ACCELERATED LIFE TIME TESTS
ACCORDING TO IEC 60 896-21 AND IEEE 535 - 1986

E. Gietz, W. Rusch, Chr. Serger and S. Zarske, BAE Batterien GmbH

1. ABSTRACT

For accelerated life time tests the standard IEC 60 896-21 requires test temperatures of 40°C and 55 or 60°C and the standard IEEE 535 - 1986 requires 62,8°C. To meet the toughest challenge we made a life time test at 62,8°C for the VRLA-types BAE OPzV and the VLA-types BAE OPzS and BAE OGi.
The batteries were placed in a steel tray, tempered to 62,8°C. The cells were float charged at the standard values: 2,25V for VRLA and 2,23V for VLA.. During the test the growth of the poles, the increase in float current and the change of the 3h-capacity was monitored every 50 days.
After 250 days – which simulates according to IEEE 535 - 1986 a life time of 15 years at 23°C – seismic tests according to US, French and German requirements were successfully performed.
After the severe seismic tests the cells were still in good shape, so we continued with the accelerated life time test.
We have observed total float charge times at 62,8°C:

OPzV	OPzS	OGi
450 days at 62,8°C	550 days at 62,8°C	425 days at 62,8°C
34,8 years at 20°C	42,6 years at 20°C	33,0 years at 20°C

The failure modes were corrosion and growth for all types. The low float current of the tubular GEL type at 62,8°C of 100 to 300 mA/100Ah shows that no thermal runaway has to be expected and the normal float voltage of 2,25V can be maintained for higher temperatures, i.e. up to 45°C in operation.
After the test all cells have had still a good integrity. No damage of the container and lid. The BAE Panzerpol was in perfect condition after the test, because it can afford a growth of up to 20 mm without leaking.
To calculate the life time at 20°C we have used an activation energy of the Arrhenius equation of 15.280 cal/mol, which is derived from IEEE 535-1986 (20days at 62,8°C correspond to 365 days at 25°C).
The comparison of VLA batteries in the tubular and flat plate batteries clearly show the better operational life time of the tubular design versus the flat plate design.

2. INTENTION OF THE TEST

The intention of the test was to qualify our stationary batteries for nuclear power plants according to IEEE 535-1986 and for all stationary purposes according to IEC 60 896-22.
IEEE 535-1986 requires an accelerated life time test for Lead-Calcium batteries, where one year at 25°C has to be simulated by 20 days at 62,8°C (145°F). Our customer has required a life time of 15 years at 23°C, which corresponds to 250 days at 62,8°C. For the calculation we used an Arrhenius approach (see chapter 5). With those cells at the end of their life time the seismic tests (earth quake and air plane crash) had to be made.
The IEC 60 896-21 defines under § 4.15/16 tests at elevated temperatures of 40°C and 55 or 60°C. The highest quality level in IEC 60 896-22 is specified with 350 days at 60°C, which corresponds to 290 days at 62,8°C (see chapter 5). So we could meet with 250 days at 62,8°C nearly the highest level with the IEEE 535-1986 test and in case the cells were still in good condition after the seismic test we may continue with the test.
Every 50 days we monitored the 3h-capacity down to 1,75V at room temperature. The float current and the growth of the poles were measured frequently and at the end of the test a tear-down analysis had to be made to find out the failure modes of the batteries.

3. EXPERIMENTS

The following cells from normal production were used for the test:

			
	BAE *OPzS* vented	BAE *OPzV* valve-regulated	BAE *OGi* vented
type	tubular	tubular - GEL	flat
density float V	1,24g/ml 2,23V	1,24g/ml 2,25V	1,24g/ml 2,23V
samples	6 cells 200Ah	3 cells 200Ah	3 cells 480Ah
samples	6 cells 490Ah	3 cells 490Ah	3 cells 800Ah
samples	6 cells 2000Ah	3 cells 2000Ah	3 cells 1520Ah

The cells were placed in a steel tray, which was filled with water. The water could be heated with a 1,5kW heater and was permanently circulated. The temperature could be controlled at 62,8+-1°C. No mechanical support of cells against bulging was made, even not for the largest cells. Water level control was in operation for safety reasons. Exchange of water with tap water reduced cell temperature to 23°C for measuring the 3h-capacity. During the high temperature test no water or water vapour should enter the VRLA-cells. Instead of placing the cells in hot air environment with a controlled humidity we housed the VRLA-cells in a water- and water-vapour-tight special foil bag made out of layers polyethylene, aluminium and polyester.

Fig.1 Thermal management for 62,8°C test

Every 50 days we measured and recorded the 3h-capacity.

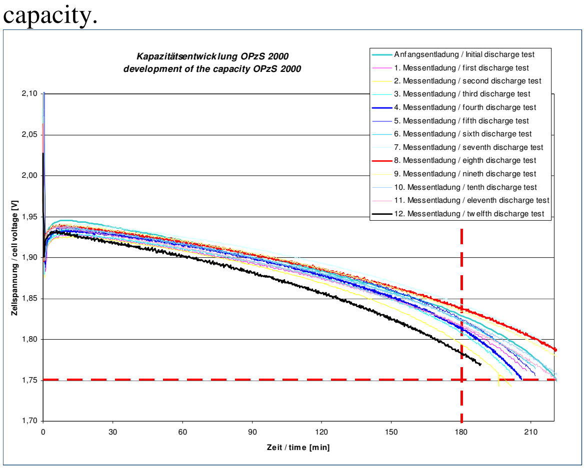


Fig. 2 Records of the 3h-capacity

After 5 periods of 50 days at 62,8°C the cells were transported to the seismic test station of the IABG, Ottobrunn near Munich. There we placed each 6 cells in a special designed seismic rack and mounted them on a steel table with the dimensions 2m x 2,5m, which can carry up to 10t, can be accelerated up to 50m/s² in x-direction, up to 40m/s² in y-direction and up to 80m/s² in z-direction in a frequency spectrum from 1Hz to 150Hz.

With the aged OPzS and OPzV cells - mounted in racks - we determined first the resonance frequencies between 1Hz and 100 Hz, then performed tri-axial time history tests of each 30s duration: Five times the earth-quake simulation (OBE) and once the airplane crash simulation (SSE). The actual acceleration can be recognized in Fig.3.

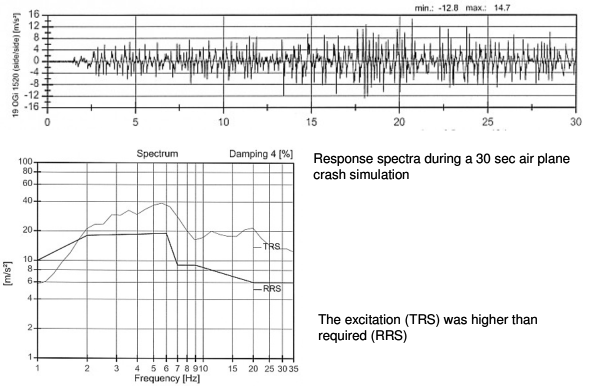


Fig. 3 Response spectra during the airplane crash simulation.

We detect accelerations from 4 to 12 m/s², measured on the poles of the cells. In the lower picture of Fig.3 we see, that the actual response spectrum was above 2Hz very much larger then the required response spectrum. This is a severe test and covers the requirements in France, Belgium and the United States (Building instructions 4B). In Germany the test philosophy is different: The test is made with new cells, but the accelerations are very much higher: f.e. the Airplane crash simulation is done with a sinus-beat of 50m/s² in xz and yz-direction. This test was also successfully verified with new OPzS and new OGi cells.

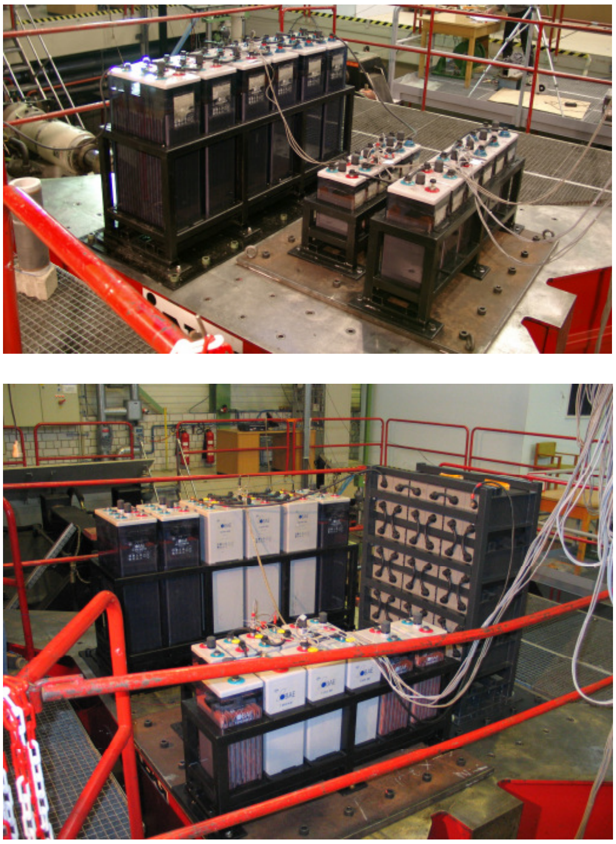


Fig. 4 Seismic test arrangement at the IABG, Ottobrunn

In Fig 4 upper picture the aged OPzS cells and in the lower picture the aged OPzV cells (each 3) can be seen. To fill the rack we used OPzS cells as dummy cells. On

the right hand side we see the BAE SPzV battery, which consists of OPzV plate sets in traction containers and lids, mounted in a steel frame rack. Also this 48V 6 SPzV 360 – battery has successfully made the seismic and airplane crash tests of IEEE 535-1986.
After the seismic test the OPzS and OPzV cells were put back in the heating chamber on float at 62,8°C.
Every 50 days we measured besides the 3h-capacity also the growth of the poles with a special measuring device and formed the average of the positive and negative poles. The float current was continuously measured.
After the end of the float charge test we opened from each type 2-3 cells, took pictures and analysed the active material.

4. RESULTS

4.1 BAE *OPzS*

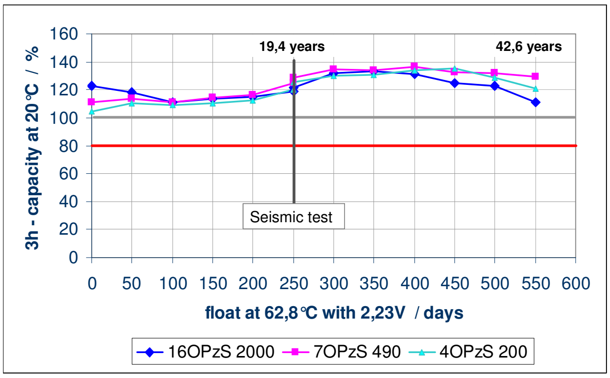


Fig. 5 OPzS 3h-capacities within 550 days at 62,8°C

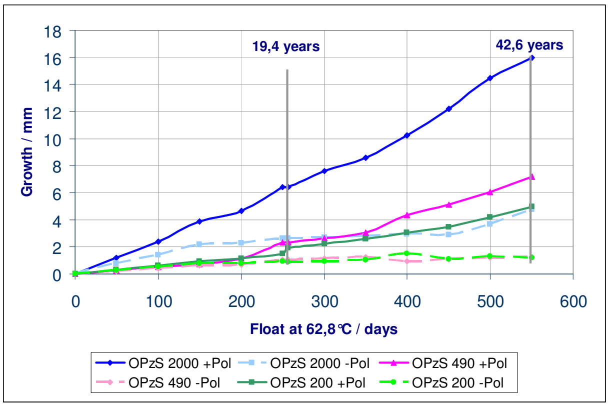


Fig. 6 OPzS Pole growth

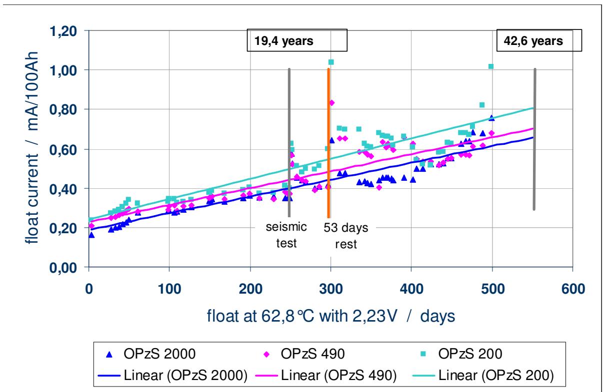


Fig.7 OPzS Float current over life

Fig.8 OPzS plates set after 550 days at 62,8°C

The tear-down analysis of the OPzS cells after 550 days at 62,8°C showed a normal corrosion of 30% of the positive grid. Lead sulphate in the positive and negative mass was below 3%. A slight short circuit in one of OPzS490 cells at the bottom of the cell is a consequence of the rupture of the outer tube.

4.2 BAE *OPzV*

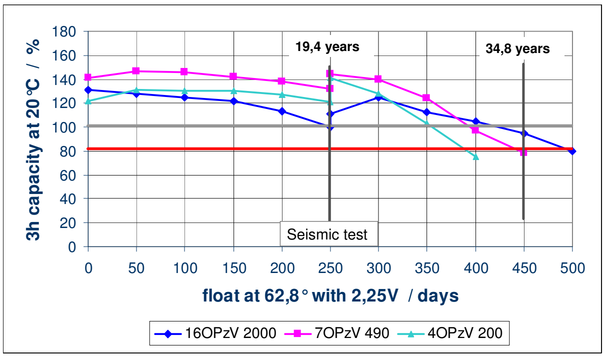


Fig. 9 OPzV 3h capacities within 450 days at 62,8°C

Interesting is the increase of capacities after the seismic test, shown in Fig.9. This has nothing to do with the vibration during the seismic test, but with the extra charging of the cells. We found out, that the capacity test – directly after 50 days at 62,8°C and cooling down to room temperature - was 10 to 15% lower than the second capacity test after charging back with float voltage at room temperature. Apparently the first capacity measured the state of charge and not the state of degradation. Consequently we used the second capacity value after 250 days. The reason for the incomplete charge will be discussed in chapter 5.

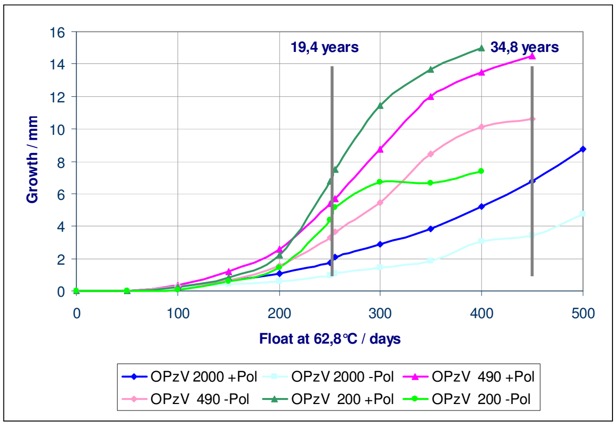


Fig. 10 OPzV Pole growth

The plate length of the type OPzV 200 is 220mm, the OPzV 490 is 315mm and the OPzV 2000 is 600mm. One would expect the highest growth for the longest plate-cell. The lowest growth of the OPzV 2000 can be explained by a purpose-designed compression of a styropor block at the bottom of the cell.

Fig. 11 OPzV2000 after 450 days at 62,8°C, Compression of the styropor block at the bottom

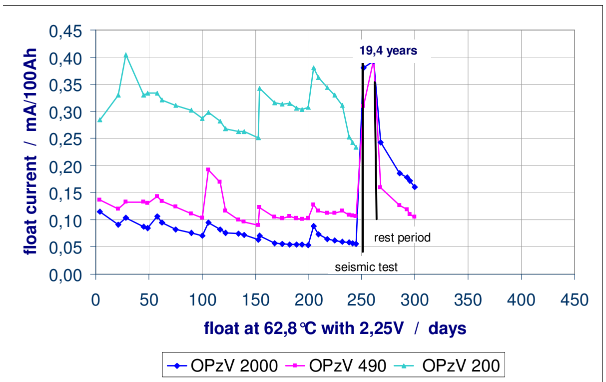


Fig. 12 OPzV float current

The float current per 100Ah is by a factor 3 larger for the smallest cell, which we attribute to the higher contribution of the poles and pole bridges related to the plate length for the internal recombination. The general reduction of the float current is opposite to the current opinion of increasing with growing dry-out of the GEL-battery and has to be discussed further.

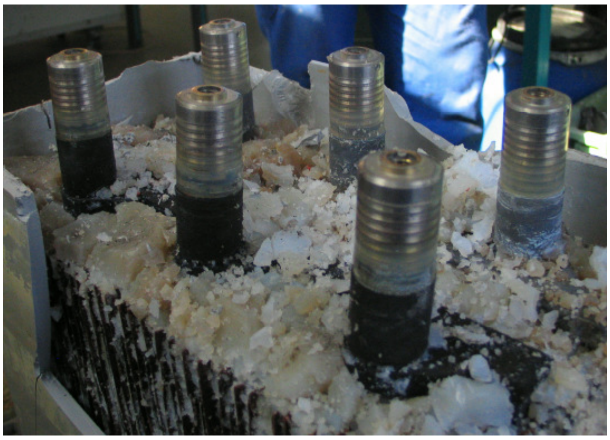


Fig. 13 OPzV 2000 opened after 450days at 62,8°C

The first observation after opening the OPzV2000 cell is the excellent, uncorroded condition of the BAE Panzerpole after this very long test.
The GEL is wet – no signs of dry-out – and covers safely the lugs and pole bridges.
The plates are without signs of deterioration. Approximately 30% of the positive grid are corroded.
Interestingly the negative mass has 8,4% lead sulphate, although the cell was in charged condition. The positive mass was perfect with 95,2% PbO_2.

4.3 BAE *OGi*

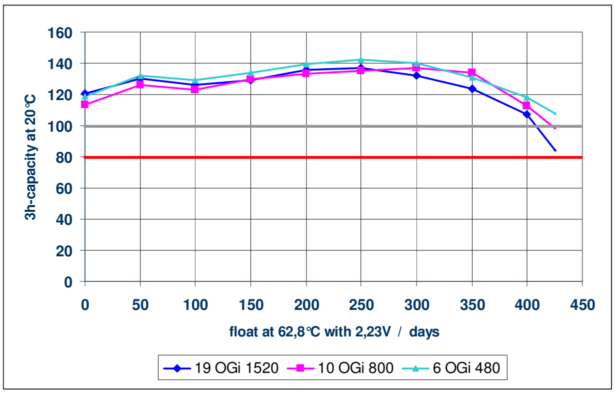


Fig. 14 OGi 3h-capacity within 425 days at 62,8°C
The 3h-capacities after 400 days (Fig. 14) are still above 100%. An extrapolation results in 425 days.

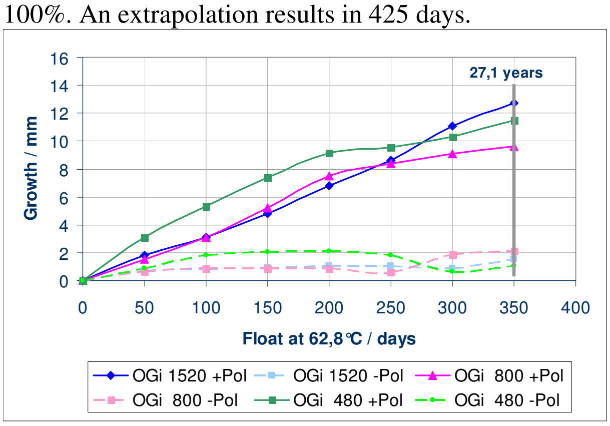


Fig. 15 OGi pole growth

.

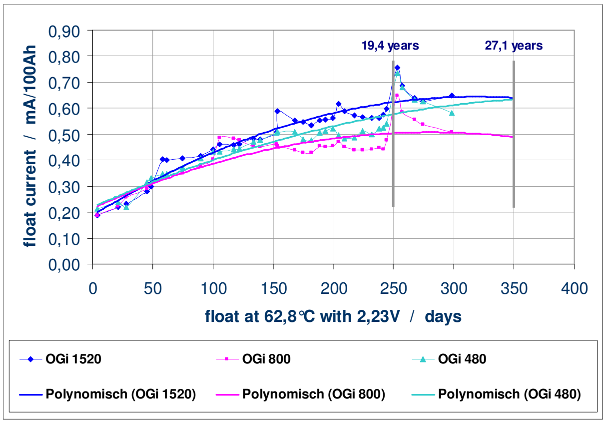


Fig. 16 OGi float current

5. DISCUSSION

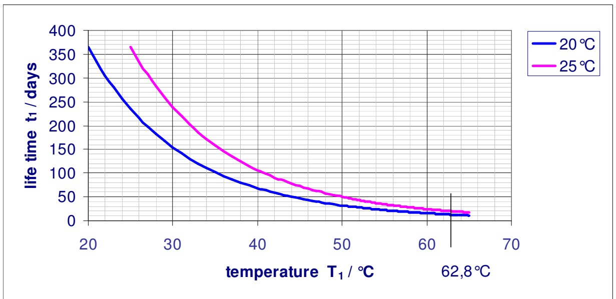
5.1 ARRHENIUS APPROACH

The rate of degradation of lead acid batteries at different temperatures obeys nicely the activation energy model of Arrhenius

$$t_1 = A * \exp(E/RT_1)$$

where t_1 is the life time at the temperature T_1, E is the activation energy in cal/mole. R is the gas constant 1,987cal/mole/K. A is a factor, which will vanish, if two states with different temperatures are compared. The temperature dependence is ruled by one constant, the activation energy. The Arrhenius approach was successfully tested before (see for example [1]). It works properly for lead acid batteries, as long as the life time limiting factor is the corrosion process of the positive grid. In case the life limiting factors are others, like crevice corrosion on poles, dry-out of AGM batteries or disintegration of container and lid, the activation energy can be by a factor two or more lower, which has the consequence that periods at higher temperatures count only for shorter periods at the lower room temperature.
We get a life time t_1 at the varying temperature T_1, having at the reference temperature T_2 a life time t_2 :

$$t_1 = t_2 * [\exp(-E/RT_2) / \exp(-E/RT_1)]$$



In IEEE 535-1986 the following data are given:
T_2 = 297,2°K, t_2 = 365 days
T_1 = 335°K, t_2 = 20 days
The red line of the above diagram is calculated with an activation energy of 15,280 cal/mol.

In IEC 60 896-22, § 4.15/16 different test times at different temperatures are given:

High temperature	40°C	55°C	60°C
Brief duration	500 days	150 days	105 days
Medium duration	750 days	250 days	175 days
Long duration	1100 days	350 days	250 days
Very long duration	1700 days	500 days	350 days

In average an activation energy of 15.650cal/mol can be derived from these data. The 350 days at 60°C correspond then to 290 days at 62,8°C.
Comparing with other values in literature and with the thumb's rule, every 10K temperature increase the life time is half, we get the following table:

	Activation energy	One year at 25°C	20 years at 20°C
	cal/mole	days at 62,8°C	days at 62,8°C
IEEE 535-1986	15.280	20	**257**
IEC 60 896-22	15.650	18,6	237
FIAMM INTELEC 2002, 5-2	15.500	19,2	245
Catella Generics Sonnenschein	17.677	12,7	169
Thumb's rule every 10K half of life	-	26,6	376

Besides the thumbs rule, who requires the longest time at high temperature, the IEEE 535-1968 is the safest value for evaluation of the life time at room temperature, because we need a longer time at high temperatures.

5.2 LIFE TIME COMPARISON

	20°C	25°C
BAE *OGi*	**33,0 years**	**21,3 years**
BAE *OPzV*	**35,0 years**	**22,5 years**
BAE *OPzS*	**42,7 years**	**27,5 years**

The tubular plate design (**BAE *OPzV*** and **BAE *OPzS***) provides a longer life time than the flat plate design (**BAE *OGi***), because their grid corrosion is lower by two reasons: The pressure-casted grid of the tubular plate has a perfect dense structure of the grains, which makes it superior to the gravity casted grid of the flat plate. Secondly is the corrosion reduced by the tubular design, because the tube presses the active material onto the corrosion layer.
The earlier capacity reduction of the OPzV cells is caused by a slight discharge during float at 62,8°C. This is proven by the fact, that the capacity test directly after 50 days float at 62,8°C is 10 to 15% lower than the capacity test after recharge (see chapter 4.2).
It is interesting that in the IEEE 535-1968 standard § 8.2 Test procedure a remark is made for the case of partial

discharge during high temperature float: *If the capacity test indicates less then 80%, the cells may be recharged, returned to float at ambient temperature for 72h minimum, and retested.*
By the tear down analysis of the OPzV2000 we found in the negative mass 8,4% lead sulphate, although the cell was charged before (see chapter 4.2). Apparently the lead sulphate has formed over the long period of 450 days larger crystals, which were not rechargeable during normal charging procedures. So we could identify, that the **negative** plate is not fully polarized during float at 62,8°C. D.Berndt [2,3] has explained the processes in detail.

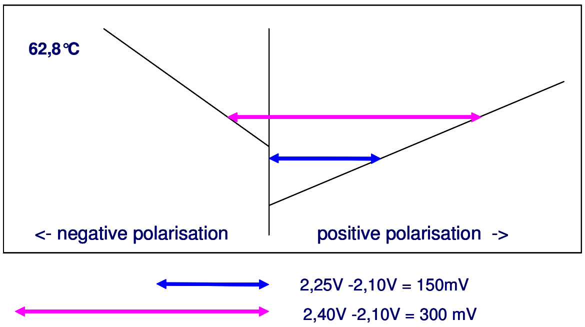


Fig.17 Unsufficient charge at 62,8°C

The float voltage of 2,25V/cell is apparently not high enough for the extreme high temperature of 62,8°C. Up to the maximum operation temperature of 45°C the float charge voltage of 2,25V/cell is fully alright. Recommendations of other lead acid battery manufacturer to reduce the float voltage of VRLA batteries are leading in the wrong direction. At higher temperatures as 45°C the voltage has to be increased at least time wise. The small level of float current of the BAE OPzV excludes any risk of a thermal runaway.

5.3 GROWTH OF POLES


Fig. 18 Pole growth of OPzS cells at the end of life

Although the pole growth for the OPzS 2000 has reached 16mm at the end of its life, the pole bushing is tight. No corrosion or deterioration happens. This is the advantage of the patented **BAE *Panzerpole***.

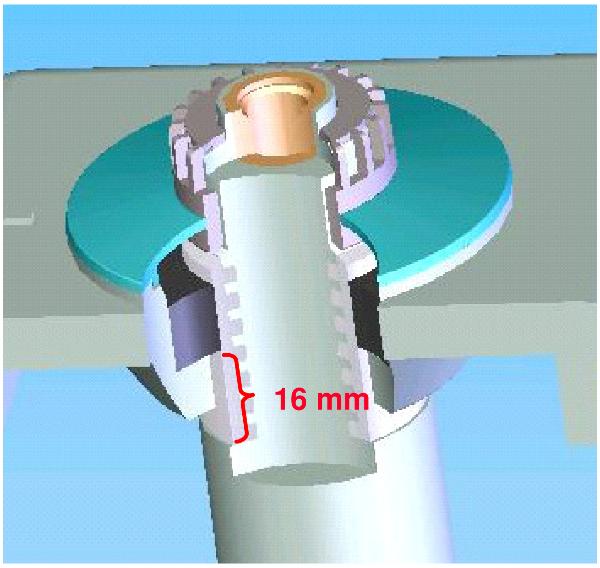


Fig. 19 Design of the **BAE *Panzerpole***

It has a plastic injection around the pole, which embraces the lead pole like a panzer. In case the poles are pressed upwards by the growth of the positive plate, while the rubber ring remains in position, the clean and plane surface of the plastic injection moves upward, keeping the perfect seal. After a 16mm-growth the corrosion area has reached the rubber seal. Then the corrosion layer is lifting up the rubber ring. A further 4mm growth can happen, before the pole cover is lifted.

5.4 FLOAT CURRENT

Float current at 62,8°C			
	initial	**After 19,4 years**	**factor**
	mA/100Ah	**mA/100Ah**	
BAE *OPzS*	**220**	**443**	**2,01**
BAE *OGi*	**193**	**567**	**2,93**
BAE *OPzV*	**177**	**130**	**0,69**

The increase of the float current during normal life by a factor two for the OPzS cells averaged over all types and samples is low. No frequent watering and high current consumption. The flat plate type has typically a slightly higher value. In both cases the same alloy PbSb1.6Se is used.
The OPzV float current is low and even reduced during the test. It demonstrates the stability of BAE OPzV, no thermal runaway and no dry out has to be expected.

6. CONCLUSIONS

The accelerated life time tests of IEEE 535-1986 and of IEC 60 896-21 are very similar and can be applied to VRLA and VLA batteries. The requirements of IEC 60 896-22 are realistic.
The **BAE *OGi***, the **BAE *OPzV*** and the **BAE *OPzS*** batteries have exceeded the expectations of the standards. The IEC 60 896-22 has as the highest requirement 350 days at 60°C or 290 days at 62,8°C.
In our accelerated life time test we demonstrated with VRLA-type in tubular-GEL – design **BAE *OPzV***
450 days at 62,8°C.
This increase of 55% is expressed in life times:
22,2 years **BAE *OPzV*** instead of 14,3 years at 25°C in the standard IEC 60 896-22 and
34,8 years **BAE *OPzV*** instead of 22,5 years at 20°C in the standard IEC 896-22.

7. AKNOWLEDGMENTS

It is a pleasure for us to thank our customer for guiding our tasks and targets for many years during the experiment documented above.

3 / 26.09.2005

Reference

[1] G.Lodi, J.McDowell, S.Rossellini, “VRLA Battery Ageing Characteristics” INTELEC 1996, Session 2-5

[2] D. Berndt, R.Bräutigam and U.Teutsch, “Temperature Compensation of Float Voltage – The Special Situation of VRLA Batteries” INTELEC 1995, Session 1-1

[3] D.Berndt, Maintenance-Free Batteries, A Handbook of Battery Technology, John Wiley & Sons Inc.