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Influence of float and charge voltage adjustment on the service life of AGM VRLA batteries depending on the conditions of use

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Abstract

Valve-regulated lead-acid (VRLA) batteries with absorptive glass mat (AGM) separators have been in use for over 20 years in different standby applications. These applications are increasingly varied, especially regarding environmental conditions. Standby batteries are not only for use in applications where conditions are strictly defined and controlled (air conditioning) and it is therefore necessary to review and clarify the key parameters for the use of VRLA batteries with respect to the optimum conditions. Several series of chemical and electrochemical reactions occur in VRLA batteries particularly when in a charge or float charge condition. These reactions give specific properties such as minimal water loss (low maintenance) but also create specific precautions for use.

VRLA battery functioning is limited by four main phenomena that are positive grid corrosion, irreversible active mass sulfation, active mass degradation by cycling and dry-out by loss of water. Positive grid corrosion is the usual failure mode in float operation or due to persistent overcharge. Irreversible active mass sulfation occurs due to lack of charge. In cycling, dependent upon the frequency and depth of discharge, the active mass undergoes numerous structural changes that cause degradation.

These four limiting phenomena define a framework inside which several parameters determine the service life of VRLA batteries. These parameters are commissioning, temperature, and frequency and depth of discharge. Commissioning is necessary to equalise and fully charge the cells before use. Temperature, and temperature dispersion, is the main factor determining the rate of corrosion. The frequency and depth of discharge determine how the active mass is utilised. This paper, by considering these parameters both qualitatively and quantitatively, attempts to indicate how and why to adjust the charge and float voltages to optimise the use of AGM VRLA batteries according to the environmental conditions.

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1. Introduction

Valve-regulated lead-acid (VRLA) batteries have been used for more than 20 years in the most important standby applications. Although the reliability is generally established it is important to remember the main key drivers that exist within a VRLA battery, and with respect to standby application the rules to apply in terms of float and charge voltage adjustment depending on the conditions of use in order to have the best use of the batteries.

2. VRLA technology

VRLA technology has been known since 1960 but only industrialised from 1980. The main principle is to minimize water loss by recombining oxygen within the battery. These batteries offer high service life and performance. This is the reason why they have been chosen as the first solution in telecommunication and UPS applications (Fig. 1).

3. Principle

Each cell consists of positive plates, negative plates and electrolyte absorbed in separator. For lead–acid batteries the

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Nomenclature

I_{fl}	current flowing through battery on float charge
	(see Fig. 2)
$I_{\rm rp}$	partial current related to recharge of positive
1	electrode (see Fig. 2)
$I_{\rm corr}$	partial current related to positive grid corrosion
com	(see Fig. 2)
Invd	partial current related to hydrogen evolution
-nyu	(see Fig. 2)
L	nartial current related to oxygen evolution (see
Toxy	Fig. 2)
I	nartial current related to ovvgen recombination
rec	(aso Fig. 2)
	(see Fig. 2)
N+	positive electrode overpotential
N-	negative electrode overpotential
U_{end}	voltage at the end of the discharge
Uc	float voltage applied on the cell in Section 4.1
01	nout voltage applied on the cen in Section 4.1

positive plates are composed of lead grids (current collector) pasted with lead dioxide (active material). Whilst the negative plates are lead grids (current collector) pasted with spongy lead (active material). The electrolyte is dilute sulphuric acid, which is also an active material. This is unusual in battery systems.

3.1. Chemical and electrochemical reactions occurring in a VRLA battery

Several chemical and electrochemical reactions occur at battery plates [1]. Chemical reactions occur without electrical current passing through the battery, for example, the self-discharge of active materials. Electrochemical reactions need electrical current to pass through the battery, for example the recharge reactions. When a cell is put on float charge there is a current that flows through the battery and this current is divided in to different partial currents (Fig. 2). On the positive plate these currents are recharge,

Ca





Fig. 2. Distribution of partial current during float charging.

grid corrosion and oxygen evolution. On the negative plate these currents are recharge, hydrogen evolution and oxygen recombination.

3.2. Gas recombination principle

During float charging, oxygen evolution occurs at the positive plate before hydrogen evolution occurs at the negative plate. Oxygen is transported through the separator to the negative plate where it reacts with charged negative active material (Pb) to produce water (H_2O) and discharged active material (PbSO₄). This is the gas recombination process. This can be achieved when the electrolyte is absorbed in absorptive glass mat separator (AGM technology) or is gelled with silica particles (gel technology). In VRLA AGM batteries the amount of acid is adjusted in order to create a free path for oxygen transport, facilitating the oxygen recombination process, which is then followed by the recharge reaction, and the sequence of reactions is:

 $Pb + 1/2O_2 \Leftrightarrow PbO$

 $PbO + H_2SO_4 \Leftrightarrow PbSO_4 + H_2O$

 $PbSO_4 + 2H^+ + 2e^- \Leftrightarrow Pb + H_2SO_4.$

Several trials have been carried out to clarify the behaviour of AGM VRLA batteries in different applications. The different trials and the results are described in this paper.

4. Electrode overpotential situation

4.1. Experimental

Typical Tafel plots [2] were established using a AGM VRLA cell (Powersafe 2V400), by putting the cell at different voltages. The cell was specially equipped with a reference electrode (Hg/Hg₂SO₄/K₂SO_{4sat}) and put on constant voltage charge at a temperature of $23 \degree C \pm 2 \degree C$. After a period of stabilisation current individual positive and negative electrode voltages were measured.

Table 1 Experimental values

1				
$\overline{U_{\mathrm{f}}\left(\mathrm{V} ight)}$	I (mA/100 Ah)	<i>N</i> + (V)	<i>N</i> – (V)	
2.24	37	0.074	0.007	
2.33	117	0.119	0.052	
2.38	160	0.140	0.077	
2.48	360	0.158	0.162	
2.58	948	0.189	0.237	

4.2. Theory [2]

When a charging current is applied to a charged battery, the battery plates experience an over potential. There is an exponential relationship between overpotential and the charging current. Overpotential is the difference between the actual potential of the plate when on charge and the equilibrium potential of the plate when no current is passing through the battery.

The level of overpotential governs the rate of the different electrochemical reactions that occur at the plates. In a fully charged battery the partial currents of recombination plus oxygen and hydrogen evolution dominate the overall charge current.

4.3. Results

The results obtained are shown in the Table 1 and the resulting Tafel plots in Fig. 3.

From Table 1 and Fig. 3 it can be seen that the charge current and the level of overpotential on the plates is dependent on the applied charge voltage.

The reaction corresponding to the positive overpotential is oxygen evolution. The situation of the negative plates is more complex. It can be seen in Fig. 3 that there is no initial overpotential of the plate in response to an increasing current until a critical value is achieved. This area is dominated by the recombination current. After which the hydrogen evolution current becomes predominant.

This illustrates the following important points:

- To maintain the negative electrode in a charged state overcoming self-discharge, it is necessary to overcharge the positive electrode.



Fig. 3. Experimental Tafel Plot on AGM cell.





- If the charge voltage is too high, recombination is overcome and water is lost by electrolysis.

5. Factors determining VRLA working life

Theoretical consideration and experience in the field in the VRLA batteries identifies the main factors constraining float service life to be (Fig. 4):

- Corrosion of positive grids.
- Active mass degradation during cycling.
- Active mass sulfation.
- Dry-out by loss of water.

Other failure modes due to poor manufacturing quality (shorts, leakage, negative group bar corrosion) are not discussed in this paper [3].

5.1. Typical capacity evolution according to ageing process

VRLA cells in service are always subjected to one or more factors constraining VRLA life. Each factor has a typical impact on the evolution of the capacity (Fig. 5).

5.2. Positive grid corrosion

Gas recombination induces in VRLA cells a higher positive plate overpotential than occurs in flooded cells. Positive grid corrosion is a normal electrochemical process and de-



Fig. 5. Schematic capacity evolution depending on failure mode.

termines the cell design life. Positive grid corrosion depends on lead alloy composition, grid design and grid casting conditions [4].

In this paper only lead calcium tin gravity cast grids and the influence of acid density are considered. Ageing tests have been conducted by increasing the temperature whilst maintaining the voltage at that specified for 20 °C. This kind of test on AGM VRLA cells is conducted to determine battery life as limited by positive grid corrosion and has been used here to demonstrate the influence of acid density on battery life.

5.2.1. Experimental

A test at 71 °C has been done on four of VRLA AGM batteries with different acid densities (1.260, 1.300, 1.340, 1.360 at 20 °C) put on float at 2.28 V per cell. Every period of 13 days at 71 °C the capacity was checked by a constant current discharge at the 10 h rate to 1.80 V per cell at 20 °C. The test was stopped when the capacity was lower than 80% of the initial capacity.

5.2.2. Theory

The rate of positive grid corrosion is influenced by current, temperature, float voltage and acid density. By applying a high temperature it is possible to accelerate grid corrosion to determine the effect of acid strength on both capacity and design life at $20 \,^{\circ}$ C.

5.2.3. Results

The result of the test clearly indicates that the higher the acid density, the higher the capacity, but the lower the life (Fig. 6).

5.3. Water loss

Electrolyte drying out is not a normal failure mode in float applications. In fact the recombination process is to a certain extent self-regulating. When the battery loses water by electrolysis, more paths for oxygen transport are created increasing gas recombination and reducing water loss. However, when the float voltage is too high, recombination is over-



Fig. 6. Influence of acid density on battery capacity as a function of periods on float at 71 $^{\circ}\text{C}.$

Table 2	
Positive active material degradation	

Battery	Acid quantity	Active mass porosity
A	High	High
В	High	Medium
С	Medium	Medium

come until the separator becomes too dry reducing battery function.

5.4. Positive active material degradation

This phenomena appears mainly in batteries in cycling applications. Several studies have been carried out to describe the phenomenon of active material softening [5]. This degradation depends on the paste formulation and on the detailed design of the cell.

5.4.1. Experiment

Experimentally three batteries (A–C) were put in cycling conditions according to the new IEC standard 60896-21 in order to show semi-quantitatively the effect of acid quantity and active mass porosity on cycle life (Table 2).

5.4.2. Theory

During discharge lead dioxide is converted to lead sulphate. Lead sulphate has a higher volume [5] than the lead dioxide from which it was made. During cycling the expansion and contraction of active material degrades its integrity. The speed of this depends on the depth of discharge and on the initial structure of active material.

5.4.3. Results

With a high quantity of acid due to volume or density and high active material porosity it is possible to discharge more of the active material giving a high capacity but resulting in more rapid degradation of active material during cycling (Fig. 7).



Fig. 7. Influence of quantity of acid and active mass porosity on cycling test according to IEC 60896-21.

5.5. Sulfation

5.5.1. Experiment

To demonstrate the effect of float voltage on sulfation, two VRLA AGM batteries (A and were tested by cycling (3 h discharge at $0.2 C_{10}$ followed by 21 h recharge at constant voltage at 23 °C ± 2 °C). Battery A: float voltage 2.27 V per cell. Battery B: float voltage 2.35 V per cell.

5.5.2. Theory

Sulfation happens when the voltage used for recharge is too low. It can be seen from the Tafel plot that a minimal voltage needs to be applied on a VRLA cell to maintain charged battery plates and especially the negative. If the voltage is too low lead sulphate crystals formed during discharge are not fully converted to active material during recharge and grow in an irreversible manner [5]. This induces a step by step lost of capacity by both, loss of active material surface area and a decrease of active material porosity.

5.5.3. Results

Fig. 8 demonstrates the reduction in cycle life when the recharge voltage is reduced below that required to effectively recharge the battery plates. Battery A failed not because of positive active material degradation or positive grid corrosion but because of active material sulfation (this capacity loss was reversed by increasing the float voltage) and battery B failed due to active material degradation. In case A charge factor (that is the ratio Ah recharged/Ah discharged) is too low compare with case B to completely recharge active material.

5.6. Temperature dispersion within a monobloc

5.6.1. Experiment

A test was carried out on a Powersafe V 12V 80 Ah monobloc that consisted in changing the outside temperature from 25 to 55 °C. Then measuring the response of cell 1 (edge) and cell 3 (internal) in temperature and voltage.



Fig. 8. Influence of recharge voltage on behaviour.



Fig. 9. Temperature dispersion within a 12 V AGM monobloc.

5.6.2. Theory

The temperature of the cell influences the float voltage of the cell in the battery. The six cells constituting a 12 V monobloc are not equivalent in the way they respond to a temperature change. The cells in the middle of the monobloc respond less rapidly to external variation compared to the border cells. This means that when the external temperature changes, the cells temperatures and voltages will not change at the same rate.

5.6.3. Results

It is observed (Figs. 9 and 10) that differences within a monobloc arise when the external temperature changes rapidly. It takes approximately 24 h to homogenize the temperature and the voltages within a monobloc.

Applications that undergo rapid changes in temperature are seen to have reduced service life due to the unbalancing of blocs within a battery and cells within a monobloc by temperature dispersion. Thus it is necessary to optimise charge algorithm to optimise the service life where the environmental conditions cannot be corrected.



Fig. 10. Temperature and float voltage difference within a $12\,\mathrm{V}$ AGM monobloc.



Fig. 11. Typical adjustment of float voltage with temperature for AGM cells.

6. Discussion: general rules to respect for a correct use

6.1. Float voltage adjustment

Float voltage adjustment is a very important parameter that influences directly the service life. A too high voltage will induce premature corrosion on the positive grid and a too low float voltage will induce a lack of charge and irreversible sulfation of the active material. Float voltage must be also adjusted according to the temperature of use of the battery but also according to the frequency of discharges. Depending on the sophistication of the charging equipment it is possible to adjust finely or in steps (Fig. 11).

In AGM cells it is observed that a temperature increase induces an increase in float current and consequently the float voltage must be reduced in order to reduce positive grid corrosion whilst maintaining state-of-charge.

6.2. Frequent discharge

Standby batteries are designed to be principally used under a constant floating voltage. Nevertheless, there are sometimes conditions where discharges are frequent. In this case full state-of-charge maintenance is a critical parameters and it is recommended to use either a slightly higher float voltage or a two step recharge mode. This mode consists of applying a high level voltage (typical 2.35–2.40 V) and after recharge a lower float voltage. This method allows rapid recovery of autonomy and full state-of-charge. However Fig. 7 shows that in the absence of boost charge a standard AGM VRLA product can meet and exceed the IEC standard cycle test requirement (only float voltage available for recharge).

6.3. Influence of temperature on available capacity

Temperature has a direct influence on the battery's service life and it is known now that an increase of $10 \,^{\circ}$ C halves the life. Temperature has also a direct influence on the capacity. Because of the ionic mobility the lower the temperature the lower the capacity. The higher the rate of discharge is, the more important is this phenomenon (Fig. 12).

During use at low temperature there is usually little risk of electrolyte freezing, but this phenomenon can oc-



Fig. 12. Temperature influence on performances of AGM cells.

cur when a discharged battery is stored at low temperature.

6.4. Storage and commissioning

Storage conditions are critical. It is technically possible in laboratory controlled conditions to store recharged cells during 3 years at 20 °C. Capacity can be recovered by applying a specific profile of current. The cell storage life in controlled conditions is not applicable in service because the conditions are not well defined and may be heterogeneous (different temperature, sun shining, humidity). For this reason it is recommended to not store more than 6 months to 1 year in order to avoid large float voltage dispersions that are not eliminated with time or with boost charge voltage.

6.5. Recharge mode

Several possibilities exists to recharge a battery.

6.5.1. Single step

In this mode of constant-voltage recharge the same voltage is used for float and for recharge. This mode is convenient when there is not frequent use and when long periods are available for recharge. In the case of frequent discharge and short periods to recharge increased float voltage is required to find a compromise between sulfation and corrosion.

6.5.2. Two step

This mode of constant-voltage recharge is recommended in case of frequent discharge use (Section 6.2) where possible in the end application. It allows rapid recharge without increasing excessively positive grid corrosion.

6.5.3. Intermittent charging mode

Initially developed to reduce as much as possible the positive grid corrosion by limiting the period where the battery is under charge. This mode of charge is relatively delicate to adjust well and runs the risk of under charging the cell, especially the negative electrode. This kind of charge is desirable when application temperature is higher than $35 \,^{\circ}$ C [1].

7. Conclusion

VRLA batteries have reached a high level of reliability and are the batteries of choice for standby applications both technically and economically. VRLA technology is well established and there are several factors that can affect the service life. It is often thought that by reducing the float voltage the service life is increased by reducing corrosion that is the normal way of ageing. This is not true especially for VRLA cells where the risk of undercharge is more important because of gas recombination. Therefore, in order to maximise the life of the battery in service the charge mode must be selected to match the requirements of the application, and not a laboratory ideal. The factors that must be considered when selecting an appropriate charging mode are frequency of discharge, depth of discharge, temperature, temperature stability, and time available for recharge. It has been described here how the basic principles of the VRLA technology underpin application guidelines that are designed to maximise service life. There is still progress in techniques, quality and standards like the new IEC 60896-21 and that will contribute to the advance of VRLA technology.

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