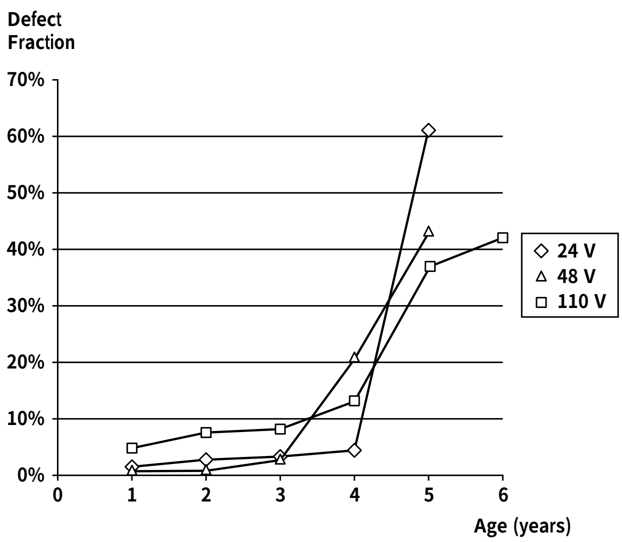


Fig. 8: Battery Defect Fraction(Fig. 1 of INTELEC Paper [26])

While the results show some differences, depending on the overall voltage of the battery plants involved, their results are certainly in close agreement with the overall results of both our 1995 and 1998 studies. Further, the authors note that because of the frequency of failures, two makes of AGM designs were withdrawn from the Swedish market. While this has not yet been publicly stated in the US, there are statements which have been made as to the intentions of some telecoms to ban all further purchases of VRLA products, especially for outdoor applications. For controlled environment use, flooded cells of proven reliability are considered a more desirable option and are increasingly being considered and selected, where space and use conditions permit.

Unfortunately, the above statements represent the “GOOD NEWS”. The “BAD NEWS” is that the largest use of VRLA products is in outdoor, uncontrolled temperature cabinets. Here we have no quantitative test data, primarily since the user has come to expect such a short life in these outdoor environments, that he generally replaces the batteries automatically after no more than 2-3 years. Under these circumstances, the user cannot justify the economics of performing capacity discharge tests. In addition, in many cases he cannot justify either the use of ohmic techniques to detect failures, nor in many cases can he justify the cost of monitors with remote access, especially since in their attempts to lower the cost of the field monitors, some manufacturers have produced products of questionable accuracy in their ability to detect significant cell failure for these outdoor installations.

While there can be some questions raised as to the statistical significance of some of the aging failures, for some individual manufacturers, there can be no doubt as to the overall message. Despite all claims to the contrary, there is no evidence, either from the 1995 paper or from the 1998 data, that any of these designs will achieve their 20 year design life, even in benign temperature environments. Any claim to reliability has to be contrasted against our long-term experience with flooded cell reliability. That reliability has resulted from our understanding of its failures modes and their dependence upon the interrelationships among the metallurgical, electrochemical, and mechanical interactions that govern flooded cell float behavior and life, coupled with the development of the necessary manufacturing processes and controls to ensure that reliability. Unfortunately, that degree of understanding has not yet been achieved for VRLA technology. **However, it should be noted that it required more than 25 years of failures and associated studies to achieve that degree of understanding for flooded cells. This gives hope that, in time, the same degree of understanding will be achieved for VRLA.**

PERIOD V- Correlation of ohmic measurements:

As indicated earlier, the development of the capacity failure data evolved as an unintended and unexpected by-product of the search for a correlation between some type of ohmic measurement and cell capacity or “State of Health”. Using proprietary conductance techniques, in early 1992, in cooperation with several telecoms and UPS

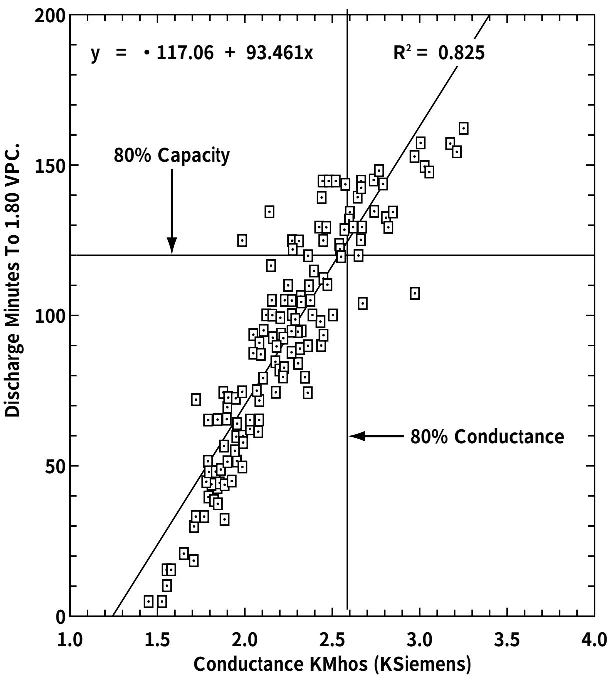


Fig. 9　Discharge Capacity vs Conductance.
VRLA 1000 Ah. 168 Cells Consolidated Date (Strings 9-15).
263 Amps. To 1.80 Volts Per Cell.

users, Midtronics, Inc. initiated a program to determine whether such a correlation existed and how it could be most usefully employed in the search for defective VRLA cells and batteries. This program resulted in a series of papers published at INTELEC from 1992-1997, in addition to papers published at ILZRO, VARNA and the ASIAN POWER CONFERENCE in Indonesia [18,19,20,21,22, 23,24]. In addition several papers were published independently in 1993, 1994 and 1998 by British Telecom [27, 28, 29]. All of these papers utilized conductance (G) as the measuring technique. Other papers reported on results using impedance (Z) or resistance(R) measuring techniques [30].

While the initial "headlines" resulting from these papers highlighted the widespread, unexpected premature capacity failures described in the previous sections the conductance/capacity correlation was progressively strengthened with the additional data provided by each presentation over this 6-year period. Early data are shown in Fig. 9, taken from the 1992 INTELEC paper [19]. It represents 168 cells in 7 parallel 48-volt strings from a working telephone transmission office. It indicates discharge time vs. conductance over a capacity range from zero to 2.5 hours, with a strong correlation coefficient of $R^2 = 0.825$. These results are typical of the literally hundreds of conductance/capacity correlation plots published throughout this period, which are far too numerous to reproduce in this paper, but which the reader can verify from the references cited. In all cases, those data represent tests in the "as found" condition and are a "snapshot" at a particular time in the life of the cells and batteries. Ideally, conductance data would be taken on the cells, as installed, and then repeated periodically, so that the data could be trended, on a cell by cell basis, until it had reached indication of cell capacity failure. Only in the last year or two has this begun to be done by some users, with data not yet available for publication .

Table 2

PUBLISHED VRLA CAPACITY TEST RESULTS: 1991-1995
WITH ASSOCIATED CONDUCTANCE/IMPEDANCE RESULTS

DATE PUBLISHED	# CELLS TESTED	# CELLS FAILED	% FAILED	CELL FAILURES CORRECTLY INDENTIFIED BY CONDUCTANCE/ IMPEDANCE	
				# FAILURES CORRECTLY INDENTIFIED	% FAILURES CORRECTLY INDENTIFIED
3/91	12	0	0	-	-
5/92	442	337	76%	324	96%
6/93	633	502	79%	483	96%
9/93	1494	907	61%	849	94%
4/94	2496	1246	50%	1172	94%
5/94	6891	4410	64%	4336	98%
5/95	23176	15813	68%	15086	95%

However, an indication of the overall accuracy of both the conductance and impedance techniques in predicting cell capacity failure is shown in Table 2 (also shown earlier in the text), taken from the INTELEC paper presented in 1995 [25]. In that table, results of capacity and ohmic tests on 23,176 cells are shown. Of these, 15,813 or 68% had failed to meet the 80% capacity criteria.

Conductance or impedance correctly identified 15,086 or 95% of the failed cells overall. In the years prior to 1995, even as the test population grew from fewer than 500 cells in 1992 to almost 7000 cells in 1994, the accuracy on the ohmic techniques stayed essentially constant from 94% to 98%, compared to the overall 95% value for the full 24,000 cell population in 1995.

Those results and those presented by others [30,31] would seem to provide solid support for the use of ohmic techniques as a suitable diagnostic tool to determine battery "state of health". However, as originally anticipated, that conclusion remains controversial. For obvious warranty/economic reasons, the battery vendors focus exclusively on cells in the 80-100% capacity range and strongly emphasize the number of "good cells" (i.e.:

>80%) mistakenly listed as “bad” (i.e.: <80%) by the ohmic technique. Conversely, the user tends to focus on the group below 80%, which affect his actual reserve. He notes the accuracy in detecting “bad” cells, only being concerned as to the cells which tested “good”, but actually are “bad”.

Typical results are shown here as Figure 10 and Table 4. For the entire 336 cell plant, made up of 14 parallel strings of 24 cells/string, the figure shows the correlation of capacity vs. conductance, with a correlation coefficient of R^2 = 0.855.

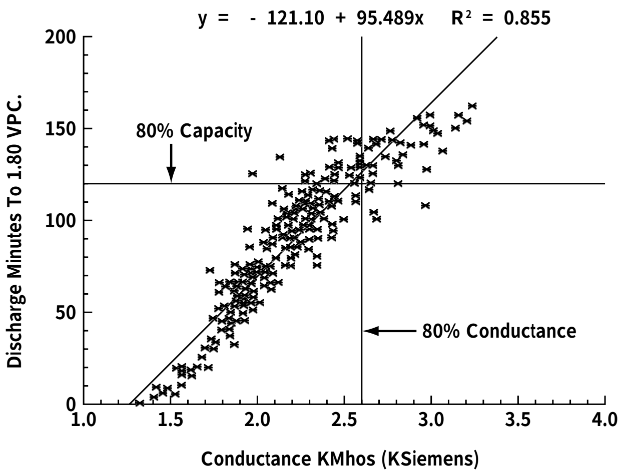


Figure 10

Table 4

Conductance Test Outcome

Capacity Test Outcome	Bad	Good	
Good	37	34	Correct Assessment: 293/336 = 87%
Bad	259	6	Correct Assessment of Failures: 259/265 = 98%

Analysis of Strings
(2-15) 336 Cells.

A box score technique (Table 4) indicates 37 + 34 =71 cells tested >80%, while 265 tested <80%. Of these, conductance correctly identified 259 of the 265 bad cells (98% correct) and 34 cells as good, or 259 + 34 =293/336 or 88% correctly identified, overall, good plus bad. However, 37 of 336 (11%) were mistakenly called bad. The benefit to the user is obvious, but in accepting the technique, the vendor subjects himself to an 11% overall error, in mistaken identification of “good” called “bad”.

Resolution of this dilemma has been negotiated by some supplier/users [29], but by no means accepted yet on an industry-wide basis. However, manufacturers have grudgingly accepted the fact that ohmic techniques can accurately identify “poor” cells, which some have taken to mean 50-60% of rated capacity. However, they generally remain fixed in their reluctance to accept replacement at 80%, based on ohmic techniques. In one case, replacement at 50% of original conductance (which is actually less than 50% of original capacity) has been accepted by both the telecom and one manufacturer, with some warranty correction allowed for service life at temperatures higher or lower than 25O C.

Period VI-Some new failure modes:

As evidence of widespread premature failures continued to mount, concern increased as to whether all VRLA failure modes had been correctly identified, were sufficiently understood and appropriate correctives developed. This author attempted to predict VRLA cell lifetime from published information on basic lead corrosion studies, laboratory and field results of cell and battery positive grid corrosion and laboratory weight and volume gassing studies. The results were presented at INTELEC 1996 [32]. In that paper, all results were normalized to a common base, to allow direct comparison among the different techniques. Using 10% water loss as an indication of significant dry-out and capacity loss, values of cell lifetimes ranged from 6 to 1300 years, depending on the technique employed! Clearly, either the theories or the experimental procedures to detect failure modes needed further study.

At INTELEC 1995, Jones [33] presented the first in a series of papers based on careful laboratory studies of gas evolution, positive and negative plate polarizations and conductance results of cells held on pure, continuous float for periods of one to two years. He noted the significant differences in the rate of hydrogen evolution from otherwise identical cells, all operating in a fully recombinant mode. This raised serious doubts that the hydrogen evolution was only a reflection of the rate of positive grid corrosion. The reference electrode values indicated severe depolarization of the negative electrodes, due to oxygen recombination, with some negatives floating below their open circuit voltage. This strongly reinforced theories of negative plate self-discharge, while on normal float. Under those conditions, a new source of hydrogen evolution is possible:

$$Pb + H_2SO_4 \rightarrow PbSO_4 + H_2$$

Further studies by Jones, Brecht, Berndt and most recent results by Fleming [34,35,36,37,38,39,40], have confirmed that negative self discharge and the resulting hydrogen evolution can be a significant VRLA failure mode, causing an entirely different type of cell capacity loss due to negative plate sulfation. This has been confirmed by actual discharge tests, in which the negative plate is the capacity-limiting element in the discharge.

From this discovery, these authors have evolved a unique (if somewhat complex) new understanding of the interrelationship among the reactions which occur within a recombinant VRLA cell on float. For a detailed examination and understanding of the complex figures and equations involved, the reader is referred to the actual references cited above. Here we will simply say that a new concept of “hydrogen balance” has emerged, within a recombinant cell on float. This concept may be described in words, as follows:

1. The partial current responsible for positive grid corrosion offsets the self-discharge of the negative electrode, and if sufficient, can polarize the negative electrode, with subsequent electrochemical generation of hydrogen gas.

2. If the partial current responsible for positive grid corrosion, i.e. the rate of positive grid corrosion, is greater than the partial current required to recharge the negative self-discharge, then the negative electrode will maintain its capacity throughout its float life.

3. If however, the partial current responsible for positive grid corrosion is less than the partial current required to recharge the negative self-discharge, then the negative electrode will self-discharge and progressively lose capacity until it becomes the capacity limiting element during discharge.

These effects lead to a curious anomaly:

If the positive electrode is made of a short life, rapidly corroding alloy, then the negative electrode will stay healthy, but the cell will fail prematurely from capacity loss due to positive grid corrosion and growth and loss of contact between the grid and active material.

However, if the positive grid is made of a pure alloy, designed to last 20 years on float, then the negative electrode will self-discharge and premature capacity failure will occur, due to negative plate sulfation.

In theory, it might be possible to balance these effects so that the exact amount of positive grid corrosion occurs, which exactly balances the negative self discharge. In practice, this is more easily said than done.

Impurities, which cause local action and depolarize the negative electrode, further complicate this delicate balance. One author has suggested that sufficient elimination of these impurities will allow the “balanced cell” to be designed and produced [40].

A simpler approach, proposed first by Jones and then reinforced by Brecht, Berndt, Dick and others [36,37,38,39,41], involves the introduction of a small catalyst into the head-space of the cell. The catalyst acts to recombine some of the oxygen with hydrogen, before the oxygen can reach the negative and completely depolarize it. With the catalyst, the positive can be highly corrosion resistant, the negative will polarize and not self-discharge, leading to a simple design, long life, balanced cell. The theories have been tested in the laboratory, on cells of several different manufacturers and are currently being used on all cells being shipped by several manufacturers, for full production and field evaluation. [41]

A further result of Jones work indicates, as might be expected, that as negative self-discharge proceeds, conductance decreases proportionately. **Thus, negative self-discharge may be added to the list of VRLA failure modes which can be detected by ohmic measurement techniques.**

Period VII-Monitors-Can they help? Are they realistic?

The attempt to develop and market remote monitors for VRLA telcom batteries in the US, has followed a wavering curve related to the situations described in the above Periods.

In Period I, when “no maintenance/20 year life” was the “Market Talk”, thoughts of a monitor would have been considered as heresy.

In Period II, as users (and some vendors) faced the realities of cell performance, possible problems and possible aging/failure mechanisms, some type of monitor was considered significant. Both national and international standards groups initiated efforts to define and standardize some type of monitor technology. At the same time, equipment manufacturers began to market monitoring devices, generally based on some type of voltage measurement.

In Periods III and IV, the initiation of capacity/ohmic correlation studies stimulated initial development of monitors based primarily on some type of ohmic measurement, with additional voltage and temperature parameters included. Publication of significant correlation between “State of Health” and ohmic techniques further stimulated the development of suitable monitoring devices by several manufacturers and accelerated the work of the various standards committees.

However, the widespread premature capacity failures resulting from the tests in Periods IV and V raised a serious dichotomy for the user. The likelihood of premature failure heightened his interest in some type of monitor. At the same time the unexpected, unusually short life for VRLA product raised serious questions as to the economic viability of a high cost, high technology monitor for a short life product, which might most economically be replaced on an arbitrary “Years of Life” basis. An additional concern involved the reluctance of the vendors to provide warranty coverage based on results from a monitor, without actual capacity discharge test information. Thus using the monitor to indicate cells in need of more detailed (and expensive) evaluation became questionable, probably uneconomic, both in utilization of capital, scarce maintenance funds and especially manpower, the most scarce commodity involved.

In recent discussions with both users, monitor equipment manufacturers and others, it appears that several approaches are being offered. One approach involves manufacturers of simple, relatively inexpensive monitors, with very limited capability, such as battery voltage, sometimes individual cell voltage and in some systems, temperature measurement. Another approach is being taken by the original equipment manufacturers, who normally supply the complete installation, "Hut" or "Controlled Environmental Vault" (CEV), which normally includes all the telephone interconnect and switching equipment as well as the necessary power equipment. They supply the entire unit, including enclosure, and ship them as a "Turnkey Facility". Some of these manufacturers are beginning to include some type of battery monitoring as part of the initial equipment package. These may include some type of ohmic technology and in at least one case, the manufacturer is offering "Cradle to Grave" follow up of the monitoring signals with associated maintenance, notification or trouble shooting services. These are relatively new and it is far too soon to make predictions as to their market acceptance by the telecom user.

The status of monitors, is therefore once more, passing through a period of change and some uncertainty. Added to this one must include the new information involving failures attributed to negative self-discharge, the possible life-enhancing capability of catalyst techniques, or the possibility that rigid adherence to new standards of purity will minimize or eliminate local action at the negative electrode, resulting in routine manufacture of "balanced cells" with sufficiently extended lifetimes to allow reconsideration of the economics of monitoring technology.

It is probably too soon to gauge these effects on the design, sophistication, reliability, cost and market acceptance of the monitor technology which will emerge.

Conclusions:

1. The Bell System's 1950 introduction of the new Pb-Ca cells, in transparent plastic jars, to replace the well understood Pb-Sb designs, in hard rubber jars led to a 15 to 20 year period of unpleasant "surprises". These included unanticipated extreme voltage variations, battery fires and significant premature capacity failures, as determined by a System-wide Capacity Test Programof more than 5000 Pb-Ca cells.

2. These problems clearly indicated that there was no basic understanding of Pb-Ca float behavior, positive grid growth, or capacity aging phenomena, by either the manufacturers or the user. Likewise the technology for design and manufacture of leakfree post and jar/cover seals had not been properly adapted to Pb-Ca technology from the earlier Pb-Sb/rubber jar era.

3. A 6-10 year study of Pb-Ca float characteristics by Dr. E.H. Willihnganz of C&D Batteries developed the necessary basic understanding and technology for the measurement and control of cell float behavior, in design. manufacture and use.

4. A parallel study at Bell Labs developed the basic metallurgical, design and operational factors, which allowed the designer to "select" the desired rate of positive grid corrosion and growth to meet any design life target, from 5 to 70 years. This allowed design of a unique circular grid, which actually caused positive plate capacity to increase throughout life.

5. Bell Labs also developed and substantiated short term accelerated life testing techniques to allow accurate prediction and validation of long term positive grid growth and cell life prediction.

6. It required the experience gained from 25-30 years of field performance problems, with the associated laboratory research, testing and development to fully understand and predict the performance of Pb-Ca flooded cells. **Just as we learned how to make**

flooded cells reliably, VRLA technology appeared!

7. The introduction of VRLA technology resulted in a series of extraordinary claims for performance, freedom from maintenance and very long life which stimulated an unusually rapid and widespread market acceptance into telecom standby service.

8. Within a few years, the apparent simplicity of the basic recombinant technology involved gave way to initial realization of its electrochemical complexity. More careful thought, coupled with initial user experience led to refutation of many of the initial claims, with beginning appreciation of the multiplicity of potential failure modes. Unlike the “graceful” aging and death of its flooded predecessor, new failure modes of dry-out, unexpected gassing behavior and thermal runaway were found, in addition to the initially expected capacity loss due to positive grid corrosion and growth.

9. Also, the apparent design simplicity began to be replaced by a greater appreciation of the critical design features needed and the fact that the “design window” for VRLA technology was far tighter than for long life flooded cells.

10. The “maintenance-free” concept was replaced with an understanding that the technology was, effectively, “maintenanceproof”, stimulating the search for a passive diagnostic to allow indication of cell capacity or “state ?of-health”, without the need to perform a full capacity discharge test.

11. Initial indications that so-called “ohmic” techniques, such as conductance and impedance might prove useful, resulted in an ongoing program among equipment manufacturers and telecom users to perform both conductance and discharge capacity tests, in the hopes of establishing a correlation which would allow conductance or impedance to be used as a suitable diagnostic.

12. While the correlation looked promising, the astonishing result of this program was to highlight widespread premature capacity failures of the VRLA technology. In an initial study of 25,000 cells, representing products of nine manufacturers, some 68% of the product tested failed to meet capacity end of life requirements. **A second study of 15,000 cells confirmed those results. A European study of 35,000 cells indicated basically similar conclusions.**

13. The series of studies of the correlation between conductance or impedance and cell capacity produced promising results, for the user looking to replace seriously failed cells. However, for the manufacturer, the possibility of his replacing even a small percentage of cells with greater than 80% capacity led to his consideration that his warranty risk was unacceptable, even though the bulk of the cells, indicated as failures by conductance/impedance, might have capacities ranging , literally, from 0%-70%. This is an economic issue which has not yet been universally resolved between manufacturers and users.

14. Concern over the widespread VRLA failures led various investigators to re-think the possible reactions taking place within these cells on long term float. The result has been to recognize the reality of self-discharge of a fully depolarized negative electrode in a recombinant system. This has led to inclusion of negative self-discharge as a major, previously unrecognized failure mode. It has highlighted the need for some degree of polarization of the negative as a requirement for satisfactory performance.

15. From this has emerged the concept that a slowly corroding positive results in negative self-discharge and subsequent premature, negative-limited capacity failure. A rapidly corroding positive provides a healthy negative, but premature failure results from capacity loss due to positive grid corrosion and growth.

16. This results in the "balanced cell" concept, in which these opposing reactions are balanced, either by the use of a small catalyst inserted into the VRLA cell or perhaps, by the use of ultra-pure materials, to reduce "local action" at the negative electrode. The catalyst is simpler and is already in use, on a production basis, in several manufacturers'products.

17. These new insights give hope to the search for solutions of the problems which have plagued VRLA life and performance, at a critical time when their use as 42 volt systems to replace the 14 volt SLI automotive battery is seriously being planned.

18. All of the above "twists and turns" in developing understanding of the fundamental behavior and performance deficiencies of the VRLA technology has led the proponents of some type of monitoring technology through the same confusing cycles, with the net result that any firm statements about monitoring are probably premature, at this time.

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