Life-test on Tubular Plate Accumulators for Stationary Applications

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1 Introduction

Today the total energy requirements of the telecommunication installations of the Swiss PTT are, as far as electrical energy is concerned, satisfied exclusively by stationary tubular plate accumulators. These are lead-acid batteries with positive plates consisting of plastic or glass-cloth tubes filled with active material. Each tube contains a current carrying lead core. The negative plates are the usual grid plates. The active mass is placed between the grid meshes. The positive and negative plates are separated by plastic separators.

With the introduction of this type of battery 25 years ago, the question of optimum battery, respectively cell voltage has again become actual. With the nowadays generally accepted practice of floating charge operation, the cell voltage is held constant. Various investigations have shown [1, 2, 3] that the favourable voltage range is between 2.18 and 2,23 V $\pm$ 1 to 2%. Some results are based on short-time observations only. In some cases battery capacity was tested several times during a few months, so that one can hardly speak of an undisturbed, typical floating charge operation.

An earlier study undertaken at the Swiss PTT to determine the optimum charge conservation voltage for tubular plate batteries was based on a 5 years' testing period [4]. Thus the number of disturbing measurements was kept at a minimum. The present test was designed as a life-test up to the total failure of all cells [5]. Besides the expected information about the optimum voltage, the test yielded data about the longtime behaviour of the capacity, floating charge currents, cell resistance, electrolyte composition with age, and naturally, about the life-span. This article contains all the important results of this experiment. Since the subject of long-time characteristics of tubular plate accumulators does not find exhaustive treatment in the technical literature, this article should be useful for both manufactures and uses as well as for maintenance personnel.

For the sake of completeness let it be mentioned that a cell voltage of 2.23 V $\pm$ 1% specified for stationary accumulators must be regarded as a compromise between the ideal floating charge voltage and the 48 V nominal supply voltage. It results from a somewhat higher operating voltage U = 49 V and the number of cells N = 22, yielding U/N = 2.227 $\approx$ 2.23 V/cell. In the concluding part (Sect. 8), the possibility of a lower operating voltage is examined.

2 Test-material, test-conditions and acquired data

Tests were conducted on standard tubular plate accumulators, as they are used in the telecommunication services of the PTT. There were:

24 batteries of 3 cells each, 20 Ah rated capacity
 6 single cells (elements), 600 Ah rated capacity
Acid density: 1.24 g/cm³

As usual in normal tubular plate accumulators, the negative grids, the lead cores of the positive plates as well as all other conducting parts consisted of a lead-antimony alloy, which is responsible for the so-called antimony contamination. The antimony contents were:

8.0 to 11.5% in the lead cores
6.5 to 8.5% in the negative grids
Year of manufacture: 1960

All the batteries and cells were connected to constant voltage sources. The 20 Ah batteries were divided into 6 test-groups having the following cell voltages:

2.15 V 2.20 V 2.25 V 2.30 V 2.35 V 2.40 V

The 600 Ah cells were initially connected to 2.30 V, then to 2.20 V. The mean voltage variation was $\pm$ 5 to $\pm$ 8 mV/cell.

The temperature of the environment was thermostatically maintained at 20° C. The following data were taken periodically: capacity (discharge current I in amperes, corresponding to $1/_{10}$ of the nominal capacity), semiannually during the first 5 years, then yearly; cell voltages; current at constant voltage; internal cell-resistance; acid concentration; water consumption; perchloric acid content of the electrolyte.

All cells were disassembled after their failure, some of them just before the end of the test-period, in order to examine their internal state. The published results are generally based on a collective of 20 Ah batteries since voltage-dependences could only be measured here. However, the different behaviour of the various types is indicated, especially when correlations between life-time and typical characteristics exist.

3 Capacity and life-span

Figure 1 illustrates the change of capacity as a function of time for 6 test voltages. It can be seen that the maximum
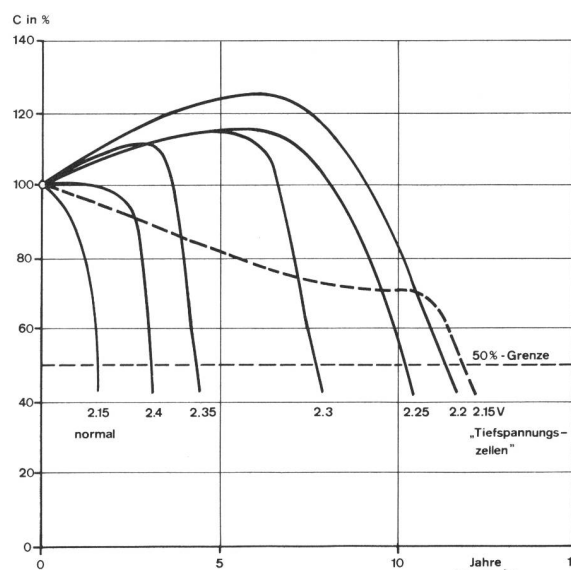

Fig. 1
Capacity shape for various voltages
50%-Grenze – 50% limit
Tiefspannungszellen – Low voltage cells
Jahre – Years

capacity in the 2.4 to 2.2 V range increases with decreasing voltage. The time for the capacity to fall to 50% of its initial value also increases. This 50% value is defined in this test as the end of battery life. At 2.15 V this means a life of 2 years («normal» curve on the left of the diagram). By recharging after deep discharges, the life of the cells used in this way can be extended to a maximum of 4 years (reversing the sulphatization). The dashed 2.15 V curve stands for the so-called «low voltage cells» which are characteristic for certain battery types.

In *Table I* the following data of interest are summarized:

$\overline{C}$ average capacity during the test period

C_{max} maximum capacity

$t_{C\,=\,max}$ time to attain C_{max}

$t_{C\,=\,50\%}$ time to reach half the initial capacity (= life-span)

$t_{N\,=\,50\%}$ time elapsed till 50% of the cells fail

Q quality factor $Q = \overline{C} \cdot t_{C\,=\,50\%}$

Table I. Capacity, life-span, and quality factor

U Volt	$\overline{C}$ %	C_{max} %	$t_{C\,=\,max}$ Years	$t_{C\,=\,50\%}$ Years	$t_{N\,=\,50\%}$ Years	$Q = \overline{C} \cdot t_{C\,=\,50\%}$
2,15 normal	90	100	0	2	2	2,0
2,15 special	80	100	0	12	8	9,5
2,20	108	124	7	11	11	12,0
2,25	105	116	7	10	10	10,5
2,30	104	115	4	8	7	8,0
2,35	103	111	3	4	5	4,5
2,40	96	110	0	3	3	3,0

As can be seen from *Figure 2,* the especially significant quality factor Q reaches its maximum at 2.20 V.

4 Current and voltage relationships, effect of antimony

Because of the antimony contamination mentioned earlier, the current necessary to maintain a given constant cell
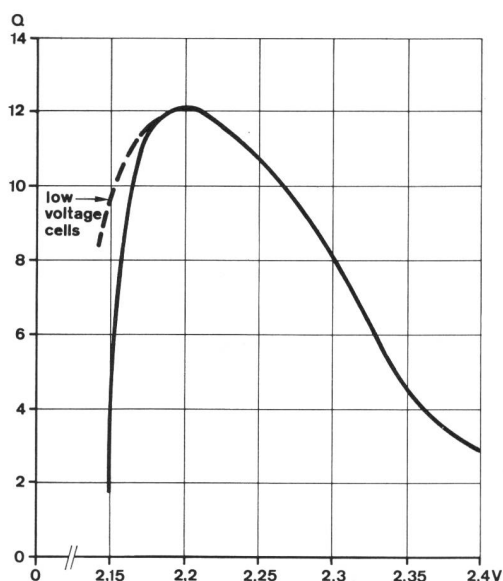

Fig. 2
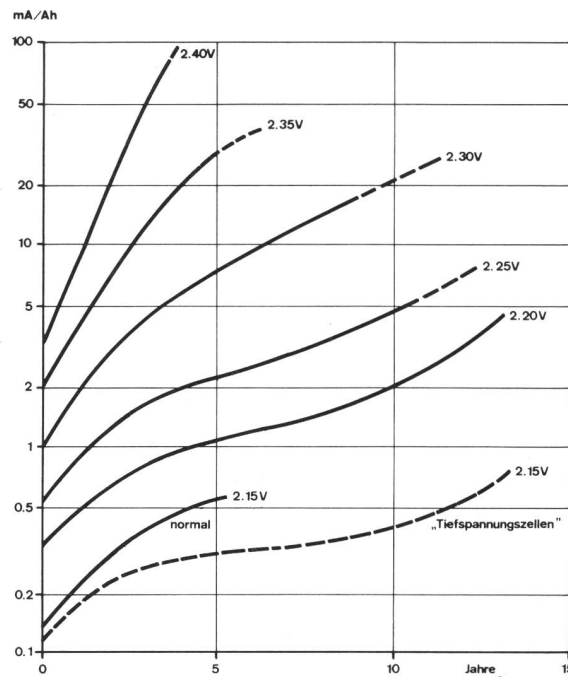Quality factor Q as a function of cell voltage

Fig. 3
Time-behaviour of currents as a function of voltage
Tiefspannungszellen – Low voltage cells
Jahre – Years

voltage will show a marked increase with time. In *Table II* the currents with respect to an initial capacity of $C_o = 1$ Ah are summarized. *Figure 3* illustrates them as functions of time (with voltage as parameter), while *Figure 4* shows their dependence on voltage (with age as parameter). The dashed auxiliary line was chosen so that a voltage increase of 50 mV (test-voltage increment) corresponds to a doubling of the current. Note that over a wide range the family of curves has approximately the same slope as the auxiliary line and thus the current-doubling effect is valid to a large extent. With large cells (600 Ah) it was found that a voltage increase of 50 mV will not double the current but merely increase it by a factor of 1.5.

It is well known that the extent of the antimony contamination, and with it the current-rise, depends on the hardness of the negative plates. In the upper part of *Figure 5* the current is plotted for cells with extremely soft plates which, as a result of effective expander additives, swoll up considerably. The lower part represents plates that remained hard because very little or no expanding agent had been added. In both cases the antimony contents of 8% in the negative plates and of 10 to 11% in the lead

Table II. Current as a function of cell voltage and age of battery

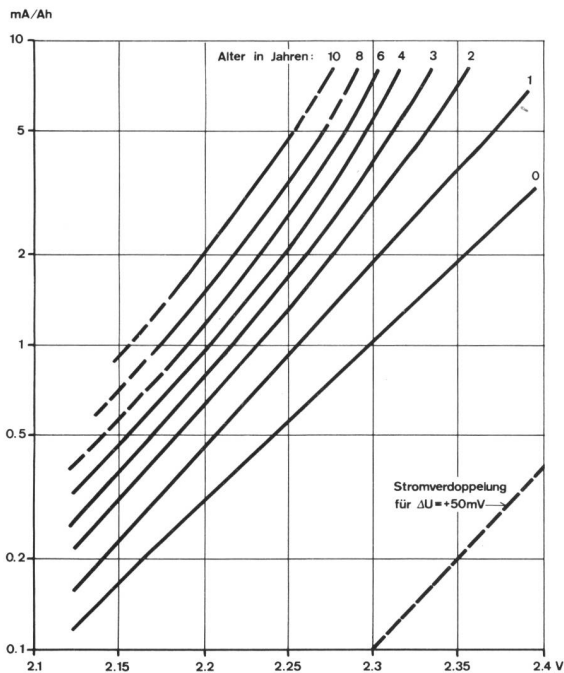| Age in years	Current in mA/Ah at cell voltage (V)						
	Average 2,15	Special 2,15	2,20	2,25	2,30	2,35	2,40
0	0,15	0,10	0,35	0,55	1,0	2,0	3,5
1	0,20	0,15	0,50	0,85	1,8	3,9	8,0
2	0,30	0,20	0,65	1,3	3,0	7,4	25
3	0,40	0,25	0,85	1,7	4,5	12	50
4	0,50	0,29	1,0	2,0	5,9	19	~100
5	0,60	0,30	1,1	2,3	7,4	30	–
6	–	0,32	1,2	2,6	9,0	40	–
7	–	0,33	1,3	2,9	11	–	–
8	–	0,35	1,5	3,4	14	–	–
9	–	0,38	1,7	4,0	17	–	–
10	–	0,42	2,0	4,8	20	–	–
11	–	0,50	2,6	5,8	25	–	–
12	–	0,60	3,3	7,2	30	–	–
13	–	0,70	4,5	~10	–	–	–

Fig. 4
Voltage-dependence of currents in the various age-groups
Alter in Jahren – Age in years
Stromverdoppelung für – Doubling of current for

Fig. 5
Effect of antimony contamination on soft and hard negative plates: current-evolution in the voltage range 2.20 to 2.25 V
Weiche negative Platten – Soft negative plates
Harte negative Platten – Hard negative plates
Jahre – Years

cores are equal. A comparison of the two parts, both being valid in the voltage range of 2.20 to 2.25 V, reveals that, on the average, the current in soft-plate cells is twice as high as in hard-plate types. *Table III* contains some representative values.

Table III. Currents as a result of antimony contamination for soft and hard negative plates, valid for 2.20 V

Age in years	I_{soft} mA/Ah	I_{hard} mA/Ah	Ratio $I_{soft}:I_{hard}$
1	0,61	0,40	1,5
3	1,16	0,61	1,9
6	1,80	0,82	2,2
9	2,73	1,09	2,5
12	5,06	1,96	2,6

Additional information about the «state of health» of the cells is gained from the *rates of current growth*. These are illustrated in *Figure 6,* where growth rates were obtained as difference quotients

$$I' = \frac{\triangle I}{\triangle t}$$

with $\triangle t = 0.5$ years. The increase during the first years is due to the antimony contamination which sets in right away. In a second phase a marked decrease follows for voltages below 2.30 V, but above 2.30 V a further increase sets in until these cells fail completely. After 5 to 6 years the rates of growth increase even in the favourable voltage ranges. The increase becomes again as strong as at the beginning. This is due to extensive antimony contamination, corrosion and sulphatization damage.

The optimum charge preservation voltages can already be obtained from the so-called relative current curves after testing for only 1 or 2 years. The conditions for this are accurate current measurements during undisturbed constant voltage operation which can only be obtained under laboratory conditions. This *relative current* is defined as
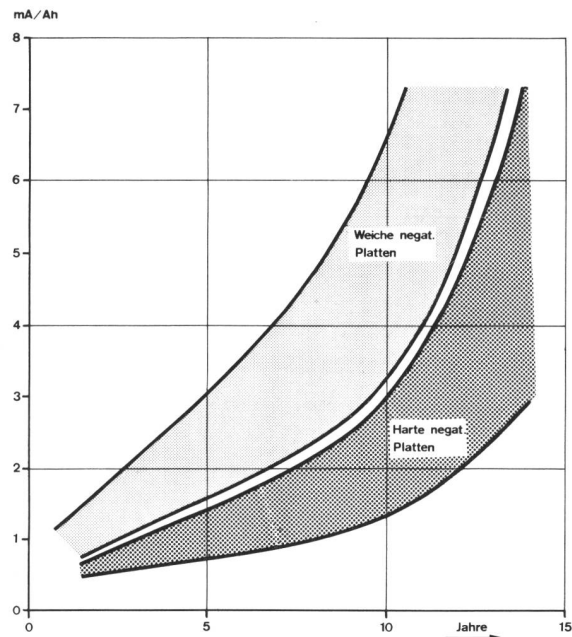
$$I_{rel}(U) = \frac{I_t(U)}{I_o(U)}$$

where:

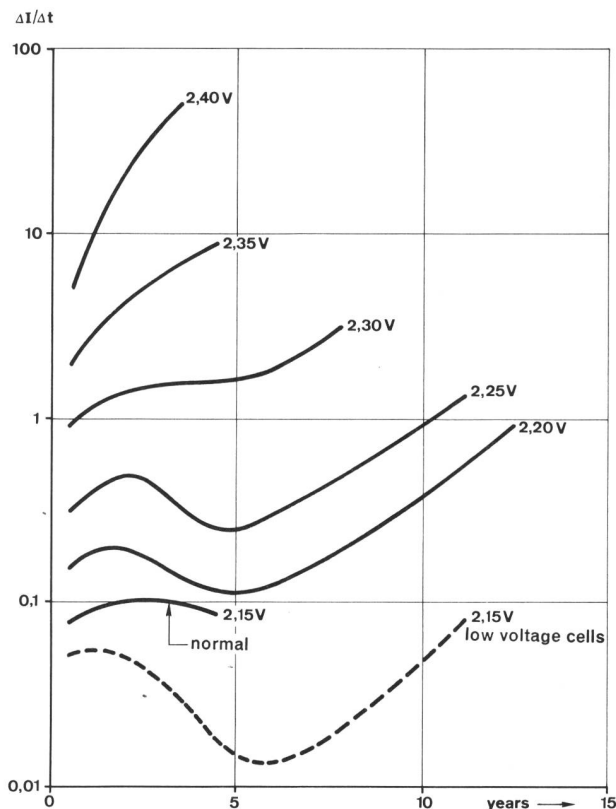I_t current at a time $t > 0$
I_o current at a time $t = 0$

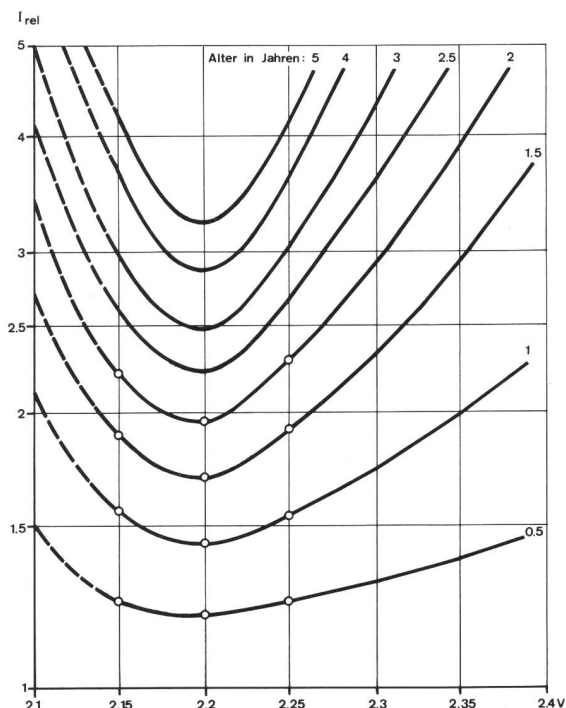**Fig. 6**
Yearly growth-rates of currents

Fig. 7
Voltage-dependence of relative currents in the various age-groups
Alter in Jahren – Age in years

The family of parabola-shaped curves resulting for I_{rel} as a function of voltage with age as parameter is illustrated in *Figure 7*. For the accumulator collective tested the minima of these curves lie very nearly at 2.20 V. It is plausible that these voltages correspond to the stationary state of the cells, i.e. to the optimum voltage. It is worth mentioning that the aforementioned «low voltage cells» have very flat minima between 2.15 and 2.20 V, which suggests that they can be operated at a lower voltage.

5 Internal resistance

The question, whether internal resistance measurements can give clues about the possible failure times of the cells (as a result of decreasing capacity), may be answered in the following way: For small cells the resistances tended only to increase towards the end of their life-span. However if a marked increase followed, the cells had already failed (corrosion damage). For large cells the resistance rose quite markedly up to the 50% capacity value – by a factor of 1.1 in the case of rapid capacity loss and about 1.5 for slower capacity losses that require three years to take place.

6 Water consumption, acid density, perchloric acid content

Table IV gives the yearly *water consumption* referring to a cell with $C_o = 1$ Ah. Because the battery cases are closed, there is no evaporation and water is consumed only by electrolysis. Thus the dependence on voltage and age is found to be the same as for the current, analogously to Figures 3 and 4. The doubling rule is again approximately valid for $\triangle U = +50$ mV.

Table IV. Water requirement

| Age in years | Water consumption in cm³/Ah per element and year at cell voltage (V) | | | | | |
	2,15	2,20	2,25	2,30	2,35	2,40
1	1,5	2,0	3,0	5	10	20
2	2,5	3,5	4,5	9	20	40
3	3,0	4,0	6,0	13	40	120
4	3,5	4,5	6,0	17	60	200
5	3,0	4,0	6,5	22	90	–
6	(2,5)	3,5	6,5	27	–	–
7	(2,0)	3,5	6,5	33	–	–
8	(1,5)	3,5	7,0	40	–	–
9	(1,3)	3,5	8,0	–	–	–
10	(1,2)	4,0	10	–	–	–
11	(1,1)	5,5	15	–	–	–
12	(1,0)	8,0	20	–	–	–
13	–	13	30	–	–	–

Values in brackets are valid for «low voltage cells» only

The *acid density* as a function of time has a characteristic similar to that of the capacity (*Fig. 8*). After the density has initially increased mainly at higher voltages, due to the advancing formation of the active material, it decreases as a consequence of diminishing capacity, i.e. with the material becoming inactive.

Nascent oxygen produced constantly in the floating charge operation attacks the polyvinylchlorid (PVC) of the tubes and separators and produces *perchloric acid* ($HClO_4$). The $HClO_4$ content of the electrolyte was periodically checked during the test period. *Figure 9* shows that even in the favourable voltage range (2.20 V), $HClO_4$ contents of 1000 to 3000 ppm are not uncommon in the presence of strongly chlorinating PVC. When hard PVC, polyester or terilene with glass-cloth is used, the $HClO_4$ content remains low: for the accumulators tested it is about 10 times smaller (Fig. 9) and amounts to only 100 to 200 ppm. The corrosive effect of the perchloric acid will be discussed in the following section.

7 Qualitative examination of disassembled cells

Following disassembly, which as a rule was performed on all the cells that failed and, to gain additional informa-
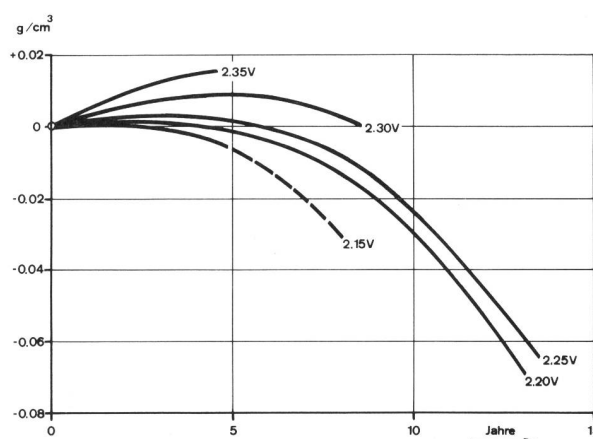

Fig. 8
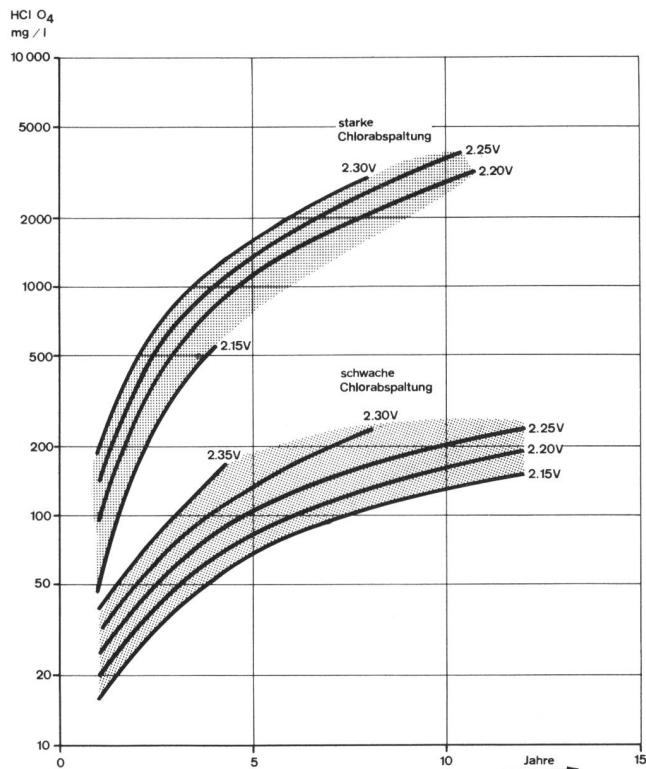Changes in specific gravity of the acid
Jahre – Years

HCl O₄ mg / l

Fig. 9
Perchloric acid content
Starke Chlorabspaltung – Heavy chlorine formation
Schwache Chlorabspaltung – Light chlorine formation
Jahre – Years

Table V. Damage to tubes and positive plate-lugs due to ageing

Voltage Volts	Age Years	State of tubes	State of plate-lugs
2.15	12	No damage	1st oxide layer peeled off
2.20	8	Partly intact, partly cracked	1st oxide layer peeled off
	12	Mostly cracked	Lugs strongly corroded, partly broken off
2.25	7	Some cracked	1st oxide layer peeled off
	10	Almost all cracked	2nd oxide layer peeled off
	14	All burst	Lugs mostly broken off
2.30	5	Partly intact, partly burst	Several oxide layers peeled off
	10	Almost all burst	Mostly through-corroded
2.35	3	Partly cracked, partly burst	Several oxide layers peeled off
	6	All cracked	Majority of lugs through-corroded
2.40	3	All burst	Strongly corroded, lugs partly broken off

The corrosive effect of large *perchloric acid concentration* can be seen from the results summarized in *Table VI.*

Table VI. Formation of oxide layers on positive plate-lugs by small and large perchloric acid concentration

Voltage Volts	Age Years	Small ppm	HCIO₄ content Degree of corrosion	Large ppm	HCIO₄ content Degree of corrosion
2.3	0.5	–	–	120	1st oxide layer formed
2.3	1	40	Slightly oxidized	200	1st oxide layer flaked off
2.3	3	80	1st oxide layer formed	600	2nd oxide layer formed
2.2	5	110	1st oxide layer flaked off	1000	2nd oxide layer flaked off

tion, also on the cells still working, the following headings were established:

– State of the separators
– State of the negative plates
– State of the tubes
– Degree of corrosion of the lead cores
– Degree of corrosion of the positive parts immersed in acid
– Amount of mud deposition

As a digest of the large amount of results, the following were deemed significant:

In all the cells the *separators* remained in perfect state. They prevented mud deposition even when the negative plates were very much swollen and the tubes were cracked. For this reason additional information about mud deposition becomes superfluous.

As to the *negative plates*, the loss of capacity can be attributed either to sulphatization (at 2.15 V) or hardening (with less effective expanding agents), or even to excessive swelling (too much expander additive). As to the *positive plates*, cracked tubes (producing loss of the active mass), broken lead cores as well as corroded conducting parts (especially plate lugs) are responsible for cell failures. The resulting tube and positive plate damages can be seen in *Table V.*

The reduction of the cross-section of the lead cores as a result of corrosion may be evaluated quantitatively. This can be seen in *Figure 10.* At 2.23 V (interpolated value) and after 15 years the diameter is reduced to half of its original value which may be considered as the permissible minimum.

Figure 11 illustrates the condition of a positive plate-joint of a 600 Ah cell after 3 years of operation at 2.3 V, the HCIO₄ content having risen to 600 ppm. The first, thick oxide layer had completely peeled off, the second one was already forming. For a HCIO₄ content of 300 ppm, the first layer had just begun to peel off. In an other cell with only 80 ppm but, on account of a lower degree of antimony contamination, with only half the current, merely a thin, very adhesive oxide layer was formed during the same time.
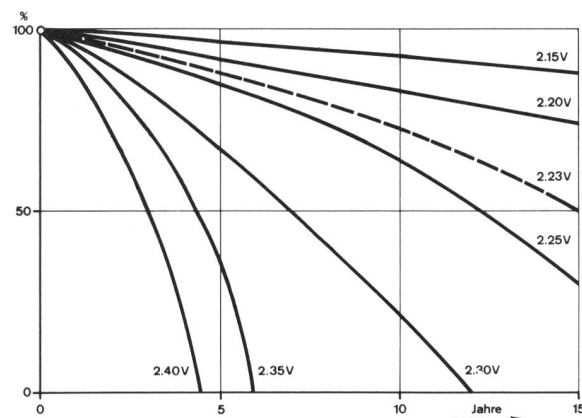

Fig. 10
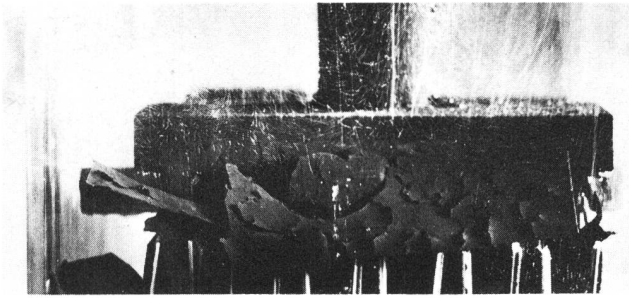**Relative diameter of lead cores**
Jahre – Years

Fig. 11
Peeled-off oxide layer on a positive plate-joint

8 Conclusions

The experiments have produced some relevant results. The most important ones are:

- Of the 6 test-voltages used with the battery collective the value of 2.20 V proved to be the most favourable. This is valid for an acid density of 1.24 g/cm³. The most important criteria are: evolution of capacity, life-span and quality factor (Sect. 3); behaviour of the charge conservation currents (Sect. 4); results from disassembling (Sect. 7).
- The upper limit of the cell voltage, which is specified as $U = 2.23 \text{ V} \pm 1\%$ and can thus be as high as 2.25 V was definitely proved to be too high.
- It still has to be demonstrated whether, for reasons of operating conditions, it is possible to reduce the average cell voltage to 2.20 V or perhaps even to 2.18 V. The question is, whether it is possible to switch from 22 to 23 cells in the 48 V installations.
- Further, it may be argued that the acid density should be lowered from 1.24 g/cm³ to 1.21 g/cm³. The advantages would be: lower charge conservation voltages, smaller current and thus slower ageing.
- From an electro-chemical point of view, the optimum voltage is 2.18 V at an acid density of 1.24 g/cm³ [6, 7]. Such a low voltage can be guaranteed only if all cells connected in series are homogenous and differences in cell voltage are smaller than 10 mV. This homogeneity must be achieved at the negative plates.

- As further improvements in manufacturing, in case they are not yet practised to-date, there may be mentioned:
- Optimizing the composition of the positive mass (ratio of lead powder and minium) in order to reduce the pressure on the tubes due to ageing.
- Minimizing the perchloric acid content of the electrolyte (max. 200 ppm, see Sections 6 and 7).
- Using lead with the least possible amount of alloyed antimony or a lead alloy with another metal (see Sect. 4).
- Optimizing the hardness of the negative plates in order to reduce the antimony contamination (see Sect. 4).
- Developing so-called «low voltage cells» (see Sect. 3 and 4) which at 2.17 to 2.18 V do not sulphatize too early.

Finally, let it be mentioned that with power supplies an improvement would also be desirable:

- If possible, a time- and load-independent voltage with a regulation accuracy of $\pm 0,25\%$.

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