# The Effects of Mechanical Electrolyte Mixing on VLA Cells in Renewable Energy Applications

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## Abstract

Changes in the energy sector worldwide require more and more decentralization of the power supply to relieve pressure on the electric grid and distribution network and to increase efficiencies. Where energy storage is used to balance these networks, additional efficiencies are needed in the energy storage systems to address operation under partial states of charge as well as cyclic load conditions.

Precisely controlled mechanical mixing of electrolyte in flooded lead acid cells can have significant benefits in cycling applications. It has been known that this process can reduce stratification in flooded lead acid cells in standby applications. Here we will present data to demonstrate how this can be applied in renewable energy applications and how this process can affect the final state of charge, energy consumption (Ampere-hour and Watt-hour efficiencies) and overall life of the battery system.

Details will be provided on effects of electrolyte stratification on the life of a battery and how mechanical mixing of the electrolyte affects lifetime and availability of energy.

The outline of a mechanical system design will be discussed along with data to show the benefits of such a system, for cycling and renewable energy applications.

## Introduction

All battery systems exhibit a change in their electrolyte concentration during discharging and charging, the result is stratification in the specific gravity of the electrolyte. This affects all types of lead acid batteries, flooded as well as valve regulated. Taller cells are affected more so than shorter cells. This paper only deals with the effects of stratification in flooded battery systems and not with that in VRLA batteries.

Acid stratification in a cell can be identified by a lower specific gravity at the top and a higher specific gravity at the bottom of the cell. In addition to gravitational effects, the electrochemical interaction between the acid and the lead electrodes during charge and discharge contributes to this process. To understand the mode of electrolyte stratification in lead acid batteries it is helpful to consider the equivalent circuit diagram of a single electrode (**Figure 1**). In this figure the battery is fully charged and the electrolyte is a homogenous mixture and insures that all resistances and voltages in the equivalent circuit diagram are equal.

U battery:          Battery voltage
I battery:          Battery current
I1-3:               Current of each path
U1-3:               Single equilibrium voltages of the electrode
RC1-3:              Double layer capacitor on the boundary
                    between electrode and electrolyte
Ra-Rc:              Resistance of the grid
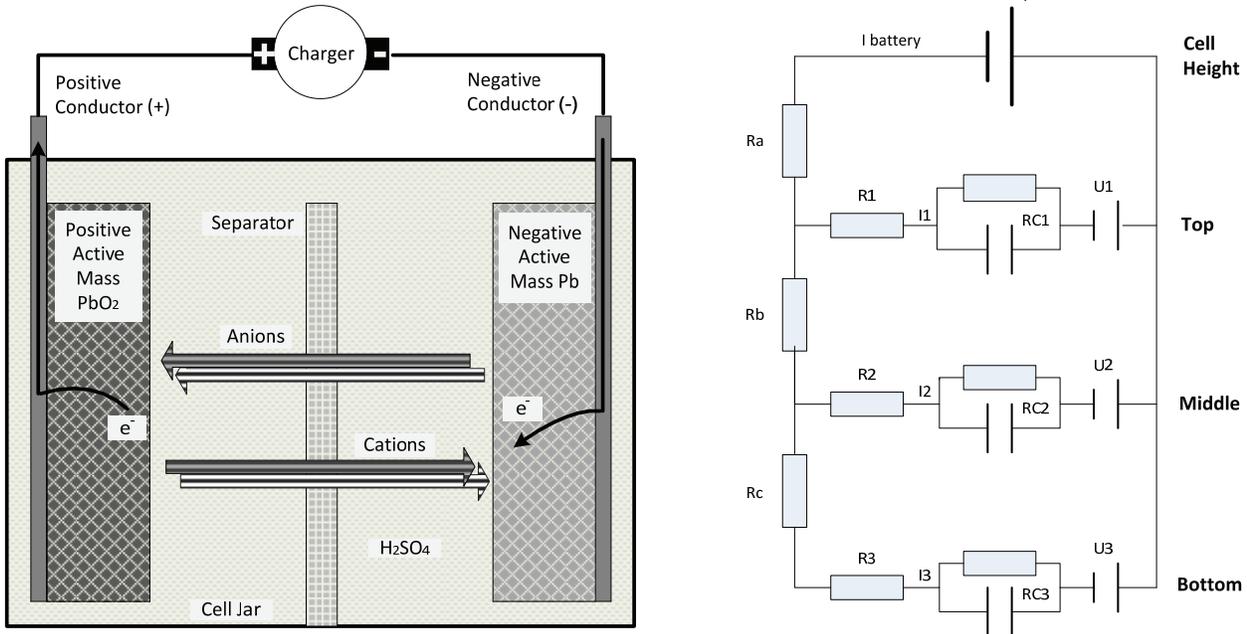R1-R3:              Resistance of the active mass

**Figure 1 - Equivalent circuit diagram of an electrode**

**Definitions:**

- U = Voltage

- I = Current

- Ia charge characteristic = constant current charge

- IU charge characteristic = a method of charging a battery where the first part of the charge is constant current at a fixed value and when the voltage reaches a pre-set value the characteristic changes to constant voltage.

- IUIa charge characteristic = a method of charging a battery where the first part of the charge follows the IU charge characteristic, followed by a constant current charge (Ia) either at the same current level as the original IU charge or at a different current level.

**Discharge cycle:**

- During discharge of the cell voltages $U_{1-3}$ are equal, but the appropriate currents differ over the electrode due to their different internal resistances ($R_{a-c}$) within the grid. For example ($I_1 > I_2 > I_3$). Therefore the electrolyte consumption at the top of the cell is dependent on a discharge current significantly higher than at the bottom.
- The reserve electrolyte above the plates migrates downwards due to gravity and replaces the exhausted sulfuric acid in the area surrounding the plates.

- The voltages $U_{1\text{-}3}$ are dependent on the local electrolyte specific gravity, which leads to an increase of the currents $I_{2+3}$ during discharge until an equilibrium state is reached. The voltages $U_{1\text{-}3}$ can be calculated according to the approximation $U_0 = 0.84 +$ acid gravity.

  For example:    $SG_1 = 1.220$,           $U_1 = 084 + 1.220 = 2.06$ V

  $SG_2 = 1.230$           $U_2 = 0.84 + 1.230 = 2.07$ V

  $SG_3 = 1.240$           $U_3 = 0.84 + 1.240 = 2.08$V

- After discharging, acid stratification is observed and level of stratification will depend on the discharge current and the internal resistance of the cell.

**Charge cycle:**

- During the charge cycle the upper area of the plate set has a higher current consumption than the lower area of the plate set. This is due to the differing internal resistances of the electrode ($R_{a\text{-}c}$) as well as the difference between the charging voltage and the equilibrium voltages $U_{1\text{-}3}$.
- Sulfuric acid, which leaves the active mass of the upper area of the plates settles out due to gravity and increases the acid density in the lower part of the plates. Hence, charging in the lower area of the plate will be more and more difficult and result in an insufficient state of charge in this region. Additional effects in this region are sulfation and capacity loss.

Over time electrolyte stratification promotes uneven current distribution within the electrodes. The top of the electrodes are mainly overcharged and the bottom of the electrodes undercharged. The result is higher corrosion at the top of the plate and sulfation at the bottom of the plate, overall premature capacity loss and shortened life of the cell.
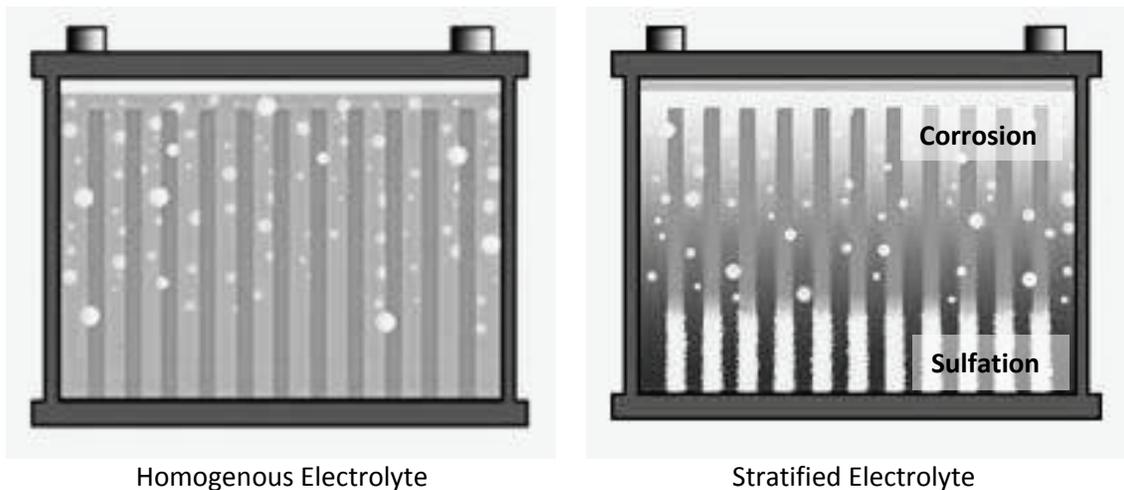


Homogenous Electrolyte                    Stratified Electrolyte

**Figure 2 - Consequences of electrolyte stratification on lead acid batteries**

In standby operation, electrolyte stratification is compensated by the gassing that occurs during overcharge at the end of the charge cycle (absorption phase). Flooded lead acid batteries in applications with daily discharge and recharge cycles generally require a higher charging factor of around 120% to help compensate for the development of electrolyte stratification. Additionally, these renewable energy applications have limited charging resources resulting in this overcharge phase not being available. Depending on the operational parameters such as depth of discharge (DOD), available charging time, charging voltage and charging current, we can look to a precise mechanical recirculation of the electrolyte to accomplish removal of electrolyte stratification.

# Mechanical electrolyte recirculation system

The main properties of a battery used in a renewable application, is its ability to cycle in difficult operating conditions. This means time limited cycling at shallow depths of discharge as well as operation in a partial state of charge condition. Additionally these applications are characterized by limited energy resources for recharging. It is important to keep these facts in mind when evaluating suitable battery products for use in a renewable energy system.

What happens to a flooded lead acid cell after only several discharge/recharge cycles? In **Figure 3** below the values 1, 2 and 3 are specific gravity readings taken at the top of the cell and values 11, 12, 13 and 14 are specific gravity readings taken at the bottom of the cell. After only 5 cycles a large concentration gradient has developed in the electrolyte (0.16 kg/l) and the capacity has dropped by 12%. This subsequently has an influence on the electrical performance of the cell and causes an uneven utilization of the active mass. Mixing the electrolyte in this situation by a standard IU-charging characteristic is not possible, as the time required to accomplish this is not available. Another possibility is to extending the standard IU charge characteristic using a second Ia (constant current) phase generating an IUIa-characteristic, which has shown to be suitable in establishing the necessary charging factor for the battery to mix the electrolyte.
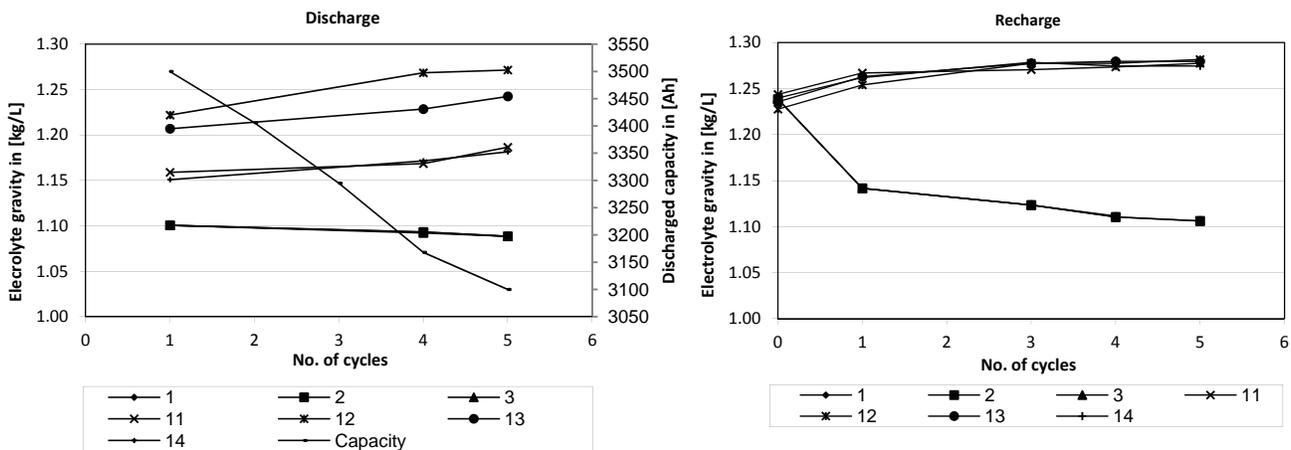


**Figure 3 - Electrolyte stratification of a 3219Ah tubular positive plate battery after cycling**

**Figure 4** shows what happens with an Ia (constant current) recharge following an initial IU (constant current/constant voltage) charge. The result is adequate mixing of the electrolyte and elimination of stratification. In Figure 4 we used an Ia charge characteristic at 5A/100Ah (150A) after 5 discharge / recharge cycles on a cell with initial capacity at the 10hr rate of 3,219Ah, discharge Vf = 1.80 V/Cell and T = 20°C/68°F. Adequate electrolyte mixing by charging to eliminate stratification under this condition took 350 minutes which corresponds to a total charge factor (CF) of 127.2% (100% CF from the standard IU-charge plus 27.2% CF from the Ia-charge).
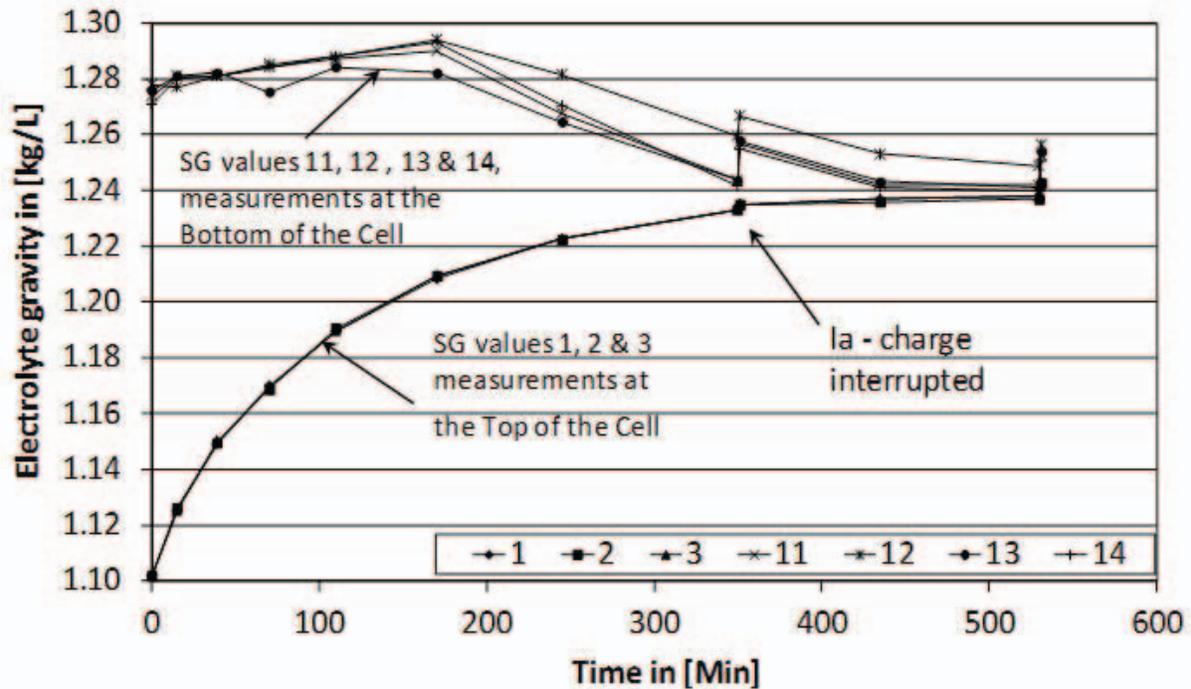
**Figure 4 - Electrolyte mixing using an Ia-charging with 5A/100Ah (150A) after 5 cycles with IU charging**

**Test parameters used in development of Figures 3 & 4 (conditions for electrolyte stratification):**
Discharge: 300A for 10hr to an end voltage of 1.80 V/Cell; Recharge IU-characteristic: 300A up to 2.40 V/Cell, switched off when current drops to 150A, Charge factor: 100%; Followed by an Ia charge characteristic: 150A up to 2.60 V/Cell. Specific gravity measurements were taken at the top of cell: Curves 1, 2 and 3; and taken at bottom of cell: Curves 11, 12, 13 and 14 )

Clearly, an IU charge followed by an Ia constant current charge will reduce the electrolyte stratification if sufficient charge time is available. Other than lack of available charge time, the main disadvantage of this charge characteristic is the high charging voltage required in the second constant current phase. These voltages can typically reach 2.60 – 2.70 V/Cell, which are often destructive to downstream electronic components.

## Ampere-hour and Watt-hour Efficiencies

Two properties used to evaluate the effectiveness of a battery system are the Ampere-hour and the Watt-hour efficiency. Ampere-hour efficiency or Coulombic-efficiency is the fraction, expressed as a percentage, of the electrical charge stored in a battery by charging that is recoverable during discharge. These inefficiencies arise from losses such as gassing and self-discharge. The Ampere-hour efficiency is defined as the reciprocal value of the charge factor (CF). Additional losses due to polarization voltages and internal resistances, are considered in the Watt-hour efficiency. The equations below illustrate clearly that the Watt-hour efficiency is always less than the Ampere-hour efficiency.

**Definition:**

$$\eta_{Ah} = \frac{Q_{Discharged}}{Q_{Charged}} = \frac{1}{CF} \qquad \text{(Ah efficiency)}$$

$$\eta_{Wh} = \frac{Q_{Discharged} \times U_{Discharge}}{Q_{Charged} \times U_{Charge}} \qquad \text{(Wh efficiency)}$$

where

| | |
|---|---|
| $Q_{Discharged}$ | = Discharged Ah, |
| $Q_{Charged}$ | = Charged Ah, |
| CF | = Charge Factor, |
| $U_{Discharge}$ | = Average discharge voltage, |
| $U_{Charge}$ | = Average charge Voltage |

The goal is to increase both the Ampere-hour and Watt-hour efficiencies of the battery in these cycling applications. This is achieved in the equations above by reducing the losses due to gassing (Ampere-hour efficiency) and reducing the average charge voltage (Watt-hour efficiency). The following discussion will demonstrate how a mechanical electrolyte recirculation system in a cycling application can achieves this goal.

A simplified diagram of a mechanical electrolyte recirculation system is described in **Figure 5**. During charging precisely controlled air bubbles are injected into the bottom of the cell via tubing and a membrane pump. Immediately after injection, the air bubbles rise in the electrolyte and mix the electrolyte by kinetic energy. The volume, pressure and the interval of air injection have to be closely controlled to eliminate potential issues such as, forced active mass-shedding and entrainment of sediments and sludge from the bottom of the cell.
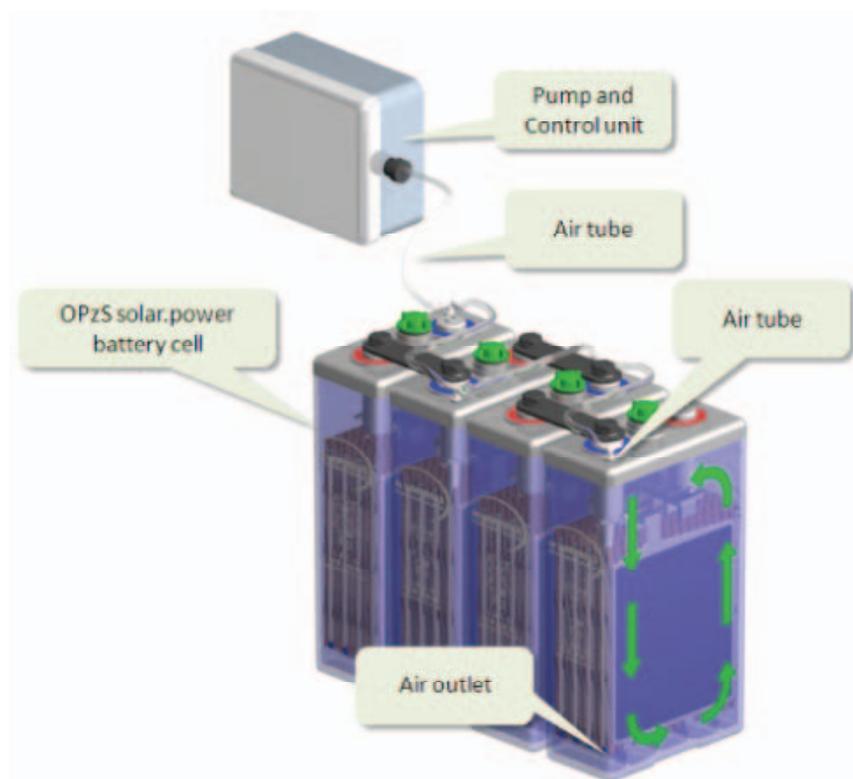


**Figure 5 - Electrolyte recirculation system (system overview)**

Two test conditions were established for the mechanical electrolyte recirculation system that corresponds exactly to the parameters given at **Figure 3**. This would ensure that conclusions could be drawn regarding the effectiveness of such a system in direct comparison to standard charging procedures.

Parameters were established for the time of start of the air injection:

a.) Immediately and continuously at the onset of charging. **Figure 6a**
b.) Injected after a cell voltage of 2.18 V is reached. **Figure 6b**

**Figure 6a** shows the first test using continuous air injection and beginning with a battery at 36% state of charge and using a standard IU charge characteristic. The result clearly shows that with injection of air-bubbles during the whole charge cycle the stratification is eliminated when a charge factor of 100% is achieved.
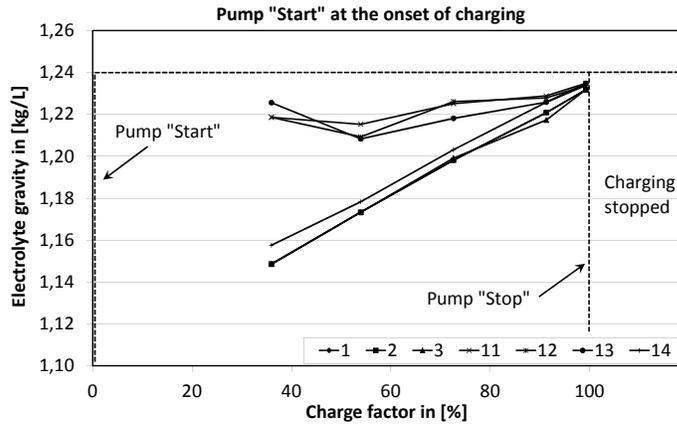


**Figure 6a - continuous pump operation during charging**

The flooded tubular lead acid battery used in this test is sized to use no more than 50% of its nominal capacity on discharge and therefore provides around 2,500 charge/discharge cycles over its lifetime. With this in mind, each recharge cycle requires approximately 6 hours' time to reach a charge factor of 100%. Therefore, the runtime of a mechanical recirculation system being operated continuously over the life of the system will result in approximately 15,000 pump operating hours.

Since the operating life of the pump is critical to the reliability of the system, it would be beneficial to reduce the operating hours of the pump and its subsequent maintenance. A second test was performed by starting the pump later in the charge cycle to see if this had an effect on the charge time or the charge factor. **Figure 6b** shows the pump starting after the charge voltage reaches a value of 2.18 V/Cell. Based on the result in Figure 6b, it is clear that the same result in charge factor and reduction in electrolyte stratification can be achieved under these conditions. For this scenario, the estimated run time of the pump over the life of the system is estimated to 8,125 operating hours.
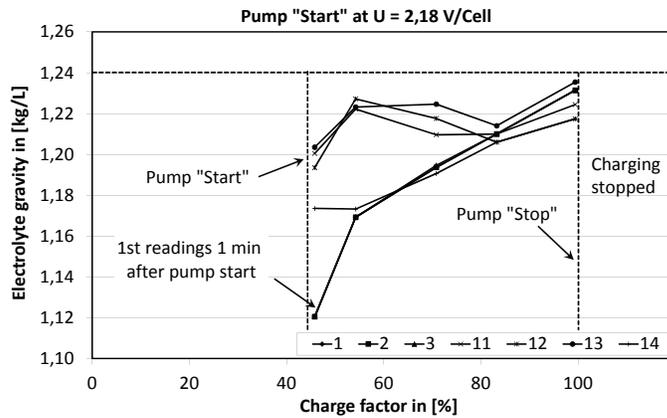
**Figure 6b - pump starting only after charge voltage reaches 2.18 V/cell**

The possibility of reducing the pump operating time further by using Intermittent air injections during the charging process presents additional possibilities for lowering the run time for the recirculation pump with the same result., However, these tests are still ongoing and will be discussed in a later paper.

Finally, **Figures 7a and 7b** describe the same 3,219Ah battery, discharged with 300A for 5 h (50% DOD) followed by recharging under two conditions:

**Figure 7a**: Recharge with IUIa-characteristic without mechanical electrolyte mixing
(IU charging with 300A up to 2.40 V/Cell until the current drops to 5A/100Ah (150A) followed by an Ia-characteristic of 150 A for an additional 6 hours up to a voltage of 2.60 V/Cell. Total Charge factor CF = 106%).

**Figure 7b**: Recharge with IU-characteristic with mechanical mixing of the electrolyte starting at U = 2.18 V/Cell. (IU charging with 300A up to 2.40 V/Cell for 12.5 hours. Charge factor CF = 106%).

A charge factor of 106% was chosen for both conditions to compensate for losses due to internal resistance and polarization. As we saw in **Figure 4** above, without the use of mechanical electrolyte mixing, a charge factor of at least 120% is needed during every recharge with an IUIa-characteristic to eliminate electrolyte stratification. **Figure 7a** shows the electrolyte stratification developed in the battery after 7 charge / discharge cycles with the IUIa charge characteristic described above and no mechanical mixing. Clearly even this IUIa charge characteristic cannot compensate for the acid stratification in this example.
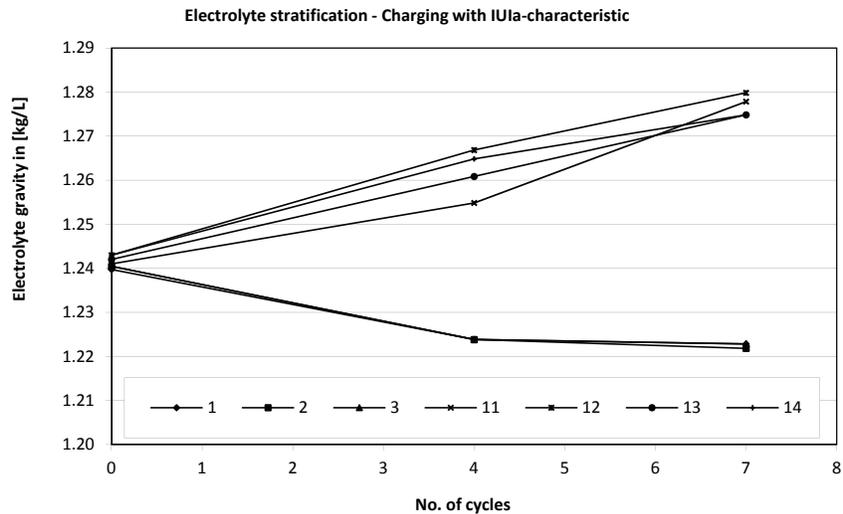
**Figure 7a - Recharge with IUIa-characteristic without mechanical electrolyte mixing**

The addition of the air circulation pump in the battery, as shown in **Figure 7b** below, along with the change of the charge algorithm to an IU characteristic, shows significant improvement in the reduction of stratification of the electrolyte. After 7 cycles the final result has a specific gravity variation of less than +/- 0.01 kg/l.
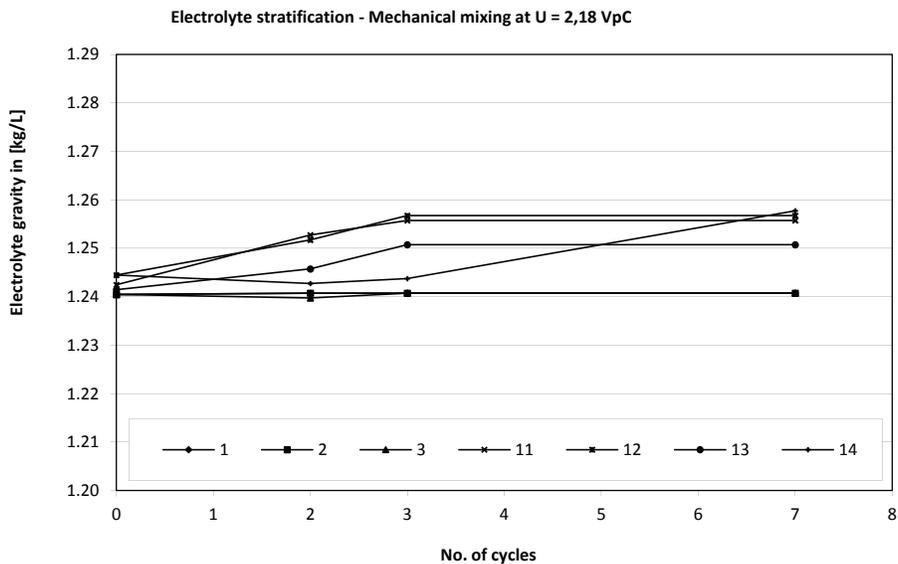


**Figure 7b - Recharge with IU-characteristic with mechanical mixing of the electrolyte starting at U = 2.18 V/Cell.**

## Results

Use of the mechanical electrolyte mixing system with an IU charge characteristic and 106% charge factor gave nearly the same result as the IUIa charge with a charge factor of 120% shown in Figure 4. In other words a 3 times higher charge factor 20% / 6% = 3.33. The following matrix provides a good comparative summary of the performance of the battery systems described in Figure 7a and 7b (with and without mechanical electrolyte mixing based on 50% DOD cycles).

**Table 1 - Standard Charges with and without Electrolyte mixing**

|  | Standard IUIa-Charge Without Mechanical Electrolyte Mixing | Standard IU-Charge With Mechanical Electrolyte Mixing |
| --- | --- | --- |
| Charge Factor CF [%] | 120 | 106 |
| AH - Efficiency [%] | 83.3 | 94.3 |
| WH- Efficiency [%] | 71.7 | 80.0 |
| Water Consumption / SERVICE COSTS [%] | 333 | 100 |
| Capacity loss due to electrolyte Stratification (sulfation and operation at reduced states of charge) | YES | NO |
| MAX. Charging Voltage | Up to 2.70 V/Cell    (112%) | 2.40 V/Cell    (100%) |
| System Costs [%] | 100 | 110 |

## Conclusions

In the cyclic applications discussed, there are clear advantages to the use of a mechanical electrolyte mixing system over the traditional charging methods.

The key effects of electrolyte stratification are clear:
1. Corrosion at the top lead and upper parts of the cell as a result of low specific gravity
2. Undercharge of the lower part of the plate due to higher specific gravity resulting in sulfation and loss of capacity.

The benefits of mechanical electrolyte mixing are demonstrated by the tests and data presented in this paper.
1. Reduced charge factor
2. Operation at a higher state of charge
3. Higher Ahr and Whr efficiencies
4. Reduced water consumption by reducing the overcharge phase.
5. Extended battery life due to reduced sulfation and corrosion at the plate surface.

One benefit that is still under investigation is the possibility of extending the life of the battery due to lowering of the average battery temperature by eliminating the heat generated during the overcharge phase. From a theoretical perspective electrolyte stratification also affects battery performance during cycling over lifetime (**Figure 3**), but conclusive investigations regarding this are ongoing.

## Summary

The beneficial aspects in efficiency and reduced service costs for the energy storage system with mechanical electrolyte mixing are clear. This paper shows conclusively that flooded lead acid batteries equipped with mechanical electrolyte recirculation system have significant advantages in round-trip Whr efficiency, service costs and life-time. These battery systems can often be retrofitted and typically the total retrofit cost corresponds to a fraction of the total battery costs, so that life cycle costs are generally not in question.

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