GLOBAL ENERGY INNOVATIONS

TECHNOLOGY BRIEF

Dynapulse™ Systems
Principles of Desulfation

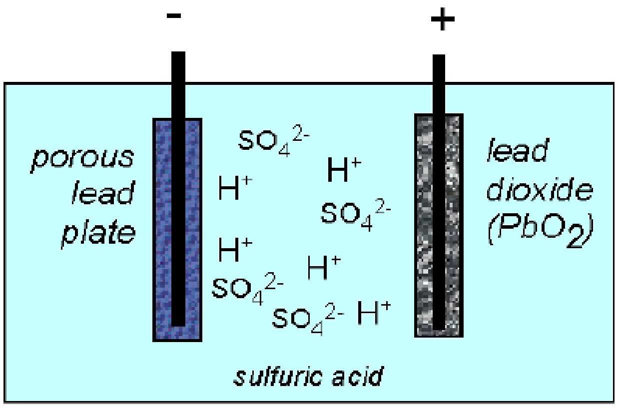
This technical brief reviews the problem of lead-acid battery sulfation and shows how the Dynapulse™ technology works to overcome the problem quickly, economically and safely.

ABSTRACT

The lead sulfate that forms on each plate of a lead-acid battery during discharge starts out as microscopic crystals that are easily converted back to active material during recharge. Over time, however, the smallest crystals tend to shrink and larger ones tend to grow. Left untended, the lead sulfate crystals eventually become so large that no amount of DC charging (even at elevated voltage) can reverse the process. At that point, the battery will not accept charge and is said to be ***sulfated***. After reviewing the causes and effects of sulfation, this document outlines a 3-stage conditioning regime that has proven highly effective for restoring capacity to sulfated batteries.

INTRODUCTION

As illustrated in **Figure 1**, the discharge reactions of a lead acid battery yield lead sulfate at both the positive and negative plates.



Discharge reaction at the negative

$Pb + HSO_4^- \rightarrow PbSO_4 + H^+ + 2e^-$

Discharge reaction at the positive

$PbO_2 + 3H^+ + HSO_4^- + 2e^- \rightarrow PbSO_4 + 2H_2O$

Figure 1. Discharge reactions at the plates of a lead acid battery.

The overall discharge reaction is:

$$Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$$

The lead sulfate produced on each plate during discharge starts out as microscopic crystals that are easily converted back to active material when the battery is recharged. Over time, however, the smallest (high surface-energy) crystals tend to shrink and larger (low surface-energy) crystals tend to grow. The physical process whereby differences in surface energy drive the transfer of material from small to large crystals is known as ***Ostwald Ripening*** and is illustrated in **Figure 2**.

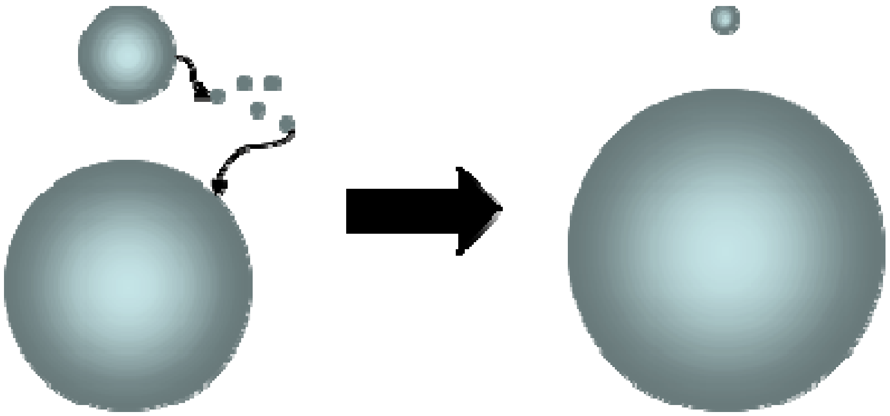


Figure 2. Schematic of the Ostwald ripening process[i]

If battery operation is not well controlled, the surviving lead sulfate crystals become progressively larger, eventually "hardening" into a dense layer that can no longer be recharged. The condition, which represents a permanent loss in capacity, is commonly known as ***sulfation.***

WHAT CAUSES SULFATION?

Experience shows that sulfation can develop on the plates of a lead acid battery when it is:

- Left for more than a few hours at a low state of charge state;
- Allowed to self-discharge for long periods after charging;
- Consistently undercharged;
- Operated at elevated temperatures;
- Consistently overcharged;
- Subjected to excessive AC ripple;

As indicated in **Figure 2**, the growth of lead sulfate crystals takes place via the diffusion of Pb^{2+} ions in solution. Consequently, factors that raise either the solubility or the diffusivity of Pb^{2+} ions tend to accelerate the sulfation process. The most important of these factors are temperature and acid concentration. A temperature change from 25 to75ºC can raise the diffusivity of Pb^{2+} ions by orders of magnitude[ii]. Similarly, as shown in **Figure 3**, ionic solubility and diffusivity can increase up to five fold as a battery is discharged[iii].

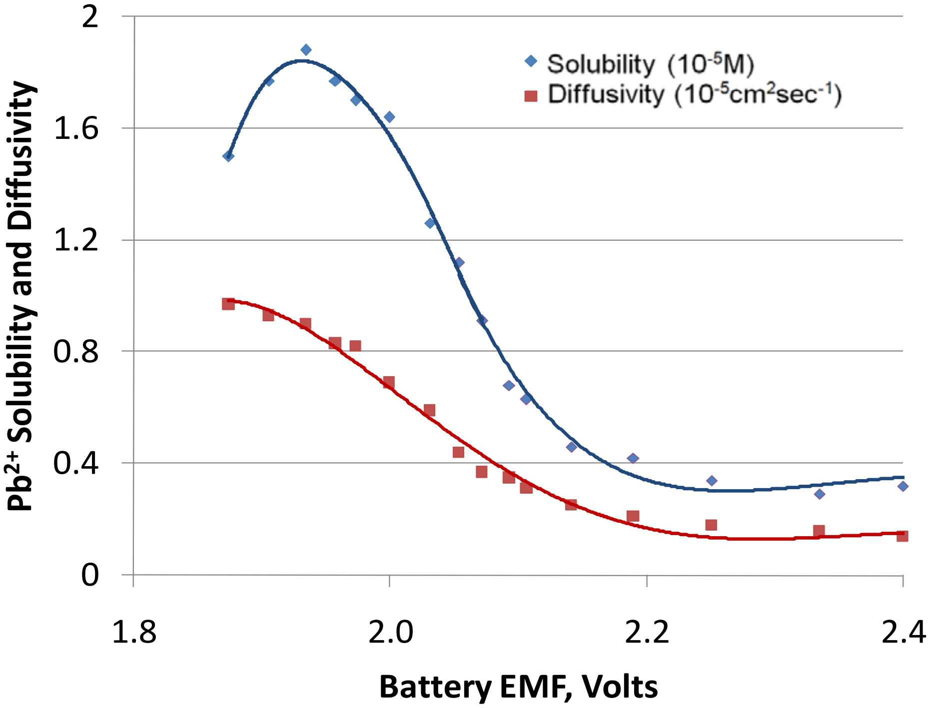


Figure 3. Discharging a battery can increases Pb^{2+} solubility and diffusivity five-fold.

While increased ionic solubility and diffusivity can explain many risk factors for sulfation, a variety of other causes may also contribute. For example, gas pressure within VRLA cells that are charged too rapidly (or at voltages that are too high) can exceed the valve pressure, releasing water vapor to the environment and raising the concentration of the remaining acid. The increased corrosivity of the acid can lead to negative-plate sulfation, even on float. Similar effects can occur in VLA cells that are not regularly topped off with DI water. Sulfation can also develop as a secondary result of operating conditions that degrade the active materials. These conditions include high rate cycling, deep discharge, and large-amplitude AC ripple (coming either from poorly regulated power supplies or from active loads). In batteries that use Pb-Ca alloy grids, sulfation may be an indirect consequence of a resistive oxide layer that builds up on the positive grid. During charge, the ohmic drop in this layer lowers the true voltage applied to the battery, a primary cause of sulfation.

Once sulfation has begun, the process tends to progressively worsen any irregularities in the distribution of charging and discharging currents within the plates. Furthermore, sulfation of just one cell in a string can degrade the performance, capacity, and ultimately the life of every other cell in the string. The degradation occurs because the increased resistance and reduced capacity of a sulfated cell leads to uneven states of charge among the other cells, promoting sulfation in undercharged cells and multiple failure modes in overcharged cells.

WHAT CAN BE DONE TO REVERSE SULFATION?

Physical Effects

Some of the factors that lead to sulfation can also speed up the reverse process. For example, the conversion of lead sulfate back into active material is more rapid at elevated temperature and low states of charge because of the increased solubility and diffusivity of Pb^{2+} ions. Agitation can also aid ionic movement; hence the gas bubbles evolved towards the end of charge may be helpful.

DC Charging

Mild sulfation can often be reversed simply by overcharging the battery for several hours. When performed on a string of batteries cells, the process is known as "equalization". The desulfation results primarily from the increased charging voltage. Agitation by the gas bubbles produced during overcharge may also be beneficial.

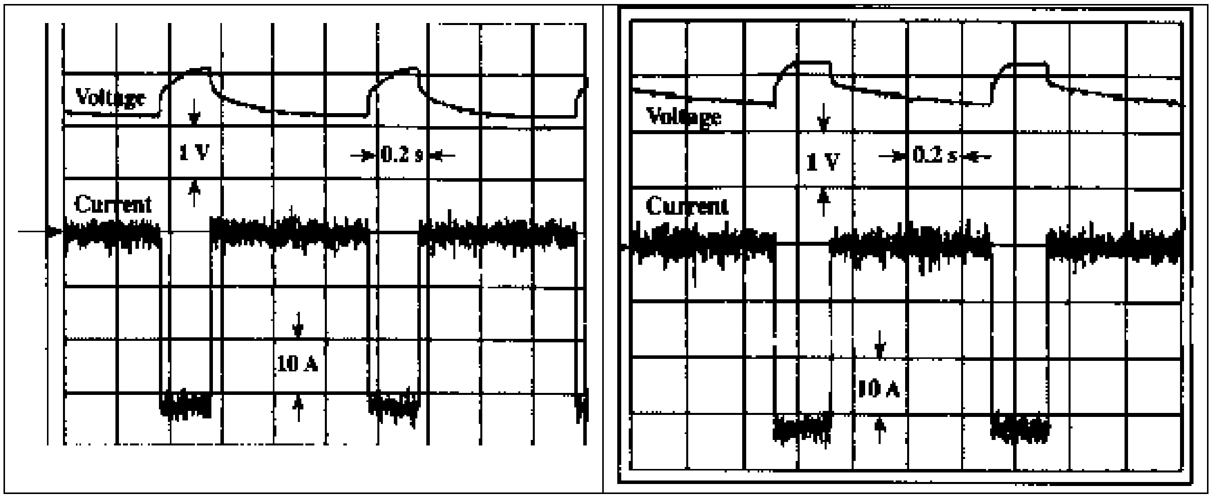
Equalization is not effective for reversing hard sulfation because the long times and high voltages required would promote other failure modes. These limitations can be circumvented by the adoption of pulsed charging regimes.

Pulsed Charging

Low-power "desulfators" promoted in the popular literature are probably no more effective than DC equalization methods. Conversely, high-power pulses, when applied without proper controls, can damage the battery and introduce the risk of fires or explosions. Fortunately, significant advances have been made in the theory and practice of pulse charging and the requirements for reconditioning lead acid batteries are better understood. A major contribution to this understanding came from the work of Lam et al[iv]. **Figure 4** (taken from Lam's paper) shows the applied current and resulting voltage waveforms during the initial and final stages of the pulsed-current charging of cells with Pb-Ca-Sn alloy grids. Each current pulse produces a sharp increase in voltage (the ohmic or IR effect) followed by a slowly rising voltage. The end of the pulse was marked by a sharp fall in voltage. The cell resistance calculated from the IR drops decreased from ~15mΩ at the beginning of charging to ~5mΩ at the end. Similar resistance changes were observed for cells with Pb-Sb alloy grids.

Lam's work highlighted several advantages of pulsed charging over conventional DC charging:

- Recharging times were reduced tenfold;
- Cycle life was increased by a factor of three to four;
- Applying pulsed-current charging to a cycled battery that had lost 20% of its nominal (or "nameplate") capacity restored the full nameplate capacity;
- For cells with Pb-Sb grids, capacity loss caused by high rate discharges was associated with an increase in the crystalline of the positive active material (PAM). A crystallinity change was also seen in cells with Pb-Ca-Sn grids but the major cause of capacity loss in those cells was the development of a resistive barrier layer on to the positive grid. Pulsed-current charging delayed the capacity loss in both kinds of battery by slowing down both the crystallization of PAM and the development of a barrier layer.



(a) (b)

Figure 4. Applied current and resulting voltage at (a) initial and (b) final stages of pulsed-current charging. (After Lam *et al.,* 1995.)

A more recent study demonstrated that additional benefits are gained by adjusting pulse parameters as the cell approaches full capacity[v]. Such adjustments are implemented automatically in the Dynapulse™ battery conditioning technology.

DYNAPULSE™ 3-STAGE CONDITIONING TECHNOLOGY

While detailed aspects of Dynapulse™ battery conditioning technology remain proprietary, they involve the patented 3-stage regime outlined in Table 1. Current and voltage values given in the table are typical for a 12 Volt, ~100Ah lead-acid battery. For other battery ratings, the values would be scaled appropriately.

Table 1. Three-stage desulfation regime[vi]

			Output Waveform			**Response Waveform**	
Stage	**Function**	**Duration, mins.**	**Frequency, Hz**	**Pulse Width, mS**	**Peak Voltage, V**	**Peak Current, A**	**Average Current, A**
1	Breakthrough	~20	120	~4mS	42	~90	0-12
2	Activation	20	0-120	1-4mS	42	~90	20
3	Charge	~200	DC	DC	14.8-15.0	~30	0-30

To avoid the possibility of thermal runaway, battery temperature is monitored throughout the conditioning regime: output power is interrupted if the temperature reaches 113°F and restored only after the battery cools to 85°F.

In **Stage 1**, (*"Breakthrough"*) the process of desulfation begins at pre-existing pin-holes in the dense layer of lead sulfate that coats the active material. Because all of the input power is concentrated at a few small sites, the local temperature at those sites rises, speeding up the dissolution of lead sulfate. In this way, the pinholes grow in size, breaking through the sulfated layer. In **Stage 2**, (*"Activation"*) openings in the lead sulfate layer are progressively enlarged, re-exposing the active electrode material. On a macroscopic scale, these changes lower the battery resistance and restore lost capacity. In **Stage 3**, (*"Charge"*) the restored capacity once more accepts DC charge.

Stag3 1 – Breakthrough

A train of 42V pulses (initially of 4 mS duration and 50% duty cycle) is applied to the battery. Because the battery is sulfated, its internal resistance is high and the amplitude of the initial current pulses may be only a few milliamps. A typical sequence is illustrated schematically in Figure 5. (Note that time scale between the pulses has been greatly compressed.)

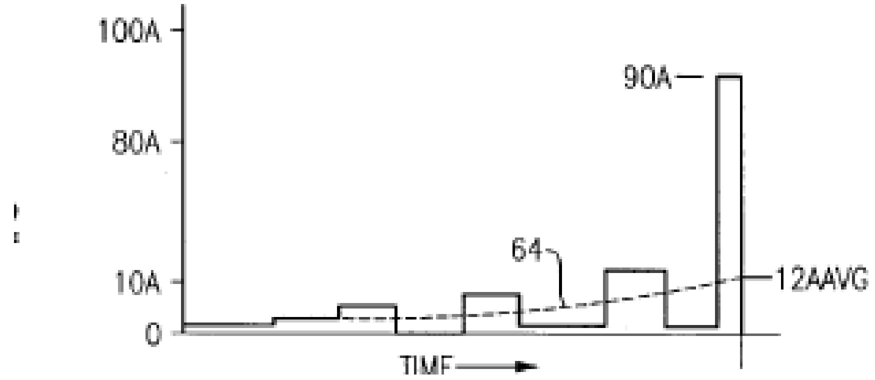


Figure 5. Current responses of a sulfated battery at intervals during **Stage 1**.

Towards the end of **Stage 1**, the peak current rises rapidly and the waveform pulse width is cut back to keep the average current below 12 Amps. The duration of **Stage 1** depends on battery condition. For a typical degree of sulfation, the end point is reached after about 20 minutes. For particularly severe sulfation, the time may be longer, however, if no improvement is seen in 20 minutes, the battery (which may also be suffering from failure modes other than sulfation), is probably unrecoverable. For batteries with good capacity and low internal resistance, **Stage 1** will be completed within milliseconds. Hence, Dynapulse™ Systems can be used with either sulfated or non-sulfated batteries because they continuously monitor the current response and adjust the output waveform accordingly.

Stage 2 – Activation

The transition from **Stage 1** to **Stage 2** is triggered when the average current reaches 12A. At that point, the output waveform is adjusted to limit the average applied voltage to 14.8V while allowing the average current to reach 20A. The increased current allows the small areas of active material uncovered during **Stage 1** to grow more rapidly, fully exposing the active material to the battery acid. At the same time, the 14.8 voltage limit ensures a net energy input that is low enough to avoid overheating and excess gassing.

Typical current pulses observed at intervals during **Stage 2** are shown in **Figure 6**. As before, the time intervals between pulses have been greatly compressed.

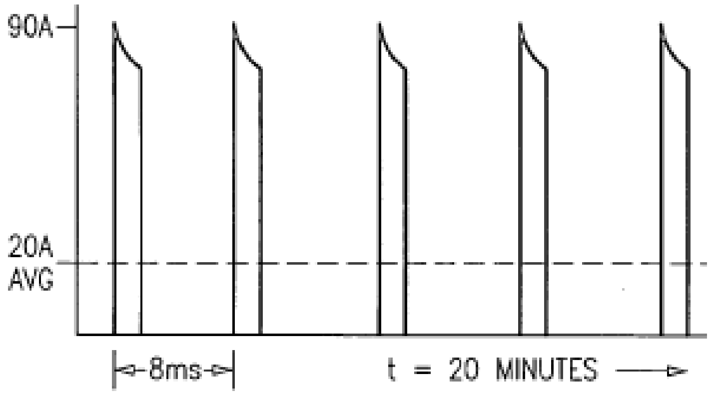


Figure 6. Current responses of a sulfated battery at intervals during **Stage 2**.

The shape of each current pulse is characteristic of an RC response to constant voltage pulses. It is equivalent to the curved voltage pulses observed by Lam *et al.* in response to constant current pulses (**Figure 4**). If **Stage 2** were continued for long enough to bring the battery close to a full charge, the RC decay would become more pronounced and the average current would decline towards zero.

As noted previously, pulse charging is significantly faster than DC charging, so in some circumstances, continuing Stage 2 until the battery reaches full charge may be advantageous. Indeed, the benefits of **Stage 2** charging are not limited to sulfated batteries: the pulsed currents are also more effective than DC methods for charging healthy batteries. However, if multiple batteries need to be conditioned, the extra time per battery may be impractical. For this reason, the transition to **Stage 3** normally takes place after a predetermined time of 20 minutes.

Stage 3 – Charge

The third charging stage consists of a low-ripple DC charge at 14.8 volts with a current limit of about 30 amperes. **Stage 3** is normally continued until a total elapsed time of 4 hours (including all three stages). At that point, the battery should be at, or very close to 100% state of charge.

CONCLUSIONS

The lead sulfate that forms on each plate of a lead-acid battery during discharge starts out as microscopic crystals that are easily converted back to active material during recharge. However, left untended, the lead sulfate crystals can grow, eventually becoming so large that no amount of DC charging (even at elevated voltage) can reverse the process. The battery will no longer accept charge and is said to be ***sulfated***. Applying a patented, 3-Stage charging regime, Dynapulse™ technology overcomes the problem of sulfation quickly, economically and safely.

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