HYDROGEN GAS MANAGEMENT FOR FLOODED LEAD ACID BATTERIES

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INTRODUCTION

Despite the enormous growth in the use of VRLA batteries as a primary energy storage solution over the past two decades, the flooded lead acid battery remains a preferred and reliable solution for many truly mission critical back-up applications in the telecommunications, utility, and industrial/switchgear industries. To many, the longer service life and performance predictability of a flooded cell battery is an acceptable trade-off to the generally higher maintenance requirements and increased footprint.

A primary consideration for any user considering a flooded battery solution centers on the issue of hydrogen evolution. In addition to the primary focus on human and system safety, this chemical reaction also impacts battery life and maintenance economics, much of which centers on maintaining proper liquid electrolyte levels and concentrations in the flooded battery. Proper watering maintenance is critical to the long-term life and performance of the flooded lead- acid battery.

Therefore understanding the phenomenon of hydrogen evolution is an important part of the engineering for any battery system. While it is particularly critical for flooded lead acid battery systems, even VRLA batteries will vent hydrogen gas under certain conditions.

The objectives of this paper are the following:

1.) To provide a general overview of the problem, and to discuss the main factors involved in hydrogen gas evolution and its primary impact on battery system design, operation, and maintenance. Primary safety considerations will be discussed and stressed.

2.) To discuss the primary methodologies for managing and mitigating hydrogen gas evolution, from initial system design, installation, and long-term operation and maintenance of the battery.

3.) To introduce and discuss the external recombinant catalyst, a relatively new technology gaining popularity in Europe and the US for mitigating hydrogen gas evolution. We will discuss how the recombinant catalyst works, review the pro's and con's, and present both laboratory and field data regarding the impact of this catalyst technology on battery performance, life, and maintenance economics.

I. AN OVERVIEW OF HYDROGEN GAS EVOLUTION

All lead acid batteries, particularly flooded types, will produce hydrogen and oxygen gas under both normal and abnormal operating conditions. This hydrogen evolution, or outgassing, is primarily the result of lead acid batteries under charge, where typically the charge current is greater than that required to maintain a 100% state of charge due to the normal chemical inefficiencies of the electrolyte and the internal resistance of the cells. This excess charge electrolyzes the water in the electrolyte mix of sulfuric acid and water, causing free hydrogen and oxygen to be vented from the battery.

In fact, flooded lead acid batteries will outgas at varying rates under almost all conditions, even in storage where minor amounts of gas will be produced due to the normal evaporation of water and the tendency to self-discharge. In normal operation (float voltage), flooded lead acid batteries are kept in a state of maximum voltage potential in order to maintain maximum power reserve. This constant state of charge current causes the flooded battery to outgas hydrogen and oxygen continuously; room temperatures higher than the recommended ambient (typically 20°C-25°C) will accelerate this outgassing.

Outgassing is increased under conditions of battery recharge following an event which would discharge the battery. The higher the voltage under re-charge, the greater the outgassing. This tendency is greatly accelerated under abnormal conditions like charger over-voltage, or in the case of VRLA batteries under conditions known as ‘thermal runaway’, which can be caused to by a variety of conditions like charger failure or excess voltage, high ambient temperatures, cell failure, or any combination of these variables. In either case, abnormal conditions can cause significant outgassing of hydrogen and oxygen with lead acid batteries..

Water decomposition: A secondary reaction of all lead acid and nickel/cadmium battery technologies

Here we can take a closer look at the phenomena of hydrogen evolution, or ‘water decomposition’.

Water decomposition, or outgassing, is a secondary and negative reaction in lead-acid and nickel/cadmium batteries. It influences the volume, composition and concentration of the battery electrolyte, and is the result of the decomposition of water into its chemical elements hydrogen and oxygen according to $H_20 \rightarrow H_2+1/2\ O_2)$ [Eqit. 1]

Oxygen outgassing is generated at the positive electrode, while hydrogen evolution occurs at the negative electrode. The water decomposition voltage equilibrium of the reaction is: Uo (Eo) = 1.227 Volt

Figure 1 shows the single electrode potentials of flooded lead acid batteries at the x-axis of the diagram, the positive electrode range on the right (+1.7 V), and the negative-electrode range on the left side (-0.23V). The y-axis represents the gas development rate (corresponding to water decomposition current), which is equivalent to the rate of the electrochemical reaction .

Thus, when the cell voltage is higher than 1.227 V, water decomposition is unavoidable, and varies accordingly. The rate of the decomposition of water and the corresponding volumes of oxygen and hydrogen that are formed, depends on the position of the individual electrode potential, or overcharge voltage.

In lead-acid batteries, water decomposition is a significant issue, because of the high open circuit voltage of lead acid batteries that are typically far above the 1.227 V.

Fig. 1 illustrates the typical parameters of this outgassing reaction:

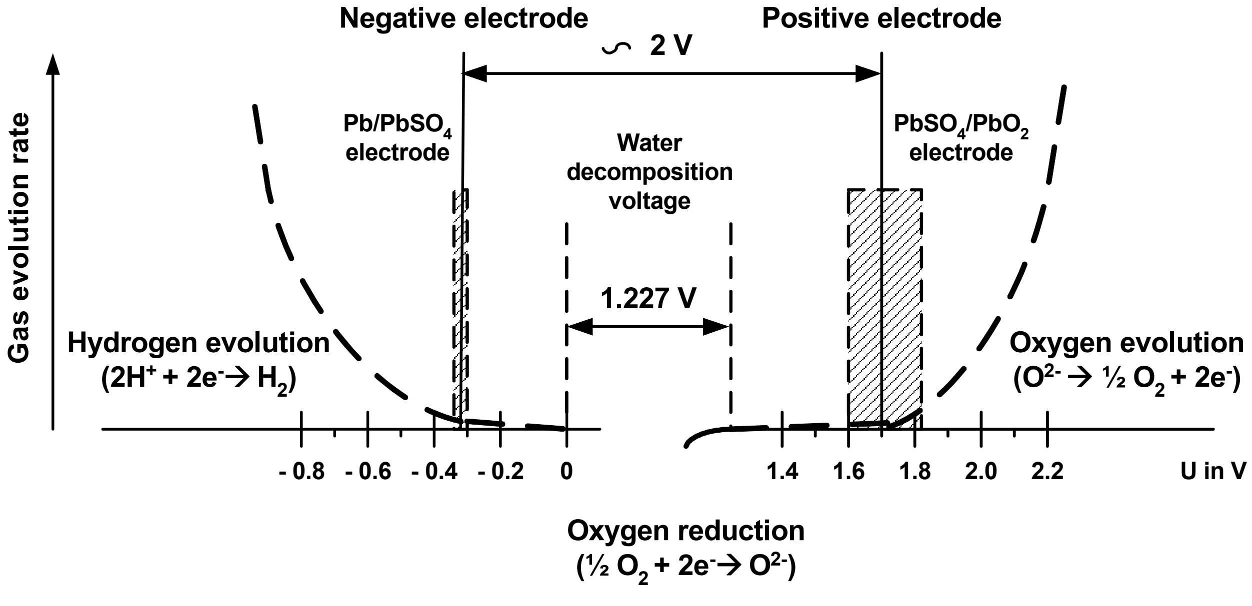

Fig. 1 - Open circuit (equilibrium) potentials of the positive and negative electrodes in a lead acid battery and the evolution of hydrogen and oxygen gas

The gradual increase at the beginning of the two curves indicates that both hydrogen and oxygen generation reactions occur more slowly, as long as the potential difference relative to their original overvoltage remains fairly small. But if the overvoltage exceeds certain values (e.g. 2.40 V), then both curves show a steep increase. This means that hydrogen as well as oxygen generation increases substantially in volume when the electrode potential is increased, typically during boost or equalizing charge.

When the battery is overcharged, hydrogen and oxygen evolution are primary reactions (except for a small content of current related to corrosion) that occur. Then the potential of the positive electrode is shifted to a more positive value (more to the outer side of the diagram), while the potential of the negative electrode is shifted to more negative values (more to the outer side of the diagram). This, compared to the state of open circuit voltage, results in current flow through both electrodes that is shifted to a higher value. When the overcharge current is the constant parameter, e.g. during equalizing charges, the cell voltage follows to the required polarization of both electrodes in dependence to the adjusted current. When the overcharge voltage is fixed (like at float operation +2.23 V or boost voltage + 2.40 V), a corresponding current is reached in dependence on the required polarization of both electrodes.

The fact that hydrogen evolution starts at potentials lower than the open circuit voltage potential of the Pb/Pb electrode means that hydrogen evolution can never be avoided completely. This is important for design of valve regulated sealed batteries. (Obviously a 100 % sealed design is not possible and should be avoided.)

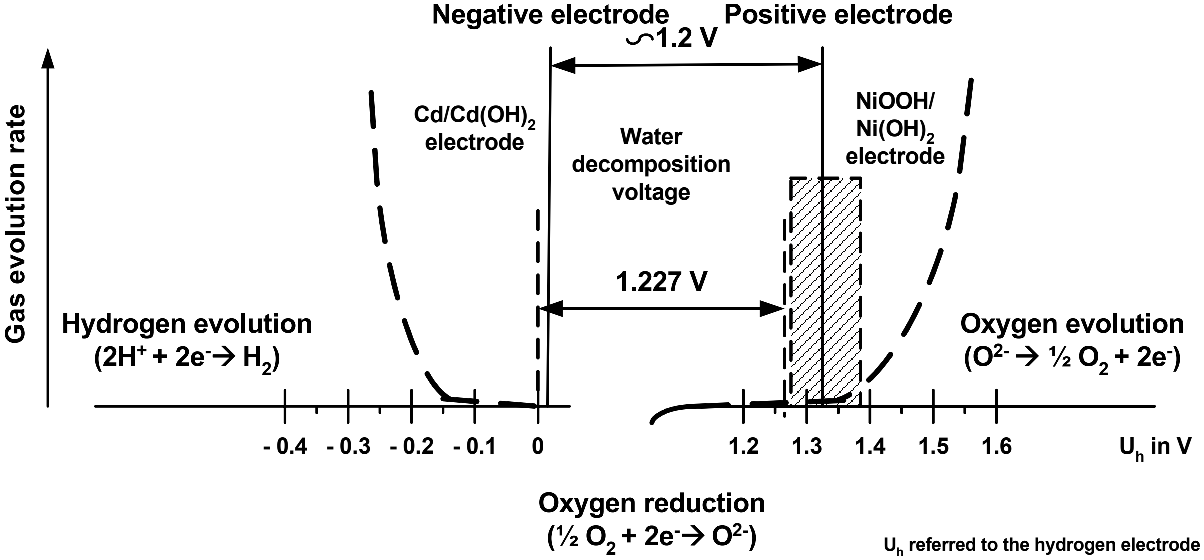

Fig. 2 - Open circuit (equilibrium) potentials of the positive and negative electrodes in a nickel cadmium battery and the evolution of hydrogen and oxygen gas

The figure 2 illustrates the situation for the nickel/cadmium battery, similar to what was depicted in Fig. 1 for the lead-acid battery. The electrode potential is shown at the x-axis.

The most significant difference between the NiCad and the lead-acid battery with respect to water decomposition, is that the equilibrium potential of the negative electrode (cadmium electrode) is more positive than the potential when hydrogen starts to be evolved. Oxygen evolution cannot be avoided at the positive electrode, because the potential of this electrode exceeds the equilibrium value of oxygen evolution. But the evolution rate und normal conditions is rather low in comparison to the lead acid batteries under open circuit conditions

Influences on the gas development rate

- **Charging voltage**

The relationship of the current / voltage dependence is demonstrated by the following test, carried out on six vented lead selenium cells with a capacity of 1500 Ah (for clearer statistical demonstration). The battery under test was subjected to a variety of different charging conditions for a period of 24 hours. After 24 hours the charging current of the 6 cells were measured. The test was carried out in a climate chamber, to avoid significant influences by the temperature on the test result.

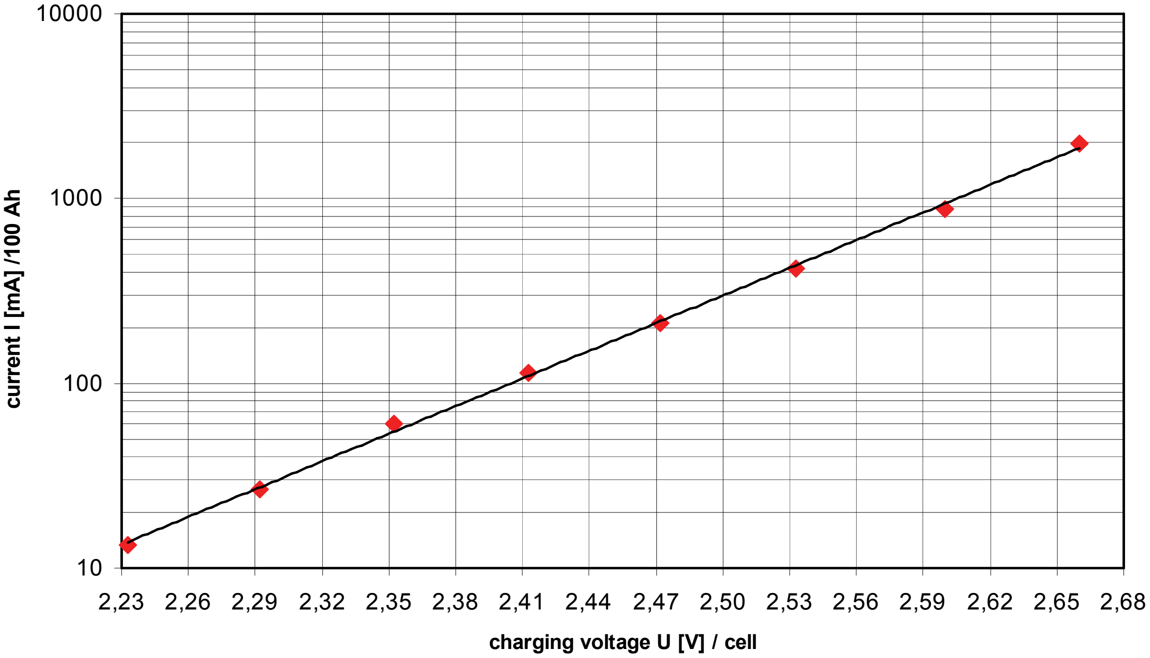

Fig. 3 - Charging current and the impact of overcharge voltage measured on new, flooded lead selenium cells

The curve shows a direct relationship (dependence) of the charging current (corresponding to the gas development rate) and charging voltage. In calculating a single measurement that best fits the values from the diagram, a common logarithm dependence (alternatively a logarithm to basis 2 dependence) can be observed.

From a recalculation, the following dependence is then given:

$U_1 - U_2 = 0{,}2 \times \log_{10}\left(\frac{I_1}{I_2}\right)$ [Eqit. 2] alternative $U_1 - U_2 = 0{,}06 \times \log_2\left(\frac{I_1}{I_2}\right)$ [Eqit. 3]

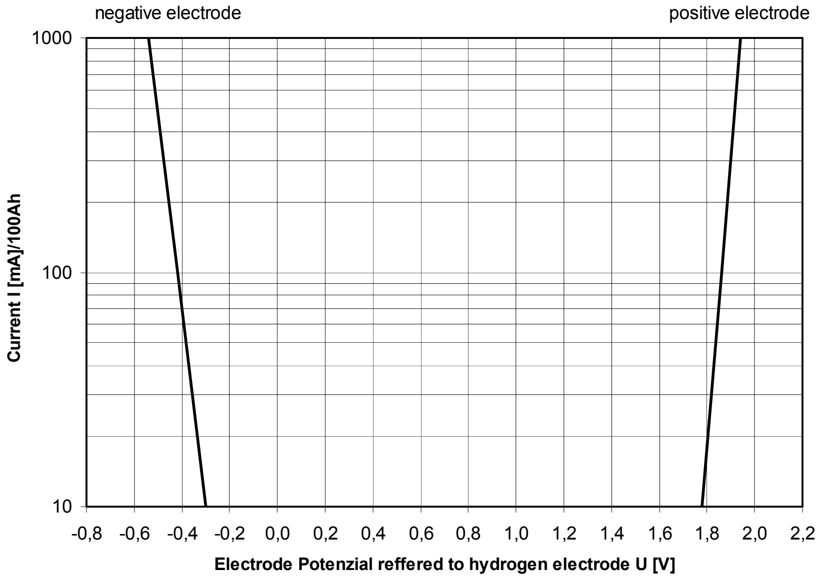

Fig. 4 - Charging current and the impact of overcharge voltage measured on new, flooded lead selenium cell

The two lines in the diagram represent slopes of 0.12 volt per current decade for hydrogen evolution and 0.08 volt per current decade for oxygen evolution, and clearly explains the results of the test above. The addition of the slopes of the two lines (0.12 + 0.08 volts) leads to the above calculated rule for flooded lead-acid batteries, which demonstrates that the increase of the overcharge voltage by 0.2 volt increases the current tenfold, and that a 0.06 volt increases the current two times.

- **Temperature**

The kinetic speed of the chemical reactions inside the battery depends on the temperature. The general approximation is that the increase of the temperature by 10K (10 °C) doubles the reaction rate of the internal processes, e.g. corrosion (aging), self discharge and the corresponding hydrogen and oxygen gas development rates.

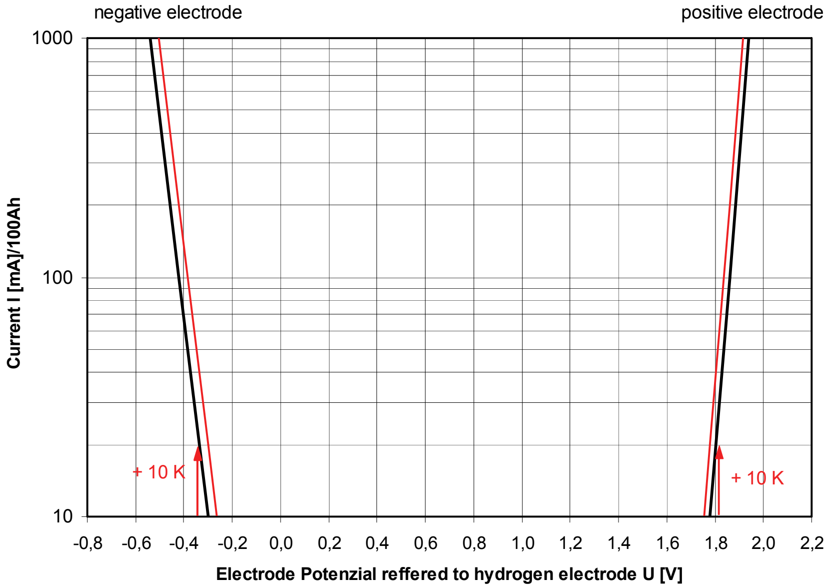

Fig. 5 - Charging current and its dependence on temperature, measured on new, flooded lead selenium cells

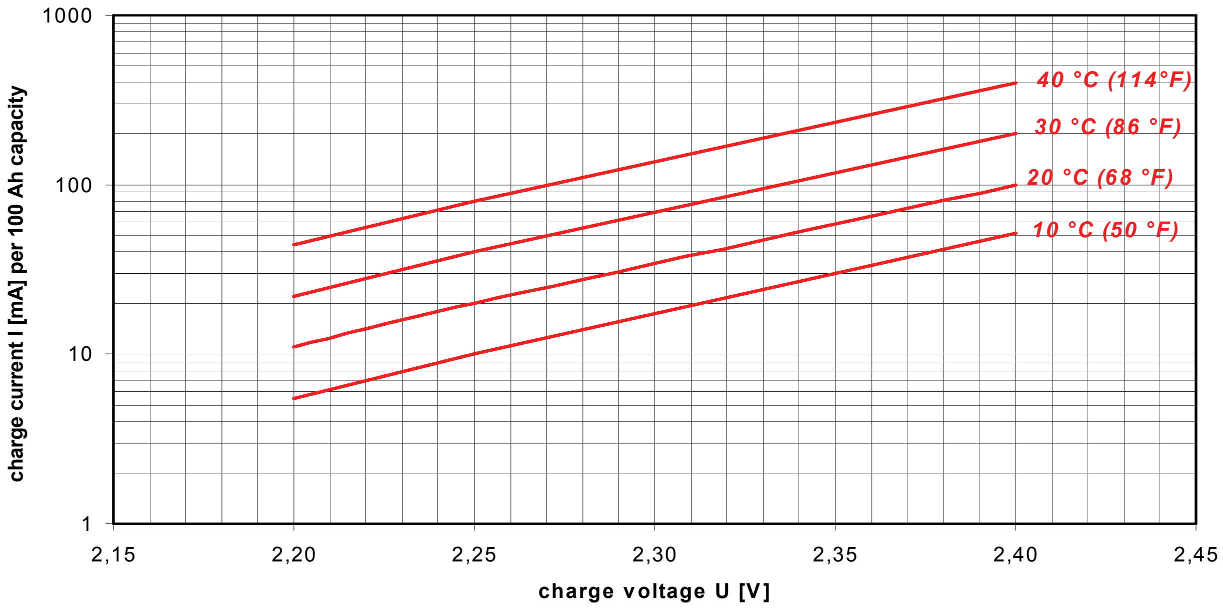

Fig. 6 - Charging current and its dependence on temperature and charging voltage, measured on new, flooded lead selenium cells

- **Impact of accidental alloy additions by the use of contaminated water for maintenance**

The high potential voltage (related to the standard hydrogen electrode) of the lead electrodes have a high influence on the hydrogen gas development, particularly if the lead electrode is connected in conductive electrolyte (like sulfuric acid) along with a metal with lower potential voltage. The result is the implementation of a local element and a higher self discharge of the lead electrode and a higher gas development rate. That effect can be observed if contaminated water (not distilled, purified water) is used to refill flooded batteries. The addition of metal contaminants with lower potential causes higher water consumption and a higher hydrogen development rate. This is also valid for electrochemically intercepted metals, such as when the corrosion process dissolved grid additions, like calcium or antimony. This situation can occur as a consequence of grid corrosion during the aging of the battery. The dissolved substance is precipitated at the negative electrode surface and forms a large surface area. As soon as the antimony content of the grid alloy is reduced to a smaller content and combined with an addition of selenium to the grid alloy (positive influence on grid hardness and corrosion speed) the antimony effect is extensively diminished.

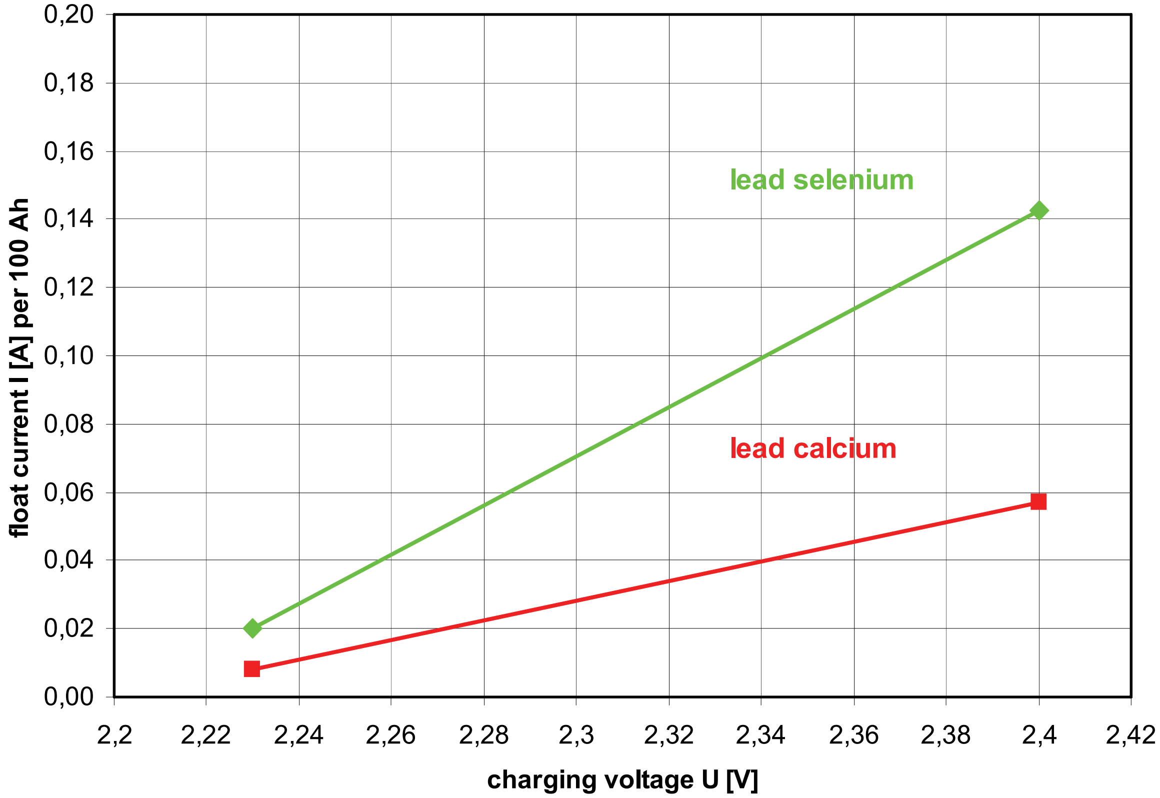

Fig. 7 - Charging current and its dependence charging voltage measured on flooded lead selenium and lead calcium cells

Amount of hydrogen gas per overcharged Ah

The relationship between current and the amount of decomposed water or the equivalent volumes of gas generated can be evaluated from using the Faraday constant. (Faraday constant is the amount of electric charge per mole of electrons = 96487 coulomb (As)/mole) of 26.8 Ah.)

Negative electrode: $2H^+ + 2e^- \rightarrow H_2$ [Eqit. 4]
Positive electrode: $O^{2-} \rightarrow 1/2\ O_2 + 2e^-$ [Eqit. 5]

The molar weight of H_20 is = 1g + 1 g + 16 g = 18 g. Based on 1 Ah it means

1 Ah decomposes = 18 g (Water) / 53.6 Ah (transferred energy)= 0.3360 g/Ah [Eqit. 6]

The level of the resultant gas volume generated by the decomposition reacion depends on temperature and pressure.
For normal ambient temperatures of 20°C (68 °F), or respectivle 25°C (77°F) and normal pressure of 0.1013 Mpa (1 atm), the amount of created gas is 0.4488 litre (68°F)/ 0.4564 litre (77°F) of hydrogen gas and 0.2244 litre / 0.2281 litre (77°F)of oxygen gas per overchagarged 1 Ah capacity.

The IEEE 484 norms confirm this value.

"... *5.4 Ventilation*
Maximum hydrogen evolution rate is $\underline{1.27 \times 10^{-7}\ m^3/s}$ *(0.000269* ft^3*/min) per charging ampere per cell at 25 °C (77 °F) at Standard pressure. The worst-case condition exists when forcing maximum current into a fully charged battery. ..."*

So if we recalculate seconds to hours the value from the IEEE norm is very close: $\underline{1.27 \times 10^{-7}\ m^3/s}$ x 3600 x1000 =

$$V_{H2} = 1.27 \times 10^{-7} \frac{m^3}{s} \times 3600s \times 1000 = 0.4572 \frac{l}{Ah}$$ litre per cell per overcharged Ah.

II. PRIMARY EFFECTS AND IMPACT OF HYDROGEN GAS EVOLUTION

Human, System, and Facility Safety – Threat of Fire and Explosion

Oxyhydrogen is a mixture of hydrogen and oxygen gases, typically in a 2:1 atomic ratio; the same proportion as water. At normal temperature and pressure, oxyhydrogen can burn when it is between about 4% and 94% hydrogen by volume**.** The most critical issue with regard to hydrogen outgassing is the potential risk of fire and explosion, and it is the most important consideration in the planning for flooded battery installations. Hydrogen is an odorless, colorless gas, which exists in the atmosphere at natural concentrations of 0.01%. Battery outgassing releases free hydrogen into the room environment, and at a concentration of 4% it reaches the lower explosion level (LEL) where it is combustible, and a potential threat to human and system safety. Oxyhydrogen explosions can be a hazard where the hydrogen gas concentration is higher than 4 % in total volume, for example in large lead-acid batteries. Ignition sources are open fire, sockets, and even sparking from light switches is possible. This outgassing scenario, while rare, can become an issue typically under unusual conditions, like abnormal over-voltage to the battery or abnormal high ambient heat conditions (e.g. failure of HVAC room cooling systems). Most codes and regulations mandate facility design to ensure a maximum allowable limit of 1% hydrogen concentration in battery rooms.

Self discharge of batteries

Flooded lead-acid batteries are often delivered filled with electrolyte. Once the electrodes of a battery are filled with electrolyte, the corrosion and self-discharge processes begin. During long-term storage, vented lead-acid batteries require periodic refresher charges for the equalizing of these corrosion and self-discharging side effects. Technically, the initial electrolyte filling date represents the beginning of service life of the battery. A self discharge rate of 2-3 % of the nominal capacity per month is a typical value at 20 °C (68°F) ambient temperature

Watering Maintenance Cycles

Probably the most noticeable consequence of hydrogen outgassing is the direct impact it has on the watering maintenance of flooded batteries. In fact, it was the problems of significant watering maintenance requirements with the original high antimony lead acid flooded batteries that drove the original development of both lead calcium and lead selenium grid alloy designs. Users are directly impacted, as batteries with higher rates of outgassing will increase the costs and effort required to maintain proper levels of electrolyte for proper battery operation and life expectancy. There are numerous factors which impact watering maintenance, including grid alloy type, ambient temperatures, voltage charging levels, and battery age.

The maintenance intervals for battery watering are dependent on the water decomposition rates at ambient temperature, number of cycles (charge/ discharge) and aging effect. Other factors would include any conditions of over voltage leading to unusually high levels of outgassing. The net effect is the assumption that water decomposition rates will increase over the life of the battery, where the increase in float current is generally linear and the water volume consumed can be described as an integral (polynomial of the second order). This would typically result in a scenario where if the normal practice of watering maintenance (which depends on the cell type) is initially every 3-5 years, then we might see that interval reduced toward the end of battery life (depending on the water reservoir and cell) with intervals that can shrink to a couple of times a year.

III. PRIMARY STRATEGIES FOR MITIGATING HYDROGEN GAS EVOLUTION

Proper Ventilation System Design

The IEEE 484 says:

“ ... 5.4 Ventilation

The battery area shall be ventilated, either by a natural or mechanical ventilation system, to prevent accumulation of hydrogen. The ventilation system shall limit hydrogen accumulation to less than 2% of the total volume of the battery area. ...”
“... A battery area that meets the above ventilation requirements should not be considered a classified (hazardous) location; thus special electrical equipment enclosures to prevent fire or explosion should not be necessary. ...”

There are a number of regulatory agencies and bodies that have established well defined standards and guidelines on proper ventilation design and facility requirements/calculations for battery rooms and power systems, including OSHA, ANSI/ASHRAE, IEEE, NFPA, and others here in the US. While hydrogen has an LEL of 4%, it is a universal guideline to design proper ventilation systems that would view 2% hydrogen gas levels as the absolute upper limit, with 1% concentration maximum limits being specified in most cases. Ventilation systems are designed to maintain human safety, to ensure fire safety, and to promote maximum equipment reliability and safety, in that order. An additional consideration in the design of ventilation systems is the regulation of temperature, as higher room temperatures can significantly increase outgassing while reducing battery life.

There is a wide difference in the outgassing rates between sealed VRLA batteries and flooded (vented) batteries. Flooded batteries outgassing levels can be at least 50 times greater than sealed VRLA batteries, particularly with its liquid electrolyte venting gas continuously under normal float operation. For this reason flooded batteries are typically located in dedicated battery rooms removed from personnel and most systems, and are installed in step or tier open battery racks for access and maintenance. Proper ventilation is critical for dedicated flooded battery rooms, both in terms of preventing gas buildup as well as to separate the battery room air from the rest of the facility. At a minimum, the general assumption is that dedicated battery rooms should have ventilation systems in place capable of moving or replacing room air two times per hour.

In most cases, VRLA batteries do not require special ventilation considerations, and small to medium size systems can often be installed in system enclosures, racks, or cabinets using the available building ventilation system. This is primarily due to the sealed design of the product, the growing use of internal recombinant catalysts, and the use of safety pressure valves to vent potential gas, particularly under abnormal or fault conditions. The VRLA will typically produce very low levels of gas under normal float and charge/recharge conditions. (One exception is in the event of a condition known as ‘thermal runaway’, which can be caused by a number of factors including improper charging, high temperatures, charger overvoltage failure, and internal cell failure. A VRLA battery in thermal runaway will continuously vent potentially significant levels of hydrogen gas until corrective action is taken to reduce the charging voltage or shut the system down. Flooded batteries are largely immune from the scenario of thermal runaway.)

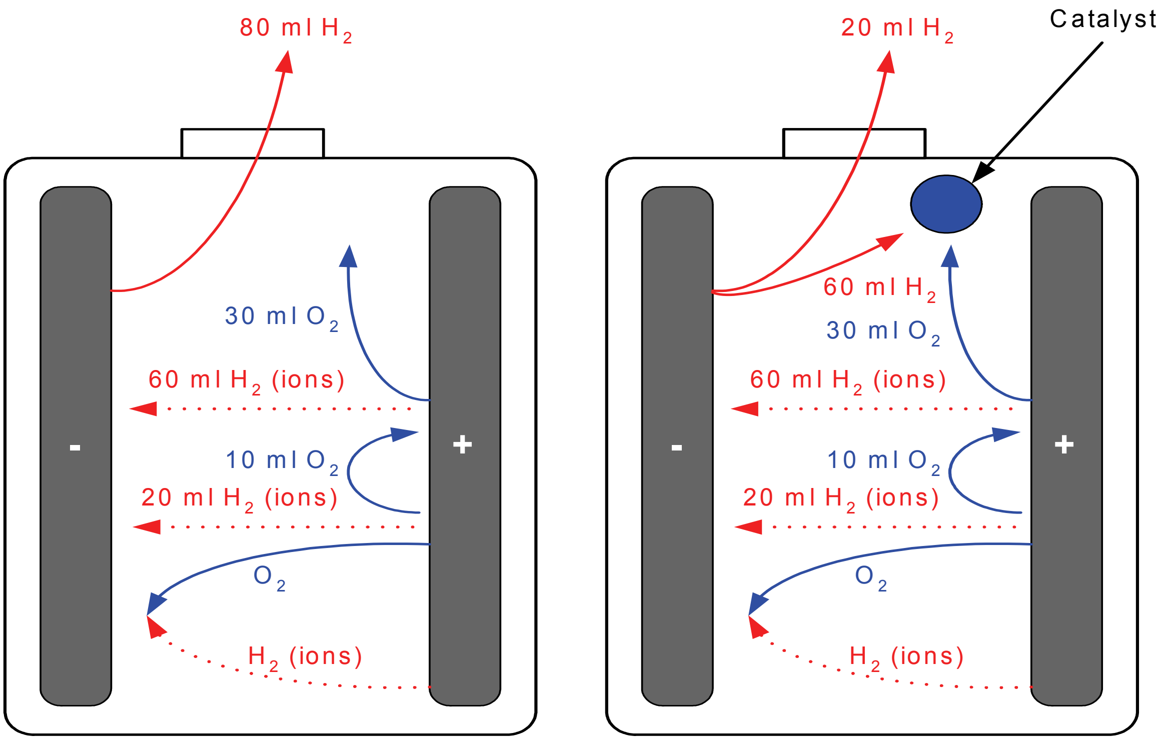

Figure 8 – Recombinant activity within VRLA cells.

Outgassing occurs even with the use of VRLA AGM cells, though at lower levels. With the use of a catalyst vent cap, oxygen gas and hydrogen gas in the upper cell space recombine to form water, thus preventing dry out of the cells.

In either case, the primary tool for evaluating the ventilation system requirements is the use of precise manufacturers' data for battery outgassing characteristics and established formulas from groups such as the IEEE (US) and EN (Europe) to calculate the maximum potential hydrogen gas evolution in any flooded battery installation. (This could even apply to certain VRLA installations in the absence of accurate MSDS sheets or manufacturers' data. In such cases, there are Codes that will mandate a minimum continuous ventilation rate (typically one CFM/minute/sq.ft. of floor area for a VRLA battery system.)

European and North American conventions for calculating hydrogen ventilation requirements are similar. The ventilation requirements in Europe are based on the DIN EN 50272 part 2 (German version). The basis for the calculation is an absolute concentration limit of the hydrogen gas at 4 % in ambient air, and a safety factor of 5.

While hydrogen evolution is a mandatory consideration with any battery type, users can begin by minimizing the amount of hydrogen outgassed from the battery. Maintaining low electrolyte temperatures, maintaining float voltages at the low end of the battery manufacturer's recommendation, and limiting frequency, amplitude and duration of boost charging, are all valuable battery management techniques in reducing the amount of hydrogen produced, and reducing watering intervals.

A comparison of the typical calculations and formulas used for determining hydrogen evolution under both IEEE and EN standards are available upon request. Please contact Carey O'Donnell at codonnell@mesa-tec.com

Hydrogen detection systems and alarms

Though there is no specific OSHA requirement or standard for the use of hydrogen detection systems, it can be an effective and increasingly cost effective means of monitoring potentially dangerous levels of hydrogen gas. Gas monitoring can initiate alarms warning of dangerous gas levels, and be configured to initiate appropriate actions to mitigate the gas buildup. Typical remedial actions can include initiating ventilation systems for maximum airflow capacity, initiating a system shutdown, and sounding audible, visual, and network alarms to evacuate personnel if necessary.

Though the LEL for hydrogen gas is 4%, most hydrogen detection systems are configured to initiate the first alarm when hydrogen gas reaches a level of 1%, and then to sound a primary alarm when the gas concentration reached 2% to initiate a direct response, to include actions like evacuation and energizing ventilation systems. In all cases, hydrogen detection systems are intended to augment human and system safety in sites with flooded batteries. Additionally, systems often include the monitoring of oxygen levels, as reduced oxygen levels can lead to dizziness and loss of consciousness in personnel. Early warning of lowered oxygen levels (typically set if oxygen levels drop below the OSHA mandated volume level of 19.5%) can help prevent injury and accidents.

Dedicated flooded battery rooms and separation

Most codes and regulations will require flooded battery systems to be installed in dedicated battery rooms, which are physically separated from other areas in the facility. The room location and layout needs to ensure that the batteries are not located near a localized source of heat, and that the room, structure, and doorways/openings meet all applicable Fire and Building Codes for fire resistance. It is not a good practice to co-locate other electrical or electronic systems in this same battery room area.

Minimizing Static and Electrical Discharge

Static electricity is a resting electrical charge, which is usually caused by friction (e.g. from friction of a plastic sheet and battery lid) and separation. Friction can generate a small heat exchange between two different ‘partners’. This change of temperature activates the material molecules. If two materials are then separated, then it is possible to realize a transmission of electrons from one material to the other. During the transmission an electrical field results from a deficiency or a surplus of electrons, which is called static electricity. The simple separation of two materials, like a plastic (vinyl) sheet and lid of a battery, can cause the same kind of electron transfer between the materials and thus produce static fields. The level of static energy produced depends on the friction or separation of the submitted materials, the extent of the friction or separation, and the relative air humidity of the environment. Plastics produce generally the strongest static charge. Low levels of humidity, typical in the winter with heated areas, increase the likelihood of static discharge. Materials, which are not detrimental to the transmission of electrons are called insulators. Examples of these are vinyl, Styrene/Acrylnitrile–SAN or Acrylonitrile-Butadiene-Styrene-ABS, glass and air.

We should keep in mind that even insulators can load “themselves" statically. This is important to remember as even during normal battery states such as float operation or storage, the development of oxygen and hydrogen gas is present. With an energy input of 19µJ, the hydrogen / oxygen gas can be ignited, thus a static discharge has enough energy to ignite the hydrogen gas. Safety practices should include:

- When handling batteries, all clothing and materials should have a surface resistance of $\leq 10^{8}$ Ω and an insulation resistance of $\geq 10^{5}$ Ω. Cotton clothing should be used when working on flooded batteries.
- After cleaning, dry the battery with appropriate means, e.g. with compressed air or cleaning cloths. Never clean batteries with cloths made from synthetic material.
- Never cover batteries with plastic or synthetic material sheets.
- Use proper personal grounding straps when working on flooded batteries, and always use insulated tools.

Safety distance

In close proximity to the battery dilution of explosive gases does not always occur, and hydrogen, for example can pool in higher concentrations in small areas close to the battery. Therefore a safety distance between the battery and spark, flame or heat sources (max. surface temperature 300 °C) must be observed. The extension of explosive gas depends on the gas release rate and the ventilation close to the source of release. The safety distance requirements are base on the DIN EN 50272 part 2 (German version). For calculation of the safety distance from the source of release, there are well established formulas which apply to the hemispherical dispersal of gas.

Typical calculations and formulas for safety distance calculations in accordance to EN standards available upon request. Please contact Carey O’Donnell at codonnell@mesa-tec.com.

External Recombinant Catalysts: Hydrogen Gas Mitigation Technology

Another way to reduce the hydrogen gas dvelopment and water loss of flooded lead-acid batteries is to use catalytic devices to recombine the gaseous hydrogen and oxygen to water. This idea is very old; as early as 1912 a patent was granted to Edison to remove gases from storage batteries by using an electrically heated platinum wire in the gas for the recombination of hydrogen and oxygen.

In the past two decades, there has been a significant increase in the research and development of external recombinant catalyst technology as a primary mechanism for reducing the problems associated with hydrogen gas evolution in flooded lead acid batteries. Much of this research and development into external catalysts has been centered in Europe, given the overwhelming installed base of older antimony and newer lead selenium flooded batteries.

The basic concept is to create a self-contained recombinant catalyst system, which is installed externally to the flooded battery. This recombinant catalyst must be able to capture the bulk of the hydrogen gas that escapes from the battery under normal float and charge/recharge conditions, and recombine the outgassed hydrogen with free oxygen in the air to form water, which is returned to the battery. Integral to a properly designed water recombination system is the use of an encapsulated catalyst, typically palladium, to promote the chemical recombination of hydrogen and oxygen. Care must be taken in the design of a palladium catalyst, to ensure that it is encapsulated, or ‘sealed’ to prevent the potential of palladium poisoning of the battery electrolyte. The entire catalyst system is encased in a plug, to capture the outgassed hydrogen gas, as well as the resultant water vapor from recombination.

When the catalyst recombination system is used, the hydrogen and oxygen gases which evolve during water decomposition are fed into the catalyst recombination plugs. The gas does not pass the catalyst, but flows along its surface. A layer of porous active carbon protects the catalyst against substances that might escape from the battery in traces and deactivate the catalyst. (Sulphur, arsenic and antimony are such substances.). Empiric field data supports that if the catalyst is designed properly with sufficient protection, the life expectancy of the catalyst can exceed that of the battery life time of 20 years.

Fig. 9 – With proper design the catalysts can reach an age of more than 20 years (units installed in 1984)

Fig. 10 - RWE Mülheim / electric power transformation substation for steel mill (installed 20.04.1984 / replaced 2007)

By means of an integral catalyst, these gases are recombined in the form of water vapour. This water vapour condenses on the sides of the catalyst vent plugs. The resultant drops of water flow downwards and are returned to the battery.
The entire recombinant plug is mounted over the vents of the flooded cell, in lieu of traditional flame arrestors.
The efficiency of the catalytic-recombination device is always limited to less than 100%, because a small part of the gas leaves the device without being recombined. In stationary applications, typical efficiencies of 85% can be achieved. More recent catalyst product development in Europe includes improved valve design to increase the prevention of escaping gas. Recent recombination catalyst designs in Europe claim recombination efficiencies of up to 99% of all outgassed hydrogen under normal float and charge/recharge conditions for flooded batteries.

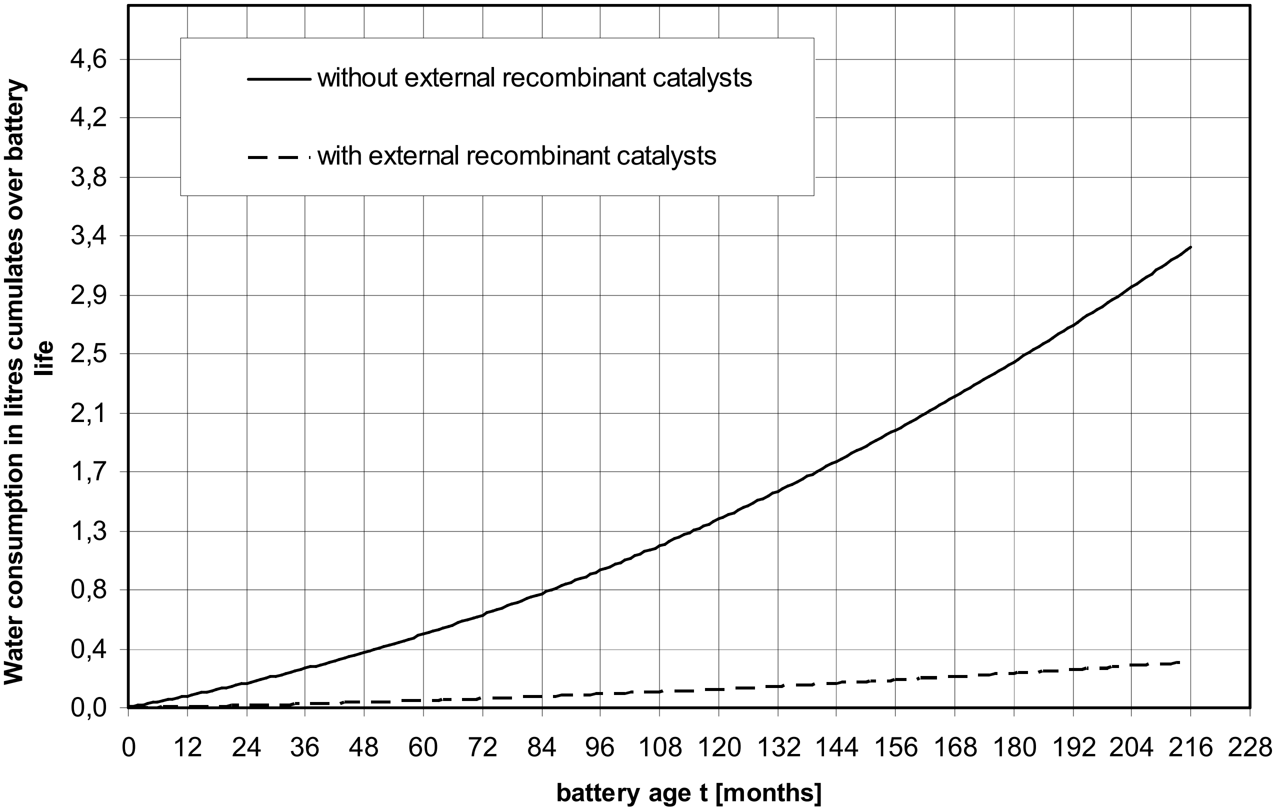

Fig. 11 - **Comparison of flooded battery water consumption with and without external recombinant catalyst**

Making the catalyst system an external component to the battery was a carefully considered choice. The recombination of hydrogen and oxygen is an *exothermic* process, where heat is generated as a by-product of this chemical recombination process. The recombination reaction is heat-intensive (ΔH = - 285.8 kJ/mole: and consequently catalytic recombination devices in general are faced with the problem of heat dissipation. 30% of the heat is generated by the condensation of vapour at the side walls.) Locating the recombination process outside of the active battery system eliminates a source of internal heat which would be potentially detrimental to the battery.

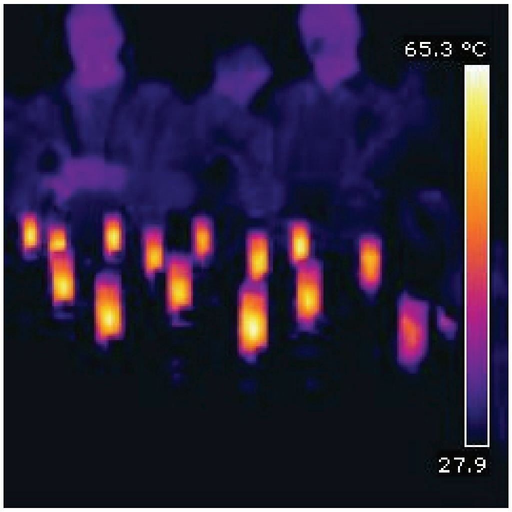

Fig. 12 - **Heat development of catalyst plugs during recombination process (infrared image)**

Proper design for safe operation, even in the event of over-voltage charging is important. Designing the recombination process to be self-limiting is a subtle but effective method to ensure safe operation of the catalyst. In a self-limiting design, when the recombination rate exceeds a certain value, the stream of water vapour flowing back from the catalyst stops further access of the hydrogen/oxygen mixture to the catalyst. Under overcharge or excess outgassing conditions, the catalyst will vent the increased gas pressure directly for safety; under these abnormal conditions the recombination rate and the heat generation are reduced, as is the efficiency, because a larger share of gas must leave the device without being recombined.

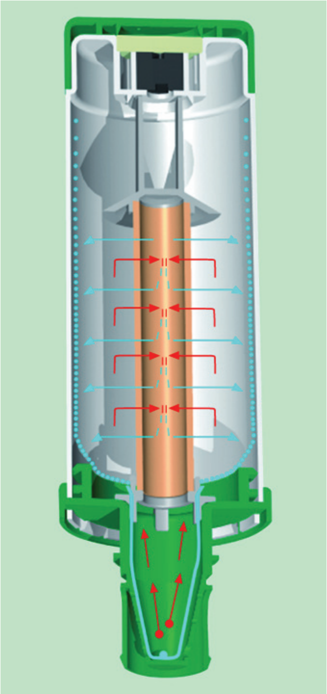

Fig. 13 - Catalyst plugs during recombination process

This was a concern with the adaptation of recombinant catalysts in sealed VRLA batteries, which was included to address some of the problems of premature dry out and failure, due to insufficient recombination of the hydrogen gas.. Early experience with the internal recombinant catalysts in VRLA demonstrated a variety of potentially significant life-reducing impacts, due to the increased heat generation from exothermic recombination, particularly at the negative electrodes. The use of an external recombinant catalyst, fitted to the battery as a component outside of the battery, avoids the potential for heat rise within the battery. Advocates for the external catalyst design view this separation of the recombination process from the active internal components of the flooded battery as a step in creating a flooded battery with a low-maintenance profile of a sealed battery with the attendant increased life expectancy and no restrictions on battery operation.

There are a number of important considerations in the proper design of any external recombinant catalyst technology. First is the need to include a spark arrestor system into the entire catalyst design, as the external catalyst is typically mounted over the battery vents where traditional flame arrestors are placed. Also, an external recombinant catalyst must be equipped with a high reliability bi-directional valve, particularly under higher-voltage events like equalize charging and worse, over-voltage conditions due to malfunctioning or improperly set battery chargers. Under these conditions, the external catalyst will realize significant reductions in the efficiency of the recombination process, but will allow for the venting of substantially increased gas pressures within the battery, avoiding problems which could occur with an over-pressured battery. On opening at low pressure the valve helps maintain the stoichiometric relationship of hydrogen and oxygen gas in an optimal balance. In other words, the bi-directional valve should be designed to promote positive pressure with negative pressure security (in the event of over voltage conditions).

The potential benefits of this technology are significant. In Europe, regulatory bodies are increasingly recognizing the performance impact of properly designed recombinant catalysts. In particular, new ventilation guidelines established, outlined in EN 50272-2 / DIN VDE 0510 Part 2 (European standards), now allow for up to a 50% reduction in ventilation requirements for flooded batteries equipped with properly designed recombinant catalyst systems. This recognition is based on demonstrated performance over two decades of the reductions in hydrogen gas realized from recombinant catalysts systems installed on flooded batteries.

Additionally, the use of an external recombinant catalyst has a significant impact in reducing the watering maintenance requirements for flooded batteries. The economic benefits are substantial, as field data from certain catalyst designs increasingly supports the design goal of achieving flooded battery maintenance profiles approaching those of sealed lead acid batteries.

IV. CONCLUSIONS

Hydrogen gas evolution is an unavoidable and inherent characteristic of flooded battery installations. In fact, flooded batteries outgas hydrogen continuously, under all states of operation, including storage (self-discharge), normal float voltage, and particularly under over-voltage conditions like equalize charge.

The potential impact of hydrogen outgassing, if not addressed, can be serious. At levels approaching 4% concentration, hydrogen gas build-up can present a danger to personnel, facility, and system safety. Hydrogen outgassing can cause problems with corrosion of the battery and components. Over the life of the battery, the rate of outgassing will directly impact watering maintenance, as the greater the outgassing, the greater the cost in ensuring that the batteries are maintained with proper electrolyte levels. Additionally, frequent watering can introduce other variables into the life expectancy of a flooded battery, such as using contaminated (non-distilled) water to refill battery levels.

There are a number of well-established methodologies for mitigating outgassing in flooded batteries. These include the separation of flooded batteries in dedicated rooms with enhanced fire protection design, the critical need for proper ventilation of battery rooms, the use of hydrogen detection systems to notify personnel and networks of potential problems, and good practice to eliminate static electricity and electrical discharge as a potential energy source for combustion..

A relatively new technology that has emerged in this effort is the external recombinant catalyst. The external recombinant catalyst is a potentially significant technology in the battle to mitigate the negative impact of hydrogen gas evolution in flooded batteries. While it is not a direct substitute for the well established methodologies described above, the external recombinant catalyst has significant potential to the US battery industry..

Two decades of empiric field data in Europe, from an installed base of external recombinant catalysts on over 3 million batteries, strongly supports the idea that properly designed external recombinant catalysts are a significant addition to the arsenal of tools aimed at mitigating the problems of potentially dangerous hydrogen gas evolution. Newer EN ventilation guidelines in Europe now officially recognize the impact of external recombinant catalysts on reducing hydrogen gas associated with flooded batteries, allowing for a reduction of 50% in ventilation requirements for flooded battery installations using this technology.

Additionally, a primary justification for the use of external recombinant catalysts centers on the substantial economic benefits of significantly reduced watering maintenance for flooded batteries, with an external recombinant catalyst technology design goal of helping flooded batteries achieve a maintenance profile similar to that of sealed batteries.

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