ELECTROCHEMICAL INVESTIGATION OF VALVE REGULATED LEAD ACID BATTERIES

by

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A thesis submitted in fulfilment of the requirements for the degree of

DOCTOR TECHNOLOGIAE
(CHEMISTRY)

In the Faculty of Applied Science at the Port Elizabeth Technikon, Port Elizabeth

January 2004

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Abstract

One of the technical advances made by the lead-acid battery industry in the field of portable power supply was the development of the valve regulated lead-acid battery (VRLA). This battery reduced the necessity for periodic servicing in terms of having to replenish the cells with distilled water. Further, this new type of battery can now be installed near sensitive electronic equipment without the danger of acid spill or dangerous fumes being emitted. In addition, longer service performance is achieved in terms of life cycle capacity, when compared to the conventional flooded type batteries. However, the new type of battery requires the manufacturing of high precision electrodes and components with low tolerances for error. In order for the manufacturers to produce such a premium product, a thorough understanding of the electrochemistry of the inner components is necessary.

None of the South African lead-acid battery manufacturers are currently making VRLA batteries to supply a very competitive global market, where a large range of sizes and capabilities are available. In order to introduce the VRLA battery into such a competing market in South Africa, a niche area for its application was identified in order to establish the viability of manufacturing such a battery locally. This is done by integrating the VRLA concept into an existing battery, such as the miners cap lamp (MCL) battery. Its application is specific with well-defined performance criteria in a relatively large consumable market in the South African mining industry.

The study looked at various components within a local manufacturing environment that required a better understanding and modification of the processes to build VRLA MCL batteries. This included a detailed study of the manufacturing processes of the positive electrode. The study involved the investigation of the types of grid alloys used, the type of electrode design, such as tubular or flat plate, the addition of red-lead to the paste mixing process and subjecting the batteries to accelerated life cycle testing. A better understanding of the oxygen recombination cycle was also performed in order to evaluate the correct use of certain design criteria in the manufacturing process. This included the study of the pressure release valve and the type of positive electrode used.
The study also looked at developing an inexpensive analytical technique to evaluate the porosity of cured and formed electrodes using a glycerol displacement method.

The monitoring of the state of health (SoH) of VRLA batteries on a continuous basis is an important parameter in unique applications such as remote power supply. A device was developed to monitor the SoH of VRLA batteries on a continuous basis. The working principle of the device was tested on a MCL VRLA battery. With the development of other types of VRLA batteries for specific applications such as in stand-by power supplies, the monitoring device would then be integrated in the battery design.

**Keywords:** Lead-Acid battery, Valve Regulated, Miner’s Cap Lamp Battery
Acknowledgment

1. Prof. Peter Loyson, for his encouragement and guidance as mentor and promoter. He continuously reminded the students in class and in the laboratory, that when it comes to the field of electrochemistry; “Let the electrons do the work”. This phrase has become the theme for the following thesis.

2. Prof. Ben Zeelie, for his support as Head of the Chemistry Department.

3. Nico Rust, Laurence Geyer, Pumza Ndgalvan and Nadia Williams as students and research assistants in helping with some of the analysis and experiments.

4. Willard Batteries for their financial support and supplying various samples used in the study, especially Andrew Poorun as technical manager for valuable discussion and assistance given.

5. South African NRF (THRIP) for their financial contribution.

6. “Commit your way to the Lord; trust in him and he will do this.” (Ps 37:5). I thank God for giving me the passion and ability to complete this study.

7. To my wife Ingrid, who patiently supported me throughout the years.

Related publications by the author that are part of this thesis

- A part of this work was presented at the 8th European Lead Acid Battery Conference (ELBC) in Rome, September 2002.


Declaration

I declare that this thesis is my own, unaided work. It is being submitted for the degree of Doctor of Technology at the P.E. Technikon, Port Elizabeth. It has not been submitted before for any degree or examination in any other Institution.

E. E. Ferg
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List of Abbreviations

VRLA – Valve Regulated Lead Acid
SLI – Starting, Lighting and Ignition
UPS – Uninterruptible Power Supply
AGM – Absorptive Glass Microfiber Mat
RAPS – Remote Area Power Supply
SG – Specific Gravity
MCL – Miners Cap Lamp
DoD – Depth of Discharge
PCL – Premature Capacity Loss
OCV – Open Circuit Voltage
PAM – Positive Active Material
NAM – Negative Active Material
CAP – Calcium lead alloy for positive electrode
SoH – State of Health
SoC – State of Charge
VH – Vickers Hardness
ToCV – Top of Charge Voltage
PSoC – Partial State of Charge
CHAPTER 1.

1. Introduction

South Africa has two main lead-acid battery manufacturers that supply over 90% of all the batteries used for the local automotive industry. They also manufacture a large range of industrial type batteries that are used in a variety of applications such as electric vehicle traction, uninterruptible power supply (UPS) and miner’s cap lamp (MCL) lighting. However, in a competitive global economy, the local manufacturers will have to continuously work to improve their product and processes, since batteries will need to be supplied in increasing numbers, and will need to be more efficient and reliable under extreme conditions. These industries have to be aware of the global trends in electrical power sources which require suppliers to continuously modernize their manufacturing processes of batteries for the optimal utilization of natural resources in order not only to reduce the cost per unit, but also to remain economically competitive. This includes the introduction of new globally competing technologies such as the valve regulated lead acid (VRLA) battery.

The primary aim of the present study will be to assimilate those aspects of present manufacturing processes, consumer market demands and technological limits to develop a unique VRLA battery for the South African market. A successful entry into the highly competitive market for VRLA batteries by South African manufacturers will require a thorough understanding of, inter alia:

1. The limitation of high technology batteries in various applications;
2. The exact relationship between tolerance levels at every stage of the production process and battery failure in various applications;
3. Improvement of existing processes and the scope of reducing manufacturing costs and
4. The effect of locally manufactured components upon the performance and reliability of VRLA batteries.

A battery is one of a few devices that were invented by man, which can be regarded as having the ability to convert energy from one form to another in a controlled fashion. When Alessandro Volta first described his electrochemical cell in 1800,
scientists across the world were quick to take advantage of the idea of harnessing chemical energy that could be converted into electrical energy in a controlled and predetermined manner\(^1\). With the onset of the industrial and communication revolution, an increase in the importance of utilizing electrical energy for portable power was evident with the first commercial batteries being manufactured in the 1830s for the use in telegraph systems. Today, virtually every electrical device makes use of a battery in some form or other. This can range from the portable hearing aids and cell-phones to peak load levelling in household and industrial electricity.

The history of the lead acid battery goes back to 1854 when Sindsteden published data where lead electrodes could be permanently polarized by an external electrical source\(^2\). The independent research and inventions by Planté in 1860 showed that lead strips immersed in sulphuric acid can be utilized to supply electricity. The early applications of the lead system were in providing electrical load levelling in industrial electric plants. The system had found little use in the portable energy system until the onset of the Second World War, where portable batteries were required for the starting and lighting of military vehicles\(^3\).

Since then, substantial research and development have taken place in the field of lead-acid batteries. This battery can be considered as one of the most commercially used system in terms of high power portable energy\(^3\). The battery was successful in remaining a viable commercial article for over a century, which is mainly due to its main use in vehicle starting, lighting and ignition (SLI) and as back-up power for a range of applications. This has made a relatively old technology survive the technology age with its versatility and ease in manufacturing and still remains the most value for money as a portable energy storage device. Many books have been published dealing with the chemistry and applications of lead acid batteries, not only from an electrochemistry point of view but also for portable power electronics\(^1\text{-}^6\).

Many advances in the development of the lead-acid battery occurred in leaps and bounds where some aspects were discovered by accident. There are still a few aspects concerning the theory of electrochemistry in the lead-acid cell that can be considered as unsolved. A familiar example is the use of expanders in the manufacturing of the negative electrode. Wooden separators were used to separate
the positive and negative electrodes until the 1950s when rubber and plastic separators were introduced. The failure in the battery’s capacity was high until it was discovered that the wood lignin found in the wooden separators contributed to the formation of the spongy lead of the negative electrode. Even to this day, wood extracted lignin is used as an additive to the manufacturing of the negative electrode. Significant research is carried out to try to explain the exact chemistry of the lignin additive and why it could not be replaced with a more conventional synthetic chemical.

The 1970s energy crisis stimulated more research into advanced energy systems. This saw the introduction of viable systems such as the Nickel Metal Hydride, Li-ion and fuel cells into the commercial market. However, at the same time, further development in the lead-acid manufacturing technologies and improvements in long-life systems, allowed the lead-acid battery to remain to this day a low cost versatile power source. One large contributing factor is the fact that most lead-acid battery types contain no other major metals besides lead. Combined with the low material and manufacturing cost and the ease of complete recycling, new energy storage systems will find it hard to compete. Consumers of battery power calculate the cost in using a battery in terms of kWh. For example, the relative cost per kWh obtained for various battery types is shown in table 1.1. Even though the data might be slightly outdated, the comparison can still be relevant considering that no major competing systems have since emerged in the market over the last 20 years. The cost of the raw material (Pb) is not expected to increase considerably over the next few years. Since lead is used primarily in the battery industry, and noting that the system is completely recyclable, the only increase to be expected is in manufacturing costs.
Table 1.1: Relative Cost of secondary battery systems compared to lead-acid

<table>
<thead>
<tr>
<th>System</th>
<th>Application</th>
<th>Relative Cost/kWh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead / Acid</td>
<td>SLI</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>Traction</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>Stationary</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>Portable</td>
<td>7.0</td>
</tr>
<tr>
<td>Nickel / Cadmium (NiCad)</td>
<td>Pocket plate</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>Sealed</td>
<td>20</td>
</tr>
<tr>
<td>Nickel / Metal Hydride (NiMH)</td>
<td>High pressure storage</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>alloy</td>
<td></td>
</tr>
<tr>
<td>Zinc / silver oxide</td>
<td></td>
<td>23</td>
</tr>
<tr>
<td>Rechargeable MnO₂</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Lithium / ion</td>
<td></td>
<td>30</td>
</tr>
</tbody>
</table>

When comparing battery types, there are many factors to consider. These factors revolve around the desired application. Things like energy density (Wh/kg), shelf life or charge retention, useful capacity or cycle life, operating temperature and cost per kWh or the initial unit cost must all be considered. Other factors, external to the battery, such as the charge controllers and maintenance cost must also be considered. It is difficult to say if one battery type is better than another, but in some cases, newer technologies do out-perform the older systems and start to replace them. A typical example is the fact that Ni-MH cells and batteries are replacing the older Ni-Cad systems. Table 1.2 gives some comparative properties that can be considered between battery systems.

Table 1.2: Comparing battery properties between Ni-Cad, Lead-Acid and Ni-MH.

<table>
<thead>
<tr>
<th></th>
<th>Ni-Cad</th>
<th>Lead-Acid</th>
<th>Ni-MH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy Density (Wh/kg)</td>
<td>35</td>
<td>35</td>
<td>50</td>
</tr>
<tr>
<td>Shelf Life</td>
<td>3-6 Months</td>
<td>6-9 Months</td>
<td>3-6 Months</td>
</tr>
<tr>
<td>Calendar Life</td>
<td>4-6 years</td>
<td>3-8 years</td>
<td>4-6 years</td>
</tr>
<tr>
<td>Life-cycle (100% DoD)</td>
<td>400-500</td>
<td>200-250</td>
<td>400-500</td>
</tr>
<tr>
<td>Operating temp (°C)</td>
<td>-20 to 45</td>
<td>-40 to 60</td>
<td>-20 to 45</td>
</tr>
<tr>
<td>Relative cost per kWh</td>
<td>20</td>
<td>10</td>
<td>30</td>
</tr>
</tbody>
</table>

The SLI automotive function is the main consumer of the lead acid battery. With its high rate ability, suitable life-cycle capability and wide temperature operation, there is currently no new battery technology that can compete, especially with regards to the cost per unit. There are however suitable competing battery technologies in the field of uninterruptible power supply (UPS) and in batteries used for general portable
power for machinery, such as the Ni-MH. There are limited uses for the lead-acid rechargeable system in the small portable market of the AA and AAA cell sizes. Even though the cells are cheaper than the conventional Ni-MH or Li-ion, they never increased in their market share due to their limited life-cycle capabilities.

Continuing advances in manufacturing technologies and battery design allow for the battery to be tailor-made for end-user specifications\textsuperscript{11-14}. The improvements and advances in technology in the SLI battery are customer-driven by the automotive manufacturers. The advantage of this is that these advances are often then applied to other lead-acid battery type systems. A typical example is the use of non-antimonial grid alloys developed for automotive batteries in order to reduce the water loss, which are now also used in industrial type batteries.

1.1. Chemistry of lead-acid batteries

A fully charged lead-acid cell can be considered to have a negative electrode made from porous lead (sponge lead) and a positive electrode made of lead dioxide (PbO\textsubscript{2}). Both are immersed in an electrolyte that is a sulphuric acid solution which has a specific gravity (SG) between 1.25-1.28 (32-37 % by weight).

As the cell discharges, the active material on both electrodes converts to lead sulphate. The reaction is reversible, and on charge the reaction is reversed. The properties of the simple reactants under such conditions contribute to the success of the system. Beneficial properties include the low solubility of the active materials in the aqueous medium, the highly reversible electrochemical reactions and the high electronic conductivity of the major components.

The electrochemical reaction mechanism of the lead-acid cell has been extensively studied, and can be summarized in the following discharge and charge equations\textsuperscript{1-5}.

Discharge Reactions.
At the cathode (positive electrode), lead dioxide reacts with sulphuric acid to form lead sulphate.

\[
PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O \tag{1.1}\]
The $E^0$ potential for the half reaction versus the hydrogen-hydrogen ion couple at 25°C is +1.685 V.

At the anode (negative electrode), lead reacts with the sulphate ion to form lead sulphate.

$$\text{Pb} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + 2e^- \quad (1.2)$$

The $E^0$ potential for the half reaction versus the hydrogen-hydrogen ion couple at 25°C is +0.356 V.

Adding the two half-cell potentials would give the approximate observed electromotive force for commercial cells.

$$\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O} \quad E^0 = 2.041 \text{ V} \quad (1.3)$$

The basic electrode process involves a dissolution / diffusion and precipitation mechanism. It is known as a double sulphate reaction and is shown graphically in figure 1.1. Sulphuric acid in the electrolyte is consumed during the discharge process, producing water. In some battery designs, it can be the limiting component in the capacity of a discharged cell.
Theoretical Capacity of lead acid cells.

An important consideration in designing lead-acid batteries is their theoretical and actual capacity per mass of active material. According to Faraday's law, 96,500 coulombs or 26.80 Ah would transform 1 mol of electrons. The atomic mass of lead is 207.2 g/mol and the valency is 2, giving an equivalent mass for lead of 103.6 g. On the negative electrode, 3.866 g of lead are transformed into lead sulphate for every 1 ampere-hour of electricity. Hence, assuming that all the lead is used in the reaction, a 1 Ah cell would require 3.866 g of Pb, or the maximum theoretical capacity for the negative electrode would be 258.7 Ah/kg. Similarly, 4.463 g of the lead dioxide on the positive electrode would be required for every ampere-hour, or the maximum theoretical capacity for a positive electrode is 224.1 Ah/kg. In most battery designs, the negative electrode would contain excess active material, and the battery would be designed according to the positive active material. Not all the active material is used in the discharge reaction, and depending on the battery design, the efficiency of the cell would vary between 30-50%.
In some battery designs, the electrolyte also becomes a limiting component. In the reaction, two molecules of sulfuric acid in the electrolyte are used for each molecule of lead or lead dioxide, according to the equation (1.3). The molecular weight of sulfuric acid is 98.076g/mol and since the valency is 2, the amount of acid consumed for every 1 Ah is 3.660g. It is noted that this is the theoretical requirement; in practice, excess acid would be required in order to maintain the conductivity of the electrolyte. There is a net change in the weight of the electrolyte during charge or discharge; however, the total weight change in the battery would be zero, since the electrolyte is contained in a closed system.

As the cell is charged, the reverse reactions of equations (1.1-1.3) occur as shown in figure 1.2. As the cell becomes fully charged, most of the lead sulphate on the two electrodes is converted back to Pb and PbO$_2$ respectively. The cell voltage increases and becomes greater than the gassing voltage (about 2.39 V/cell) where the overcharge reactions then begin. In a commercial cell, a number of overcharge reactions take place such as the electrolysis of water to hydrogen and oxygen, the corrosion of the positive electrode grid and some minor side reactions such as the oxidation of organics present in the electrode material. Energy is also converted to heat in the process.
The charge and overcharge reaction mechanisms at the positive and negative electrodes can be summarized as follows.

Positive Electrode
\[
PbO + H_2O \rightarrow PbO_2 + 2H^+ + 2e^- \tag{1.4} \\
PbSO_4 + 2H_2O \rightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \tag{1.5}
\]

Negative Electrode
\[
PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-} \tag{1.6}
\]

The electrolysis of water in an acid medium is as follows:

Positive electrode: Oxidation of oxygen: \( H_2O \rightarrow \frac{1}{2} O_2 + 2H^+ +2e^- \tag{1.7} \)

Negative electrode: Reduction of hydrogen ions: \( 2H^+ + 2e^- \rightarrow H_2 \tag{1.8} \)

Overall Reaction: \( H_2O \rightarrow H_2 + \frac{1}{2} O_2 \tag{1.9} \)

The equilibrium cell voltage for the reaction is \( E^0 = 1.229 \text{ V} \).
However, the equilibrium cell voltage in a lead acid cell for the charge reaction (reverse of equation 1.3) has an equilibrium cell voltage of $E^o = 2.041 \text{ V}$. Hence, the cell voltage is much greater than the electrolysis potential for water; however, kinetic parameters govern the rate of the water decomposition reaction, thereby limiting the water decomposition reaction. As the cell approaches 80-90% of charge, the recharge reactions become less efficient and the positive electrode begins to evolve oxygen according to equation (1.7). As the charge potential continues to increase, the negative electrode starts to produce hydrogen according to equation (1.8).

Figure 1.3 summarizes the secondary overcharge reactions in a lead acid cell².

![Figure 1.3: The electrolysis of water in a Pb-acid cell.](image)

The two vertical columns at the two electrode sides represent the equilibrium potentials of the negative and positive electrodes in a range of the concentration of the electrolyte. The gas evolution rates are represented by the dashed lines that correspond to the current potential curves of hydrogen and oxygen evolution. Hence the rate at which gas is generated is a function of the electrode potential. The theoretical water decomposition potential starts already at 1.23 V with a gradual increase in gassing as the potential increases slowly until the over-voltage is reached where both curves show a steep increase in the rate of gas evolution.
If a cell is overcharged, the main reactions that occur are the hydrogen and oxygen evolution. Hence the equivalent current that flows through the cell can be related to the amount of gas generated. When the overcharge current is the determined parameter, the cell voltage follows the current required for the polarization of both electrodes. This simple approach is an approximation since in an actual cell application other secondary reactions take place such as oxygen recombination, positive electrode grid corrosion and organic decomposition. The fact that the hydrogen evolution potential is always larger than the equilibrium potential of the Pb/PbSO$_4$ electrode, implies that hydrogen gassing can never be avoided even if the cell is at open voltage. The gas evolution at the open circuit voltage characterizes the self discharge of the electrodes. Hence, the net reactions for self discharge are as follows:

For the negative electrode: \[ \text{Pb} + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + \text{H}_2 \]  \hspace{1cm} (1.10)

For the positive electrode: \[ 2\text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O} + \text{O}_2 \]  \hspace{1cm} (1.11)

During charging, the water consumption reactions are in competition with the active mass reaction. As the voltage increases, the water consumption reaction increases. The H$_2$ evolution increases at the negative electrode, and if any trace metals such as Sb or Cu are present, the hydrogen over-potential for that element is reached sooner, and the gassing rate increases. Antimony is present in older battery designs, where the element was used in grid manufacturing. It can easily leach into the sulphuric acid and plate onto the negative electrode. Copper and other metal impurities are often introduced during the service life of a battery, where un-distilled water was used to replenish the electrolyte that was lost during overcharging. The self discharge of the cell during the open-circuit voltage also increases with Sb present. Modern designs and manufacturing processes have moved away from negative electrodes containing Pb-Sb grids. However, Pb-Sb alloys are still used in the positive electrode manufacturing process for some large industrial battery systems. The main reason is that the Pb-Sb grids have a higher corrosion resistance, a higher rigidity and a reduction of the passivation layer at the interface between the current collector and positive active material$^{12}$.

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1.2. Chemistry of VRLA batteries

Water loss in lead acid batteries seemed to be the main issue concerning the maintenance and loss of perceived usage of a lead acid battery. The formation of hydrogen gas during charging is considered dangerous with the result that some explosions have occurred during actual applications\textsuperscript{10}. The introduction of flash arrestors that are connected to the vent outlet of a battery has helped reduce the dangers of hydrogen to open flames such as sparks from electrical systems. One of the biggest challenges the automotive industry gave the Pb-acid battery manufacturers was to reduce the maintenance of the SLI battery. Many problems in terms of customer satisfaction were related to the need of regular servicing the battery. The fact that the automotive battery was not a sealed unit and was dependant on the user to maintain its electrolyte levels was considered as a problem. Many problems with regards to warranty claims, acid spills and incorrect servicing of the battery were experienced. It was important for the automotive manufacturer to have almost all components of a vehicle independent of the consumer’s requirement to service the component themselves. This was where the concept of “maintenance free” batteries started.

It is important to note that a maintenance free battery is not necessary a valve regulated lead acid (VRLA) battery. Maintenance free or low maintenance implies that the battery requires no or very little filling of the electrolyte during its expected lifetime application that can range from 2-3 years for a SLI battery. There is an additional premium paid for the concept of “maintenance-free”; however, certain maintenance on the battery would still be required. This would involve the periodic checking of the terminals for corrosion and recharging after the battery has been standing in open voltage for extended storage (self discharge). Another form of maintenance would be the additional boost charge required when batteries were used for excessive deep discharge cycles. In general, the term maintenance-free usually relates to the replenishing of lost water during the life of a battery. The concept of maintenance-free is different when one considers different battery systems such as traction batteries, stand-by or portable batteries. In such systems, a battery that is spill-proof and can be kept next to sensitive electronic equipment would be regarded as maintenance-free.
In order to reduce the electrolyte loss in flooded type batteries, some battery manufacturers inserted a catalytic gas recombination device in their battery design\(^2\). The catalyst would recombine the hydrogen and oxygen in a container device that was attached to the vent plugs of a battery. The problem with these devices was the dissipation of the heat that was generated in the process. The catalyst made use of expensive metals and complex designs that would increase the unit cost of the battery. These devices were also limited in their efficiency to about 85%, where small amounts of gas still escaped the converter.

The initial development of a spill-proof battery with reduced water consumption was started in the 1950s with the use of silica gel (SiO\(_2\))\(^2\). Later, the combination of a pressure release valve and the use of glass-matt micro-fibres as an electrolyte support was introduced. The development of using an absorptive glass mat separator was similar to the sealed spirally wound nickel cadmium cells that were developed in the 1970s, of which the first patents of the technology appeared in 1975\(^16\). This development increased the possibility of a low maintenance battery where the initial research was done in replacing the flooded SLI battery with a VRLA type system\(^17\). However, over the years, very few VRLA batteries were used for SLI automotive applications and the battery found a niche market in the stationary and portable battery market. Some of the reasons why the battery failed in the SLI market where its failure under high temperature and high current applications and that the cost per unit was much higher than the conventional flooded system\(^18\).

These VRLA batteries are only different from conventional batteries in their use of gelling or adsorptive porous materials with the replacement of vent caps by pressure release valves and are often referred to as completely sealed systems. This is however not true, since the pressure release valve regulates the pressure during the charge cycle of the battery, where under normal use, some gas (mainly hydrogen) would escape. The pressure release valve is built into the battery to allow a pressure build up, to maintain the pressure and for safety purposes where excessive gassing could occur during malfunctioning\(^5\).

The concept in the VRLA battery is that the electrolyte is maintained in the pores of the electrodes and in the separator. The separator between the two electrodes is
either an absorptive glass microfiber mat (AGM) or an immobilized gelled silica. The system operates in a starved electrolyte condition, where just enough electrolyte is added to coat the electrodes and partially saturate the separator. The recombination cycle of oxygen is discussed by a number of authors\(^{21-26}\).

In addition to the normal charge reaction products described in equations (1.4-1.6), the following additional reactions take place, which are referred to as the oxygen cycle and is illustrated in figure 1.4.

\[
\begin{align*}
\text{Positive Electrode: } & \quad \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2} \text{O}_2 + 2\text{e}^- \\
\text{Negative Electrode: } & \quad \text{Pb} + \frac{1}{2} \text{O}_2 \rightarrow \text{PbO} \\
& \quad \text{PbO} + \text{H}^+ + \text{HSO}_4^- \rightarrow \text{PbSO}_4 + \text{H}_2\text{O} \\
& \quad \text{and} \\
& \quad \text{PbSO}_4 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Pb} + \text{H}_2\text{SO}_4
\end{align*}
\] (1.12) (1.13) (1.14) (1.15)

During the charging process, oxygen is evolved at the positive electrode before the electrode is fully charged and before hydrogen evolution occurs at the negative electrode. The oxygen gas can channel through the partially saturated separator to the negative electrode\(^{26}\). The oxygen then reacts with the sulphuric acid and Pb at the electrode to partially discharge the negative electrode preventing it from reaching the over-potential where hydrogen will start to evolve sufficiently. This results in a lower hydrogen production, since the electrode will still be in a partially charged state. Since the negative electrode is still on charge, the reaction product will then convert to Pb. The resulting net reaction product is therefore zero where no chemical change has occurred. The electrical energy that was required during the process is converted to heat. This additional formation of heat must be sufficiently dissipated and controlled in order to prevent overheating and subsequently overcharging. The oxygen reduction that takes place at the negative electrode, which governs the internal oxygen cycle, requires the potential of the negative electrode to have reached the equilibrium value or more of the open circuit potential of the negative electrode.

During the manufacturing process, the positive and negative active material ratio is kept close to unity, so that gassing can occur at the positive electrode first before the negative electrode, allowing the liberated oxygen to diffuse to the negative to
recombine. This means that the cell potential must be equal or more positive than the open circuit voltage in order to maintain an efficient oxygen recombination reaction. Some VRLA designs can maintain recombination efficiency up to 99%, where very little hydrogen is released under normal charging conditions\(^{13}\). During the charge and overcharge of a VRLA cell, a number of other side reactions can occur besides the ones described above.

![Figure 1.4: Schematic diagram of the oxygen cycle in a VRLA cell.](image)

These reactions would include positive electrode grid corrosion, conversion of residual lead oxides and sulphates at the positive electrode and the oxidation of organic materials and lignins\(^{13,21}\).

The reversal of the hydrogen evolution reaction is the oxidation of hydrogen according to the following equation:

\[
H_2 \rightarrow 2H^+ + 2e^- \tag{1.16}
\]

In theory, the hydrogen formed at the negative electrode could form part of the hydrogen cycle that would correspond to the oxygen cycle described previously. From
a theoretical thermodynamic system\textsuperscript{13}, the reaction should occur as soon as gaseous hydrogen molecules reach the positive electrode. But this reaction is very slow and for all general applications in lead acid batteries, the hydrogen oxidation reaction can be ignored\textsuperscript{4}. The amount of hydrogen given off during overcharge is difficult to measure since many factors contribute to the loss of hydrogen present in the cell. Hydrogen can easily permeate many materials, such as the cell walls of the containers and through the tight rubber seals of the cell inter-cell connectors\textsuperscript{26}.

The oxygen cycle described above is not the same as the recombination of hydrogen and oxygen that is aided by a catalyst for forming water. It is fundamentally different in that the oxygen is reduced rather at the negative electrode (oxidizes the lead) and the oxidized lead is then recharged. As a result of this reaction process, the acid concentration is increased at the positive electrode in continuous overcharge conditions such as float type applications. A continuous increase in a concentration or stratification of the acid gradient between the two electrodes would then occur. However, sufficient diffusion can act as a counter reaction that would level the concentration forming an almost stationary concentration gradient between the two electrodes\textsuperscript{2}. This form of acid stratification or acid depletion at the negative electrode could have detrimental effects in reducing the effective capacity of the electrode under high load.

The problem of stratification occurs mainly in batteries that are used for standby applications. Further stratification in VRLA batteries can also occur simply due to the density difference between sulphuric acid and water in contact with the AGM separator. With time, the separator’s pores at the bottom of the cell would become filled and the pores at the top become starved, reducing the effectiveness of the recombination cycle. Conventional flooded standby batteries are usually slightly overcharged during the float charge or capacity cycling in order to produce gas bubbles for the mixing of the electrolyte. However, this increases corrosion and water loss. Some manufacturers of larger flooded type batteries have made use of air pumps to circulate the electrolyte in applications such as submarine batteries\textsuperscript{39}. VRLA batteries used for standby applications are therefore limited to the size and height to which they can be built because AGM cells can undergo severe acid stratification\textsuperscript{14}.
Other factors that influence the gas evolution and recombination efficiencies are the amounts of other metal impurities present in the grids, active material, electrolyte and separators. These metals would either deposit on the positive or negative electrode during charge and form active sites for the electrolysis of water. Their influences on the water loss properties of lead acid batteries have been studied and each manufacturer would specify the levels of various elements allowed in their raw material. A summary of selected specifications required by the manufacturer for raw materials is shown in Appendix A.

Additional factors such as the age of the battery and its service history would also influence the recombination efficiency. The oxygen and hydrogen recombination rates and efficiencies of both glass mat and gel-type batteries have been extensively studied and reported on in the literature\textsuperscript{21-23}.

The self-discharge in a lead-acid battery which occurs during storage is unavoidable and can be approximated to about 2% per month for a modern stationary battery\textsuperscript{1}. This can be influenced by the storage temperature and would increase significantly with increased temperature, where the increase could be as much as a factor of 2 for every $10^\circ C$. This is usually an approximation since the self-discharge current densities of the cells depend on the porosity and surface area of the electrodes. In stand-by applications of grid electrical supply systems, batteries are maintained on a so-called float charge. This charge is usually regulated at a constant voltage and is kept just above the cell potential in order to keep both cell electrodes polarized. This ensures that the battery is always fully charged and can be used in cases of emergencies. However, maintaining the battery at the constant charge potential has long term detrimental effects such as positive grid corrosion and eventual water loss, even in a VRLA battery. In order to overcome the limited shelf-life of lead acid batteries, some manufacturers make a “dry charged battery”\textsuperscript{25}. This battery is made by assembling the positive and negative electrodes in a fully formed state, and adding the electrolyte before application. These types of batteries can have a shelf life of up to 5 years. However, this method of dry-charged batteries is not possible with VRLA systems.
Substantial research has been carried out on the recombinant battery separator mats also referred to as “Absorptive Glass Mat” (AGM) and their characteristics in VRLA applications\textsuperscript{29, 30 & 31}. The most important properties of the separator are its ability to maintain a porous structure through the width of the matt allowing for the oxygen to move through to the negative electrode, and at the same time able to retain enough electrolyte to allow for the discharge of the electrodes. The matt must not be completely saturated with the electrolyte; however, the electrolyte bound in the glass matt system is influenced by gravity and would cause the pores at the bottom of the cell to be more filled with time and the pores at the top would be empty, even the smaller ones. This property limits the practical plate height where recommendations are given for using the battery in stationary type applications on their side in a battery rack rather than in their upright position. Research into suitable small diameter fibre and the packing of them into a matt for VRLA application had only recently become important\textsuperscript{31}. The modern AGM separator is made from a blend of fibres that comprise different thickness and lengths where appropriate stack pressure is required between cell group and battery container to maintain the effectiveness of the recombination property. It seems that glass is the only suitable material, which is sufficiently wetted by sulphuric acid\textsuperscript{30}. Another important property that is required from the glass-matt separator is that their respective pores must be small enough to prevent the formation of dendrites that can grow from the positive electrode due to active material shedding. With sufficient shedding and time, these can grow through the separator and cause a short circuit at the negative electrode, thereby causing the battery to fail prematurely.

The characteristic of the recombination process is that the water loss increases during the service application. This process increases the gas channels through the glass matt making the moving of the oxygen to the negative electrode easier. There is however a slight increase in the float current during the service life and is a good indication of the effectiveness of the recombination\textsuperscript{2}. The increase in the water loss would also result in an increase in the internal resistance of the battery. When sudden high current application loads are required from the battery, a lower discharge voltage would occur resulting in a lower than expected discharge capacity than when the battery was new.
The VRLA batteries have found applications in UPS, Electric vehicle propulsion, standby power emergency lighting, computer standby, RAPS, telecommunications and SLI in motor-cycles\textsuperscript{12, 14}. Even though the NiCad systems offer longer service life than the equivalent VRLA type, the cost effectiveness (factor of 5) will keep the battery as a competitive portable power source.

Some disadvantages of using VRLA type batteries are their use in inconsistent life cycle regimes such as in RAPS applications. The poor performance occurs due to insufficient recharging, where partial state of charge capacity cycling reduces the effective life of the battery tremendously\textsuperscript{32, 33 & 34}. For RAPS applications, micro-processor controls with well-established algorithms are required. In particular, the charging of VRLA batteries needs to be carefully controlled due to the additional heat that is generated as compared to normal flooded type batteries. In addition to the fact that the heat dissipation of the battery is lower due a lower amount of sulphuric acid and if the environmental temperatures of the battery are relatively high (above $40^\circ$C), a considerable increase in water loss could be experienced that could permanently damage the battery. These battery types are more suitable for UPS systems where discharge and recharge conditions are more predictable.

1.3. Manufacturing processes of lead-acid batteries

The manufacturing process of lead acid batteries involves the expertise from a variety of fields such as metallurgy, electrochemistry and polymer chemistry. The following will be a short review of some of the basic principles relevant to this study in the manufacturing of lead-acid batteries applicable to VRLA systems.

1.3.1. Flat plate manufacturing.

Figure 1.5 summarizes the manufacturing process for flat plate electrodes.
Pure lead is converted to lead oxide either in a Ball-Mill or using a Barton-Pot process. The former relies on the oxidation of lead pellets by friction and the latter process relies on molten lead being oxidized with water and air. The powdered material that results from the process forms two types of crystallite structures of lead oxide\textsuperscript{35}. These are referred to $\alpha$-PbO (litharge or tetragonal) and $\beta$-PbO (yellow or rhombic). The oxide used in the manufacturing process consists mostly of $\alpha$-PbO and Pb (20-30%). The $\beta$-PbO phase occurs mainly during the Barton Pot process at
higher temperatures and is less desirable due to its lower reactivity when compared to a-PbO.$^{37}$

The fine oxide powder is then mixed into a paste with water and sulphuric acid and applied to a lead grid. The curing process involves the hydrosetting of the plate at high temperature and humidity which results in a hardened porous material that is made up of lead oxide and various basic lead sulphates. Any free lead that remained in the active material should have also oxidized during the curing process. Free lead that remains in the cured active material can lead to lower formation efficiencies and possible self-discharge in the final product. Other additives in small amounts are often included during the pasting process. For the positive electrode, carbon fibres are added to aid the conductivity of the active material and a mixture of carbon, lignin sulphates and barium sulphate is added to the negative paste.

After curing, the active materials on the plates are lead monoxide (α- and β-PbO), monobasic lead sulfate (PbO·PbSO$_4$), tribasic lead sulphate (3PbO·PbSO$_4$), and depending on the curing conditions, especially if higher temperatures occurred, tetrabasic lead sulphate (4PbO·PbSO$_4$). Much work was published on the characteristics of the various cured basic sulphates and their performance in formed plates.$^{35, 36 \& 37}$ Most literature agrees that the tribasic lead sulphate is preferable as a cured product because it can change easier to lead dioxide during the formation stage as compared to the tetrabasic lead sulphate. Mixtures of the two phases in relative proportions have shown to be beneficial for formation and increase the live cycle ability of the positive active material.$^{36}$ After the plates and active cured material have dried, they are then assembled for either jar or tank formation.

The formation process starts with a soaking stage, where the cured electrodes are allowed to stand for a period of time in the formation electrolyte that has a specific gravity (SG) between 1.19 to 1.25. The soaking stage occurs before any current passes through the electrodes, allowing the lead oxide and basic lead sulphates to change to lead sulphate.$^{38}$, according to equation 1.17 – 1.20.
\[
\begin{align*}
PbO + H_2SO_4 & \rightarrow PbSO_4 + H_2O \\
PbO.PbSO_4 + H_2SO_4 & \rightarrow 2PbSO_4 + H_2O \\
3PbO.PbSO_4 + 3H_2SO_4 & \rightarrow 4PbSO_4 + 3H_2O \\
4PbO.PbSO_4 + 4H_2SO_4 & \rightarrow 5PbSO_4 + 4H_2O
\end{align*}
\]

Equations (1.17) - (1.20)

A significant amount of heat is generated during the soaking period and depending on the type of battery system, the times can range from half an hour to almost 3 hours. During this time, the sulphuric acid is consumed and the acid density decreases significantly, resulting in the increase in resistance of the acid in the unformed battery during current flow. Some manufacturers make use of red lead and graphite as an additive to the active material in order to aid the conductivity of the current flow. Sodium sulphate is commonly added to the formation acid to increase the conductivity of the electrolyte.

Once the current flow is initiated, the formation profiles would vary from manufacturer to manufacturer. Modern formation systems include pulse profiles with intermittent short discharges in order to optimize the conversion of the active material to the desired product. However, to include complicated formation profiles, would increase the cost of manufacturing. Most manufacturers rely on constant current formation profiles that are step-time and current-programmable to ensure that the optimal amount of formation capacity was used for the shortest period of time. Approximately 250% of the theoretical active mass capacity should be used as the recommended amount of formation capacity\textsuperscript{44}.

When the electrical current is switched on, the lead sulphate converts to lead dioxide on the positive plate and lead on the negative plate according to the reactions of equations (1.5; 1.6). Any un-reacted lead oxide that remained in the pasted plates would also convert to the lead dioxide or lead respectively. Sulphuric acid is regenerated during the reactions resulting in a higher final acid SG. The process generates a lot of heat and often requires external cooling systems such as water baths and the initial filling acid is usually added at a much lower temperature (typically 5°C). The formation process requires the longest time in the manufacturing process and can range between 48 to 60 h, depending on the battery size. The process
consumes a lot of energy, and the optimal formation process is critical in obtaining the most efficient conversion of active material.

The conversion efficiency for the negative plate is greater than that for the positive plate. During the process, the negative plate usually completes its formation well before the positive plate resulting in an increase in the charge potential and an increase in the gassing rate of the electrolysis products of water. A substantial amount of water is lost during the formation process. The end of formation is followed by an adjustment of the SG of the acid to the required value and a topping up of the cells to the required volume.

1.3.2. Positive tubular electrodes.

Lead acid batteries, which are assembled with tubular positive electrodes, are used in a wide range of applications such as in vehicle traction, stationary standby power (UPS) and miners cap lamp (MCL) batteries. The robust structure of the cell and in particular the tubular design of the positive electrode have resulted in a battery that can undergo deep discharge life cycles with limited active material shedding that causes cell failure\textsuperscript{3}. The tubular electrode has an improved mass utilization but the reduction in the available surface area of the active material reduces its effectiveness for high power applications. The current collector for the tubes is situated in the centre thereby reducing the grid corrosion that commonly occurs with flat plate electrodes.

One way of manufacturing stationary type batteries is to assemble dry-charged cells, where both the positive and negative electrodes are assembled in their fully formed state. The electrolyte would be added just before application. During the manufacturing process, it is possible to optimise the formation conditions for the tubular design outside the assembled cell. Many authors have investigated tubular cell designs with their variables in manufacturing and formation in order to optimise the performance of the active material\textsuperscript{44-46}. They have found that the formation acid should have a specific gravity (SG) between 1.05 and 1.15 for optimal utilization of the active material. Optimal formation can be easily achieved during the dry charge process where the SG of the formation acid can be easily controlled in a bath.
However, many tubular design cells such as those used in vehicle traction applications and MCL VRLA are assembled in their unformed state, which is followed by jar formation of the completed cell. In this process, factors such as the formation acid concentration, temperature during formation and the final electrolyte SG become important. One way of overcoming problems is to use a two-stage formation process. The cells are allowed to start their formation in a lower SG acid. This is usually followed by emptying the jars and filling them with a higher SG acid before the finishing stages of the formation\textsuperscript{47}. However, the additional step required in the process becomes costly. In order to aid the formation process of the active material in the tubular plates, red lead ($\text{Pb}_3\text{O}_4$) is frequently added to the oxide during the filling process of the tubes.

After filling the tubes with dry lead oxide, the plates are subjected to a process known as soaking or dipping in a low SG acid. Some authors also describe this as pickling\textsuperscript{1}. This process has three main advantages. Firstly, it eliminates the loose dust that coats the exterior of the tubes thereby making the plates easier to work with for assembling purposes. Secondly it would aid in the formation of mono-basic and tri-basic lead sulphates during the curing stage and thirdly, it would reduce the free lead that was present in the filling oxide. In practice, this process of dipping can vary from a few minutes up to a few hours. A number of authors have investigated the relationship between the formation efficiency and curing times\textsuperscript{45,48}.

**RED LEAD**

Red Lead ($\text{Pb}_3\text{O}_4$) is made by a batch process where a-$\text{PbO}$ is further oxidized by air at about 400$^\circ$C and is currently 56% more expensive by mass that the normal grey oxide. The addition of red lead to the positive active material during manufacturing is considered to be useful when initial low capacities of batteries are obtained which are due to the positive electrode incomplete formation. Red Lead results in the formation of $\beta$-$\text{PbO}_2$ as shown in equation 1.21, during the soaking or paste-mixing stage and indirectly during the formation stage\textsuperscript{37, 54}. The presence of $\beta$-$\text{PbO}_2$ increases the conductivity of the active material before formation and allows for seed crystals to develop that would increase the conversion efficiency of the final formed active material.
During the formation stage, the lead sulphate is then further oxidized to \( \beta\text{-PbO}_2 \) as shown in the reaction of equation (1.5). The addition of red lead has been shown to improve the conversion of tetrabasic lead sulphate thereby improving the cycle life of flat plate automotive batteries\(^{37}\). The addition of red lead to tubular electrodes can vary from 10\% to 80\% wt and up to 25\% wt for automotive flat plates\(^{46}\).

This thesis will investigate aspects of the manufacturing process of the tubular positive electrodes. The addition of red lead to VRLA MCL type batteries consisting of flat plate and tubular positive electrodes is also investigated.

1.3.3. Electrode current collectors.

Numerous books and papers have been published in the metallurgical field of lead and lead alloys and their use in lead acid batteries\(^{74-77}\). The selection of the correct grids, their shape and their alloy composition is crucial in obtaining the optimal performance of a lead-acid battery. The grids, acting as the current collectors for the positive and negative electrodes, have to have a number of properties in order to be suitable for the lead acid battery. Pure lead is seldom used in the manufacturing of grids due to it being soft and having a low corrosion resistance. A grid has to have good mechanical strength, high creep resistance during life cycle and be corrosion resistant. The composition of the alloy’s constituents would further influence the electrochemical properties of the overall cell. A number of combinations of grid alloys are used by the industry depending on the type of battery system. A few of the common alloys are summarized in table 1.3\(^2\).
Table 1.3: Grid alloys used in lead/acid batteries.

<table>
<thead>
<tr>
<th>Alloy Additives to Pb</th>
<th>Types of Battery and Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Antimony alloys</td>
<td>Flat plates, tubular spines for traction batteries, older types of stationary batteries.</td>
</tr>
<tr>
<td>4-11 % Sb</td>
<td></td>
</tr>
<tr>
<td>Various low concentrations of As, Sn, Cu, Ag</td>
<td></td>
</tr>
<tr>
<td>Low Antimony alloys</td>
<td>Flat plate, tubular spines for low maintenance or maintenance free batteries, stationary, SLI (hybrid).</td>
</tr>
<tr>
<td>0.5 – 3 % Sb. Various concentrations of Se, S, Cu, AS, Sn and Ag</td>
<td></td>
</tr>
<tr>
<td>Lead Calcium alloys</td>
<td></td>
</tr>
<tr>
<td>0.05-0.08 % Ca; 0-3 % Sn (Al)</td>
<td></td>
</tr>
<tr>
<td>ASTAG alloy</td>
<td></td>
</tr>
<tr>
<td>0.009 % As, 0.065 % Te, 0.08 % Ag</td>
<td></td>
</tr>
<tr>
<td>Small amounts of Sn</td>
<td></td>
</tr>
<tr>
<td>Pure Lead</td>
<td>Planté plates, Bell System Batteries with punched grids (GATES)</td>
</tr>
<tr>
<td>Small amount of Sn</td>
<td></td>
</tr>
<tr>
<td>Antimony/Cadmium alloy</td>
<td>GNB ‘Absolyte battery’</td>
</tr>
<tr>
<td>1.5 % Sb, 1.5 % Cd</td>
<td></td>
</tr>
</tbody>
</table>

A lead-calcium alloy was introduced in the 1970s as a grid support for lead-acid batteries. The use of the alloy reduced the water consumption considerably, introducing the low-maintenance and maintenance-free batteries that did not require water addition for its service life expectancy. In comparison, lead-antimony alloys have the advantage of giving the grid good mechanical strength and high creep resistance, but the consumption of water due to gassing was considerably high. This is due to the lower hydrogen over-potential of antimony. Antimony, used in the positive grid electrode would also dissolve into the electrolyte during grid-corrosion and electroplate onto the negative electrode during charging, thereby increasing the water consumption rate. With the use of a lead-calcium alloy for the grid, a reduction of the water consumption was observed. Calcium does not affect the corrosion properties or the electrochemical behaviour because the element does not precipitate at the negative electrode and remains in the electrolyte.

The disadvantages of the lead-calcium alloys are their relatively low creep resistance properties and lower mechanical strength, making it more difficult to manufacture. The effect of grid passivation and reduced cell capacity is also more prominent with Ca-Pb alloys\(^8^0\). The creep or grid growth of positive electrode grids occurs due to electrochemical corrosion, which is more pronounced at the grain boundaries forcing...
the grid to increase in size. This has adverse effects on the tightly packed cell where loss of contact between the active material and current collector occurs and the puncturing of the separator results in an electrochemical short-circuit between the electrodes. The problem is partially overcome by modifying the alloy with the addition of small amounts of aluminium and tin\textsuperscript{82, 83}. The addition of tin can range from 0.02 to 1.2 \%wt, reducing the premature capacity loss, capacity passivation and the grid growth effect, but the cost of tin is considerably higher than lead thereby increasing the overall price of the alloy.

The importance of age hardening of various Ca alloys for the improvement in the manufacturing process will be investigated in this study. Characteristics such as corrosion, passivation and workability of the grid will be compared between various alloy types for optimal use in VRLA type batteries.

1.4. Market trends in the use of lead-acid batteries.

The global trend in the manufacture of lead acid batteries is the reduction of the maintenance that is required by the final consumer of the battery. One of the greatest advances in the lead acid battery industry was the development of the VRLA battery. This type of modified lead acid battery is manufactured by a number of international companies in various voltage ranges and capacities. As was discussed previously, these batteries have found a niche market in the portable electronic stand-by applications from computer UPS to RAPS applications for telecommunications. Little or no progress has been made amongst the South African manufacturers to compete in the VRLA stand-by battery market. The main reason is the cost of manufacturing such batteries with a limited market demand in South Africa. The raw materials such as the AGM glass matt and battery cases need to be imported and are the most costly components in comparison to the rest of the battery. In addition, a more comprehensive manufacturing process would be required which would not justify the initial capital expenditure in a market that is very competitive. Furthermore, the market demands expect a large range of batteries in size, capacity and voltage rating at a reasonable price per unit. Typical expectations from consumers for VRLA batteries are that they should work under extreme environmental conditions of high to low temperatures (20 to 60\degree C); should have long float charge abilities (10 to 20 years);
deep discharge cycle life (1000); high specific energy (40 to 50 Wh/kg) and high
power (150 to 200 W/kg)\textsuperscript{13}.

There are new demands placed on the lead-acid battery by the automotive
manufacturers for SLI and vehicle traction batteries. The requirements for batteries
used in automotive traction applications should withstand a new form of capacity
cycling duty known as “Partial State of Charge Cycling” (PSoC)\textsuperscript{57}. A battery that is not
fully charged (50-90% below its full capacity) is required to be able to capacity cycle.
These requirements are considerably challenging for a battery system whose active
chemical components inside the battery are interdependent on each other’s state at
various stages of the batteries charge. Research in this field will have to be intensified
in order to reduce the problems associated with PSoC which cause excessive positive
grid corrosion and the accumulation of negative electrode sulphation\textsuperscript{34, 58}.

Modern automotive manufacturers of large vehicles are requiring the SLI battery to
supply 36V / battery instead of the conventional 12V / battery\textsuperscript{59, 60}. This has a number
of implications on the size and performance of the battery system, where the battery
should be preferably of the VRLA type and located in the boot of the car instead of
under the hood.

A battery must be designed and often modified for optimal reliability and performance
for specific applications, keeping in mind, limits within the technology itself. A battery
should be considered as a dynamic and not a static system. Even when the battery is
not in use, there is still “chemistry” occurring within its cell walls. No two batteries
manufactured are ever the same. They might be rated at the same capacity, but their
characteristics such as the exact discharge capacity, float current and electrode mass
utilization might be very different. These factors depend on the manufacturing
parameters, where each cell electrode assembly is not identical. There will always be
slight differences in active material pasting, curing, porosity, active material utilization
and cell plate compression. These factors must be taken into account when using
batteries or cells in a large bank application such as UPS or vehicle traction. In
addition, more expensive specialized electronic charging systems would be required
to control high rate recharges in high temperature environments. In extreme
environments, with excessively high demands on the battery in terms of recharge
rates, excessive water loss can occur with possible thermal meltdown of a battery unit\textsuperscript{43}.

The main market consumers of lead acid batteries in South Africa use the maintenance or low-maintenance flooded type battery. In 2002, the South African battery manufacturers made almost 6 million SLI-type batteries. Table 1.4 summarizes the use of lead in South Africa for various types of batteries and other applications\textsuperscript{40}.

\textbf{Table 1.4:} Use of batteries in South Africa (2002)

<table>
<thead>
<tr>
<th>Types of batteries</th>
<th>Lead (tons)</th>
</tr>
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<tbody>
<tr>
<td>SLI (OE &amp; Replacement)</td>
<td>17 779</td>
</tr>
<tr>
<td>Industrial (UPS, Traction)</td>
<td>4 933</td>
</tr>
<tr>
<td>MCL</td>
<td>166</td>
</tr>
<tr>
<td>Other (plating, cables)</td>
<td>88</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>22 966</strong></td>
</tr>
</tbody>
</table>

OE: original equipment supplier

The values show that by far, the main use of lead is for the lead-acid batteries used for the SLI automotive industry.

Due to the fact that variations in environmental temperatures influence the chemistry of VRLA batteries to a greater extent than with flooded type batteries, complete replacement of the existing SLI automotive flooded battery by a VRLA would be unlikely. The use of heat shields around the battery has been suggested. Some automotive manufacturers have moved the battery position from the front of the car, where temperatures of up to 70°C can be experienced, to the boot of the car\textsuperscript{18, 19}.

A typical use of a VRLA system manufactured in South Africa is to be found in a Miners Cap Lamp (MCL) Battery. The desire for a completely sealed unit reduces the maintenance that is required in a harsh mining environment. The introduction of impurities and other maintenance errors during the replenishing of the electrolyte is very common. A completely sealed unit would allow for only one external maintenance application such as the charging sequence after use. A variety of battery
designs have been suggested in the literature and the nominal designs are around a 4 V / 16 Ah, which are discharged at 1 A to 3.7 V\textsuperscript{41}. A typical application requires a discharge of a 0.9 A bulb for a minimum of 9 h with possible requirements to operate for up to 12 h, and to maintain a voltage greater than 3.7 V. This is equal to about 56\% depth of discharge (DoD). The recharging of the batteries is usually done on a rack that charges at constant voltage of 4.9 V for 15 h. The life expectancy of such a battery is 2 years, which equates to about 700 cycles with a 9 h working shift.

The introduction of VRLA technology in MCL batteries is ideal for the South African manufacturer due a number of reasons:

- The life expectancy of the battery is relatively short in comparison to other applications, allowing for a higher consumption of batteries in the commercial market.
- The battery has only two cells. This reduces failures that are due to inconstancies between a string of cells such as float current and charging voltages.
- Most of the raw material used in the manufacture is locally produced. The only imported component would be the glass matt separator.
- The amount of lead and other raw material used in the manufacture of such batteries is relatively low when compared to larger battery types. This implies that the cost of research and development is relatively lower in terms of raw material usage.

This thesis will investigate the optimisation and improvement of various components of the MCL battery using VRLA technology. In particular the manufacturing process and the performance differences of tubular and flat plate electrodes will be investigated.

Once the technology of the relatively small-scale battery is proven to work effectively in its specific application, a scale-up to larger types of VRLA batteries for other applications would then be possible.
1.5. Continuous monitoring of the state of health for batteries

As a battery is used in a particular application, the two factors that remain critical throughout its service lifetime is firstly, its state of charge (SoC), and secondly, its state of health (SoH). In other words, how much current or capacity can one still obtain from the battery before having to recharge and how many capacity cycles can one get from the battery before failure?

With the current technology boom in cellular telecommunications, ever-increasing demands for remote repeater stations are required with suitable power supply. Accessibility to these repeater towers is often only by four wheel drive or helicopter. It is desirable to monitor the information on the state of the batteries health through some form of remote modem computer network system. In order to obtain such information, a number of diagnostic tests have to be done on the battery system. In particular, a typical UPS remote battery can consist of up to 300 x 2 V cells. If VRLA type batteries are used, the cellblocks would be 12 V batteries, which in-turn have six 2 V cells in series. Both the state-of-charge and health parameters are important for the end user and cannot be determined by direct readings during application. In order to do suitable capacity or state of health tests on the cells or batteries, they have to be physically disconnected, followed by a rated discharge and recharge capacity test. This is often not possible in particular applications where the power supply can be interrupted. During the capacity test, the battery would not be available for supporting the system as in the case of an emergency power supply. Additional batteries or supporting batteries would have to be used and the battery in question would have to be completely removed from its application. Capacity tests are long, tiresome and dangerous when dealing with high power applications. Capacity tests as such are seldom done in the field application, unless a batch or suspected faulty batteries are under question and removed. These diagnostic tests that are done at regular intervals are important, particularly, for stand-by support systems in order to ensure that the desired power would be delivered when required. The tests aim at knowing which cell or battery of a set of batteries (or cells) is starting to deteriorate or has failed and requires replacement.
The state of charge depends largely on the particular application. In order to know how much energy was taken out of the system one can use a simple load monitoring approach and determine relatively accurately how much energy must be put back into the system. However, this is not always simple, especially in applications such as vehicle traction and RAPS. Many papers have been published on predicting and simulating the service lifetime of batteries in RAPS and UPS type systems\textsuperscript{34, 55 & 61}. These models are based on one battery type and application and would require independent configuration for different systems or conditions. In addition, the actual capacity of the battery is influenced by its aging, which in-turn is dependent on the changes that occurred during its service life such as the loss of active material, grid corrosion, sulphation and water loss. The failure modes observed for the same type of batteries used in different applications often show different characteristics that caused the battery to fail or loose capacity. Often the loss in capacity is ascribed to the aging of a battery, but in fact might be due to the uncertainty in knowing the state of charge. “Premature capacity loss” (PCL) is a term used to describe the condition when a battery fails or looses its expected capacity before its specified service life as indicated by the manufacturer.

The most common method that gives an approximate indication of the SoC in the flooded type batteries is to monitor the SG of the electrolyte. A commercial battery service centre usually tests small automotive batteries using a simple pipette type hydrometer. Some batteries have built-in SG sensitive floating ball indicators. The values obtained from the hydrometer have to be compensated for temperature variations and are usually just an approximation to the SoC. The monitoring of the electrolyte SG does however not predict the service lifetime of the battery, nor give an indication of the state of health. Failure in battery capacity can still occur even though the SG of the electrolyte was sufficient. Larger stand-by batteries make use of hand-held electronic meters that can quickly measure the SG to four decimal places with automatic temperature compensation. The process still requires the physical presence of service technicians that need to record data and need to take corrective action when large variations between cells are observed. The extent of the water loss in flooded batteries is usually determined at the same time as the SG of the electrolyte. In the servicing of larger flooded UPS type batteries, stratification of the acid can occur giving an incorrect reading of the SG if the analysed sample was taken
from the top of the cell. In order to determine the SoC by measuring the SG, the electrolyte must be circulated and a set of predetermined parameters for the particular battery must be carried out experimentally. As yet, no suitable computer monitoring SG meter is commercially available that could evaluate the SG of battery electrolyte continuously during its service lifetime.

The monitoring of the SoC by means of the SG of the electrolyte cannot be done in a VRLA battery because the battery is a sealed unit with limited amount of acid present. However, the use of novel solid-state sensors built into the casing of VRLA batteries have been reported in the literature. Another parameter that is often used to monitor the cell performance is to consider the potential of each electrode versus a reference electrode. This gives some indication of the behaviour of the individual electrodes to each other. The use of various reference electrodes in VRLA batteries have been reported in the literature.

With long float type applications or repetitive uneven capacity cycling, the cell’s capacity and their open circuit voltage (OCV) in a string of cells can become unequal. Due to the uneven performance of cells and batteries, some cell’s capacity might decrease more, relative to others. In extreme situations, during a discharge, cells in a battery can be forced into reverse polarity. These uneven capacities are due to the initial cell’s SoC, which are determined by the manufacturing process. Factors such as uneven active material pasting on the grids, differences in porosity, cell compression variations etc, can result in cells within a battery to perform differently relative to each other, but still maintain an overall capacity that is above the manufacturer’s specified rated capacity. Once a cell starts to capacity cycle at a partial state of charge, relative to the other cells in a battery, its respective capacity loss increases and the overall state of health of the battery deteriorates faster. The failure or decrease in performance of one or more cells in a large bank of batteries would cause the other cells to function out of specification and are required to work harder, thereby reducing their own useful service life. The inconsistencies due to inadequate charging conditions are more pronounced in VRLA than flooded type batteries. Additional charge and equalized overcharging at elevated temperatures are often required to maintain a relative consistent state of capacity and float charge voltage between cells or batteries.
The most common method for determining the SoH of a battery is by considering the parameters and variations in cell voltages and string current. Large variations in the battery or cell temperature in VRLA batteries can give further information about the SoH. Various authors have reported on using sophisticated impedance studies and thermography to give some indication of the SoH of batteries in various types of applications. With impedance studies, the batteries are subjected to alternating currents between 10 to 200 Hz, where increases in internal resistance indicate an increase in corrosion and water loss. Thermography makes use of the thermo effects of the outer surface of a battery in order to deduce SoH of the battery. However, these techniques require sophisticated equipment and the interpretation of results are unique to a specific battery design, where prior information of the impedance and thermo characteristics of the new battery is required and are often influenced by the surrounding “noise” of electronic equipment attached to the battery.

Akutagawa et al have suggested a life indicator in lead-acid batteries based on the growth and pressure that occurs from a positive electrode in a cell assembly. The invention relied only on one physical characteristic of a deteriorating cell, namely the growth and expansion of the positive electrode during battery application. This indicator would respond through a receiving circuit illuminating a LED light source. This was primarily aimed at preventing short-circuiting of electrodes and cell wall damage due to the aged batteries. The growth of the positive electrode was a common problem associated with the use of Ca-based lead alloys in the 1990’s. Since then, the development in lead alloy research has improved significantly, causing the grid growth characteristics experienced with positive Ca-lead alloys to be reduced significantly, so that this effect is no longer a main contributing factor to battery failure.

Manufacturers of lead-acid batteries study the failure modes that limit the cycle life of batteries such as cell shortening, positive grid corrosion, shedding of PAM, loss of surface area, porosity, sulphation and water loss. New battery designs will always look at overcoming these problems with new claims of extended cycle life by additives, improved grid alloys and advanced design features. Reports of long life cycle testing of up to 1000 cycles can take over a year to complete. These tests are
usually done under ideal conditions where accelerated testing at elevated temperatures might give some indication of the failure modes but are often difficult to relate to real life situations. Performance testing such as float charge life testing is virtually impossible to do where life expectancy of more than 10 years can be expected.

Single cells in a VRLA type battery exhibit a broader voltage distribution during float charging applications than conventional flooded types and it is important to monitor these variations. The cause of the distribution is the competition between two cathodic overcharge reactions, namely the reduction of protons and the depolarisation of the negative plate by oxygen. The broad variation in the float voltages is controlled by varying the top of charge voltages (ToCV) to a higher float charging at 2.35 V / cell instead of the recommended float charge of 2.25 V / cell for flooded systems¹.

The VRLA batteries used in a UPS or RAPS system are often closely packed in battery cabinets due to space constraints. It then becomes important to monitor the temperatures of the system with suitable passive cooling to allow sufficient dissipation of the heat. Increases in the VRLA cell temperatures during float charge and during the recharging after a deep discharge cycle can give an indication of the increase in water loss and specific temperature limits should be adhered to and built into the algorithm of the charging system controls. The measuring of high voltages across the battery and the need for cell monitoring in closed confined spaces can also become dangerous.

The monitoring system must be able to provide information to a certain confidence level that the system will provide power for the required period of time not only in the moment but in the future. Since a battery pack is dependant on the SoH of every cell, it is important to monitor the onset of weaker or poorly performing cells, which would terminate the discharge period prematurely due to one or two cells. Abnormal cell deviations in comparison to the rest of the battery pack are usually good indications of poor performing cells. The monitoring system should enable the operator to register time dependant changes of battery parameters, and should prevent high temperatures or high float currents to occur. Abnormal operating conditions should release alarm signals that could be recorded through remote modem systems for
service personnel to respond to a particular bank of batteries. Variations in the cell voltages of ±50 mV can indicate that the cells are undercharged or that a number of cells are short-circuiting.

The monitoring of each cell voltage can be complex and expensive when up to 300 cells in a bank need to be registered and recorded. What is usually done in practice, such as in a decentralized telephone exchange is the following: the data logging of comparisons of individual float and discharge currents of 3 paralleled batteries are compared to published data from the manufacture. For economic and safety reasons, current, voltage and temperature of groups of batteries are monitored continuously and any changes with time are then signalled as alarms and recorded for maintenance.

The improvements in the electronic and lower cost microprocessors have allowed for the regulation and management of the entire energy system as a whole. The microprocessor can be designed to monitor the discharge capacity used, recharge limits and control, and temperature of the cells of battery on a continuous basis. Individual cells as well as entire battery packs can be monitored and controlled for cell equalization, end of life cut-off and temperature. Other desired parameters that should be monitored are the SG and the electrode potential versus a reference electrode. Devices for such uses have limited success in application on a large scale due to their cost and complexity.

Extensive work on simulating the working of VRLA under various conditions have shown that often the failed batteries are due to environmental conditions and charge profiles. An expensive VRLA battery has warranty to last between 10-15 years. The perception of a failed battery is still, that it is the battery manufacturers fault and that the failure lies with the manufacturer. Extensive warranty claims are a constant issue with supplier and customer in the battery industry. The failures and performance of VRLA batteries lie in the fact that the limits in the technology and its diverse applications are not fully understood. The battery manufacturer makes and sells the batteries according to the specified conditions of capacity, life cycle and performance under standard conditions. However, in an application, the battery is never or very seldom under the specified standard conditions.
This thesis will investigate a technique to monitor the SoH of VRLA batteries on a continuous basis, which can be applied to give suitable information for remote access battery systems.

In summary, this thesis will examine the viability of VRLA batteries in South Africa, and specifically investigate the following related aspects of lead-acid battery manufacture:

a. The use of Pb-Ca alloys as grid material for positive electrodes,
b. The manufacturing processes of positive tubular electrodes and their comparative performance to the use of flat plate electrodes,
c. An accelerated life-cycle comparison of MCL batteries made with flat plate positive electrodes, and
d. Determining the SoH of a VRLA MCL battery under accelerated conditions.

In addition, a method will be presented that will determine the porosity of a complete electrode plate. This method can be used by the industry as a quick, reliable technique for determining the porosity of the electrodes that were manufactured.
CHAPTER 2.

2. Experimental

2.1. Positive electrode investigations

2.1.1. Microstructure and accelerated corrosion study of Pb-Ca alloys

The corrosion performance of the positive electrode grids made from various types of lead alloys was studied using an accelerated applied potential corrosion test. This was done in order to evaluate comparatively the use of various lead-calcium alloys as grids for positive electrodes in automotive batteries. The results would also give an indication of what type of grids should be used in VRLA battery designs.

Electrochemical cells were assembled with unpasted grids where each grid type was soldered onto a crossbar in parallel as the positive pole electrode. A standard gravity cast grid was used as the negative pole electrode. The cells were kept at a constant temperature of 55°C in industrial grade sulphuric acid (SG 1.25) with a constant potential across the cell of 2.31 V. R. Miraglio\textsuperscript{79} used an applied potential of 1.5 V for the positive electrode versus an Hg/Hg\textsubscript{2}SO\textsubscript{4} (K\textsubscript{2}SO\textsubscript{4}) reference electrode. In the following experiment, however, a Cd reference electrode was used intermittently to ensure that the potential was approximately 2.75 V for the positive electrode versus Cd. The Cd electrode could not be left in the acid solution on a continuous basis since, with time, some of the Cd would dissolve in the acid. The following table was used as a guideline that compared the use of various reference electrodes.

<table>
<thead>
<tr>
<th>Reference Electrode</th>
<th>Hg/Hg\textsubscript{2}SO\textsubscript{4}</th>
<th>Cd</th>
<th>Calomel</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25 V</td>
<td>0 V</td>
<td>0.63 V</td>
<td>0.30 V</td>
<td></td>
</tr>
</tbody>
</table>

The study was comparative in nature where the various grid types in one cell would be subjected to the same applied potential throughout the experiment. At regular intervals during the accelerated corrosion study, samples were cut from the various grids for evaluation. Some of the corroded grid sample would be cast into cold set resin for further Scanning Electron Microscopy (SEM) and optical microscope...
microstructure studies. The SEM was a Philips XL30 Series and the optical microscope was an Olympus PMG3.

The other parts of the corroded grid samples were evaluated for their respective grid mass loss due to electrochemical corrosion. The exposed corroded areas (lead oxide) of the grids would be dissolved in a 1:1 mixture of glacial acetic acid (UniLAB chemical pure) and hydrazine hydrate (UniLAB chemical pure). The samples would be washed and reweighed in order to determine their mass loss as an indication of the extent of corrosion. A plot of the percentage mass loss versus time and the microstructure observations for the various alloys under investigation would allow a comparative study of the degree of corrosion under constant applied potential.

Samples for micro-structural studies were prepared by using alumina-polishing solutions of 1µm and 0.3µm respectively. The samples were chemically etched using a 3:1 solution mixture of acetic acid (CH$_3$COOH) and hydrogen peroxide (H$_2$O$_2$) (Merck, chemical pure) respectively.

The elemental composition of the lead alloys used in the study were determined by ICP analysis. The technique uses an ICP Spectra Flame Modular with at least 3 standard solutions prepared in the range of the expected elemental composition for the different alloys analysed.

### 2.1.2. Age-hardening of lead alloys

The following sets of experiments were done in order to evaluate the age-hardening properties of lead alloys used for the manufacture of positive electrode grids. The problem experienced by the industry was that the hardening process required for certain Pb-Ca alloys was taking a long time to harden significantly in order to be used for further manufacturing. The problem caused unnecessary delays and the accumulation of stock. The study investigated the age hardening properties of two types of Pb-Ca alloys compared to a typical Pb-Sb alloy. The alloys are abbreviated as M5, CAP and CaO1 and their elemental composition range are summarized in table 2.2. The alloys were subjected to the following set of conditions:
a. Under normal ambient room temperature conditions as per existing processes in the factory,
b. Under various accelerated age-hardening processes in a controlled laboratory environment and
c. Under quenched age-hardening processes after casting.

**Table 2.2:** Composition of Pb-alloys received from Willard Batteries for comparative age-hardening study.

<table>
<thead>
<tr>
<th>Alloy description</th>
<th>Pb-Alloys composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% Se</td>
</tr>
<tr>
<td>M5</td>
<td>0.025-0.03</td>
</tr>
<tr>
<td>CAP</td>
<td>-</td>
</tr>
<tr>
<td>CaO1</td>
<td>-</td>
</tr>
</tbody>
</table>

Positive electrode grids were gravity cast with the alloys using the normal manufacturing process in the factory.

The age-hardening characteristics of the alloy were determined by monitoring the change in their respective Vickers hardness with time. This was carried out on a Vickers Armstrongs Eng. Limited machine with a square based diamond pyramid shaped indenter and a load of 1kg. The Vickers hardness is a method that determines a materials’ resistance to indentation. The test was performed by impressing into a specimen, the pyramid indenter under a known static load. The hardness is expressed as a number that is proportional to the load and area of impression\(^91\). The load used for all the samples studied was 1kg and the results are expressed as a Vickers Hardness (VH) number. The units are in kgf/mm\(^2\). The selected section used for all samples was the electrode lug area. The samples were left in a temperature-controlled room at 24\(^\circ\)C throughout the experiment. An average of 5 tests would be done on selected days after receiving new cast grids of the alloys and their results recorded.

The grids made from the different alloys would be subjected to the following set of conditions:
a. The grid samples were left at ambient room temperature and their normal age hardening monitored with time.

b. Grid samples were subjected to various heat-treating sequences soon after being gravity cast. Samples from each sequence were then allowed to age-harden with time at 24°C.

b1. The cast grids were quenched in water straight after casting by placing the hot grid in 0°C water. They were then placed in an oven and heat treated at 110°C for 24 h. After the heat treatment, the grids were again quenched in 0°C water before being cooled to ambient temperature before analysis.

b2. The cast grids were allowed to cool under normal conditions to room temperature after casting. They were then placed in an oven and heat treated at 110°C for 2 h, 8 h and 24 h respectively. After the heat treatment, selected grids were removed after each time interval and allowed to cool to ambient temperature before analysis.

b3. The cast grids were allowed to cool under normal conditions to room temperature after casting. They were then placed in an oven and heat treated at 80°C for 2 h and 24 h respectively. After the heat treatment, selected grids were removed after each time interval and allowed to cool to ambient temperature before analysis.

One of the concerns expressed and reported in the literature was the effect of over age hardening\textsuperscript{86}. With time, the lead alloy hardens to a maximum, and then subsequently starts to decrease in its hardening properties, to the extent that it could become unsuitable for manufacturing purposes. This effect was investigated by selecting sufficient grid samples of each of the above alloys with the addition of a sample made from pure lead. Selected samples were age hardened at 110°C for 24 h without quenching and left to cool to ambient temperature before analysis. All samples (heat-treated and non-heat-treated) were left in a temperature-controlled room at 24°C for the duration of the experiment. At regular intervals, samples from the grids were tested for their VH as described previously over a period of three months.

In order to verify the effects of the age hardening properties of the lead alloys, it was necessary to compare the tensile strength and the % elongation of heat-treated and
untreated alloy samples. The changes in % elongation of the alloys with time could indicate the change in brittleness of the alloy. If the alloy becomes too brittle, it could again be detrimental to the manufacturing process, where relatively flexible grids are required for ease of assembling. The samples for the tensile testing were made by casting 10 mm diameter by 200 mm length rods made from the different alloys listed in table 2.2. The selected alloys were heated to 400°C and poured into a pre-heated mould. The mould and rods were allowed to cool to ambient temperature, before removing. One set of rods was then heat-treated at 110°C for 24 h and the other set was left at ambient temperature. All samples (heat-treated and non-heat-treated) were left in a temperature-controlled room at 24°C for the duration of the experiment. The samples were subjected to tensile testing on a Hounsfield H25ks extensometer with a 5 kN load cell at a test speed of 5 mm/min. The rod samples were clamped into stainless steel jaw clamps and subjected to a transverse pull where the maximum strength and the % elongation at break were recorded. An average of three tests per sample were carried out at regular time intervals.

2.1.3. Pickling and curing of positive tubular electrodes

The common practice in the manufacturing industry is to leave a batch of tubular plates in the pickling acid for different time intervals ranging from 6 to 12 h, depending on the shifts and supervision of the process. The existing process involves the hoisting of large quantities of the tubular plates by crane into the acid baths. After the prescribed times, the tubes are then hoisted into a water bath, where the excess acid is supposed to be washed from the electrodes. Since the plates are tightly packed, acid could remain between the plates during the drying process, which would then lead to significant increases in acid concentration. The increase in the acid concentration then becomes detrimental to the acrylic gauntlet, which gives the electrode its rigidity. In addition, inconsistent sulphation of the positive electrodes could occur, thereby resulting in poor cell performance. This practice also occurs in the manufacturing of the tubular MCL positive electrodes, where excessive pickling processes are being used.

Battery manufacturers are always looking at improving their production processes in order to become more efficient and to produce a more consistently performing
product. It was therefore necessary to investigate the possibility of reducing the production process time in the manufacture of tubular jar-formed cells without decreasing the performance of the final product. It was also necessary to investigate the possibility of improving the existing manufacturing process in order to obtain the desired consistency in plate manufacturing.

The positive tubular plates chosen for the study of the influence of varying the dipping and curing times with its influence on the final electrochemical performance were 14 spine plates with rectangular profiled non-woven tubes. The plates were vibration-filled with an industrial grade grey oxide that contained 0.012 % Syloid (amorphous silica). The average packing densities of the spines was 3.9 g/cm³. The characteristics of the grey oxide used are summarized in table 2.3.

**Table 2.3: Characteristics of the filling oxide**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free Lead</td>
<td>15.2 %</td>
</tr>
<tr>
<td>γ-PbO</td>
<td>13.5 %</td>
</tr>
<tr>
<td>α-PbO</td>
<td>71.3 %</td>
</tr>
<tr>
<td>Acid Absorbance</td>
<td>153.0 mg / g oxide</td>
</tr>
<tr>
<td>Apparent density</td>
<td>29.42 g/cu.in.</td>
</tr>
<tr>
<td>BET surface area</td>
<td>0.71 m²/g</td>
</tr>
<tr>
<td>Particle size mean D[4,3]</td>
<td>5.51 µm</td>
</tr>
<tr>
<td>Particle size median D(v, 0.5)†</td>
<td>4.44 µm</td>
</tr>
</tbody>
</table>

The phase analysis of the oxide and active material was determined by X-ray powder diffraction (XRD) and the data was analysed using the commercial software program known as Peaks⁴⁹. The program uses a method developed by Hill⁵⁰ to determine specific peak intensity ratios of X-ray diffractograms of various solid phases used as active material in lead acid batteries. Phase identification was done using the ICDD diffraction patterns search¹⁰⁰. Some common diffractograms found in Pb-acid battery is shown in Appendix B. A Bruker D8 Advance X-ray powder diffractometer was used for all XRD measurements.

* D[4,3] is defined as the equivalent volume mean diameter or the De Broucker mean.⁵¹
† D(v,0.5) is defined as the volume (v) median diameter as shown as D₅₀ or D₀.₅.
The BET surface area was determined by nitrogen gas adsorption on the active cured or formed material, which was carefully removed from the fabric tube and inner Pb-spine. A Micromeritics Gemini III 2375 was used for all BET measurements. The absolute density of formed active material was determined by using a Micromeritics Multivolume Helium pycnometer 1305. The Hg porosimetry pore volume distribution and porosity was done on a complete 12 mm length section of a single spine containing the active material. A Micromeritics Autopore II 9215 was used for all Hg porosimetry measurements. The particle size distribution of the oxide powder was determined using a Malvern Mastersizer laser-diffraction particle size analyzer.

The oxide-filled tubular plates were dipped in 1.1 SG sulphuric acid for 5 sec, 15 min, 60 min, 5 h and 15 h respectively. The dipped plates were subsequently washed with water in order to remove any excess acid and were allowed to cure in a Labcon humidity chamber set at 25°C and 85 % humidity. The Selected plates from the different batches were removed after 12 h, 24 h and 48 h curing time. The plates were allowed to air-dry completely and reweighed before being assembled into cells. The cells were assembled with one negative flat plate on either side of the positive tubular plate. The cells were rated at 22.5 Ah at the C₅ rate‡ and contained an excess amount of acid. The formation acid used had an SG of 1.24, which was adjusted to 1.25 after formation. The assembled plates were allowed to soak for 1 hour in the acid before commencing with the formation. The formation was done at constant current (4 A) until 250 % of the theoretical active material capacity was achieved. A 3 h rest period was allowed after the first 30 h of formation. The formation conditions for all cells were kept the same. An initial C₅ discharge test to 1.75 V was done followed by a constant voltage (2.6 V) recharge of 140 % of the discharged capacity. This was followed by a high current (50 A) discharge test and a 10-cycle test at the C₅ rate. Once the 10-cycle test was completed, another 50 A discharge test was done. All discharge capacities and cycling tests were carried out at room temperature. All electrochemical testing of the cells was done using a Maccor Series 4000 multi-channel computer controlled battery tester.

The active material of duplicate cells for the different dipping and curing times were analysed for their respective phase composition, BET surface area, absolute density,

‡ C₅ is defined as the discharge rate at which the battery would discharge within 5 hours.
porosity and pore volume distribution after the curing, formation and capacity cycling steps. All discharge capacity results are recorded in Ah/kg of active cured material.

2.1.4. Addition of red lead to positive active material in MCL batteries

The following study investigated the influence of varying the red lead content to positive active material in VRLA MCL flat plate and tubular electrodes. The addition of red lead to the positive active material is known to improve the formation efficiency of batteries that have relatively thick flat plate or tubular electrodes\(^{37}\). However, the cost of using red lead is relatively greater than that of normal grey oxide made by the Barton Pot process.

One of the advantages that were investigated in using flat plate electrodes in VRLA MCL batteries rather than tubular, was the reduction of material cost per positive electrode. This included the fact that the flat plate positive electrode requires less active material for the same Ah capacity and that a more automated pasting process could be used than the corresponding tubular electrode. However, due to the plate thickness and VRLA cell type assembly, the efficient conversion of active material was often low when only grey oxide was used. It was therefore necessary to investigate the effect of adding red lead to the flat plate manufacturing process and to optimise the formation process in order to obtain a reliable product without compromising its final performance.

Red Lead oxide is exclusively used in the manufacture of tubular electrode MCL batteries. The feasibility of increasing the grey oxide content into the active material and the optimisation of the formation process was necessary.

The following was a comparative study between the two types of positive electrode manufacturing technologies with variations in red lead addition to the active material. Batches of active material for tubular and flat plate MCL electrodes were prepared by respectively adding 25, 50, 75 and 100 % Pb\(_3\)O\(_4\) to grey lead oxide that was made from a Barton Pot process. The cells were assembled with the different ratio oxides and were tested using two different formation acid concentrations and two different rates of formation sequences.
The procedures for preparing the two types of electrodes with variation in red lead content are described as follows:

**Tubular Electrodes**
A 6 spine current collector made from an antimony lead alloy (1.8 % Sb, 0.1 % As and 0.2 % Sn) with rectangular profiled non-woven acrylic tubes as active material support was used to make the positive tubular electrodes. The correct ratio of grey oxide and red lead was prepared and the plates were vibration-filled containing 0.012 % Syloid. The average packing density of the tubular plates was 3.4 g/cm$^3$ and the characteristics of the red lead and grey oxide used are summarized in table 2.4. The filled tubular plates were dipped in 1.1 SG sulphuric acid for 5-15 seconds only, since previous work had shown this to be sufficient for tubular electrodes. The dipped plates were subsequently washed with water in order to remove any excess acid and were allowed to cure in a humidity chamber set at 25°C and 85 % humidity for 48 h. The cured plates were allowed to air-dry completely before being assembled into cells or used for further analysis.

**Flat Plate**
A 112 x 55 x 4 mm cast grid current collector was made from a lead-calcium alloy (0.045 % Ca, 0.7 % Sn and 0.035 % Ag). The correct ratio of grey oxide and red lead was prepared in a Mullen Wheel Paste Mixer and pasted by a single-sided belt paster. The paste was prepared by adding 24 L of 1.24 SG sulphuric acid and 32-40 L of water to 300kg of oxide mix containing 0.1 % of floc-fibre. The paste was mixed until the correct paste properties were obtained with a density between 136 to 144 g/(2 cubic inch) and a plasticity of 27-29 using a Globe Pentometer. The characteristics of the red lead and grey oxide used are summarized in table 2.4. The pasted flat plates were allowed to cure in a humidity chamber set at 25°C and 85 % humidity for 48 h. The cured plates were allowed to air dry completely before being assembled into cells or used for further analysis.

The flat plate grids used for the negative electrodes were made by using a lead-calcium alloy (0.1 % Ca and 0.3 % Sn) pasted with a standard mixture of grey oxide and expander. The same negative plates were used in the assembling of batteries
with the tubular or flat plate positive electrodes, made with the various ratios of red lead to grey oxide.

**Table 2.4:** Characteristics of the red lead and grey oxide.

<table>
<thead>
<tr>
<th></th>
<th>Grey Oxide</th>
<th>Red Lead</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free Lead</td>
<td>27.3 %</td>
<td>-</td>
</tr>
<tr>
<td>β-PbO</td>
<td>15.4 %</td>
<td>11.8 %</td>
</tr>
<tr>
<td>a-PbO</td>
<td>57.3 %</td>
<td>4.4 %</td>
</tr>
<tr>
<td>Pb₃O₄</td>
<td>-</td>
<td>83.9 %</td>
</tr>
<tr>
<td>Acid Absorbance</td>
<td>152.3 mg / g oxide</td>
<td>-</td>
</tr>
<tr>
<td>Apparent density</td>
<td>28.64 g/cu.in.</td>
<td>-</td>
</tr>
<tr>
<td>BET surface area</td>
<td>0.686 m²/g</td>
<td>0.536 m²/g</td>
</tr>
<tr>
<td>Particle size mean D[4,3]</td>
<td>9.55 µm</td>
<td>8.31 µm</td>
</tr>
<tr>
<td>Particle size median D(v, 0.5)</td>
<td>6.16 µm</td>
<td>4.49 µm</td>
</tr>
</tbody>
</table>

The cells were assembled into polycarbonate containers with three negative flat-plates and two positive tubular or flat-plates wrapped with AGM glass matt separator. The average compression of the cells was determined to be about 12 kPa. The formation acid used was 1.19 or 1.26 SG. The cells were formed using an “open” system, where excess electrolyte was used\(^{47}\). The SG of the electrolyte was adjusted to 1.31 SG after formation. The cells were allowed to “soak” for 1 h with the acid before commencing the formation sequence. The formation was done using a multi-step constant current formation profile until 250 % of the theoretical active material capacity was achieved\(^{44}\). The formation sequences used are summarized in table 2.5. The high rate sequence was only optimised after completing the initial studies using the low rate sequence, which was used in the industry’s manufacturing process. The voltage and temperature profiles of the different batteries were simultaneously recorded during their formation process using the Maccor battery tester. The temperature of the formation process was recorded by inserting a Teflon coated PT100 probe into one of the cell openings.
Table 2.5: Sequences used in the formation of flat plate and tubular MCL batteries.

<table>
<thead>
<tr>
<th>Electrode type</th>
<th>Rest (h)</th>
<th>Charge (A)</th>
<th>Rest (h)</th>
<th>Charge (A)</th>
<th>Rest (h)</th>
<th>Charge (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat Plate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low Rate</td>
<td>1</td>
<td>1.5 for 22 h</td>
<td>1</td>
<td>2 for 21 h</td>
<td>1</td>
<td>1 for 21 h</td>
</tr>
<tr>
<td>High Rate</td>
<td>1</td>
<td>2 for 2 h</td>
<td>1</td>
<td>4 for 3 h</td>
<td>1</td>
<td>2 for 6 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9 for 3 h</td>
<td></td>
<td>3 for 3 h</td>
<td></td>
<td>1.5 for 10 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 for 3 h</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tubular</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low Rate</td>
<td>1</td>
<td>1.5 for 26 h</td>
<td>1</td>
<td>2 for 27 h</td>
<td>1</td>
<td>1 for 27 h</td>
</tr>
<tr>
<td>High Rate</td>
<td>1</td>
<td>2 for 4 h</td>
<td>1</td>
<td>4 for 5 h</td>
<td>1</td>
<td>2 for 6 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9 for 4 h</td>
<td></td>
<td>3 for 4 h</td>
<td></td>
<td>1.5 for 10 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 for 5 h</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The cells were rated at 16 Ah at the 1 A rate. After formation, an initial 1 A discharge test to 1.75 V / cell was done followed by a constant voltage (2.65 V / cell) recharge where 140 % of the discharged capacity was returned. This was followed by a high current (10 A) discharge test and a 10 cycle test at the 1 A rate. The cycle test was set to a discharge voltage of 1.75 V and a constant voltage recharge of 2.62 V until 130 % of the discharged capacity had been achieved at a maximum current of 2 A. All discharge capacities and cycling tests were carried out at room temperature. The active material of the duplicate formed cells were removed from the batteries, washed with water and dried for further analysis for their respective phase composition, BET surface area, absolute density, porosity and pore volume distribution. All discharge capacity results are recorded in Ah and Ah/kg of active cured material.

The phase analysis of the oxide and the cured and formed active material was determined by XRD as described previously. The BET surface area and the absolute density of cured and formed active material were determined as described previously. The Hg porosimetry pore volume distribution and porosity was done on the same instrument that was described previously. The tubular electrodes were analysed by using a complete 10mm length section of a single spine containing the active material and acrylic gauntlet. The flat plate electrodes were analysed by removing complete sections of the active material from the grid wire current collector.
2.2. Porosity measurements of electrodes used in Pb-acid batteries

There seems to be a need for a quick, easy-to-use analytical method for determining the porosity characteristics of a battery electrode. The following method was developed in order to allow the technical laboratory in a lead-acid factory to evaluate, on a routine basis, both the formed and cured positive and negative electrodes and draw conclusions from the results with regards to the effective porosity of the manufactured material. The electrodes could be evaluated as a complete plate, giving an average porosity distribution across the whole electrode and not just certain sections thereof. The method developed for the plate density measurement was similar to that developed by Johnson Contro\textsuperscript{93} but uses glycerol instead of water.

Various samples of cured and formed active material of both the negative and positive electrodes were analyzed using the glycerol displacement method, and compared to the results obtained using techniques of BET surface area (Nitrogen absorption), Mercury Porosimetry (Hg intrusion) and Helium Pycnometry (He intrusion). The BET surface area analysis was performed on selected active material that was carefully removed from the center of the respective electrode grid. Care was taken not to crush the samples or distort the shape of the samples. This was particularly important for the analysis of the formed negative active material, where the sponge lead can very easily be distorted when handled.

The experimental details and calculations for measuring the absolute density and porosity electrode active material by means of glycerol displacement are described below.

**Accessories and equipment required**

- Vacuum pump
- Vacuum desiccator
- 5 L glycerol
- Electronic balance with a scale hook underneath (accurate to at least 2 decimals)
- Common electrical crocodile clips
- Thin copper wire (0.5 m length)
Large container or test cell (approximately 25 cm deep to support the electrode intended for analysis)

Preparation
Figure 2.1 shows schematically the laboratory set-up for the glycerol displacement method. The electronic balance is placed on a sturdy frame structure, which is located about 50 cm above the test cell. The one end of the copper wire, bent into a hook, is allowed to extend from the bottom of the scale through a hole in the centre of the frame support. The other end of the copper wire has a common electrical crocodile clip where the plates for analysis are supported. The container used must be big enough to allow a complete plate to be immersed in glycerol. The container should however not be oversized, which would then require an excess amount of glycerol. The container was supported on a laboratory jack that could be easily moved up or down underneath the balance frame structure.

Figure 2.1: Experimental method for the determination of the porosity using the glycerol displacement method.

Method
1. The copper wire with a clip is connected to the balance and zeroed before connecting the sample for analysis.
2. The plates for analysis must be sufficiently dried prior to determining their mass. The positive formed plates can be dried in an oven at 110°C. The
negative formed plates should be dried in an inert atmosphere such as Nitrogen or Argon. Care needs to be taken that all the sulphuric acid is washed from the plates before drying. Cured positive and negative plates are placed in an oven at 110°C for a short period of time to ensure complete dryness before plate mass determination. The mass of the dry plate should be filled in table 2.5 as C.

3. One plate from a batch of both the cured positive and negative plates should be used to determine the accurate mass of their respective grids by carefully removing the active material. This value should be recorded in table 2.5 as F. The density, which depends on the type of alloy used for the grid, should be recorded in table 2.5 as G.

4. The plates to be tested are placed in the container, which is filled with glycerol. The negative and positive formed plates should not be placed in the same container, since they could touch and result in an electrical short-circuit. The filled container is then placed in the desiccator. The desiccator is evacuated by a vacuum pump for about an hour or until no more air bubbles are observed coming out of the glycerol covered plates.

5. The vacuum on the desiccator should be released slowly and the plates are then removed from the glycerol. The plates are allowed to stand freely in an upright position for about half an hour. Ensure that no contact is made with the sides of the plates.

6. After the standing time, there may still be a few drops of glycerol hanging from the bottom of the plates; these should be carefully wiped away with paper towel. The plates are re-weighed by suspending the wet plate by the crocodile clip that was set up in step 1. Their masses are recorded in table 2.5 as D.

7. The suspended wet plate is then carefully immersed into the container filled with glycerol. The sample should not touch the sides of the container and hang freely, completely immersed in the glycerol. Ensure that the crocodile clip is not immersed in the glycerol, as this will influence the results. Wait for the reading on the balance to stabilize and record the mass in table 2.5 as E.

8. Remove the plate from the glycerol and repeat the measurement for at least two plates per batch.
Table 2.6: Calculations for determining the matrix density and porosity of plates by means of the glycerol displacement method\textsuperscript{93}.

<table>
<thead>
<tr>
<th>Column</th>
<th>Description or equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Customer ID (battery type, plate size)</td>
</tr>
<tr>
<td>B</td>
<td>Plate Type (cured, formed, +ve or –ve)</td>
</tr>
<tr>
<td>C</td>
<td>Dry plate mass, (g)</td>
</tr>
<tr>
<td>D</td>
<td>Glycerol soaked plate mass, (g)</td>
</tr>
<tr>
<td>E</td>
<td>Mass in glycerol, (g)</td>
</tr>
<tr>
<td>F</td>
<td>Grid mass, (g)</td>
</tr>
<tr>
<td>G</td>
<td>Grid density, (g)</td>
</tr>
<tr>
<td>H</td>
<td>Active material mass, (g) = C – F</td>
</tr>
<tr>
<td>I</td>
<td>Absolute Density, (g/cm\textsuperscript{3}) = H/((C-E)/1.264-(F/G)) *</td>
</tr>
<tr>
<td>J</td>
<td>Bulk Density, (g/cm\textsuperscript{3}) = 1/((1/I)+K) *</td>
</tr>
<tr>
<td>K</td>
<td>Specific Pore Volume, cm\textsuperscript{3}/g = ((D – C)/1.264)/H *</td>
</tr>
<tr>
<td>L</td>
<td>% Porosity = JxKx100 *</td>
</tr>
</tbody>
</table>

\* The derivation of the formulas will be discussed in chapter 4.

The following sets of experiments were performed in order to validate the method developed and to determine its limits and accuracy. Porosity results obtained by the glycerol displacement method were compared with the results from Hg porosimetry. Pore volume distribution was determined from Hg porosimetry and BET surface area using N\textsubscript{2} adsorption technique. All these techniques were described previously.

1. Cured and formed positive and negative automotive plates were received on a monthly routine basis from a local lead-acid battery manufacturing facility. Their porosity was evaluated using the glycerol displacement method using the complete electrode. In order to verify the repeatability of the technique on various types of cured and formed electrodes, the analysis was done in duplicate, where the average and the standard deviation was recorded. To ensure reproducibility, the electrodes were taken from the same manufactured batch. Selected electrodes from the same batch that had undergone similar electrochemical processes were further analysed by BET surface area and Hg porosimetry. The samples for the two techniques were selected from active material taken from the middle section of duplicate electrodes.
2. A 12 V 50 Ah automotive battery was formed where each cell of the battery was filled with a different SG sulphuric acid. It is known that the concentration of the formation acid influences the surface area and porosity of the final active material\(^1\). The formed electrodes (+ve and –ve) were washed, appropriately dried and analysed for their porosity by the glycerol displacement method and Hg porosimetry. The BET surface area was analysed for the active material taken from the middle of the plates. The 6 cells were filled with 1.1; 1.13; 1.16; 1.20; 1.24 and 1.28 SG acid respectively, and formed in a water bath for 62 h until \(5 \times C_{20}\)\(^8\) rated capacity was achieved. After formation, the battery was cut open, and the formed positive and negative electrodes carefully removed.

3. The repeatability and versatility of analysing other types of electrodes were investigated by evaluating a cured and formed positive tubular electrode used in the study for section 2.1.3. A 10-spine electrode was used in the study, since the curing and formation conditions for each of the individual spines would be identical. The electrode was divided by cutting along the spine separator into 10 identical individual spines. The porosity of the cured active material in each spine was analysed by the glycerol displacement method and compared for their repeatability and accuracy. The mass of the single spine replaced the grid mass (F) in table 2.6 and the mass of the plastic stopper and gauntlet was also taken into consideration when doing the calculations.

\(^8\) \(C_{20}\) is defined as the discharge rate at which the battery would discharge within 20 hours.
2.3. Oxygen recombination in MCL VRLA cells.

The effective recombination of oxygen in a VRLA battery is an important parameter in order to reduce the water loss properties and to extend the service life of the battery. The rate at which oxygen in a cell can migrate from the positive electrode to the negative electrode where it can recombine to form water, can be indirectly determined by measuring the $O_2$ concentration in the free space above the cell assembly.

The oxygen recombination efficiency of VRLA MCL batteries made with flat plate and tubular positive electrodes were compared by using batteries made during previous tests as described in section 2.1.4. The batteries were made by assembling two positive plates with three negative flat plates separated with AGM separator. The positive electrodes were either made from a flat plate assembly, where active material made from grey oxide was pasted onto a lead-calcium grid support before curing and formation, or a tubular assembly where a six spine lead-antimony grid support was inserted into rectangular non-woven acrylic tubes filled with 100 % red lead oxide. The batteries were assembled and formed using standard manufacturing procedures specified by the particular battery manufacturer. The acid after formation was adjusted to 1.31 SG and after a few capacity cycles, excess acid was removed from the top of each cell. The filling hole was then closed with a suitable rubber gas-vent plug and stopper.

The MCL batteries were rated at 16 Ah and subjected to 10 x 80 % DoD capacity cycles before commencing with the recombination study to ensure that all active material had converted and that the electrolyte was in a starved condition in the separator.

A piezo-electric pressure transducer (RS 0-15 psi output) and an oxygen sensor (AO2-PTB-18.10/City Technology) were assembled into the battery case wall as shown in figure 2.2. The pressure sensor measured the change in the pressure of free space above the cell assembly with respect to atmospheric pressure. The oxygen sensor was calibrated under normal atmospheric oxygen concentration of 21% before
assembly. The influence of the variation in the cell pressure on the % O\textsubscript{2} reading by the sensor was observed to be minimal and disregarded in calculations.

![Pressure and Oxygen sensors assembled into an MCL VRLA Cell](image)

**Figure 2.2:** Pressure and Oxygen sensors assembled into an MCL VRLA Cell

The cell was allowed to stand in OCV until all the oxygen in the cell’s free space had decreased below 1 % before testing. The following test sequences were chosen to evaluate the O\textsubscript{2} recombination characteristics under normal operating conditions.

1. The discharge and charge cycle with intermittent OCV rest periods were applied as follows:
   a. Discharge the cell at 1 A to 1.75 V followed by a recharge at 2 A with a constant voltage limit of 2.7 V until 140 % of the discharged capacity was achieved. This was followed by a 48 h rest period before another discharge and charge cycle.
   b. This was followed by another 48 h rest period. The cell was then charged and discharged 4 times at the same current and voltage ratings as in (a) without any rest periods after the charge cycle.

2. The float charge characteristic at different voltages of the cell was studied as follows: a fully charged cell was overcharged at 2.45, 2.50, 2.55, 2.60, 2.65 and
2.70 V respectively for 18 h with a 48 h OCV rest period between each charge step.

The 48 h rest periods in all the studies were sufficient to allow the O$_2$ that was in the cell’s free space to decrease below 1 %. All the tests were done at room temperature and the change in the voltage, current, cell pressure and % O$_2$ in the cell’s free space was recorded using a Grant 1000 Series Squirrel Meter/Logger.

2.4. Accelerated life cycle testing of VRLA MCL batteries

2.4.1. Pressure release valve

In order to maintain a consistent recombination efficiently in a VRLA battery, it was important to ensure that the working of the pressure release valve was as specified by the manufacturer. It was important to maintain a reasonable pressure inside the cell compartment in order to reduce the loss of gases that are formed during the charging process of the battery, even after extensive exposure to sulphuric acid. The following experiment was carried out to simulate the opening and closing of a pressure relieve valve used in VRLA MCL batteries under conditions of high acid concentrations.

A transparent polycarbonate MCL battery case was modified with a glass frit and a piezo-electric pressure transducer (fig 2.3). The glass frit was connected to an air pump, which was controlled by a timing switch. Air was allowed to bubble through 1.300 SG acid at a very slow rate every hour for one minute. After every 12th hour cycle, an additional 1-hour rest period was allowed. These rest periods allowed the pressure to stabilize and indicate at what appropriate pressure the valve would close completely. The pressure sensors would measure the change in the cell pressure with respect to atmospheric pressure. The test was performed at 25°C for two weeks, which would be equivalent to 336 cycles of opening and closing the valve in a typical application.
2.4.2. **Life-cycle test of VRLA MCL batteries.**

MCL batteries made with the flat plate positive and negative electrodes were subjected to a comparative accelerated life cycle testing. Two batteries were obtained from the local manufacturer and one battery each from two different competitor suppliers. The batteries were rated at 16 Ah at the 1 A discharge rate and were tested for 3 cycles before subjecting the batteries to the life cycle testing. Only batteries that obtained 16 Ah or more during their initial cycle test were used in the following study.

**Figure 2.3:** Experimental cell for the simulation of opening and closing of a pressure release valve used in VRLA MCL batteries.
Life Cycle Test Sequence

Capacity test at 0 cycle: 1 A discharge to 1.85 V / cell and recharged at constant voltage of 2.7 V / cell for 24 h with a 2 A maximum current limit.

This was followed by:
1 life unit
- Discharge at 2.5 A to 35 % of the rated capacity (2.24 h)
- Charge at 2.6 V / cell until 6.16 Ah was returned to the battery (110 % of the rated capacity), with a maximum current limit of 2.5 A.
- This was performed 40 times (cycles) followed by a 30 minute rest period.

After the rest period, a capacity test of 1 A to 1.85 V / cell was performed followed by a constant voltage charge at 2.6 V / Cell for 24 h with a maximum current of 2 A. A charge limit of 25 Ah was used. After the capacity test, the battery was weighed in order to determine the water loss during the preceding life cycle unit. The battery was then placed back in the water bath to commence with the next life cycle unit. All life cycle units and the 1A capacity tests between the units were performed in a water bath at 40°C.

The life cycle units were repeated until the batteries had lost 50 % of their rated capacity or when the life cycle could not obtain 1.85 V / cell upon discharge during the 40 cycle sequence.

After completing the accelerated life cycle testing, the batteries were cut open in order to determine their cause for loss in capacity or cell failure.

2.4.3. Corrosion study of the strap-lug interface in MCL cells

Following the results of the life cycle testing of the MCL batteries in the previous section, it was necessary to determine the optimum strap alloy for use in the assembly of the negative electrode. Five different strap alloys (table 2.7) were used and subjected to an accelerated corrosion study that simulated long life charge cycling. Negative electrode grids made from a common Pb-Ca alloy (CAP) were assembled to each strap that contained a different alloy. The ease of assembly, the
flow of the strap alloys and its electrochemical corrosion were studied. All cells were assembled in parallel, thereby being subjected to the same charge and discharge cycle. The grids and straps were placed in sulphuric acid with an SG of 1.250 and the acid was filled to just under the strap-lug interface. The temperature throughout the test was kept at 50°C. The samples were allowed to corrode for a period of two weeks according to a profile where the cells were charged at 2.7 V for six hours and then discharged to 0.1 V followed by the next charge at 2.7 V. After the accelerated corrosion study, a cross-section was cut from the strap/lug interface and mounted in Epofix resin. The samples were ground and polished with 0.5 micron Alumina and etched appropriately in a mixture of 20 ml H₂O₂ and 80 ml Acetic Acid. The cross sections of the strap-lug interface were evaluated using an optical microscope and their corrosion characteristics reported. The following table shows the specified alloy percentage compositions of the different strap alloys used.

**Table 2.7: Specifications for the alloys used in the strap.**

<table>
<thead>
<tr>
<th>Alloy Type</th>
<th>% Sn</th>
<th>% Sb</th>
<th>% As</th>
<th>% Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAP/5HT</td>
<td>A 1:1 mixture of the two alloys was prepared</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAP</td>
<td>0.55-0.80</td>
<td>0.001</td>
<td>0.001</td>
<td>0.030-0.056</td>
</tr>
<tr>
<td>A75</td>
<td>0.10-0.15</td>
<td>2.5-3.0</td>
<td>0.10-0.15</td>
<td>-</td>
</tr>
<tr>
<td>5HT</td>
<td>0.28-0.32</td>
<td>4.50-5.00</td>
<td>0.25-0.30</td>
<td>-</td>
</tr>
<tr>
<td>3HT</td>
<td>0.20-0.25</td>
<td>3.70-4.00</td>
<td>0.10-0.15</td>
<td>-</td>
</tr>
</tbody>
</table>

2.5. **Continuous monitoring of the state of health of batteries**

The following experiment describes a component that gives an on-line continuous State of Health (SoH) sensing for lead-acid batteries that can detect the change of certain physical characteristics that indicate the progression of the batteries useful life. The SoH sensor has a detection part, a circuit, an amplification part, a receiving part and an algorithm that interprets the received data. The SoH sensor was positioned in the battery case in such a way as to detect the change between two or more sections along the width or height of an electrochemical cell assembly.
Figure 2.4 is a vertical sectional view of the placement of two sensors in the wall of the polycarbonate cell container of a MCL VRLA cell. The dimensions and placement of the SoH sensors serve only as an example and could be positioned appropriately in any other VLRA type battery, depending on the cell size and configuration. In this example the sensors are placed at the top and bottom part of the cell respectively. The top sensor was placed in such a way that it was just below the cell component assembly, ensuring that it was in contact with the AGM separator. The bottom sensor was placed near the bottom part of the cell assembly ensuring that it was in contact with the AGM separator.

Figure 2.5 shows a vertical sectional view of the sensor. The spacer was positioned inside the battery case wall with a suitable resistance strain gauge. The resistance strain gauge is commercially available and is made from a suitable grid of resistance wire, that when subjected to a change in dimensions it would result in a change in its resistance. It was placed on the inside of the spacer by solvent welding it between two thin pieces of polycarbonate. The spacer was supported by two small bridges on either side to allow the spacer to be flush with the inside wall of the battery container. A second strain gauge, defined as a dummy gauge was placed on the opposite side of the working gauge imbedded in the sensor frame. The gauges were assembled in such a way as not to be in contact with the electrolyte and still maintain the cell container’s wall integrity for the functioning of a proper cell. The gap between the working gauge on the spacer and the dummy gauge on the sensor frame was sufficient to allow movement of the spacer without compromising the strength and durability of the cell container wall.
Figure 2.4: Schematic representation of the strain gauge sensors assembled into a polycarbonate MCL battery. Only one cell is shown (all dimensions are in mm).

Figure 2.5: Cross-sectional view of a strain gauge sensor assembly in a polycarbonate battery case. Only one sensor is shown (all dimensions are in mm).

A 16 Ah MCL VRLA battery with 2 positive flat plates (112 x 55 x 4 mm) and 3 negative flat plates was used in the study. The battery case was made from see-
through polycarbonate (PC) and the strain gauges, supported on thin PC bridges, were assembled into the cell wall container, allowing the face of the bridge to be flush with the battery case inner wall. The PC mountings were solvent welded into place using chloroform. The strain gauges and their terminals were imbedded into the polycarbonate to prevent any contact with the corrosive electrolyte.

Two different sized strain gauges were used in two separate built cells and assembled into the PC cell wall. The strain gauges had a resistance of 120.0 Ω ± 0.5 % with a nominal gauge-factor of 2.00. The working temperature range of the gauges was from -30 to 180°C, well within the range of the working temperature of a battery. Their temperature coefficient factor was 0.015 %/°C. The two strain gauges are referred to as 2 mm gauge (2.5 x 6.0 mm) and 5 mm gauge (11 x 4 mm) respectively. The working and dummy strain gauges of each cell were assembled into a Wheatstone-Bridge as shown in figure 2.6.

![Wheatstone Bridge assembly](image)

**Figure 2.6:** A Wheatstone Bridge assembly of the strain gauges used in the SoH sensor in the MCL VRLA cell.

A suitable excitation voltage (12 V) was applied across the bridge. The null detector voltage (D) was suitably amplified and transmitted to a data-logging device (Squirrel) that recorded the change in the voltage with time. $R_B$ and $R_Y$ are the strain gauges situated at the bottom of the cell and $R_A$ and $R_X$ are respectively situated near the top of the cell. The use of strain gauges in any application is very sensitive to changes in
temperature. The effect of temperature was reduced by using the arrangement indicated, where the unstressed dummy gauges are exposed to the same temperature as the working gauge, thereby compensating for any temperature influences that might occur. $R_B$ would be the dummy gauge for the working gauge $R_Y$ and similarly $R_A$ the dummy gauge for $R_X$.

The test sequence chosen to evaluate the characteristics of cell wall strain variation was an accelerated capacity test of 90 % depth of discharge (DoD) with excessively high recharge voltages allowing for sufficient water electrolysis and active material shedding to take place. The purpose of the accelerated testing was to demonstrate the working principle of the SoH sensor.

The cell underwent a capacity cycle by discharging the cell at 2 A to 1.75 V limit followed by a recharge at 2.7 V until 120 % of the discharged capacity was returned with a 2 A current limit. This was done until the battery had achieved almost 50 % of its initial capacity. The cell voltage, strain difference and cell temperature were recorded simultaneously during the testing sequence. The % strain difference between the two sensors was determined by subtracting the strain difference reading ($S_F$) from the initial strain difference ($S_I$) divided by the $S_I$, where $S_I$ was determined from the amplified voltage reading of the assembled cell before the accelerated testing. A K-type thermocouple was inserted into the battery case wall in order to measure the change in temperature of the cell during the testing sequences.
CHAPTER 3.

3. Positive electrode investigations

3.1. Background

This chapter covers the experimental results obtained for the investigations carried out to evaluate the performance of positive electrodes in VRLA MCL batteries. Some of the investigations relate to components that are common to all types of lead acid batteries, such as the type of grid alloy and active material pasting procedures.

The positive electrode of any battery is considered as the “work-horse” of the battery. At this electrode, chemical oxidation takes place of the material present in the electrode, or on the electrode surface, or both. In particular, with lead-acid batteries, failure or loss of capacity is often related to the characteristics of the positive electrode, such as positive active material shedding, grid corrosion and poor initial capacity.

This chapter will specifically deal with the following:

a. The corrosion characteristics of positive electrode grids and the use of Pb-Ca alloys as grid material,

b. Additional manufacturing problems which often occur when using new types of alloys for grids, amongst them being the characteristics of age-hardening,

c. The improvement of the pickling and curing manufacturing process of industrial tubular positive electrodes, and

d. The addition of red lead to improve the performance characteristics of flat plate and tubular electrodes used in MCL batteries.

3.2. Microstructure and accelerated corrosion study of Pb-Ca alloys

The comparative corrosion performance of the positive grid made from various lead alloys was studied using an accelerated high temperature constant voltage cell. A Cd reference electrode was used at regular intervals to measure the positive electrode potential. The applied potential across the cells was measured to be 2.31 V
at 55°C. The average applied potential of the positive electrode versus the Cd reference was slightly lower than that used by R. Miraglio. However, since the experiment was comparative by nature and the grids were assembled in one cell, the electrode potential was not adjusted during the experiment.

The elemental compositions of the alloys used in the study are summarized in table 3.1.

**Table 3.1**: Composition of Pb-alloys received from the battery manufacturer for comparative corrosion study.

<table>
<thead>
<tr>
<th>Sample Number / Grid description</th>
<th>%Ca</th>
<th>%Sn</th>
<th>%Ag</th>
<th>%Al</th>
<th>%Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>I / M5: gravity cast 1.5 mm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.8</td>
</tr>
<tr>
<td>II / Std CAN: gravity cast 1.2 mm</td>
<td>0.08</td>
<td>0.35</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>III / CAP: gravity cast 1.5 mm</td>
<td>0.04</td>
<td>0.64</td>
<td>0.03</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>IV / CAP: gravity cast 1.2 mm</td>
<td>0.03</td>
<td>0.78</td>
<td>0.03</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>V / Exp CAN: made from strip</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VI / DLP: gravity cast 1.5 mm</td>
<td>0.063</td>
<td>0.76</td>
<td>0.041</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VII / CAP: strip</td>
<td>0.059</td>
<td>0.76</td>
<td>0.034</td>
<td>0.006</td>
<td>-</td>
</tr>
</tbody>
</table>

3.2.1. **Average corrosion mass loss.**

The average % corrosion mass losses for the various grids investigated are shown in figure 3.1. No corrosion study of the lead alloy strip (VII) was done (table 3.1). It was only used for microstructural evaluation.
The results show that the Pb-Sb (M5) alloy had the highest mass loss characteristics due to electrochemical corrosion over the 23 days as compared to any of the other alloys investigated containing variations of the Pb-Ca alloy.

The higher mass loss due to electrochemical corrosion of the Exp-CAN as compared to the Std-CAN alloy can be related to the amount of Sn present in the alloys. Literature has reported on the benefit of small amounts of Sn in Pb-Ca alloys to reduce its electrochemical corrosion effect\textsuperscript{80-83}. The Sn acts as an inhibitor for excessive grain boundary corrosion. Further, expanded grids are subjected to mechanical cutting and stretching of the metal sheet into a suitable grid frame. The effect of stretching of the alloy would introduce micro-strains along the grain boundaries that allows for more corrosion to take place\textsuperscript{82}. However, it is beneficial to use expanded metal grids as current collectors for the negative electrodes due to its ease of manufacturing and where very little corrosion takes place.

The alloys with low Sn to Ca ratio (<9) (sample II) exhibit a finer grain structure with more rapid age hardening and a higher corrosion rate as compared to alloys that have a higher tin to calcium ratio\textsuperscript{82, 88}. The effect of the Sn to Ca ratio on the microstructure will be discussed in more detail later.
No significant differences in the corrosion mass loss between the other three grid-alloys were observed, with the DLP type alloy showing a slightly lower mass loss after 23 days.

### 3.2.2. Microstructural investigation.

In order to obtain further information about the extent of electrochemical corrosion taking place for each grid alloy tested, the microstructural characteristics of the corroded sections after 23 days were investigated using an optical microscope and SEM.

![Microscope and SEM micrograph for M5 alloy after 23 days of corrosion.](image)

**Figure 3.2:** Microscope and SEM micrograph for M5 alloy after 23 days of corrosion.

Figure 3.2 shows the microstructure studies of the antimony-based alloy (M5) with fine dendritic grain structures that are typical for antimony-based lead alloys. The
corrosion that occurred can be seen to be predominantly along the grain boundaries at the surface of the grid. The alloy showed a much higher % mass loss over the 23 days of analysis when compared to the Pb-Ca alloys. This can be largely ascribed to the alloy containing very fine grain structures that allows for a more inter-grain corrosion and that the applied potential encourages dissolution of the Sb into the electrolyte. Corrosion occurs preferentially in the interdendritic (eutectic) regions at the surface of the alloy\(^9\). The corrosion is also associated with a type of “built-in” electrochemical cell at the grain boundary precipitates, where segregation of the alloying elements can provide the metal with slightly different electrochemical potentials, thereby encouraging corrosion.

**Figure 3.3:** Microscope and SEM micrographs for std-CAN alloy after 23 days of corrosion.
Figure 3.3 shows the microstructure studies for the std-CAN alloy (Pb-Ca) with the corrosion to be predominantly along the grain boundaries that can lead to pieces of grains to be detached from the surface. The grain structure is relatively well refined with smaller grains near the surface of the grid, which can lead to more corrosion to take place. The alloy contained no Ag and had a Sn to Ca ratio of 4.4. Lead alloys with a Sn to Ca ratio of less than 9 show a grain structure to be smaller with serrated grain boundaries. These can be explained in terms of the Pb₃Ca that encourages the moving of the grain boundaries during solidification. These alloys would have a higher corrosion rate when compared to alloys with a higher Sn to Ca ratio and are predominantly used as negative grid alloys. They were included in this study for comparison purposes.

Figure 3.4: Microscope and SEM micrograph for CAP gravity cast grid (1.5 mm) after 23 days of corrosion.
Figure 3.4 shows the microstructure studies for the CAP grid (Pb-Ca) that was gravity cast to a thickness of 1.5 mm. The pictures show that the corrosion was localized at the grain boundaries with the bulk of the corrosion occurring on the surface of the grains. The grains are irregular in shape and size with a slight preferred orientation towards the centre of the grid. There are areas of discontinuous groups of grains where the corrosion attack along the grain boundary seems to be more prevalent (fig 3.4 a.). This could be due to the quenching effect on the alloy that occurs during casting. The alloy had a Sn to Ca ratio of 16 and a small amount of Ag. Ag had been shown to be beneficial in the manufacture of positive grid alloys, reducing the grid corrosion and enhancing the active material / grid interface properties during capacity tests of electrodes\(^{75, 76}\). As discussed previously, lead alloys with higher Sn to Ca ratio (>9) show larger grain sizes with slower initial age hardening properties and lower corrosion rates\(^{82, 83, 87}\). However, inter-granular penetrating failure of grids can occur quicker if the grains are too big. If the Sn to Ca ratio is >9, the grains are larger and well defined with cellular type substructures of segregated tin. These form stable \((\text{Pb,Sn})_3\text{Ca}\) precipitates during the solidification and age hardening process of the alloy\(^{85}\).

Figure 3.5 shows the microstructure studies of the CAP grid (Pb-Ca) that was gravity cast to a thickness of 1.2 mm. The concern expressed by the manufacturer was that even though the same alloy composition was used in the casting of two grids with different thickness, would the corrosion behaviour be the same? Hence, would the effects of different cooling rates and grid size significantly influence the corrosion properties?
The results were similar to the previous alloy evaluated in that the corrosion was mainly at the grain boundaries near the surface of the grid. The grain structure was irregular in size and showed a dendritic type structure that was superimposed on the “puzzled” macro structure. This was not observed in the previous samples, and could be a result of the slightly higher Sn to Ca ratio (26) and a slightly different rate of cooling used during the manufacturing process.

The one sample evaluated microscopically showed that air cavities or pores were in the centre of grid structure (fig 3.5 b.). These pores occur during the casting process and are due to air being trapped in the bulk of the cast metal. These areas could
result in weaknesses in the grid, since during accelerated corrosion they are exposed to the surface acid causing the grid to break prematurely.

The corrosion analysis results in figure 3.1 show no significant difference between the two grids with different thickness, even though their grain structure appeared to have some differences. The presence of pores, observed in some samples, would only influence the strength characteristics of the grid if significant corrosion had taken place through the bulk of the grid wire.

![Microscope and SEM micrographs for exp-CAN grid (Pb-Ca) after 23 days of corrosion.](image)

**Figure 3.6:** Microscope and SEM micrographs for exp-CAN grid (Pb-Ca) after 23 days of corrosion.

Figure 3.6 shows the microstructure studies of the exp-CAN (Pb-Ca) grid that was made from an expanded metal grid. The pictures show that a lot of the corrosion was along the grain boundaries. The SEM micrographs show that there are large defined
precipitated regions around the grains, which are susceptible to corrosion. Smaller irregular grains can be seen extending towards the centre of the grid with preferred orientation of the grains towards the corners of the grid.

The expanded metal grid type contained only Ca (0.04%) and is primarily used as a negative electrode grid. In this study, the grid was used for comparison purposes only and showed a higher corrosion mass loss when compared to the previous Pb-Ca alloys. This can be largely ascribed to the absence of tin and silver in the alloy, which inhibits particular grain boundary corrosion. The fact that the grid was an expanded metal rather than a cast grid also has an influence on its corrosion properties. The microstructure studies show typical larger grains to be lined in preferred orientation towards the corners of the grid. This occurs during the mechanical expansion of the cold alloy into a grid during manufacturing. The corrosion of expanded metal grids is usually higher than cast grids due to the micro strains that are introduced during the cold-rolling and expanding process.

Figure 3.7 shows the microstructure studies of the DLP grid (Pb-Ca) that was gravity cast to a thickness of 1.5 mm.
The pictures show the alloy to have an irregular grain microstructure with a superimposed dendritic structure. The pictures show minimal corrosion along grain boundaries, with the bulk of the corrosion localized along the surface of the grains. The Sn to Ca ratio was 12 (>9) and contained a slightly higher concentration of Ag than the previous CAP gravity cast grids evaluated. A number of samples showed significant amount of pores that are formed from trapped air pockets. This is an indication of poor casting and quenching of the sample during the manufacturing process. These pores are areas of weaknesses in the grid structure and can cause accelerated corrosion and premature grid failure.
A large amount of pores was observed in a number of samples investigated. This suggests that the particular type of grid, with this alloy composition was more difficult to obtain as a good quality product with low amounts of internal air cavities due to the manufacturing process used. Factors such as a too low alloy or mould temperature could cause early solidification of the metal liquid thereby trapping pockets of air in the grid structure. A too early cooling cycle into the mould after casting could also have prevented sufficient time to allow the air to escape during casting, thereby trapping it in the grid structure.

The alloy used in the DLP grids had a slightly higher Ca and Ag content than the previous CAP alloys (table 3.1). In spite of the large amount of pores observed in the grids, the results of the corrosion study (fig 3.1) show it to have the lowest mass loss due to electrochemical corrosion over the 23 days of analysis, when compared to the other alloys analysed.

The above study only considered the corrosion characteristics and microstructure of gravity cast grids used for positive electrodes. The feasibility of using a suitable Pb-Ca based alloy as an expanded metal grid for positive electrode grids was also investigated. Figure 3.8 shows the microstructure studies of the CAP strip (Pb-Ca) before being expanded into a grid.

Figure 3.8: Microscope microstructure for a cross-section of a CAP strip. Optical 5 x mag.
The use of the alloy is still at the experimental stage, where neither the mechanical expanding of the grid nor corrosion studies have been completed. The purpose of the microstructure study was to compare its grain structure to that of the other types of Pb-Ca alloys investigated. However, due to the complexity of obtaining the correct alloy and the cost of producing the expanded metal, the continuation of this investigation was postponed.

The cross-section of the strip in figure 3.8 shows the large preferred orientation of the grains across the width of the strip. There are areas in the metal where grains have a superimposed binary structure near the surfaces of the strip (dark brown batches). These areas of the alloy would be more susceptible to corrosion than other more regular shaped grains. There are also large grains that in some places extend across the width of the strip and can introduce micro-fractures when subjected to mechanical stretching during the manufacturing of the expanded grid. This type of alloy with its grain structure would be unsuitable for its use as a positive electrode current collector. The grains would have to be substantially refined and modified with the possible use of grain boundary engineering\textsuperscript{85}.

### 3.2.3. Summary

The above results show that an increase in the rate of the inter-granular corrosion of the positive grid was observed with a decrease in Sn content and depended on the Sn to Ca ratio of the alloy, which agrees with results reported in the literature\textsuperscript{82-90}. The grain size and shape in calcium based lead alloys depend on its Sn to Ca ratio. Alloys with a Sn to Ca ratio below 9 (sample II) would have a finer grain structure with more grain boundaries at the surface exposed to the acid thereby showing a higher corrosion rate. Alloys with a Sn to Ca ratio above 9 (sample III and VI) have larger equiaxed grains that show a lower corrosion rate but are more susceptible to deep inter-granular corrosion which can result in grains to dislodge themselves from the bulk material.

The above study shows that a small amount of Ag in the grid alloy reduces the grid corrosion characteristics, however, with a relative increase in the cost of the alloy. The study also shows that care must be taken when gravity casting Pb-Ca alloys with
a higher Sn content. The process is more susceptible to forming small pore cavities in the grid, which can lead to a weakening of the current collector during service lifetime of the battery.

Stress in the material that is caused by the corrosion product along the grain boundaries of larger grains can also lead to grid growth. Grid growth can result in the physical deformation of the grid along its thin wire grating, causing the actual electrode to increase in size. This is detrimental in a cell where the electrodes are tightly packed, resulting in internal short-circuiting through the cell separator and in extreme cases, damage to the battery housing.

3.3. Age-hardening of lead alloys.

The introduction of Pb-Ca alloys in the manufacture of the negative and positive electrodes has lead to the pasting process of the particular battery industry to adapt the “workability” of the grid. Pure lead is very soft and would not be suitable for high rate production. The use of Pb-Sb alloys increased the hardness character of the grid significantly where they have a relatively short “age-hardening” time (3-5 days), after which the pasting process began. However, with the introduction of Pb-Ca alloys, the grids were considerably softer, requiring longer age-hardening time. This significantly reduced the manufacturing throughput rate. The following study investigated the possibility of reducing the age-hardening time of some of the more common Pb-Ca alloys used in battery manufacturing. The experimental procedures and the three alloys selected for the study, together with their composition range are summarized in chapter 2. The table with the composition range of these three alloys is again shown in table 3.2 for the purpose of discussion.
Table 3.2: Composition of Pb-alloys received from Willard Batteries for comparative age hardening study.

<table>
<thead>
<tr>
<th>Alloy description</th>
<th>Pb-Alloys composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% Se</td>
</tr>
<tr>
<td>M5</td>
<td>0.025-0.03</td>
</tr>
<tr>
<td>CAP</td>
<td>-</td>
</tr>
<tr>
<td>CaO1</td>
<td>-</td>
</tr>
</tbody>
</table>

3.3.1. Vickers hardness studies

Figure 3.9 summarizes the change of Vickers hardness (VH) of the three alloys studied with time when left to cool and age-harden at room temperature with no heat treatment or quenching after casting the grids.

![Vickers Hardness Graph](image)

Figure 3.9: VH change with time for alloy samples that were allowed to cool at room temperature with no heat treatment.

The results show that the VH for the antimony-based alloy (M5) increased within 5 days after casting to a hardness value of over 15. Previous manufacturing experience has shown that for all practical purposes of handling a grid in manufacturing, its VH hardness should be above 15. The two calcium based alloys required at least 12-14 days before their respective VH was above 15.
Figure 3.10 summarizes the change of VH of the three alloys studied with time when quenched in water after casting and after heat-treating at 110ºC for 24 h. The water used for quenching was 0ºC.

![Graph](image)

**Figure 3.10:** Vickers Hardness change with time for alloy samples that were quenched in water straight after casting and were heat treated at 110ºC for 24 h, followed by another quenching in water.

The results show that quenching the antimony alloy (M5) had a detrimental effect on the hardness properties of the alloy. Its VH did not increase above 15 even after leaving the samples 20 days to age harden. However, the quenching effect and heat treatment improved the VH hardness of the two calcium lead alloys, where a VH hardness of above 15 was obtained after removing the samples from the heat treating and quenching. The hardness of the alloys continued to increase to above a VH of 20 after 20 days. However, even though an improvement in the VH was observed when quenching and heat-treating the Pb-Ca alloys, it would not be practical to introduce this process near the grid casting machines due to the high temperatures of the surrounding, because of the 0ºC required for cooling.

The following three figures summarize the VH hardness change with time for the lead alloy samples that were heat treated at 110ºC for various lengths of time.
Figure 3.11: VH change with time for Pb-alloys heat treated at 110⁰C for 2 h and cooled to room temperature.

Figure 3.12: VH change with time for Pb-alloys heat treated at 110⁰C for 8 h and cooled to room temperature.
The figures shows that by heat-treating the M5 alloy at 110°C for 8 and 24 h respectively resulted in a decrease in its effective VH number. Heat-treating the M5 alloy for 24 h resulted in a decrease of the VH number to below 15. The VH number remained below 15 even after 20 days. However, an improvement in the age hardening time was observed for both Pb-Ca alloys that were heat treated for only 2 h at 110°C. Their respective VH number increased to over 15 within the first three days. Noticeably, by increasing the heating time to 8 and 24 h respectively, a reduction in the time required for the Pb-Ca alloy to increase in hardness was observed, especially for the CAP alloy, where a VH value close to 20 was obtained after removing the samples from the oven after 24 h of heat treatment.

The following two figures show the VH number change with time for the lead alloy samples that were heat-treated at 80°C for 2 h and 24 h respectively.
Figure 3.14: VH change with time for Pb-alloys heat treated at 80°C for 2 h and cooled to room temperature.

Figure 3.15: VH change with time for Pb-alloys heat treated at 80°C for 24 h and cooled to room temperature.

The results show that the heat-treatment of the M5 alloy at 80°C for 24 h gave a VH number above 15. However this same heat-treatment for the two Pb-Ca alloys gave
only a slight improvement in the age hardening properties when compared to the heat treatments at 110°C described previously.

3.3.2. Tensile strength and % elongation

Figure 3.16 and 3.17 show the results of the tensile strength analysis of the various lead alloys that were heat treated at 110°C for 24 h after casting. They were compared to the samples that were not heat treated after casting. For comparison purposes, the tensile strength data for pure Pb, which was similarly heat-treated, is included. All samples were kept at room temperature for the duration of the experiment.

![Tensile Strength and % Elongation Graph]

**Figure 3.16**: Tensile Strength change with time for Pb-alloys and pure Pb that were heat treated at 110°C for 24 h and cooled to room temperature.
Figure 3.17: Tensile Strength change with time for Pb-alloys and pure Pb that were not heat treated after casting, but left to cool to room temperature.

Figure 3.18 and 3.19 show the experimental results obtained for the % elongation at break as a function of time for the various lead alloys that were heat treated at 110°C for 24 h after casting. They were compared to the samples that were not heat treated after casting. For comparison purposes, the result for pure Pb, which was similarly heat-treated, is included.
Figure 3.18: % Elongation change with time for Pb-alloys and pure Pb that were heat treated at 110°C for 24 h and cooled to room temperature.

Figure 3.19: % Elongation change with time for Pb-alloys and pure Pb that were not heat treated after casting, but left to cool to room temperature.

The Tensile strength comparison between the heat-treated and non-heat treated alloys showed that there was no significant difference in strength for the M5 alloy. An
average value of 50 MPa was obtained for the tensile strength analysis after 23 days. For comparison purposes, pure lead was heat-treated and the results showed an average tensile strength of only 25 MPa with no significant difference between the heat-treated and non-heat-treated samples. The importance of alloying lead for the purpose of grid manufacturing can be seen in these results, where the tensile strength of pure lead is about half that of the antimony alloy (M5).

The calcium lead (CaP) alloy showed on average a higher tensile strength for the samples that were heat treated than those that were not. The CaP alloy showed an initial tensile strength of about 90 MPa for the heat-treated samples, which remained relatively constant for the duration of the test period. The non-heat treated samples showed an initial lower tensile strength value of about 55 MPa with an increase in strength after 17 days to 80 MPa. The CaO1 alloy samples showed a slight increase of tensile strength when comparing the heat-treated with the non-heat treated samples. The values ranged from 50 to about 67 MPa. There was little change in tensile strength for the samples as they were allowed to age harden for 23 days.

The results of the % elongation for the M5 and CaO1 alloy were similar for the duration of the 23 days of analysis. The CAP alloy showed an initial lower % elongation, with the heat-treated samples lower than the non heat-treated samples. The pure lead samples showed the highest % elongation of about 35 % for the heat-treated and non-heat treated samples.

The % elongation properties of metals can be considered as an indication of its brittleness character. The results show that the stronger alloy (CAP) in terms of tensile strength had a lower % elongation. This would imply that the CAP alloy might have a higher tensile strength but could also have a higher brittleness factor. The properties of elongation and brittleness are important characteristics to consider if an alloy is to be used in the manufacturing of expanded metal grids. A metal with poor elongation properties would give possible failure during the expansion of the sheet metal during manufacturing.
3.3.3. Over-age hardening

The properties of over-age hardening the lead alloys are shown in the following figures. The VH testing of heat-treated and non-heat treated samples were tested for a period of 100 days.

Figure 3.20: VH change with time for Pb-alloys and pure Pb that were heat treated at 110°C for 24h and cooled to room temperature.
Figure 3.21: VH change with time for Pb-alloys and pure Pb that were not heat-treated.

The heat treatment of the M5 and CaO1 alloys at 110°C for 24 h showed a decrease in their VH number towards the end of the 100 days of age hardening. The results show an initial slightly lower VH value (<15), than the non-heat treated samples for the same period of time. A further decrease in the VH number after about 60 days was observed for the two alloys. The CaP alloy that was heat-treated showed an initial increase in VH number above 20, followed by a slight decrease after about 60 days of analysis. Its VH number did not decrease below 17 after 100 days of analysis.

3.3.4. Summary

Ageing processes of lead calcium alloys are described in the literature to proceed via a number of steps that involve the properties of their grains and crystalline structure to determine aging and over-aging characteristics. The initial transformation takes place through the movement of different grain boundaries that then induces an initial hardness. All these mechanisms are thermally activated, thereby allowing for the heat-treating effect to accelerate the process. The over-ageing depends on the amount of calcium in its composition. If the alloy also contains high levels of tin, it
would cause the grains to harden by a continuous precipitation of \((\text{Pb}_{1-x}\text{Sn}_x)_3\text{Ca}\)\(^{82}\). Over-ageing occurs when the discontinuous transformations of the grains at their inter-phase precipitate allows them to move easier, thereby decreasing the metals hardness\(^{87}\).

Alloys that contain a Sn to Ca ratio of (<9) tend to harden quicker and obtain a relatively consistent VH hardness. The \(\text{Pb}_3\text{Ca}\) that is formed during the solidification process is believed to impart rapid initial hardness. For a low Sn to Ca alloy (>9), the initial hardness is low and only increases to acceptable levels after 6-10 days of hardening\(^{87}\). The slow formation of the \((\text{PbSn})_3\text{Ca}\) and \(\text{Sn}_3\text{Ca}\) precipitates at the grain boundaries are considered to harden the lead matrix at a much slower rate. When the alloys starts to over-age harden, the \((\text{PbSn})_3\text{Ca}\) increases in size thereby allowing more movement between the grain structures. The above tensile strength results were similar to the results published in the literature, where an alloy with a higher tin content showed an increase in tensile property\(^{87}\).

The results of the above study show that sufficient improvement in the age-hardening properties of the Pb-Ca alloys, used in the manufacturing of grids, can be achieved by heat treating them for short periods of time at 110\(^\circ\)C (2 h – 8 h). However, similar heat-treating Pb-Sb alloys, showed a decrease in the hardening properties of the alloy.

The tensile strength and % elongation results showed that care must be taken with the heat treatment of CAP alloys (Sn to Ca ratio > 9), where a low % elongation was obtained. This can be an indication of an increase in brittleness of the alloy, and care must be taken when handling the grids during manufacturing, where excessive strain placed on the grid can cause it to break.

No significant decrease in the hardening properties of the Pb-Ca alloys was observed during the over-age hardening study. A slight decrease in VH number was observed towards the end of the 100 days of study, but the VH values were still above the acceptable value of 15.
3.4. Pickling and curing of positive tubular electrodes

The influence of varying selected parameters in the manufacturing process of tubular electrodes was investigated in order to reduce the time required and to produce a consistent optimised performing product. Two aspects of the manufacturing process investigated were the pickling or dipping process of newly filled electrodes and the curing process. The other parameters such as the acid concentration and formation procedures were kept constant.

Figure 3.22 shows the relationship between the acid adsorption and the different dipping times. The results show that a significant amount of acid was adsorbed after only 5 seconds of dipping. The amount of acid adsorbed within the first 5 seconds was approximately one third of the acid that would be adsorbed after 15 h. M.T. Lin et al. reported that an acid adsorption of 170 mg/g oxide should be achieved for optimal formation. However, as seen from the figure, an acid adsorption of only 130 mg/g oxide could be achieved after 15 h of dipping.

![Figure 3.22: Relationship between the acid adsorption and dipping time for tubular positive plates.](image)

The cross-sectional stereomicroscope pictures (fig 3.23a-d) show the depth to which the acid penetrated after the various dipping times. By leaving a plate in acid for 15 h, the acid did not penetrate all the way through the oxide to the middle Pb-spine.
Instead, a thick crust of lead sulphate was formed on the exterior surface of the spine. This can be seen in figure 3.23d, where the tubular electrode that was dipped for 15 h has a thick layer of lead sulphate penetrating about ½ of the oxide material towards the inner lead spine. The electrodes that were dipped for 15 and 60 min show only a slight irregular penetration of the acid.

Figure 3.23a: Spine dipped for 15 min.  
Figure 3.23b: Spine dipped for 60 min.  
Figure 3.23c: Spine dipped for 300 min.  
Figure 3.23d: Spine dipped for 15 h.

Table 3.3 summarizes some of the XRD phase analysis results for the cured and formed active materials after the 12 and 48 h curing time respectively. The total sulphate content of the cured material was considerably lower than the results indicated in figure 3.22. This was because a lot of the sulphate material would have remained on the non-woven outer tube that was removed before analysis. The results show that there was an increase in lead sulphate and monobasic lead sulphate for the samples that were dipped for longer periods of time in acid. However, generally there
was no significant difference in phase composition for the various samples that were cured for 12 or 48 h. There was no significant increase in the tri-basic lead sulphate for samples that were cured for a longer time.

**Table 3.3:** XRD phase analysis of the cured and formed active material of tubular spines that were dipped in acid for various times and cured for 12 and 48 h respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cured Active Material (%)*</th>
<th>Formed Active Material (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a-PbO</td>
<td>β-PbO</td>
</tr>
<tr>
<td>D5sec C12hrs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C48 hrs</td>
<td>65</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>74</td>
<td>12</td>
</tr>
<tr>
<td>D5min C12 hrs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C48 hrs</td>
<td>65</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>66</td>
<td>10</td>
</tr>
<tr>
<td>D60min C12hrs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C48hrs</td>
<td>59</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>57</td>
<td>10</td>
</tr>
<tr>
<td>D300min C12hrs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C48hrs</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>61</td>
<td>12</td>
</tr>
<tr>
<td>D15 hrs C12hrs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C48hrs</td>
<td>52</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>44</td>
<td>11</td>
</tr>
</tbody>
</table>

D: Various Dipping Times
C: Various Curing Times
T1: Monobasic Lead Sulphate
T3: Tribasic Lead Sulphate
* The free-Pb values are shown in figure 3.25.

The changes in the surface area of the cured active material with dipping and curing times are shown in figure 3.24. These results show that there was a sharp increase in the surface area for the cured active material in going from a dipping time of 5 seconds to 15 and 60 minutes. A gradual decrease in the surface area of the active material was observed for samples that were dipped for 5 h and 15 h respectively. This trend was the same, irrespective of the curing times. During the initial stages of dipping, the lead oxide would react with the acid to form lead sulphate. If the oxide remained in the acid for longer periods of time, the lead sulphate crystals would start to grow and fuse together to form larger crystals. This in turn would cause a decrease in the surface area of the active material.
Figure 3.24: Relationship between the BET surface area and various dipping and curing times of cured active material.

The changes in the free-Pb of the cured active material with dipping and curing times are shown in figure 3.25. These results show that the free-Pb decreased considerably from 12 h to 24 h of curing. The decrease in free-Pb from 15.2% initially, after 12 h of curing was only 6%, whereas the decrease after 24 h was almost 11%. The free-Pb after 48 h of curing was only slightly lower than that after 24 h of curing. Literature recommends that the free-Pb after curing should be kept low in order to eliminate possible Pb in the final formed active material\textsuperscript{52}. No Pb was observed in the final formed material. If however, higher formation temperatures would occur due to the higher free-Pb content in the cured active material, it should not be a problem because the cells used in this study had an excess amount of electrolyte that would easily dissipate any excess heat.
Figure 3.25: Relationship between the free-Pb and various dipping and curing times of cured active material.

The surface area of the formed plates that were dipped for 5 seconds showed a greater surface area when compared to the plates that were dipped for longer periods of time (fig 3.26). It would seem that the increase in surface area takes place during the initial stages of formation, thereby allowing more active sites to develop. The crystal growth and size of the lead sulphates during this time would be critical and could increase considerably in size as the soaking time increases\(^{47}\). The results in figure 3.24 showed that the largest surface area of the cured active material was for a dipping time between 15 minutes and 1 h. Even though the surface area after 5 seconds of dipping was not optimal, the surface area would increase during the 1 h soaking time before formation. The plates that were dipped for the longer times (5 and 15 h) before curing, showed a decrease in surface area of the final formed active material when compared to the plates that were dipped for shorter times.
After formation

After 11 cycles

Surface Area (m$^2$/g)

Figure 3.26: Relationship between the BET surface area and various dipping and curing times of formed active material after formation and after 11 cycles.

This could be due to the non-conducting sulphate crystals that were already present in the active material, especially concentrated near the exterior layer of the tubular spine (fig 3.23d). These crystals would increase in size during the pre-formation soaking time and thereby decrease the available surface area and reduce the effective penetration of electrolyte to the core of the spine during formation. Hence, a high concentration of large lead sulphate crystals would reduce the formation efficiency. This can also be seen in the slightly higher sulphate content of the formed active material for the plates that were initially dipped for 15 h (table 3.3). There was a considerable decrease in surface area of the active material after 11 capacity cycles (fig 3.26). The surface area of the active material that was initially dipped for longer times (300 min and 15 h), showed a lower surface area after the 11$^{th}$ discharge cycle when compared to the samples that were dipped for shorter periods of time. Hence, the effect of a relatively lower surface area after formation is still evident after 11 capacity cycles. Even though a change in the morphology of the active material takes place during cycling, most of the active material would be lead dioxide.

Only slight variations were observed in the absolute density of the active material after formation between the samples that were dipped and cured for different times (fig 3.27).
Figure 3.27: Variation of the absolute density between the formed active material and after 11 capacity cycles for the different curing and dipping times.

However, all samples showed a slight decrease in the absolute density of the active material after 11 capacity cycling, except for the samples that were dipped for 15 h before curing, when a slight increase in absolute density was observed. These trends were irrespective of the length of curing time used.

The porosity of the cured, formed and capacity cycled plates determined by Hg porosimetry are summarized in figure 3.28. The samples studied were taken from the plates that were dipped for different times and cured for 48 h only. In order to evaluate the porosity of the active material effectively, a 12 cm complete section of spine, with the outer fabric and active material still in one piece, was used. This caused the results of the porosity to be slightly lower than the porosity of the active material alone, which was reported to be about 50 % on average\textsuperscript{53}. 

\[ \text{abs density (g/cm}^3) \]
Figure 3.28: Relationship between the porosity (%) and the various dipping times of the cured, formed and the “after 11 capacity cycled” active material. The curing time was 48 h.

The results for the cured spines show a decrease in porosity with increasing dipping time. The cumulative pore volume distributions determined by Hg porosimetry for the cured samples show that the mean pore diameter for the cured active material was about 1 µm (fig 3.29).

Figure 3.29: Relationship between the cumulative pore volume distribution and the pore diameter for the various dipping times of the cured active material. The curing time was 48h. Pore Volume: mL Hg per mass of 12 mm complete spine.
The results also show that the cured spines that were dipped for 15 h had a lower pore volume penetration than the other spines that were dipped for shorter times. These results can be largely attributed to the large amount of sulphates that formed a crust layer on the surface of the spine (see fig 3.23d), reducing the penetration of the Hg into the sample and ultimately reducing the effective penetration of the electrolyte during formation.

The incremental intrusion volume of the formed plates (fig 3.30) show that pore size distribution varied between the various dipping times.

![Figure 3.30: Relationship between the incremental pore volume distribution and the pore diameter for the various dipping times of the formed active material. The curing time was 48 h. Pore Volume: mL Hg per mass of 12 mm complete spine. The median pore diameter in brackets is shown for each respective sample.](image)

After formation all samples show two peaks of pore sizes at 1 µm and at 0.05 µm respectively. The plates that were dipped for 5 seconds showed a slightly larger pore volume at the pore size of 0.05 µm, whereas the plates dipped 300 min and 15 h showed a larger pore volume at 1 µm respectively.

The pore size distribution after 11 capacity cycles (fig 3.31) shows that the pore sizes are spread over a wider region between 5 to 0.05 µm with an increase in the median pore diameter (volume).
Figure 3.31: Relationship between the incremental pore volume distribution and the pore diameter for the various dipping times of the formed active material after 11 capacity cycles. The curing time was 48 h. Pore Volume: mL Hg per mass of 12 mm complete spine. The median pore diameter in brackets is shown for each respective sample.

A noticeable decrease in total intrusion volume was also observed when compared to the results from the formed plates alone. The Hg porosimetry results are based on the intrusion pressure alone. For all the samples studied, no extrusion results were obtainable. The reasons for this could be that the intrusion of Hg caused the internal pores and voids to collapse during the high pressures or the pores have “ink bottle” type structures preventing the Hg from extruding during the decrease in pressure.

The results of the 1st and 11th C₅ discharge capacity for the plates dipped and cured at various time intervals is shown in figure 3.32.
The 1st $C_5$ discharge capacity for the plates that were dipped for 5 seconds was similar to the capacity obtained from the plates that were dipped for 15 h (fig 3.32). However, for the plates dipped for 15, 60 and 300 minutes respectively, a slightly lower 1st capacity performance was obtained. This trend was observed irrespective of the curing times. The trends of the 1st capacity are very similar to the trend observed for the surface area of the formed plates (fig 3.26).

During the subsequent capacity cycling, the capacities of the cells increase significantly for the next 2-3 cycles and would start to plateau at a relative consistent discharge capacity until the 11th cycle. After this, some cells started to show a slight decrease in their respective discharge capacities. On average, all cells showed similar capacities (Ah/kg) after 11 cycles, except for a slightly lower value for the plates that were dipped for 15 h. Evident is the relative increase each cell could achieve between the 1st and 11th capacity cycle. The cell with the positive electrode that was dipped for 15 h showed a smaller increase in capacity during cycling when compared to the electrodes that were dipped for shorter periods of time. This trend was similar for the various curing times and was similar to the trend observed when comparing the surface area of the active material after the 11th capacity cycle (fig. 3.26). A noticeable decrease in surface area was observed between the 1st and 11th cycles. The initial increase in capacity during the cycling can be mainly ascribed to the
conversion of unformed active material to lead dioxide until they reach their maximum discharge capacity where most of the active material would then have been converted. With continuous cycling, other factors start to contribute to the decrease in discharge capacity. These include a decrease in active material porosity, available surface area and loss of contact between lead dioxide particles. Active material shedding in tubular plates is not as common as in flat plate automotive batteries and would only be noticeable after many more capacity cycles. The main contributing factors to a decrease in discharge capacity during cycling can be attributed to the decrease in porosity and surface area of the active material.

The high current discharge (50 A) tests after the 1st and the 11th C₅ discharge capacity tests are shown in figure 3.33.

![Graph showing capacity (Ah/kg) for various dipping and curing times of tubular positive cells.](image)

**Figure 3.33:** Relationship between the 1st 50 A discharge and the 2nd 50 A discharge after the 11 capacity cycle testing for the various dipping and curing times of tubular positive cells.

The first high rate capacity for the plates that were dipped for 5 seconds and 15 h were lower than the capacities for the plates dipped for 15, 60 and 300 minutes. This trend is almost the opposite of that what was observed for the 1st C₅ capacity test. The high rate capacity that was repeated after 11 cycles was considerably lower than the first one, except for the plates that were dipped for 15 h. Similarly, the absolute density determined for the formed and cycled active material showed a similar trend (fig 3.27). These results show to what extent the pore size and surface area of active
material influence the cell potential through either a diffusion-controlled reaction (concentration gradients) or through a resistance-controlled reaction (potential gradient). The high rate discharge is primarily a surface effect of the active material and is dependant on the rate and ability for the acid to penetrate to the active sites. The decrease in high rate capacity after 11 cycles can be linked to the decrease in surface area. The increase in capacity for the 15 h dipped sample can be due to the increase in active material (lead dioxide) that became available during continuous cycling. Even though the 5 seconds dipped plates showed a high surface area and an initial larger first $C_5$ capacity, the high rate (50A) discharge was comparatively lower. The lower capacity would be due to the smaller pore size that would limit the available acid to diffuse to active sites rather than available surface area. The lower discharge rate ($C_5$) is more dependent on the pore volume available for the conversion of active material than just on the surface area of the active material as in the case of the high rate discharging.

### 3.4.1. Summary

During manufacture, the positive electrodes are usually not completely formed to lead dioxide as active material. As much as 30% of the unformed material, which is mainly made up of lead sulphate, can remain in the tubular plates\(^1\). The unformed PbSO\(_4\) would reduce the amount of capacity available during the 1\(^{st}\) discharge step of the battery. The amount of capacity achieved during the 1\(^{st}\) discharge is an important parameter to which a battery is often rated by the supplier or consumer of the battery. A lower 1\(^{st}\) discharge capacity would imply a poorer performing battery, and the manufacturer would have to increase the amount of active material added to the electrodes during manufacturing in order to achieve the specified 1\(^{st}\) capacity rate.

This study showed that there was no significant difference between the 1\(^{st}\) capacity of batteries made with tubular positive plates that were dipped for 5 seconds or 15 h during the initial stages of pickling. The cell’s capacity improved with capacity cycling until it would plateau to a relatively constant capacity value during the first 11 cycles. The study showed that the length of time for which the positive tubular plates were dipped in acid prior to curing and formation does have an influence on the surface
area and pore volume distribution of the active material even after subjecting the active material to a number of charge and discharge cycles.

The study also showed that it would be sufficient to dip tubular positive plates for 5 seconds before curing. This would eliminate any loose oxide on the surface of the tubes and would give the plate enough rigidity for assembling purposes. About one third of the acid that would have been adsorbed after 15 h is adsorbed during this step. Increasing the dipping time before curing, did convert more lead oxide to lead sulphate but reduced the surface area and formed a hard crust of lead sulphate near the surface of the spine reducing the ability for the electrolyte to penetrate to the core of the electrode. The optimal surface area on the active material for optimum formation to take place would be achieved during the 15-60 min soaking stage prior to applying the formation current.

The respective high current (50A) and C₅ discharge capacity study of the cells showed that multiple diffusion and potential reaction mechanisms take place during the discharge of tubular plates. These depend on the active material conversion, surface area, porosity and pore size distribution. These parameters change considerably during the life cycle of the plates and depend on the requirements of a particular application (low or high current rates).
3.5. **Addition of red lead to positive active material in MCL batteries.**

Tubular lead dioxide electrodes are used in lead acid batteries for applications that require durability and reliability during deep discharge applications at moderately low currents. They have been successfully used in MCL applications for a number of years but their manufacturing costs are considerably higher than the use of conventional flat plate positive electrodes. These flat plate positive electrodes have a number of advantages such as their ease of manufacture, reduced cost, less active material per Ah required and better oxygen recombination efficiencies, but also have a comparatively lower life cycle capability.

The following study compares the use of flat plate electrodes with tubular electrodes in MCL VRLA batteries, from a perspective of the efficiency of formation in converting enough lead dioxide active material to allow the battery to deliver the specified capacity on its first discharge test.

In order to obtain, for the positive electrode, a higher conversion of active material to lead dioxide, red lead (Pb₃O₄) is often included in the starting material. The amounts of red lead that could be added as starting material and its effect on the physical and electrochemical characteristics of the MCL VRLA battery is investigated in this study.

**3.5.1. Flat plate electrodes**

The XRD phase composition of the various flat plate electrodes’ cured active material used in the study are summarized in table 3.4.

<table>
<thead>
<tr>
<th>Cured Sample % Pb₃O₄</th>
<th>a-PbO (%)</th>
<th>β-PbO (%)</th>
<th>Pb₃O₄ (%)</th>
<th>T3 (%)</th>
<th>PbSO₄ (%)</th>
<th>β-PbO₂ (%)</th>
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<tbody>
<tr>
<td>Flat Plate</td>
<td>42</td>
<td>15</td>
<td>-</td>
<td>43</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
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<td>50</td>
<td>11</td>
<td>11</td>
<td>35</td>
<td>38</td>
<td>-</td>
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</tr>
<tr>
<td>75</td>
<td>10</td>
<td>8</td>
<td>60</td>
<td>19</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>100</td>
<td>-</td>
<td>-</td>
<td>76</td>
<td>-</td>
<td>11</td>
<td>13</td>
</tr>
</tbody>
</table>

T3: Tribasic Lead Sulphate

**Table 3.4:** XRD phase analysis of the cured active material of the flat plate electrodes with various additions of red lead to the grey oxide.
The results show that the 0, 25 and 50 % addition of red lead to the cured active material of the flat plate still contained about 40 % T3. This T3 is formed from the reaction of PbO with sulphuric acid and is an important component in the binding of the active material during curing and formation\textsuperscript{35}. The material (T3) would be finally converted to lead dioxide during the formation process, but is considered to give the formed PbO\textsubscript{2} its structure and rigidity, that allows the electrode to undergo chemical phase changes that occur during discharge and charge capacity cycling, with limited shedding\textsuperscript{35, 36 & 37}. The results show that small amounts of PbO\textsubscript{2} had formed during the curing process for the cured electrodes that contained 25, 50 and 75 % added Pb\textsubscript{3}O\textsubscript{4}, which had come from the reaction of red lead with sulphuric acid. This shows that the predominant reaction during the curing process is the reaction of free lead and PbO to tribasic lead sulphates.

The cured material made from 100 % red lead was included for comparison purposes and showed poor active material structural bonding to the grid and to itself after curing. The reaction of the red lead with sulphuric acid would be according to equation 3.1 and its reaction product would result in no basic lead sulphates. This is needed to give the active material its rigidity and bonding capability during the curing process.

\[
Pb_3O_4 + 2H_2SO_4 \rightarrow \beta-PbO_2 + 2PbSO_4 + 2H_2O \quad (3.1)
\]

The low percentage yield of the lead sulphate and lead dioxide was due to the fact that the pasting recipe (described in section 2.1.4) was kept the same for all the electrodes manufactured, and that a minimal amount of sulphuric acid was used.

The change in the BET surface area of the cured flat plate electrodes with various additions of red lead is shown in figure 3.34.
The results show that there is a general increase in surface area of the active material with an increase in the addition of Pb$_3$O$_4$. The effect of the addition of red lead on the surface area leads at first to a slight decrease in surface area in the range 0 to 50% added Pb$_3$O$_4$, followed by an increase to above 2.5 m$^2$/g for the cured material made from 100% Pb$_3$O$_4$.

The variation of the absolute density of the cured active material of the positive electrodes made with different amounts of Pb$_3$O$_4$ is shown in figure 3.35.
Figure 3.35: Absolute density of cured active material for flat plate electrodes made with different concentrations of red lead.

The results show that the 0 and 25 % added Pb$_3$O$_4$ cured active material had a slightly lower absolute density when compared to the cured active material that container higher amounts of Pb$_3$O$_4$. These variations could be related to the ease of manufacturing, where a slightly higher pasting pressure had to be used for the higher Pb$_3$O$_4$ content plates, in order for the paste to stick to the grids during application.

The formation of the batteries was usually carried out in an air-cooled environment by using a low SG acid of 1.19. A low SG acid was primarily used in order to increase the conversion of the cured material to lead dioxide. According to literature$^{47}$, formation with lower SG acid was more efficient where smaller lead sulphate crystals are formed during the initial stages of the rest period and formation. The formation with a lower SG acid for VRLA type batteries, however, was considered as impractical, since a final higher SG between 1.29 - 1.32 was necessary for optimal functioning of the battery in a starved electrolyte condition. Additional steps would have to be introduced to increase the specific gravity of the final electrolyte. The low rate formation sequence was used only for the cells filled with the 1.19 SG acid.
The formation with the low and subsequent high rate sequence was carried out using the 1.26 SG acid. At the end of formation, only a slight adjustment in the final acid concentration was required. All cells were formed with excess electrolyte ensuring that no drying out of the electrodes would occur during the duration of the sequence. At the end of formation, all cells showed that sufficient electrolyte remained. The high and low formation rate sequences are summarized in table 2.5 (section 2.1.4).

For each battery tested, one cell of a duplicate pair was removed for analysis and the other cell was further tested for its discharge capacity. The phase composition of the formed active material for the various cells studied using flat plate electrodes are summarized in table 3.5.

**Table 3.5:** XRD phase analysis of the formed active material of the flat plate electrodes with various additions of red lead. The electrodes were formed using various acid SG strengths and formation rates described previously.

<table>
<thead>
<tr>
<th>Formed Sample</th>
<th>a-PbO₂ (%)</th>
<th>β-PbO₂ (%)</th>
<th>PbSO₄ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Pb₃O₄</td>
<td>Flat Plate Electrode</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low Rate Formation with 1.19 SG Acid</td>
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<td></td>
</tr>
<tr>
<td>0</td>
<td>28</td>
<td>56</td>
<td>16</td>
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<td>25</td>
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<td>53</td>
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</tr>
<tr>
<td>100</td>
<td>14</td>
<td>67</td>
<td>19</td>
</tr>
<tr>
<td>Low Rate Formation with 1.26 SG Acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>21</td>
<td>51</td>
<td>28</td>
</tr>
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<td>25</td>
<td>15</td>
<td>68</td>
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<tr>
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</tr>
<tr>
<td>High Rate Formation with 1.26 SG Acid</td>
<td></td>
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</tr>
<tr>
<td>0</td>
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<tr>
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<td>19</td>
<td>67</td>
<td>14</td>
</tr>
</tbody>
</table>

The results of the phase composition of the formed flat plate electrodes showed that the active material formed with the lower SG acid did result in a slightly higher conversion of the cured material to PbO₂. There was no significant difference in the conversion to lead dioxide in the active material between the two different formation rates used, when using 1.26 SG formation acid. Although the average phase composition of the formed material for the additions of Pb₃O₄ for the range 0 to 50 % was not significantly different. The visual observance of the 0 % addition electrode showed significant amounts of lead sulphate being present on the surface of the
electrode (fig 3.36a). The white lead sulphate on the surface would decrease as the Pb$_3$O$_4$ content increased in the initial cured material (fig 3.36b – 3.36e). The electrodes shown in figure 3.36 were formed with 1.26 SG acid using the low rate formation procedure.

Figure 3.36a: 0% red lead  3.36b: 25% red lead  3.36c: 50% red lead

Figure 3.36d: 75% red lead  3.36e: 100% red lead
The effect of the non-conducting lead sulphate on the surface would detrimentally influence the discharge capacity of the electrode by inhibiting the underlying active material (PbO$_2$) to be used in the discharge reaction. It would further reduce sufficient flow of the electrolyte (sulphuric acid) to penetrate and react with the inner pore structure of the material.

The results of the formation profiles (section 2.1.4 table 2.5) used by the industry for the MCL batteries using flat plate positive electrodes with the two different acid concentrations are shown in figures 3.37 and 3.39. The graphs show the change in voltage with time for the batteries made with various red lead additions to the flat plate positive electrodes. Figure 3.38 and 3.40 show the formation voltage change during the first 5 h for the respective profiles.

![Graph showing formation profiles](attachment:image.png)

**Figure 3.37:** Voltage formation profile for flat plate electrodes formed in 1.19 SG acid at the low rate with various additions of red lead.
Figure 3.38: Voltage formation profile for flat plate electrodes formed in 1.19 SG acid at the low rate with various additions of red lead showing the first 5 hours only.

Figure 3.39: Voltage formation profile for flat plate electrodes formed in 1.26 SG acid at the low rate with various additions of red lead.
Figure 3.40: Voltage formation profile for flat plate electrodes formed in 1.26 SG acid at the low rate with various additions of red lead showing the first 5 hours only.

The voltage profiles of the first hour show that there was an increase of the cell potential for the 100 % Pb$_3$O$_4$ added electrode during the rest period (fig 3.38 and 3.40). During the rest period, the acid is allowed to “soak” into the active material that converts the Pb$_3$O$_4$ to PbO$_2$ and PbSO$_4$. The batteries that were formed with the higher SG acid showed a sharper increase in the voltage graph due to more acid being available followed by a gradual decrease towards the end of the rest period. This implies that some of the PbO$_2$ would have started to convert to PbSO$_4$ during this time. The increase in voltage during the rest period was not observed for the other batteries made with lower Pb$_3$O$_4$ addition.

The graphs (fig 3.37 and 3.39) show that the overall charge voltage decreased with the addition of red lead to the positive active material. An overall lower formation charge voltage would imply better conversion efficiency. However, the phase analysis of the formed material did not show significant differences between the different formed active materials, except for the electrodes that were formed with the 1.19 SG acid.
The forming of the plates with different acid concentrations showed that there was an initial lower end voltage before the first rest period for the lower SG acid. However, the voltage profiles were very similar for the second and third stages, where only little differences in voltages were observed. A lower voltage during charge or formation implies more conversion of active material and lower water loss. Slight differences in the phase composition between the two formations were observed (table 3.5) with the active material formed at higher acid concentration having a higher percentage lead sulphate.

The temperature of the battery during formation is considered to be critical in terms of efficiency and active material conversion\textsuperscript{11, 12}. If the temperature is too high, excessive gassing and damage of the electrode’s active material would occur. Low temperatures would indicate a poorer manufacturing efficiency in terms of unnecessary time spent for the formation stage. There was no significant difference in the temperature profiles between the batteries made with different concentrations of red lead or formed with different concentrations of acid. Only selected temperature profiles from the batteries studied are shown in figure 3.41.

![Temperature profile for selected cells made with flat plate electrodes carried out at the low rate at different formation acid concentrations and red lead addition (F1.19: formation with an acid SG of 1.19; F1.26: formation with an acid SG of 1.26).](image)

**Figure 3.41:** Temperature profile for selected cells made with flat plate electrodes carried out at the low rate at different formation acid concentrations and red lead addition (F1.19: formation with an acid SG of 1.19; F1.26: formation with an acid SG of 1.26).
The results show that the initial rise in temperature at the beginning of the sequence was mainly due to the conversion of the lead oxide and basic lead sulphates to lead sulphate. The temperature during the first step of formation continued to decrease showing that a too-low current parameter was used. Even though the conversion process to form lead dioxide continued during this step, a lower rate of conversion occurred, which would not be beneficial in terms of unnecessary time taken to complete the formation sequence. After careful consideration of the temperature profiles recorded and the conversion efficiency of the formed active material during the low rate formation, a new profile labelled as “high rate” was developed that would reduce the time of formation and optimise the conversion of the active material.

Figure 3.42 shows the voltage graphs for the high rate formation profile used for the MCL batteries made with flat plate positive electrodes. The higher currents that were used during the initial stage of the procedure resulted in slightly higher charge voltages when compared to the previous procedure. However, towards the end of formation, the battery voltages were very similar to the previous ones. All batteries formed with the higher rate still retained electrolyte above the cell assembly after formation and the SG was adjusted to 1.31 ensuring excess electrolyte was present before commencing with the discharge and charge testing. The corresponding temperature profile of the high rate formation sequence is shown in figure 3.43.
Figure 3.42: Voltage formation profile for flat plate electrodes formed in 1.26 SG acid at the high rate with various additions of red lead.

Figure 3.43: Temperature profile for selected cells made with flat plate electrodes done at the high rate with 1.26 SG formation acid and different red lead additions.

The temperature graphs show that the initial stage during high rate formation sequence had a rise in temperature mainly due to the conversion of lead oxide, red lead and basic lead sulphates to lead sulphate. This reaction is exothermic and
depending on the size of the battery, the increase in temperature can cause the battery to have temperatures above 50°C before formation\textsuperscript{1, 2}. In order to reduce the initial increase in temperature after the addition of the acid, most manufacturers add “chilled” acid to the batteries (about 5°C). Due to the size of the MCL batteries and the amount of active material in this study, it was not necessary to add “chilled” acid.

The current rates for the subsequent steps were increased to charge steps of 5 to 9 A, where a significant increase in temperature to 40°C was observed. This was beneficial in increasing the conversion rates of the active material, since Dimitrov and Pavlov\textsuperscript{90} have reported that there are added benefits of high rate formation currents to final conversion and properties of the active material. The higher temperature was limited by keeping the high charge currents for a short period of time only, until the charge voltage increased significantly. It would then be beneficial to decrease the current in order to reduce the effect of water loss at a lower cell temperature and charge voltage. A significant reduction in formation time from 66 h (low rate) to 33 h (high rate) was achieved.

The BET surface area results of the positive active material formed with the low rate procedure at the different acid concentrations and red lead additions are shown in figure 3.44 for the flat plate electrodes.
Figure 3.44: BET Surface area of formed active material for flat plates with different formation acid SG concentrations using the low rate procedure for various additions of red lead. Analysis was done on duplicate samples after formation and after 11 capacity cycles.

The surface area of the active material straight after formation and after completing 11 capacity cycles showed that a general decrease in surface area after capacity cycling was observed, which has been reported elsewhere (section 3.4)\textsuperscript{71}. An increase in surface area of the formed active material was observed as the initial \( \text{Pb}_3\text{O}_4 \) content increased.

The surface area of the formed active material from the flat plate electrode showed only slight differences between using two types of acid concentrations during the formation sequence. However, the formed electrode made with 100 \% \( \text{Pb}_3\text{O}_4 \), showed a slightly higher surface area after formation when using the 1.26 SG instead of the 1.19 SG acid.

Figure 3.45 shows the change in surface area for the cells formed at the higher rate. A slight increase in the respective surface areas of the various formed flat plate electrodes was observed as compared to the same types formed at the lower rate.
Figure 3.45: BET Surface area of formed active material for flat plates formed at the high rate with 1.26 SG acid for various concentrations of red lead.

The results show that the surface area of the electrodes that were formed with the high rate procedure for the 25 and 75 % Pb₃O₄ were slightly higher than those formed with the low rate procedure, whereas the electrode that contained 100 % Pb₃O₄ was comparatively lower. There seems to be no significant influence on the surface area of the formed active material of the electrodes when formed using the two different rates.

The Hg porosimetry analysis of the formed active material from the flat plate electrodes made with different concentrations of red lead in the initial cured material are summarized in figure 3.46.
Figure 3.46: Porosity of formed active material for flat plates formed at the high and low rate with 1.26 SG acid for various concentrations of red lead.

The porosity of the various formed active material made with different concentrations of Pb$_3$O$_4$ showed only slight differences between the electrodes formed at the two different rates. A slightly higher porosity for the electrodes made with 25 %, 75 % and 100 % Pb$_3$O$_4$ was obtained.

The corresponding variation of the incremental pore volume distribution and pore diameter for the various formed flat plate electrodes using the low and high rate procedures with 1.26 SG acid, made with different concentrations of Pb$_3$O$_4$ are shown in figure 3.47 and 3.48 respectively.
The results show that the average pore diameter of the formed active material decreases as the Pb$_3$O$_4$ used in the active material increases for the cells formed with 1.26 SG acid with the low rate formation procedure (fig 3.47). The range in average pore diameter was from about 1 µm to 0.25 µm.
The pore volume distribution of the formed active material using the high rate formation procedure shows that the average pore volume distribution was slightly lower. Most of the samples analysed showed an average pore diameter of about 0.5 µm, except for the sample that contained 100 % Pb₃O₄, which showed a slightly lower average pore diameter of 0.25 µm.

The MCL battery is nominally rated at 4 V / 16 Ah and discharged at 1 A to 3.7 V. For most electrochemical investigations of battery material utilization, the capacity is reported in the Ah/kg of active cured material. It is also of interest to report the capacity results in terms of Ah at a particular rate and compare the results to the rated capacity specified by the manufacturer. The following discharge capacity results are recorded as the average capacity for the set of cells in Ah capacity at the 1 A discharge rate and the individual cells in Ah/kg of the active cured material. The variation in capacity over 11 cycles for the different batteries made from various concentrations of Pb₃O₄ in the initial active material are shown in figures 3.49, 3.50 and 3.51.

![Graph](image-url)

**Figure 3.49:** Capacity cycle of flat plate electrodes made with various concentrations of red lead formed with 1.19 SG acid in Ah/kg (a) and Ah (b). Formed at the low rate.
The results show that the cells formed with the 1.19 SG acid using the low rate procedure did not achieve the expected rated capacity of 16 Ah after the 1\textsuperscript{st} discharge (fig 3.49b). However, with further capacity cycles, the cells made with the 50, 75 and 100 \% Pb\textsubscript{3}O\textsubscript{4} achieved capacities above 16 Ah after the 2\textsuperscript{nd} capacity cycle. The cell made with 100 \% Pb\textsubscript{3}O\textsubscript{4} achieved about 17.5 Ah, which decreased to about 16 Ah after 11 cycles.
The cell made with 25% Pb$_3$O$_4$ had an initially low capacity, and only obtained the rated 16 Ah after 10 cycles. The electrodes made with 0% Pb$_3$O$_4$ achieved the rated capacity of 16 Ah after 3 capacity cycles and maintained the capacity above 16 Ah for the 11-cycle test. The 50 and 75% electrodes showed a similar increase in capacity after the 2$^{\text{nd}}$ capacity cycle, followed by a gentle decrease towards the 10$^{\text{th}}$ capacity cycle.

The cells formed with the 1.26 SG acid using the low rate procedure showed that the electrodes made with 0 and 25% Pb$_3$O$_4$ had a very low 1$^{\text{st}}$ capacity (fig 3.50). The subsequent capacity increased slowly with cycling; however, the 25% battery did not achieve the rated capacity of 16 Ah within the 11 cycles. Similar to the results in figure 3.49, the cells made with 50, 75 and 100% Pb$_3$O$_4$ achieved a higher initial capacity, followed by a gradual decrease within the 11-cycle test. The 50% electrode showed a decrease below 16 Ah after the 11-cycle test.

Overall, the cells formed with the 1.26 SG acid showed a slightly higher material utilization in terms of the Ah/kg of active material (Fig 3.49 a. and 3.50 a.). This might be explained by the use of slightly lower mass electrodes for the second study and that the final acid concentration across the cell was higher. Even though the acid in the 1.19 SG cells was increased to 1.31 SG before commencement with the capacity test, some of the lower concentrated acid could have remained in the AGM separator, especially at the bottom of the cell, and not have mixed properly during the acid adjustment, which would not have been the case with the cells formed with 1.26 SG acid.

The cells formed with the 1.26 SG acid using the high rate procedure showed that the average capacity of all cells was lower than the corresponding capacities using the low rate procedure. The cells made with 50 and 100% Pb$_3$O$_4$ achieved 16 Ah after the 1$^{\text{st}}$ capacity test. The cell made with 75% Pb$_3$O$_4$ achieved 16 Ah after the 2$^{\text{nd}}$ capacity cycle. All three cells showed a slight increase in capacity after a few more cycles, with a gradual decrease during the 11 cycles to below 16 Ah. The cells made with 0 and 25% Pb$_3$O$_4$ did not achieve the 16 Ah after the 1$^{\text{st}}$ cycle and showed a gradual increase in capacity so that only after the 8$^{\text{th}}$ cycle 16 Ah was obtained. The
active material utilization (fig 3.51 a.) showed comparatively good results when compared to the cells made with the low rate procedure.

The 10A discharge capacity test after the 1st and 11th 1 A capacity test is shown in figure 3.52. The results are in Ah/kg and showed only slight increases in capacity for the 0 and 25 % Pb₃O₄ added cells when compared to the cells formed with different SG acids. The results of the cells formed with the high rate procedure are not shown, since no significant differences between the various cells were observed.

![Graph showing capacity test results](image)

**Figure 3.52:** 10A Capacity test after formation and after 11 capacity cycles for flat plate electrodes made with various red lead concentrations.

These results show the importance of using the correct mass balance of the active material in designing the expected rated capacity (Ah) of a battery in terms of its material utilization expressed in Ah/kg. On average, the cells that contained Pb₃O₄ of various concentrations formed with the high and low rate procedure showed good material utilization in terms of Ah/kg, but were not always achieving the expected 16 Ah. This shows that the rated capacity can be achieved with a higher rated formation procedure and a high concentrated formation acid. It would be beneficial to use slightly more active material per electrode in order to ensure that the expected rated capacity of 16 Ah would be easily achieved within the first few capacity cycles.
3.5.2. Tubular electrodes

The phase analysis of the tubular cured material showed a relatively low % of corresponding PbO$_2$ and PbSO$_4$ when compared to the flat plate electrodes. This was primarily because the filled tubular electrodes were only dipped for a short time in 1.1 SG acid and the reaction product remained primarily in the gauntlet fabric. This can be observed by the immediate change in colour of the electrodes that contained Pb$_3$O$_4$, where the outer layer of the gauntlet of the electrodes changed from a red to a dark brown that is typical for lead dioxide. The phase analysis of the active material was carried out with the external gauntlet and inner spine removed.

The XRD diffractograms of the phases on the surface and of the inner core of the positive tubular electrodes made with the various concentrations of red lead are shown in figure 3.53. The corresponding phase composition analysis results, based on these figures, are shown in table 3.6.

The XRD analysis of the surface of the electrodes was done by aligning a section of a filled tube specimen into the sample holder and rotating it at 20 rev/min during analysis. This was done in order to allow for a relatively large representative sample of the surface to be exposed to the X-rays, thereby eliminating any effects due to preferred orientation of the crystals or uneven surface concentration. The diffractograms of the cured active material inside the tube and that of the surface of the tube were normalized to their most intense peak for comparison purposes and compared to the ICDD$^{100}$ reference diffractograms. Some of the more common lead oxide and lead sulphate phases encountered in the lead-acid battery manufacturing process are shown in Appendix B.
Table 3.6: XRD phase analysis of the cured active material of the tubular electrodes with various additions of red lead to the grey oxide.

<table>
<thead>
<tr>
<th>Cured Sample</th>
<th>a-PbO (%)</th>
<th>β-PbO (%)</th>
<th>PbO₄ (%)</th>
<th>T3 (%)</th>
<th>PbSO₄ (%)</th>
<th>β-PbO₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>% PbO₄</td>
<td>Tubular (gauntlet and spine removed)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>80</td>
<td>6</td>
<td>-</td>
<td>7</td>
<td>7</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>53</td>
<td>7</td>
<td>26</td>
<td>10</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>50</td>
<td>32</td>
<td>-</td>
<td>53</td>
<td>7</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>75</td>
<td>15</td>
<td>-</td>
<td>70</td>
<td>8</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>100</td>
<td>8</td>
<td>-</td>
<td>76</td>
<td>-</td>
<td>14</td>
<td>2</td>
</tr>
<tr>
<td>Tubular (surface of the gauntlet)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>39</td>
<td>11</td>
<td>-</td>
<td>50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>37</td>
<td>11</td>
<td>16</td>
<td>36</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>50</td>
<td>7</td>
<td>5</td>
<td>47</td>
<td>18</td>
<td>14</td>
<td>9</td>
</tr>
<tr>
<td>75</td>
<td>4</td>
<td>4</td>
<td>60</td>
<td>15</td>
<td>11</td>
<td>6</td>
</tr>
<tr>
<td>100</td>
<td>4</td>
<td>4</td>
<td>49</td>
<td>-</td>
<td>36</td>
<td>7</td>
</tr>
</tbody>
</table>

T3: Tribasic Lead Sulphate

Figure 3.53 a.  
Figure 3.53 b.  
Figure 3.53 c.  
Figure 3.53 d.
Figures 3.53 a-e: X-ray diffraction patterns of the surfaces and of the inner bulk active material of the cured tubular electrodes filled with various concentration of red lead. The diffraction patterns were normalized to their respective most intense peaks for comparison purposes.

The results show that there is a significant difference in the phase composition of the active material on the surface of the gauntlet as compared to that of the bulk inner core. The dipping of the filled tubular electrodes in dilute sulphuric acid for short periods of time leaves the inner core material largely un-reacted. The tubular electrode with 0 % red lead had up to 50 % tri-basic lead sulphate (T3) in the gauntlet. The T3 concentration would decrease as the red lead addition increased. No lead sulphate was formed on the electrodes that had 0 % and 25 % red lead. The lead sulphate concentration on the surface of the gauntlet increased as the red lead concentration of the electrode increased from 50 to 100 % red lead, and its formation can be described by equation 3.1. Unfortunately, the formation of $\beta$-PbO$_2$ was lower than expected. In order to aid the formation process, it would be beneficial to have a larger amount of the conductive lead oxide present, rather than the non-conducting lead sulphate.

Cross sections of selected tubes filled with 0 and 100 % red lead after acid dipping and curing, were examined under a stereo microscope and show the effect of the acid penetrating the active material (fig 3.54). The white basic lead sulphate layer near the gauntlet, extending slightly into the grey oxide, is evident in the electrodes containing
no red lead (fig 3.54a). The brown patches of lead dioxide that occur when red lead reacts with sulphuric acid (equation 21) are observed for the electrodes filled with the 100 % red lead (fig 3.54b).

(a)         (b)

Figure 3.54: Stereo microscope pictures of a cross-sectional view of a MCL tubular electrode for 0 % (a) and 100 % (b) red lead addition, after dipping in acid and curing.

The small amounts of “brown” lead dioxide at the surface of the electrodes are sufficient to reduce the effect of loose dust that coats the tubes after filling. The advantage of reducing the “pickling” time of tubular electrodes was discussed previously (section 3.4)\textsuperscript{71}. In particular, if red lead is used in the filling oxide, excessive pickling would convert all the material to lead dioxide and finally to lead sulphate. The phase analysis shows that the conversion to lead sulphate seemed to have dominated the reaction during the short exposure time, and if kept in acid for too long, ultimately all the active material in the tubes would convert to lead sulphate. The lead sulphate would continue to grow and thereby reduce the effective surface area of the active material and inhibit efficient formation. It would be beneficial to have a small percentage of conductive lead dioxide in the cured material that would act as seed crystals during the formation process, whereas lead sulphate would be considered as an insulator and would inhibit efficient formation. Once the electrodes are assembled into batteries and allowed to “soak” before formation, further lead dioxide would form thereby encouraging the formation process. The tubular electrodes made with 0 and 25 % Pb$_3$O$_4$ would form only the basic lead sulphates during the pickling and soaking steps, which would have a higher resistance during the formation process.
The change in the BET surface area of the cured flat plate and tubular electrodes with various additions of Pb\textsubscript{3}O\textsubscript{4} is shown in figure 3.55.

![Bar graph showing BET surface area of cured active material for tubular electrodes made with different concentrations of red lead.]

**Figure 3.55:** BET surface area of cured active material for tubular electrodes made with different concentrations of red lead.

The results of the BET surface area for the cured active material with no Pb\textsubscript{3}O\textsubscript{4} in the tubular electrodes, has a value very similar to that obtained for the starting material of grey oxide (0.69 m\textsuperscript{2}/g). However, upon addition of Pb\textsubscript{3}O\textsubscript{4}, followed by the short pickling and curing process, the surface area increased significantly to 1.7 m\textsuperscript{2}/g for the active material that contained 100% red lead, even though the surface area of the initial Pb\textsubscript{3}O\textsubscript{4} added was only 0.54 m\textsuperscript{2}/g (table 2.4). This effect is significant in showing that the short period of “pickling” in acid and curing increases the surface area of the starting material, which becomes important during the subsequent formation procedure, where a cured active material with a larger surface area would be beneficial.

After formation, one cell of a duplicate pair was removed for analysis, while the other cell was further tested for its discharge capacity. The XRD phase analysis of the formed active material taken from the tubular electrodes that were formed, using the various SG acid strengths and formations rates described previously, are shown in table 3.7
Table 3.7: XRD phase analysis of the formed active material of the tubular electrodes with various additions of red lead.

<table>
<thead>
<tr>
<th>Formed Sample</th>
<th>a-PbO₂ (%)</th>
<th>β-PbO₂ (%)</th>
<th>PbSO₄ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Rate Formation with 1.19 SG Acid</td>
<td>11</td>
<td>61</td>
<td>28</td>
</tr>
<tr>
<td>25</td>
<td>8</td>
<td>71</td>
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<tr>
<td>50</td>
<td>17</td>
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</tr>
<tr>
<td>75</td>
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<td>72</td>
<td>20</td>
</tr>
<tr>
<td>100</td>
<td>12</td>
<td>62</td>
<td>26</td>
</tr>
<tr>
<td>Low Rate Formation with 1.26 SG Acid</td>
<td>8</td>
<td>62</td>
<td>30</td>
</tr>
<tr>
<td>25</td>
<td>13</td>
<td>58</td>
<td>29</td>
</tr>
<tr>
<td>50</td>
<td>9</td>
<td>63</td>
<td>28</td>
</tr>
<tr>
<td>75</td>
<td>24</td>
<td>66</td>
<td>10</td>
</tr>
<tr>
<td>100</td>
<td>21</td>
<td>63</td>
<td>16</td>
</tr>
<tr>
<td>High Rate Formation with 1.26 SG Acid</td>
<td>16</td>
<td>37</td>
<td>47</td>
</tr>
<tr>
<td>25</td>
<td>14</td>
<td>43</td>
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<td>55</td>
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</tr>
<tr>
<td>75</td>
<td>7</td>
<td>69</td>
<td>24</td>
</tr>
<tr>
<td>100</td>
<td>5</td>
<td>82</td>
<td>13</td>
</tr>
</tbody>
</table>

The phase composition results of the formed tubular electrodes show that there are significant differences between the electrodes made with different amount of Pb₂O₄. The amount of lead sulphate in the various electrodes that were formed with the 1.19 SG acid at the low rate showed only slight differences in concentration. However, the amount of lead sulphate in the electrodes formed with the 1.26 SG acid increased significantly for the range 0 % to 50 % Pb₂O₄. This increase was even greater for the electrodes formed with the high rate procedure. However, the electrodes that had 75 and 100 % Pb₂O₄, showed a decrease in its lead sulphate content, as compared with the lower Pb₂O₄ addition, with the use of the 1.26 SG acid and the high rate formation procedure. This implies a better conversion rate of the active material to lead dioxide for the tubular electrodes that contain predominantly Pb₂O₄ and which are formed with a higher SG acid and a faster formation sequence.

The formation profiles (table 2.5) that are used in the industry for MCL batteries made with tubular positive electrodes with the two different acid concentrations, formed at the low rate, are shown in figure 3.56 and 3.58 respectively. The graphs show the change in voltage with time for the batteries made with various Pb₂O₄ additions to the tubular positive electrodes. Figure 3.57 and 3.59 show the formation voltage change during the first 5 h for the respective profiles.
Figure 3.56: Voltage formation profile for tubular electrodes formed in 1.19 SG acid at the low rate with various additions of red lead.

Figure 3.57: Voltage formation profile for tubular electrodes formed in 1.19 SG acid at the low rate with various additions of red lead showing the first 5 h only.
Figure 3.58: Voltage formation profile for tubular electrodes formed in 1.26 SG acid at the low rate with various additions of red lead.

Figure 3.59: Voltage formation profile for tubular electrodes formed in 1.26 SG acid at the low rate with various additions of red lead showing the first 5 h only.

The formation times used for the batteries with tubular electrodes were longer than for those made with the flat plate electrodes. This was primarily due to the fact that more
active material in the tubular electrode has to be converted and that the conversion process is less efficient than for the flat plate electrodes.

The results show that during the initial rest period in the acid, an increase in cell voltage for the 100 % and 75 % added Pb₃O₄ batteries was observed. This shows that some of the Pb₃O₄ is converting to significant amounts of lead dioxide and which would act as "seeding" crystals for the initial stages of formation to effectively convert the bulk material to the active lead dioxide. This benefit can be further seen during the first charge step, where the battery voltage started to decrease after about 2 h of formation for the 100 and 75 % Pb₃O₄, if compared to the battery made with no Pb₃O₄ (fig 3.57 and 3.59). A relatively lower average charge voltage during formation in a battery implies better efficiency in the process of converting the lead sulphate to the active lead dioxide.

The battery voltages at the end of formation were significantly different for the various batteries made with different Pb₃O₄ addition. The difference was especially significant for the batteries formed with the 1.19 SG acid, which could be ascribed to poor conversion of the cured active material. The SG at the end of formation was significantly low and had to be increased to 1.31 before capacity testing could be carried out.

The temperature profiles of the batteries during formation were recorded and were similar to those of the study carried out for the flat plate electrodes. There was no significant difference in the temperature profiles between the batteries made with different concentrations of red lead or formed with different concentrations of acid. Figure 3.60 shows the temperature profiles recorded during formation of the 0 % and 100 % added Pb₃O₄ batteries using two different formation acid concentrations.
After carefully considering the formation voltage and temperature profiles at the low rate of formation, a new formation procedure was developed that would reduce the time of formation and still maintain a good conversion to the desired active material. The sequence was labelled as “high rate” and is described in section 2.1.4 (table 2.5).

Figure 3.61 shows the voltage graphs for the high-rate formation profile used for the MCL batteries made with tubular positive electrodes. The corresponding temperature profile of the high rate formation sequence is shown in figure 3.62.
Figure 3.61: Voltage formation profile for tubular electrodes formed in 1.26 SG acid at the high rate with various additions of red lead.

Figure 3.62: Temperature profile for selected cells made with tubular electrodes at the high rate in 1.26 SG formation acid using different red lead additions.

The results show that using higher currents during the initial stages of the procedure results in a corresponding higher charge voltage, when compared to the previous low
rate procedure. However, similar lower currents were used towards the end of formation sequence, giving a battery voltage similar to that of the previous lower rate sequence. The increase in the formation voltage would increase the water loss due to electrolysis, with the danger of “drying out” the cells before completing the formation. However, all the batteries that were formed with the higher rate still had sufficient electrolyte above the cell assembly. The SG of the electrolyte of the cells was adjusted to 1.31 ensuring excess electrolyte would be present before commencing with the discharge and charge capacity testing.

The increase in the charging currents during the initial stages of the formation sequence also showed an increase in temperature to about 45°C. This step was done for a short period of time in order to prevent excessive water loss and possible damage to the active material on the electrodes due to high temperatures. However, tubular positive electrodes are less susceptible to damage due to high temperatures because of the protective gauntlet used. The temperature towards the end of formation decreased significantly, showing that possible further reduction in the formation time could be achieved with an increase in the current for those steps. A significant reduction in formation time from 83 h (low rate) to 41 h (high rate) was achieved.

The BET surface area of the formed positive active material from the tubular electrodes made with different concentrations of Pb₃O₄, formed at the low rate with different acid SG concentrations, is shown in figure 3.63. The corresponding BET surface area results of the electrodes that were subjected to 11 capacity discharge and charge cycles are included on the graph. The BET surface area of the formed active material from the electrodes formed at the high rate is shown in figure 3.64. The active material of these electrodes after capacity cycling was not further analysed since there was only little differences when compared to the previous analysis.
Figure 3.63: BET Surface area of formed active material for tubular electrodes at different formation acid SG concentrations at the low rate for various concentrations of red lead.

Figure 3.64: BET Surface area of formed active material for tubular electrodes formed at the high rate with 1.26 SG acid for various concentrations of red lead.

The surface area of the formed active material from the tubular electrodes showed no significant difference in surface area for cells formed with the low SG acid using various concentrations of Pb₃O₄. However, a significant increase in the surface area was observed for cells that were formed with the higher SG acid using either low or
high rate procedures. The surface areas of the formed material, using the low rate procedure, with no Pb$_3$O$_4$ and 100 % Pb$_3$O$_4$ are 4.4 and 8.4 m$^2$/g respectively. Similarly, the formed material using the high rate procedure gives a surface area of 3.5 and 8.7 m$^2$/g, respectively, for the corresponding no Pb$_3$O$_4$ and 100 % Pb$_3$O$_4$.

The surface areas of the active material after the 11 capacity tests were slightly lower than the corresponding cells that were evaluated after formation (fig 3.63). Noticeably, the surface areas for all the cells after capacity cycling were approximately 2.8 m$^2$/g. The corresponding decrease in surface area for the 100 % Pb$_3$O$_4$ electrode is from 8.4 to 2.8 m$^2$/g, which is comparatively a greater decrease when compared to the other electrodes, which had a relatively lower initial surface area. This implies that the surface area of the various tubular electrodes, after 11 capacity cycles, become relatively similar, irrespective of the amount of initial Pb$_3$O$_4$ in the cured material. However, the surface area, straight after formation, is significantly influenced by the amount of Pb$_3$O$_4$ present in the initial cured material.

The characteristic property of the formed active material, having a higher surface area after formation is important for the utilization of the active material during the subsequent capacity testing. The greater the surface area, the more active sites are available for reactions to take place, thereby resulting in a higher utilization of active material and better battery capacity per active material.

Figure 3.65 shows the change in % porosity of the cells formed with 1.26 SG with the low and high rate procedure. The % porosity was determined by Hg porosimetry on a 10 mm cross-sectional piece of complete spine cut from the tubular electrode. The outer gauntlet and inner active material was not complete and the two ends of the sample were sealed with a wax. This was done in order to ensure that the Hg intrusion would flow through the outer section of the sample and not through the two open sides.

The corresponding variation of the incremental pore volume distribution and pore diameter for the various formed tubular electrodes using the low and high rate procedures with 1.26 SG acid, made with different concentrations of Pb$_3$O$_4$ are shown in figure 3.66 and 3.67 respectively.
**Figure 3.65:** Porosity of formed active material for tubular plates formed at the high and low rate with 1.26 SG acid for various concentrations of red lead.

The results show that the % porosity of the formed active material increased significantly as the Pb$_3$O$_4$ content of the tubular electrodes increased. There was only a slight difference in the % porosity of the active material between the two low and high formation procedures.

**Figure 3.66:** Variation of the incremental pore volume distribution and pore diameter for the various formed tubular electrodes at the low rate in 1.26 SG acid, made with different concentrations of red lead.
The pore volume distribution results show that the average pore sizes for the formed active material were between 1 and 2 µm. The pore volume of the samples that were formed using the high rate procedure had a slightly larger corresponding pore intrusion volume. This implies that the Hg could penetrate the core of the sample easier. This is an indication of the extent to which the electrolyte in the cell can penetrate the core of the material in order to utilize the active material.

The discharge capacity results of 11 cycles for the various cells made with positive tubular electrodes formed under the different conditions, discussed previously are shown in figures 3.68 to 3.70. The capacities in terms of Ah/kg of cured active mass and in terms of Ah are shown. The cells were rated at 16 Ah at the 1 A discharge rate. The SG of the cells after formation was adjusted to 1.31.
Figure 3.68: Capacity cycle of tubular electrodes made with various concentrations of red lead with 1.19 SG acid in Ah/kg (a) and Ah (b) with the low rate formation procedure.

Figure 3.69: Capacity cycle of tubular electrodes made with various concentrations of red lead with 1.26 SG acid in Ah/kg (a) and Ah (b) with the low rate formation procedure.

Figure 3.70: Capacity cycle of tubular electrodes made with various concentrations of red lead formed with 1.26 SG acid with the high rate formation procedure.
The results show that the cells containing 50, 75 and 100 % Pb\textsubscript{3}O\textsubscript{4} formed with the 1.19 SG acid did achieve the expected 16 Ah capacity after the 1\textsuperscript{st} discharge test. The cells made with 0 and 25 % did not achieve the rated 16 Ah, even after 11 capacity cycles (fig 3.68).

The cells that were formed with the 1.26 SG acid showed on average a slightly lower capacity (fig 3.69) when compared to the cells formed with the 1.19 SG acid (fig 3.68). The cells made with 0 and 25 % Pb\textsubscript{3}O\textsubscript{4} did not achieve the rated capacity of 16 Ah, even after 11 capacity cycles. The cell made with 100 % Pb\textsubscript{3}O\textsubscript{4} achieved capacities just below 16 Ah, which could be due to the lower active mass per electrode when compared to the other cells. The results in figure 3.69 a. show that the 100 % cell did, however, achieve a comparatively higher Ah/kg when compared to the other cells. The cells made with 50 and 75 % Pb\textsubscript{3}O\textsubscript{4} achieved the rated 16 Ah capacity after the 1\textsuperscript{st} discharge test, and maintained a relatively higher capacity during the 11 cycle test.

The capacity cycle results of tubular electrodes that were formed with 1.26 SG acid using the high rate procedure showed on average a lower active material utilization when compared to the cells formed with the lower rate (fig 3.70 a). The cells made with 0 and 25 % Pb\textsubscript{3}O\textsubscript{4} had very low 1\textsuperscript{st} capacity value (12.2 and 12.5 Ah respectively. The capacities increased during the 11 capacity cycles, where the cells obtained capacities just below 16 Ah after the 11\textsuperscript{th} cycle. This shows that a lot of unformed material remained in the electrode and only through repetitive cycling, did the unformed material convert to active lead dioxide. The cells made with 50 and 75 % Pb\textsubscript{3}O\textsubscript{4} did not achieve the rated 16 Ah and maintained a relatively consistent capacity during the 11-cycle test. The cell made with 100 % Pb\textsubscript{3}O\textsubscript{4} achieved a discharge capacity above 16 Ah after the first discharge test. This value remained relatively consistent throughout the 11-cycle test.

The 10 A capacity test that was done after the 1\textsuperscript{st} and 11\textsuperscript{th} 1 A discharge test, is shown in figure 3.71.
The results show no significant trend between the various cells formed with 1.19 and 1.26 SG and using the low rate formation procedure respectively. The test was not repeated with the high rate formation procedure.

### 3.5.3. Summary

The addition of red lead to the positive active material for flat plate electrodes has been compared in depth with tubular electrodes for VRLA MCL batteries. The following are the most important experimental findings:

1. The time required to electrochemically form the two types of MCL batteries made with flat plate or tubular electrodes was reduced by half, when compared to the existing process, and still maintained a relatively good first discharge capacity. The reduction in time was achieved by using a multi-step charge profile, and by carefully monitoring the temperature during the process, ensuring that it does not exceed $50^\circ$C.

2. The use of red lead improves the formation efficiency of both types of batteries by producing lead dioxide seeding crystals during the initial soaking stage before applying the formation current.
3. The results show that tubular electrodes were on average 30 % less efficient than flat plate electrodes in terms of utilizing the active material per Ah. Hence, a lower Ah/kg of active material was obtained for the cells made with the tubular electrodes as compared to the cells with flat plate electrodes.

Furthermore, the following points apply specifically to the batteries made with flat plate electrodes.

1. It is beneficial to add small amounts of red lead (25 %) to the paste preparation of the flat plate, since this improves the formation efficiency and results in first discharge capacities that are close to the rated capacity of the battery. Increasing the red lead content causes an increase in the first capacity, but gives a slightly weaker active material strength.

2. Even though the batteries that contained 100 % Pb$_3$O$_4$ in the original paste show very good initial capacity results, the cured pasted electrodes did not have a very good paste-bond to the supporting grid. This would result in a formed active material that is considerably weaker, which can be seen in the slight decrease in capacity during the first 11 cycles. The cured material should contain some tribasic lead sulphates in order to give the plate some rigidity. However, the tribasic lead sulphates do not form in the cured material if the red lead content is above 50 %. The paste density of the cured material increased for electrodes that contained 50 % Pb$_3$O$_4$ or more, showing that significantly more pressure was required during the pasting process in order to obtain a suitably pasted plate.

3. The use of 25 % red lead decreases the effect of the surface lead sulphate that is normally found on the formed electrodes that contain no Pb$_2$O$_4$. Even though the lead sulphate content in the rest of the active material is above 20 %, reasonably quick conversion of the material was observed with an improvement in capacity during subsequent cycling. This was not observed for electrodes that contained no Pb$_3$O$_4$, where many more capacity cycles were required in order to achieve the necessary capacity. An important parameter is the visual presence of surface sulphates that remain on the formed electrodes, which was especially observed for plates containing no Pb$_3$O$_4$. The layer of
surface sulphate inhibits the utilization of the underlying lead dioxide active material.

Regarding the use of tubular electrodes, the following important points can be noted:

1. There was no significant benefit in reducing the Pb$_3$O$_4$ content of tubular MCL electrodes. The results show that it would be better to use 100 or 75 % Pb$_3$O$_4$. From the manufacturing point of view, it would be easier to use the 100 % Pb$_3$O$_4$ material, which would reduce the unnecessary step of adding the grey oxide.

2. The results show that active material of electrodes that contain 75 and 100 % Pb$_3$O$_4$, had a higher surface area for both cured and formed cells, and that the formation procedure has a better utilization. However, with subsequent capacity cycling, the surface areas of all samples decreased and were very similar in value, irrespective of the initial amounts of Pb$_3$O$_4$ present in the cured material.
CHAPTER 4.

4. Porosity measurements of electrodes used in Pb-acid batteries

4.1. Background

The active surface area of the electrode material used in lead-acid batteries is directly proportional to the amount of capacity that can be achieved during discharge. Another important parameter that is related to the discharge performance is the porosity of the active material. This influences the rate and the amount of electrolyte that can penetrate the active material within an electrode. An electrode with a high porosity might give good results during high power discharge applications such as the starting of a car engine, but if the porosity is too high, a reduction in the cycle life ability of the electrode would occur because of poor adhesion between the particles in the active material.

Various techniques are available to evaluate the porosity of a porous material such as Mercury Porosimetry and Helium pycnometry. These techniques require expensive equipment and are usually limited to the sample size, which its sample chamber can accommodate. Some lead-acid battery manufacturers have developed their own technique using a water displacement method to determine the porosity of cured positive and negative electrodes. However, the method of using water as the displacement medium cannot be used to evaluate the porosity of the negative formed electrodes, which consist of sponge lead. The wetting of the negative formed electrode by water would accelerate the oxidation of the lead, thereby decreasing the effective pore size, and would not give a true reflection of the porosity of the active material.

The importance of the porosity of the active material in lead acid battery electrodes has been widely debated with many references quoting the optimal porosity and its role in the battery electrochemistry during charge and discharge. The importance of porosity as a function of the activity of the electrodes relates to the availability of active material sites for reactions to take place and the ease at which the electrolyte, can access the active sites. The porosity of a material is related to its density about which a number of important terms should be clearly defined.
The density of a solid substance is defined as the mass of a quantity of the solid divided by the volume of the same quantity, where the units are expressed as g/cm\(^3\) or kg/m\(^3\). If a solid object has a rigid well-defined shape, the density is simply related to the shape of its geometry that determines its volume. Many substances however have pores of varying shapes and sizes and often consist of cracks and crevices that extend through the bulk of the solid matrix. This leads to a number of different definitions of density and require different analytical techniques for their determination.

**Absolute Density.** Other terms that are used in the industry are true, matrix, real, apparent and skeletal density. This density is obtained when the volume that is measured excludes the pores within the sample material. The absolute density is determined from the absolute volume of the material\(^92\).

**Bulk Density.** This is also referred to as the envelope density and is determined for porous materials where the pore spaces within the material are included in the volume measurement. For fine powders, the term “tap” density would be the same as bulk density\(^92\).

\[
\rho_a = \frac{M}{V_a} \quad (4.1)
\]

\[
\rho_b = \frac{M}{V_b} \quad (4.2)
\]

where \(V_a\) = absolute volume and \(\rho_a\) = absolute density
\(V_b\) = envelope volume and \(\rho_b\) = envelope density

Porosity (\(P\)) and the specific total pore volume (\(V_P\)) can be determined from the following relationships:

\[
P = 100 \left(1 - \frac{\rho_b}{\rho_a}\right) \quad (4.3)
\]
There are a number of analytical techniques available that determine the porosity of porous material. The most common technique used in a wide field of applications is Mercury Porosimetry where Hg is forced under pressure to fill the pore volume of a porous object. The rate at which the volume of Hg changes with pressure can then give an indication of the object’s porosity. Other techniques such as He pycnometry and Dry-powder envelope density have been developed and used successfully in the industry\textsuperscript{92}. He pycnometry measures the absolute density of a solid sample by placing the sample into a known fixed volume sample chamber. The chamber is then filled with a known volume of He, which fills all the free space around the sample, including the pores. The absolute volume of the sample is determined by measuring the amount of He that did not fill the sample chamber. The Dry-powder envelope density method uses Archimedes’ principle to measure the encompassing volume of a sample. The displaced medium is a free flowing powder made from small hard spherical beads that flow easily around the outer “skin” of the solid sample. The difference in volume of a specific sample chamber with and without a sample is then used to determine the envelope density.

4.2. Glycerol displacement method to determine porosity

It was considered important to develop a rapid, reliable and cheap method for determining the porosity of battery plates in the plant laboratory. This method should require only elementary equipment and should be simple to operate, so that low-level lab workers can use it as a routine method during manufacturing. The method should be able to determine accurately the porosity of both cured and formed electrode plates.

As was pointed out earlier, a method based on water displacement has been used in the battery industry\textsuperscript{93}. However this method cannot be applied to negative electrodes, due to the interaction of water with the lead. For this reason, water was replaced by glycerol in the current analytical method. The method is based on Archimedes’ principle, which states, “That a body wholly or partly immersed in a fluid is buoyed up
with a force equal to the weight of the fluid displaced by the body. Table 4.1 summarizes the data and the relevant formulas.

**Table 4.1:** Calculations for determining the matrix density and porosity of plates by means of the glycerol displacement method.

<table>
<thead>
<tr>
<th>Column</th>
<th>Description or equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Costumer ID (battery type, plate size)</td>
</tr>
<tr>
<td>B</td>
<td>Plate Type (cured, formed, +ve or –ve)</td>
</tr>
<tr>
<td>C</td>
<td>Dry plate mass, (g)</td>
</tr>
<tr>
<td>D</td>
<td>Glycerol soaked plate mass, (g)</td>
</tr>
<tr>
<td>E</td>
<td>Mass in glycerol, (g)</td>
</tr>
<tr>
<td>F</td>
<td>Grid mass, (g)</td>
</tr>
<tr>
<td>G</td>
<td>Grid density, (g)</td>
</tr>
<tr>
<td>H</td>
<td>Active material mass, (g) = C – F</td>
</tr>
<tr>
<td>I</td>
<td>Absolute Density, (g/cm$^3$) = H/((C-E)/1.264-(F/G))</td>
</tr>
<tr>
<td>J</td>
<td>Bulk Density, (g/cm$^3$) = 1/((1/I)+K)</td>
</tr>
<tr>
<td>K</td>
<td>Specific Pore Volume, cm$^3$/g = ((D – C)/1.264)/H</td>
</tr>
<tr>
<td>L</td>
<td>% Porosity = JxKx100</td>
</tr>
</tbody>
</table>

Essentially the battery plate is dried and weighed (C). The dry plate is then immersed in glycerol and a vacuum is applied above the glycerol, so that the glycerol can penetrate the pores of the material. It is then removed from the glycerol and allowed to drip-dry so that excess glycerol is removed. Once no more surface liquid is visible, the wetted plate is weighed again (D). Now it is weighed again whilst completely immersed in glycerol (E). The grid mass of the plate (F) is based on the average mass per batch of plates, and the grid density (G) is determined using conventional methods and depends on the type of lead alloy used. Further experimental details of the method are described more fully in the experimental section (2.2). Analysis of at least two plates from a batch is done simultaneously, and the average result is then reported.

The derivation of the formulae given in table 4.1 will now be covered:
With reference to H in the Table, the active material mass is simply the difference between the dry mass of the plate (C) and the grid mass (F).

According to Archimedes’ principle, the apparent loss in mass of an immersed body is equal to the mass of liquid displaced, from which the volume of the immersed body can be determined. However the apparent loss in mass of the plate will be the sum of the apparent loss in mass of the paste on the plate and that of the grid of the plate. The absolute density (I) of the paste is given by equation 4.5:

\[
I = \frac{\text{mass of dry paste}}{\text{volume of dry paste}} = \frac{C - F}{\text{volume of plate} - \text{volume of grid}} = \frac{C - F}{\text{volume of plate} - \frac{F}{G}} \quad (4.5)
\]

However the volume of the plate is equal to the volume of glycerol displaced, which equals the apparent loss in mass (C – E) divided by the density of glycerol at 25°C, which is 1.264 g/cm\(^3\). The absolute density (I) of the paste of the plate is therefore given by equation 4.6:

\[
I = \frac{H}{\frac{C - E}{1.264} - \frac{F}{G}} \quad (4.6)
\]

The pore volume = volume of all open pores = the volume of glycerol that was soaked up by the dry plate = mass of glycerol soaked up divided by the density of glycerol. Hence the pore volume is given by equation 4.7:

\[
Pore \text{ volume} = \frac{[D - C]}{1.264} \text{ and specific pore volume in cm}^3 g^{-1} = K = \frac{[D - C]}{1.264 \times H} \quad (4.7)
\]

Now, since the total volume of the paste is the geometric volume of the paste + the pore volume, it follows that:

\[
\text{Total volume of paste} = \frac{[C - E - \frac{F}{G}]}{1.264} + \frac{[D - C]}{1.264} \quad (4.8)
\]
and the bulk density of the active material, \( (J) \), is simply the mass of active ingredient, \( (H) \), divided by the total volume of the paste:

\[
\text{Bulk density } = J = \frac{H}{\left[ \frac{C - E}{1.264} - \frac{F}{G} \right] + \left[ \frac{D - C}{1.264} \right]}
\]  

(4.9)

Equation 4.9 can be simplified, since the geometric volume of the paste can be expressed as \((H/I)\) and the pore volume itself is equal to \((KxH)\). Hence:

\[
\text{Bulk density } = J = \frac{H}{\left[ \frac{C - E}{1.264} - \frac{F}{G} \right] + \frac{D - C}{1.264} + \frac{H}{I} + KH} = \frac{1}{\left[ \frac{I}{J} \right]} + K
\]  

(4.10)

Finally the % porosity is given by equation 4.11:

\[
\text{% porosity} = \frac{\text{volume of pores}}{\text{total volume of the paste}} \times 100 = \frac{KH \times 100}{\frac{H}{J}} = JK \times 100
\]  

(4.11)

In order to test the glycerol method for determining porosities on battery plates, duplicate plates from the same batch of battery plates were tested over the year and some of the results are shown in table 4.2. These tests were carried out on four different battery plate types: formed negative, formed positive, cured negative and cured positive.
Table 4.2: Porosity of duplicate plates using the glycerol displacement method.

<table>
<thead>
<tr>
<th>Type of plate</th>
<th>Sample 1 porosity (%)</th>
<th>Sample 2 porosity (%)</th>
<th>Average porosity (%)</th>
<th>Standard deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formed negative</td>
<td>73.07</td>
<td>73.48</td>
<td>73.28</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>68.16</td>
<td>68.91</td>
<td>68.54</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>67.89</td>
<td>67.46</td>
<td>67.68</td>
<td>0.30</td>
</tr>
<tr>
<td>Formed positive</td>
<td>51.45</td>
<td>51.86</td>
<td>51.66</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>51.54</td>
<td>52.05</td>
<td>51.80</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>49.71</td>
<td>50.21</td>
<td>49.96</td>
<td>0.35</td>
</tr>
<tr>
<td>Cured negative</td>
<td>40.62</td>
<td>39.49</td>
<td>40.06</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>39.51</td>
<td>40.51</td>
<td>40.01</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>36.13</td>
<td>35.25</td>
<td>35.69</td>
<td>0.62</td>
</tr>
<tr>
<td>Cured positive</td>
<td>40.70</td>
<td>39.68</td>
<td>40.19</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>45.13</td>
<td>44.23</td>
<td>44.68</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>41.34</td>
<td>42.05</td>
<td>41.70</td>
<td>0.50</td>
</tr>
</tbody>
</table>

The tabulated results show that the glycerol method gives consistent readings for the % porosity of the different plates. Both the negative and positive formed plates give, however, a slightly better average standard deviation than the cured plates. Taking into account the small standard deviations obtained, it becomes apparent that this is a workable method to determine, in situ, the porosity of battery plates.

This method will now be compared with mercury porosimetry.

4.3. Comparing the glycerol method with Hg porosimetry

Four different types of plates are being compared, namely the negative and positive formed plates, and the negative and positive cured plates. The results reported for the glycerol method represents each time the average analysis carried out on duplicate plates of the same batch, whilst the corresponding Hg porosimetry result represents only one analysis carried out on sample taken from the center of a plate from the same batch. The results are spread over a number of batches of plates obtained from the industry over a time period of one year. The forming and curing conditions were
different depending on the type of plate and its particular manufacturing process. More studies were carried out on the formed positive plates, since this was the main area of the investigation.

Using statistical testing, one can analyze the data obtained for both methods and decide whether there is a significant difference between the results of the two methods\textsuperscript{95}. One starts with the null hypothesis, assuming that the two methods give the same result, and the t-test is carried out, which yields a t-value. If this t-value exceeds a certain critical value at a particular confidence level, then the null hypothesis must be rejected and the two methods then give significantly different results.

For samples, which are not identical but are compared by two similar techniques, the paired t-test is used\textsuperscript{95}. This method is applied to the data shown in table 4.3, which is for the formed negative plates only. The results shown in table 4.4 are for all the plate types analyzed, and the t-test method was done on each group of plates separately.

Since the samples are not identical, it is meaningless to calculate the mean and standard deviation of each series, since any differences between the two methods will be swamped by differences in the samples. For each series of results, the differences (d) between each pair of results are calculated, and the mean deviation (d), is obtained. The square of the deviations from the mean deviation is calculated, and the standard deviation (s\textsubscript{d}), of the differences is calculated using equation 4.12, where N is the number of different pairs of results.

\[
s_{d} = \sqrt{\frac{\Sigma (d - \bar{d})^2}{N - 1}} \tag{4.12}
\]

For the results in table 4.3 the data calculations for the negative formed plates is shown in the adjacent columns.
Table 4.3: Calculation for paired t-test for the negative formed plates.

<table>
<thead>
<tr>
<th>Hg porosimetry porosity (%)</th>
<th>Glycerol displacement porosity (%)</th>
<th>D</th>
<th>d - d</th>
<th>(d - d)^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>51.41</td>
<td>60.46</td>
<td>+ 9.05</td>
<td>- 6.70</td>
<td>44.89</td>
</tr>
<tr>
<td>54.87</td>
<td>59.92</td>
<td>+ 5.05</td>
<td>- 2.70</td>
<td>7.29</td>
</tr>
<tr>
<td>54.34</td>
<td>59.81</td>
<td>+ 5.47</td>
<td>- 3.12</td>
<td>9.73</td>
</tr>
<tr>
<td>57.07</td>
<td>60.53</td>
<td>+ 3.46</td>
<td>- 1.11</td>
<td>1.23</td>
</tr>
<tr>
<td>51.82</td>
<td>59.35</td>
<td>+ 7.53</td>
<td>- 5.18</td>
<td>26.8</td>
</tr>
<tr>
<td>55.46</td>
<td>56.96</td>
<td>+ 1.50</td>
<td>+ 0.85</td>
<td>0.72</td>
</tr>
<tr>
<td>65.95</td>
<td>63.63</td>
<td>- 2.32</td>
<td>+ 0.03</td>
<td>0.0009</td>
</tr>
<tr>
<td>59.34</td>
<td>54.80</td>
<td>- 4.54</td>
<td>- 6.89</td>
<td>47.47</td>
</tr>
<tr>
<td>55.21</td>
<td>51.17</td>
<td>- 4.04</td>
<td>- 6.39</td>
<td>40.8</td>
</tr>
</tbody>
</table>

\[
d = + 2.35 \quad S(d - d)^2 = 178.9
\]

The value \( s_d \) given by equation 4.12:

\[
s_d = \sqrt{\frac{178.9}{8}} = 4.73
\]

Finally the t-value is determined using equation 4.13.

\[
t = \frac{d \sqrt{N}}{s_d} = \frac{2.35 \sqrt{9}}{4.73} = 1.49
\]  
(4.13)

For a two-tailed test, with 8 degrees of freedom, the accepted critical statistical value for t at 95 % confidence level ( \( P = 0.05 \) ) is 2.31\textsuperscript{95}. This shows therefore that the null hypothesis is valid and there is no significant difference between the glycerol displacement method and the Hg porosimetry method for the negative formed plates analyzed.

The data for the other plates was similarly calculated and the t-values are displayed in the table 4.4. For each of these, the null hypothesis was valid, and therefore there is no significant difference between the two porosity methods.
Table 4.4: Comparison between the % porosity determined from Hg porosimetry and the glycerol displacement method for various cured and formed electrode material selected from positive or negative electrodes. Statistical verification was done at the 95% confidence level.

<table>
<thead>
<tr>
<th>Negative formed</th>
<th>Positive formed</th>
<th>Positive cured</th>
<th>Negative cured</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hg Por. (%)</strong></td>
<td><strong>Glycerol disp. (%)</strong></td>
<td><strong>Hg Por. (%)</strong></td>
<td><strong>Glycerol disp. (%)</strong></td>
</tr>
<tr>
<td>51.41</td>
<td>60.46</td>
<td>59.24</td>
<td>55.66</td>
</tr>
<tr>
<td>54.87</td>
<td>59.92</td>
<td>52.36</td>
<td>46.99</td>
</tr>
<tr>
<td>54.34</td>
<td>59.81</td>
<td>50.36</td>
<td>50.44</td>
</tr>
<tr>
<td>57.07</td>
<td>60.53</td>
<td>51.00</td>
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</table>

The results in table 4.4 are shown graphically in figure 4.1. The comparative results between the two techniques are indicated for each type of electrode analysed. The linear equation shown is fitted using all the results.
Even though the statistical verification at the 95 % confidence level showed that the two techniques are comparable and that the null hypothesis is valid, slight deviations from the simple linear relationship between the two techniques for all samples analysed was observed. The graph (fig 4.1) shows the slight deviations from linearity, in particular the results of the formed negative electrodes. The porosity results obtained for these negative electrodes using the glycerol displacement method were, on average, slightly higher than the corresponding values obtained using the Hg porosimetry method. This can be attributed to the sample preparation for the two techniques. The negative formed electrode after drying in an inert atmosphere was analysed within a few hours using the glycerol displacement method; instead, the samples taken for Hg porosimetry analysis were also taken from plates that were dried in an inert atmosphere, but by pushing the “sponge” lead from the grid support and analysing it only a few weeks later, could have influenced the porosity of the active material. The soft “sponge” lead can easily distort, thereby closing the respective pores and lead oxidizes, which can also lead to closing of the pores.
It must be remembered that the two techniques differ in their analytical methodology in that the Hg porosimetry analysis uses only a small section of the active material that was removed from the grid support. The material in the above study was always taken from the middle of the plate and was about 3 grams in mass. The Hg is pressurized into the pores of the sample thereby filling most available space. Under these high pressures, certain pores in the active material can also collapse. On the other hand, the glycerol displacement method uses an entire electrode for analysis without the active material being removed from the grid support. The glycerol is only slightly forced into the pores by vacuum and relies on the volume and mass displacement of the glycerol. The samples that have predominantly larger pores could, in comparison, give slightly lower results when using the glycerol displacement method than Hg porosimetry, since some of the glycerol that had filled the larger pores could start to leak out due to gravity during the set rest period during analysis.

4.4. Comparison between porosity and surface area

The porosity of a material would be indirectly related to the surface area of the solid material matrix. This relationship will be investigated in the following study.

Samples of electrodes manufactured by the local battery company were obtained on a monthly basis for more than a year and analysed for their porosity using the glycerol displacement method and the results were compared to the BET surface area of the same material.

Figure 4.2 shows the porosity results plotted against the BET surface area results obtained from a number of cured and formed active material obtained from positive and negative electrodes used in the manufacture of automotive lead-acid batteries.
Figure 4.2: Comparison of the % porosity using the glycerol displacement method versus the BET surface area of various cured and formed active material.

The graph shows that there are clear groupings of the resulting values between the various types of active material analysed. In theory, there should be a relationship between the surface area of a material and its porosity. The more pores and the greater the porosity of a material, the greater its surface area. However, the above results show that it is possible to obtain a material that has a relatively large porosity with a smaller surface area. This can be seen from the results obtained for the formed negative active material. The samples of the active sponge lead found on negative electrodes could have a very similar surface area but significantly different porosities. The porosity of the formed negative active material showed a considerable variation from 57 to 74 % without any significant change in their respective surface area. This shows that the internal material’s structure can change considerably during the formation time of the negative plate and can then result in an increase of the respective porosity, without significantly changing the available surface area.

The porosity and surface area of the cured positive and negative active material were very similar in that they reported a lower porosity and a lower respective surface area, with the negative cured material having a slightly higher average surface area. The porosity of the cured samples is between 35 to 45 % and their surface area between
0.5 to 2.1 $m^2/g$. There is not a great difference in the manufacturing process between the two cured electrodes, except that the negative cured material contains an expander consisting of very fine carbon powder, barium sulphate and lignin as an additive. These might contribute to the slightly higher surface area of the cured negative material.

The small variation in porosity and surface area results of the cured electrodes can be due to the fact that the manufacturing process during the time of analysis remained relatively consistent.

The results for the positive formed active material show that the surface area of a sample could change significantly without varying the available porosity. The surface area of the formed active material varied between 4 to 11 $m^2/g$ with only a slight variation in the respective porosity between 45 to 50 %.

The results show that the formation conditions of the battery used during manufacturing, influences the porosity and surface area of the final active material for both the negative and positive electrode.

The following investigation considered varying only one parameter, namely the concentration of the acid used during the formation, and its influence on the porosity and surface area of the final formed positive and negative active material.

4.5. Porosity of electrodes as a function of formation-acid concentration

It is well known that the acid concentration used during formation influences not only the active material composition but also the porosity and surface area\(^1\). Furthermore, it was important to verify the unusual trend observed previously of surface area and porosity for various formed active materials (fig 4.2).

4.5.1. Positive electrode

Figure 4.3 shows the porosity and surface area results for active material taken from the formed positive electrode as a function of the formation acid concentration. The
electrodes were well rinsed with water and dried at 100°C for several hours. Two plates from the same cell were analysed for their porosity using the glycerol displacement method and active material taken from the centre of another plate were analysed by Hg porosimetry and BET surface area respectively.

![Figure 4.3: Comparisons of the porosity and BET surface area of the active material from a positive electrode formed with different acid concentrations.](image)

The variation of the porosity, using Hg porosimetry and glycerol displacement methods, for the positive active material shows similar trends in that the porosity of the active material at first decreases slightly as the SG of the formation acid increases, followed by an increase at SG values of 1.2 and higher. The variation in porosity with the SG of acid used for formation ranged only from 45 % (1.16 SG) to 53 % (1.28 SG).

The variation in the surface area for the active material with SG of the acid is significantly larger. There is an almost linear increase in surface area from 4.5 m²/g (1.1 SG) to 9 m²/g (1.24 and 1.28 SG). This confirms the results observed in figure 4.2, where a larger variation in the surface area of the positive formed active material was observed than in the variation of its porosity.

The one advantage of using Hg porosimetry is that the pore volume and their size distribution of the active material can be determined at the same time. The distribution
of the pore volume of the formed active material versus the pore diameter is shown in figure 4.4. The corresponding median pore diameter distribution for the formed positive is shown in figure 4.5. For comparison purposes, the median pore diameter distribution for the negative electrodes is also shown, and will be discussed later.

**Figure 4.4:** Relationship between the incremental pore volume distribution and the pore diameter for the formed positive active material formed with different acid SG concentrations as determined by Hg porosimetry.

**Figure 4.5:** Median pore diameter distribution for the formed positive and negative active material formed with different acid SG concentrations.
The results for the positive electrode show the decrease in the average pore diameter as the SG of the acid used for formation increased. The positive active material formed at the lower SG acid, has predominantly larger pores of about 2 µm (median of 0.75 µm), whereas the material formed with 1.16 and higher SG acid has pores sizes predominantly below 1 µm (median of 0.25 µm).

The trend for the surface area of the active material formed at the higher SG can be explained in terms of the material having predominantly smaller pores. The smaller pores do, however, not decrease the porosity of the material, since, there could simply be more of them at the smaller diameter, thereby increasing its porosity only slightly but the surface area would increase then significantly. This is confirmed by figure 4.3 where the surface area increased as the SG of the formation acid used increased.

4.5.2. Negative electrode

The comparative porosity of the formed negative active material using the two techniques for porosity is shown in figure 4.6, together with the BET surface area determinations.

Figure 4.6: Comparison of the porosity and BET surface area of the active material from a negative electrode formed with different acid concentrations.
The results show that no significant change in the porosity of the negative active material occurs with a change in the formation S.G acid. The porosity values obtained from the glycerol displacement method are generally higher than those obtained from the Hg porosimetry analysis.

Similar to the results observed in figure 4.2, the surface area of the negative formed active material does not change significantly, even by changing the acid concentration during formation over the SG range of 1.10 to 1.28. This implies that very little influence on the active material’s surface area and porosity can be achieved by changing the formation acid concentration. There are, however, probably other factors that could influence the porosity of the negative formed active material such as the use of various expanders or formation currents, rates and temperature.

The pore volume distribution of the negative-formed active material did show a larger average pore size for the material formed using the 1.20 and 1.16 SG acid concentration than for the material that was formed using 1.28 and 1.24 SG acid respectively. The pore volume distribution for the material formed at 1.10 and 1.28 SG had similar pore volume distributions (fig 4.7).

![Figure 4.7: Relationship between the incremental pore volume distribution and the pore diameter for the formed negative active material formed with different acid SG concentrations.](image-url)
The median pore diameter (volume) for the Hg pore volume intrusion for the different formed negative active material with various formation SG acid is shown in figure 4.5. The results show that the negative formed material had a significantly larger median pore diameter than the corresponding positive formed material, with little or no differences between the ones formed in different acid concentrations.

4.6. Glycerol displacement method used for positive tubular electrodes

The summary of a study that used the glycerol displacement method in the analysis of tubular cured and formed electrodes is shown in tables 4.5 and 4.6. This study would show the viability and precision of using the glycerol displacement method for the analysis of tubular positive electrodes. The study involved the measurement of a single cured and formed 10 spine tubular electrode that was carefully separated into its individual spines. This ensured that no variation in curing or formation of the active material could have influenced the results since each spine would have been exposed to the same experimental conditions.

Table 4.5: Summary of the density and porosity of single spines analysed from a tubular positive cured plate, using the glycerol displacement method.

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>C dry mass (g)</th>
<th>D Glyc.wet mass (g)</th>
<th>E in glycerol mass (g)</th>
<th>H Mat. mass (g)</th>
<th>I Abs density (g/cm³)</th>
<th>K Sp.pore volume (cm³/g)</th>
<th>J bulk density (g/cm³)</th>
<th>L % porosity</th>
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<tr>
<td>Cured tubular spines</td>
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<tr>
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Table 4.6: Summary of the density and porosity of single spines analysed from a tubular positive formed plate, using the glycerol displacement method.

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>C dry mass (g)</th>
<th>D Glyc.wet mass (g)</th>
<th>E in glycerol mass (g)</th>
<th>H Mat. mass (g)</th>
<th>I Abs. Density (g/cm³)</th>
<th>K Sp.pore volume (cm³/g)</th>
<th>J bulk density (g/cm³)</th>
<th>L % porosity</th>
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The abbreviated letters used in the tables are described in table 4.1.

Total Spine mass (F) = lead spine + plastic + gauntlet = 17.4 g
Spine density (G) = 10.6 g/cm³
Glycerol density = 1.264 g/cm³

The results of the individual spines of a 10-spine electrode showed that the glycerol displacement technique could be used to determine the porosity of tubular electrodes with a relatively low standard deviation and span of results. The standard deviation for the porosity of the cured electrode spines was 1.84 % and for the formed electrode 0.81 % respectively.

For comparison purposes, 10 cured and 10 formed spines which were treated in section 3.4 by varying the curing and dipping conditions of tubular electrodes where analysed for their porosity by using the glycerol displacement method. The variation between the porosity and surface area of formed and cured tubular electrodes active material are shown in figure 4.8.
Figure 4.8: A summary of % porosity results versus BET surface area for formed and cured positive tubular electrodes.

The results are similar to those observed for the flat plate automotive electrodes discussed previously (fig 4.2). However, a significant variation in porosity of the cured material is observed between samples with little change in their respective surface area. The formed active material showed again a different trend, in that the surface area between samples would vary significantly with little change in their respective porosity.

4.7. Summary

The technique of using Archimedes’ principle to determine the porosity of cured and formed plates used in the manufacture of flat plates as well as positive tubular electrodes was shown to be successful. The use of glycerol, instead of water, for determining the porosity was shown to be feasible for not only the cured plates, but also formed negative plates, where the sponge lead is sensitive to oxidation. The method is comparative to Hg porosimetry, a well-known technique and differences between some of the results could be explained due to the nature of sample preparation. The technique is relatively quick and inexpensive, and can be easily implemented as a routine procedure in a manufacturing environment.
The variation of electrode porosity and surface area seems to be more evident for some plate types than others. The cured automotive electrodes (positive and negative) did not show large variations in their porosity and surface area over the range of samples analysed. They were between 35 – 45 % and 0.5 – 2.6 m²/g respectively. However, for the tubular cured electrodes studied the porosity values had a much larger variation than the corresponding surface areas. They were between 25 - 50 % and 1.0 - 1.5 m²/g respectively.

Significant variations in the porosity of negative formed electrodes were obtained with very little change in their corresponding surface area. They were between 55 - 75 % and 0.2 – 0.7 m²/g respectively. The variation of the surface area of the positive formed electrodes was much larger with very little variation in their corresponding porosity. They were between 45 - 55 % and 4.5 - 10.5 m²/g respectively.

The formation parameters used during the formation of the battery contribute to the surface area and porosity of the active material on the positive and negative electrodes. One of these parameters, namely the acid concentration, was evaluated and this study showed that by changing the acid concentration, used for forming a Pb-acid flat plate car battery, only slight changes in active material porosity took place, but there was a significant variation in the corresponding surface area for the positive electrode; the change in surface area would correspond to a similar change in the respective pore size median, where smaller pores were obtained for active material that was formed with a higher SG acid.

No significant influence on the porosity and surface area of the negative formed active material was observed when using different acid concentrations during formation. The median pore size of the negative formed electrode was considerably larger than the formed positive electrode.
5. Oxygen recombination in MCL VRLA cells.

5.1. Background

The comparative study of the oxygen recombination and cell pressure cycle for MCL VRLA batteries using positive flat plate and tubular electrodes was carried out using various charge/discharge and float charge voltage profiles. The intention of the study was to obtain an indication of the efficiency of the recombination of oxygen in VRLA batteries using these two different positive electrode designs. The pressure and % Oxygen above the cell assembly in the sealed battery was measured continuously during various discharge and charge profiles. It should be remembered that the gas that was released and measured in the upper part of the battery may not have the exact same composition as the gas that is contained in the whole free volume of the battery. The free volume includes the micro pores of the active material of the electrodes and capillary channels of the separator, which form part of the cell assembly, and can vary depending on the charge or discharge condition of the test sequence.

5.2. Oxygen cycle of MCL VRLA cells during capacity cycles

5.2.1. MCL batteries with tubular electrodes

For a MCL VRLA battery made with tubular positive electrodes, the changes in cell pressure and the oxygen concentration in the free space above the cell assembly was measured during the open circuit voltage (OCV), discharge and charge cycle tests with intermittent OCV rest periods, followed by discharge and charge cycles without any rest OCV. The charge / discharge tests are described in the experimental section 2.3. These results are shown in figures 5.1 and 5.2.
Figure 5.1: Changes in cell pressure and relative oxygen concentration during the discharge and charge cycles with intermediate rest periods of a MCL VRLA cell made with positive tubular electrodes.

Figure 5.2: Changes in cell voltage and current during the discharge and charge cycles with intermediate rest periods of the same MCL VRLA cell made with positive tubular electrodes indicated in figure 5.1.

Figure 5.3 a and b represent the O$_2$ composition for the first two discharge and charge cycles shown in figure 5.1.
Figure 5.3 a & b: Change in oxygen concentration during first and second recharge cycles for the MCL VRLA cell made with positive tubular electrodes.

The pressure of the cell shown in figure 5.1 increased during the first 48 h OCV step. There was, however, no noticeable increase in the oxygen concentration. The pressure increase may be attributed to the possible self-discharge effect in the cell during OCV where hydrogen was formed at the negative electrode according to reaction (5.1). The oxygen that was formed in the tubular cells (equation (5.2)) might be trapped in the acrylic tubes and separator and be released at a later stage during the discharge and charge steps into the free head space above the cell assembly, or migrate to the negative electrode to recombine with Pb.

\[
\text{Negative Electrode: } \text{Pb} + 2\text{H}^+ + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + \text{H}_2 \\
\text{Positive Electrode: } \text{PbO}_2 + 2\text{H}^+ + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2
\] (5.1) (5.2)

With reference to figure 5.3 (a), a small amount of about 3 % O$_2$ was observed to form in the cell space during the discharge step (A) that followed the OCV. This could be the O$_2$ trapped in the pores and acrylic gauntlet that was forced out during the volume expansion of the active material on discharge. During the charging cycle, at 2.3 V and 2 A charge current, O$_2$ was formed rapidly with a noticeable increase in cell pressure. This is in agreement with literature, which reports that above 2.3 V, the gassing rate of O$_2$ would increase significantly$^1$. As the cell reached the constant charge voltage of 2.7 V, the current started to decrease when the oxygen content in the free space was about 62 % (B) (fig 5.3). The cell pressure continued to increase
and the relative O₂ concentration rose to a maximum of about 90% (C) until the cell vent pressure was reached and a small amount of gas was released. A decrease in O₂ concentration and a slight drop in cell pressure followed this drop when the O₂ recombination at the negative electrode became greater than the O₂ generation at the positive electrode. A slight increase in cell pressure was noted at the end of charge (fig 5.1) which may be due to the increase in hydrogen concentration, when the negative electrode’s polarization had decreased significantly to allow hydrogen gas to develop (D in fig 5.3).

The % O₂ decreased to about 50% at the start of the next OCV (D). This was followed by a gradual drop (E) in concentration according to a first order kinetics reaction described by Henn et al. 28 Exponential graphs that correspond to first order reactions were obtained for the OCV steps with a reaction rate constant (k) = 0.1358 h⁻¹ for the 1ˢᵗ cycle and 0.1412 h⁻¹ for the 2ⁿᵈ cycle respectively (fig 5.3 a & b). The cell pressure (fig 5.1) dropped over the initial stages of the 2ⁿᵈ OCV period, followed by a slight increase towards the end of the OCV even though no increase in the % O₂ was observed.

The charge current profiles during the constant voltage charge step (fig 5.2) did not reach a constant float current as was typically observed at the end of charge for common flooded type lead acid cell systems, but rather showed a slight increase towards the end of the charge step. This characteristic is typical for VRLA cells where the charge current can be considered as the sum of the float charge current (gassing, grid corrosion and slight active material conversion) and the recombination current that occur at the negative electrode.

Figure 5.4 represent the % O₂ for four repeating discharge and charge cycles shown in figure 5.1.
**Figure 5.4:** Change in Oxygen concentration for the charge and discharge cycle with no intermittent OCV rest period for MCL VRLA cell with positive tubular electrode.

The repetitive cycle test in figure 5.4 showed similar results to that of the intermittent charge cycle with extended OCV (fig 5.3). The increase in O$_2$ concentration from (A) to (B) to (C) was similar to the profiles discussed previously (fig 5.3). During the constant voltage recharge step, the % O$_2$ decreased to about 45 %, before the next discharge step occurred (F). This showed that recombination of the O$_2$ was still taking place at the negative electrode even though the cell was in discharge. Once the cell reached a discharge voltage of 1.75 V, a charge step was followed of 2 A (G) with about 15 % of O$_2$ remaining. The O$_2$ concentration continued to drop slightly until the charge voltage of 2.3 V was reached, where an increase in the O$_2$ concentration was observed.

The characteristics of the cell pressure at the end of the charge profile were similar in that the cell pressure would peak during the constant voltage charge of 2.7 V. This was followed by a slight “dip” in pressure even though the oxygen concentration during this time was decreasing (C). The second peak in the pressure cycle would be due to the active material on both electrodes being almost fully converted to lead and lead dioxide, respectively, and due to the hydrogen over-potential been reached, allowing for hydrogen gassing to start at the negative electrode, increasing the cell pressure.
Only part of the negative active material becomes electrochemically active during recharging where the recombination cycle of oxygen at the negative electrode suppresses hydrogen gas evolution during overcharge and initiates $O_2$ recombination\textsuperscript{22, 23 & 27}.

5.2.2. MCL batteries with flat plate electrodes

A MCL VRLA battery, made with flat plate positive electrodes, was evaluated electrochemically as for the battery made with tubular electrodes discussed previously. The results are shown in figures 5.5 and 5.6.

![Graph showing changes in cell pressure and oxygen concentration during discharge and charge cycles with intermediate rest periods of a MCL VRLA cell made with positive flat plate electrodes.]

**Figure 5.5:** Changes in cell pressure and oxygen concentration during the discharge and charge cycles with intermediate rest periods of a MCL VRLA cell made with positive flat plate electrodes.
Figure 5.6: Changes in cell voltage and current during the discharge and charge cycles with intermediate rest periods of the MCL VRLA cell made with positive flat plate electrodes.

Figure 5.7 a and b represent the change in the $O_2$ composition for the first two discharge and charge cycles shown in figure 5.5.

Figure 5.7 a & b: Change in Oxygen concentration during first and second discharge and recharge cycles for MCL VRLA cell made with positive flat plate electrodes.

With reference to figure 5.7 (a), the $O_2$ concentration change during the discharge, charge and OCV profiles of the MCL VRLA batteries made with positive flat plate
electrodes was considerably different to the profiles observed for the batteries made with the positive tubular electrodes (fig 5.3 a & b).

The \( \text{O}_2 \) concentration during the initial discharge step (A) in figure 5.7 (a & b) increases considerably with a corresponding increase in the cell pressure (fig 5.5). The increase from (A) to (B) obeys a typical kinetic first order reaction to a maximum of 10 % \( \text{O}_2 \) (B) to the end of discharge at 1.75 V as shown by the fitted curves and correspond to equations (5.3) and (5.4) for the 1\(^{\text{st}}\) and 2\(^{\text{nd}}\) discharge respectively. The second discharge reaction deviates slightly from a first order reaction towards the end of the discharge. This could be due to some of the \( \text{O}_2 \), formed during the discharge having migrated to the negative electrode to recombine. This process was further encouraged by the slight increase in cell pressure and an increase in the capillary porosity of the glass matt separator at the top of the negative electrode, giving access for oxygen to recombine at the grid of the negative electrode. The increase in pressure can be seen in figure 5.5.

\[
\begin{align*}
1^{\text{st}} \text{ discharge:} & \quad Y = 10^{-7} e^{0.3035X} \quad R^2 = 0.99 \quad (5.3) \\
2^{\text{nd}} \text{ discharge:} & \quad Y = 5 \times 10^{-19} e^{0.3475X} \quad R^2 = 0.97 \quad (5.4)
\end{align*}
\]

Where \( k \) for the 1\(^{\text{st}}\) discharge = 0.3035 h\(^{-1}\) and \( k \) for the 2\(^{\text{nd}}\) discharge = 0.3475 h\(^{-1}\).

Note: The preceding term before the exponent (concentration at time zero) of the two equations are considerably different and is due to the fact that point (A) on the graph did not originate at time zero. The concentration at “time zero” is not of significant interest and is a relative term depending on the point of origin. For calculation and discussion purposes, the slope of the graph is of more interest.

A decrease in available active material and a subsequent reduction in capacity that occurs during OCV are known as self-discharge. Self-discharge processes take place whether the electrodes are charged or discharged or standing without load. The decomposition of the active mass occurs with gas evolution and formation of lead sulphate. Bode\(^1\) reported that the amount of gas being produced during discharge could be as high as 19 cm\(^3\) for a 2.7 h discharge test done at 1 A.
Referring to figure 5.7, as the cell starts to charge at 2 A (B), the \( O_2 \) concentration decreases to almost 1 \% (C), which corresponded to about 2.25 V on the charge voltage profile (fig 5.6). As the charge voltage increases to 2.3 V, the \( O_2 \) concentration of the cell increases to a maximum of 45 \% (D). This corresponds to the constant charge voltage of 2.7 V, where the charge current starts to decrease. The current does not decrease significantly, due to the contribution of the recombination current occurring at the negative electrode. This is followed by a decrease in the \( O_2 \) concentration in the cell space, due the recombination of \( O_2 \) at the negative being greater than the formation of \( O_2 \) at the positive electrodes. However, an unusual “dip” with an increase in the oxygen concentration and a corresponding increase in pressure is observed towards the end of the charge profile (E). Towards the end of charging, the negative electrode becomes sufficiently polarized to allow for the gassing of \( H_2 \) to take place. The increase in \( H_2 \), which moves upwards in the cell, may have caused \( O_2 \) that was near the negative electrode to be caught in the upward movement of the gas, thereby preventing it from recombining with the lead electrode.

During the OCV step of the test sequence, the \( O_2 \) concentration in the cell decreases rapidly (F) following a linear decrease with time (equation 5.5 and 5.6) rather than an exponential decrease observed for the tubular electrode cells discussed previously and also reported by Henn et al\(^{28}\).

The linear equations fitted to figure 5.7 (a) & (b) are as follows between (E) and (F).

1\(^{st}\) OCV (a): \[ Y = -8.2784X + 615.68 \]
\[ R^2 = 0.99 \] (5.5)

2\(^{nd}\) OCV (b): \[ Y = -7.6174X + 1093.4 \]
\[ R^2 = 0.99 \] (5.6)

Note: The Y-axis intercept of the two equations is considerably different and is due to the fact that point (E) on the graph did not originate at time zero. The Y-axis intercept parameter is not of interest and is a relative term and depends on the point of origin. For calculation and discussion purposes, the slope of the graph is of more interest.

The average of the slopes of the two equations is about 8 \% \( O_2 \)/h. The negative sign implies a decrease of the relative \( O_2 \) concentration during OCV of the cell. This implies that if a cell produces a maximum of 40\% \( O_2 \) during its charge cycle in the free space above the cell, it would virtually all be recombined during the OCV cycle within
5 h. This is considerably different when compared to a similar situation for a cell made with tubular electrodes, where a relative \( O_2 \) concentration after 5 h would still be 20% (fig 5.3).

For these positive flat plate electrodes, the decrease in \( O_2 \) concentration to about 2% during OCV was within 5 h, whereas for the cells made with tubular positive electrodes it took 21 h to reach the same \( O_2 \) concentration in OCV. This was unusual in that the same type of negative electrodes were used in the manufacturing of the flat plate and tubular batteries. The characteristic of the rapid decrease in \( O_2 \) during OCV might be explained by an increase in the capillary channels made available in the AGM separators between the two flat plate electrodes allowing for more \( O_2 \) to move to the negative electrode for recombination. This may be especially significant near the top of the cell space where the \( O_2 \) concentration is measured.

The rapid decrease in \( O_2 \) concentration during the initial stages of the OCV for the flat plate electrodes caused the cell pressure to go below atmospheric pressure (fig 5.5). This was followed by a similar trend to the case of the cells with tubular electrodes. It was observed that during OCV here was an increase in cell pressure even though there was no noticeable increase in \( O_2 \). The increase was attributed to the self-discharge gas that was formed during OCV according to equations (5.1) and (5.2). The oxygen formed during the self discharge could be considered as occluded gas in the pores of the electrode and separator, which then was released during the discharge reaction\(^1\).

Figure 5.8 represents the relative % \( O_2 \) change for four repeating discharge and charge cycles as shown in figure 5.5.
The repetitive cycle test in figure 5.8 shows similar results to that of the intermittent charge cycle with extended OCV (fig 5.7). The increase in \( \text{O}_2 \) concentration during discharge (B) followed by a decrease at the beginning of the following recharge cycle (C) was discussed previously. As the cell voltage reached 2.3 V, the \% \( \text{O}_2 \) increased to about 50 \% until constant charge voltage of 2.7 V was reached (D). This was followed by a characteristic “dip” in the \( \text{O}_2 \) concentration towards the end of charge (E).

The charge step was immediately followed by a discharge step to a voltage limit of 1.75 V. During this step, the relative \( \text{O}_2 \) concentration continued to decrease during the first half of the discharge step up to point (F). This is followed by an increase in the \( \text{O}_2 \) concentration towards the end of discharge (B).

The decrease from (E) to (F) was initially similar to that observed during normal OCV after a charge cycle observed previously. At the low discharge rate (1 A), the \( \text{O}_2 \) had sufficient time to recombine at the negative electrode during the early stages of discharge. However, after about 50\% DoD, an unusual increase in \( \text{O}_2 \) was observed, with a slight increase in the cell pressure, even though the cell was in discharge. This indicates that gases were released during the discharge process of the VRLA cell.
Once the cell reached a discharge voltage of 1.75 V, a charge step of 2 A was applied. The O$_2$ concentration continued to drop for a short time and then at 2.3 V charge voltage, the O$_2$ concentration increased rapidly.

The characteristics of the cell pressure at the end of each charge profile for both tubular and flat plate electrodes were very similar in that the cell pressure would peak followed by a slight decrease and then an increase in pressure even though the oxygen concentration was decreasing. The second peak would be due to the active material on both electrodes being almost fully converted to lead and lead dioxide respectively and that hydrogen gassing would start at the negative, increasing the cell pressure and causing some of the O$_2$ gas not to recombine at the negative electrode and subsequently increasing its concentration slightly. During the following step, the cell pressure would decrease below atmospheric pressure whilst the O$_2$ concentration was decreasing after discharge (fig 5.5), showing that a rapid and efficient recombination process is taking place.

5.3. **Oxygen cycle of MCL VRLA cells during over-charge**

When a fully charged lead-acid battery is charged at constant voltage, the corresponding current decreases to a relatively constant value in order to maintain the respective charge voltage. This is referred to as the overcharge or float current and gives some indication of the electrochemical characteristics of the battery’s components. Applications that require the use of batteries in a constant charged state (UPS) would charge the battery sufficiently on a continuous basis in order to prevent self-discharge. The setting of the charge voltage in such applications depends on factors such as the battery design type and variations in ambient temperature. In a simple flooded lead-acid cell, the contribution to the float current comes primarily from the electrolysis of water, corrosion of the positive electrode current collector, decomposition of organics and the conversion of small amount of lead sulphate still present in the active material. The float current at a specific charge voltage can also vary with the ageing of the battery, where metal impurities introduced into the cell (Sb, Cu) can electroplate onto the negative electrode thereby increase the decomposition rate of water.
The float current in VRLA type batteries becomes more complex, when contributions from the recombination of the oxygen at the negative electrode have to be taken into consideration. The extent of the recombination current contribution would an indication of the efficiency of the recombination. The following results are from charging a fully charged battery at certain pre-programmed constant voltage settings for 18 h. Every charge period was followed by a 48 h OCV rest period in order to allow the $\text{O}_2$ that was formed in the cells to recombine before commencing with the next charge period at a higher voltage setting.

### 5.3.1. MCL batteries with tubular electrodes

Figure 5.9 summarizes the changes in $\text{O}_2$ concentration, cell pressure and cell current during different float charge voltages with intermittent OCV rest periods for tubular electrodes.

![Figure 5.9](image)

**Figure 5.9:** Changes in cell pressure, oxygen concentration and current during various constant voltage float charge steps with intermittent OCV rest periods for a MCL VRLA cell made with positive tubular electrodes.

Figure 5.10 shows the change in $\text{O}_2$ concentration with first order reaction curves (equations 5.13 to 5.18) fitted to each of the OCV rest periods.
Figure 5.10: Changes in cell oxygen concentration at various constant voltage float charge cycles with intermediate OCV rest periods for a MCL VRLA cell made with positive tubular electrodes.

The maximum \( O_2 \) concentration and current measured at each of the float voltage steps are summarized in table 5.1.

**Table 5.1:** Comparison of charge voltage, maximum \( O_2 \) concentration and the average float current for MCL VRLA cells made with tubular positive electrodes.

<table>
<thead>
<tr>
<th>Float Voltage (V)</th>
<th>% ( O_2 )</th>
<th>Average Float Current (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.45</td>
<td>32</td>
<td>0.102</td>
</tr>
<tr>
<td>2.50</td>
<td>61</td>
<td>0.173</td>
</tr>
<tr>
<td>2.55</td>
<td>79</td>
<td>0.215</td>
</tr>
<tr>
<td>2.60</td>
<td>86</td>
<td>0.278</td>
</tr>
<tr>
<td>2.65</td>
<td>76</td>
<td>0.277</td>
</tr>
<tr>
<td>2.70</td>
<td>66</td>
<td>0.380</td>
</tr>
</tbody>
</table>

At every float charge voltage step, the \( O_2 \) concentration would increase to a relatively consistent maximum value over the duration (18 h) of the test. The corresponding float charge current would decrease to a relatively constant value with some cases showing a slight increase towards the end of the step. The increase in current would be attributed to the \( O_2 \) recombination occurring at the negative electrode. The increase in float charge voltage to 2.65 and 2.70 V shows a decrease in the maximum \( O_2 \) concentration formed in the cell. This can be ascribed to an improvement in the
recombination where more capillary channels in the AGM separator between the positive and negative electrodes are forced open due to higher gassing rates. A decrease in the water content of the separator due to the preceding test would also contribute to the increase in the channels improving the recombination of O₂.

Even though the float current measured was influenced by the recombination current, the relationship between the float voltage and current follows a typical Tafel plot relationship shown in figure 5.11.

![Tafel plot](image)

**Figure 5.11**: Tafel plot of float voltage versus the ln I for the MCL VRLA cell made with tubular positive electrodes.

The slope of the straight-line equation (0.1953 V) is similar to that reported elsewhere in the literature\(^1\). Assuming that the cells are fully charged, the current during the float charge can be described as follows\(^2\):

At the positive electrode:

\[ i = i_{O_2(\text{gas})} + i_{(\text{other})} \]

Where \( i_{O_2(\text{gas})} \) is the current due to the oxygen formed at the positive plate (equation 5.7) and \( i_{(\text{other})} \) the current due to reactions such as positive grid corrosion, small amounts of unformed PbSO₄ (equation 5.8) and oxidation of organic species.
At the negative electrode:

\[ i = i_{H_2(gas)} + i_{O_2(red)} \]

Where \( i_{H_2(gas)} \) is the current due to the hydrogen forming (equation 5.9) and \( i_{O_2(red)} \) is the current due to the oxygen recombining (equation 5.10 - 5.12) at the negative electrode.

\[
\begin{align*}
2H^+ + 2e^- &\rightarrow H_2 \\
Pb + \frac{1}{2} O_2 &\rightarrow PbO \\
PbO + H^+ + HSO_4^- &\rightarrow PbSO_4 + H_2O \\
\text{and} & \\
PbSO_4 + 2H^+ + 2e^- &\rightarrow Pb + H_2SO_4
\end{align*}
\] (5.9) (5.10) (5.11) (5.12)

The cycle can repeat itself. The total current observed during the charging step is shown in equation 5.22 and will be discussed in more detail later. The recombination of \( O_2 \) that takes place during the OCV steps between the various float charge cycles obeys a similar first order reaction mechanism described previously by Henn et al.²⁸ The equations for the OCV graphs in figure 5.10 are given as follows.

\[
\begin{align*}
\text{At } 2.45V: & \quad Y = 16.1e^{-0.1513X} \quad R^2 = 0.91 \\
\text{At } 2.50V: & \quad Y = 43.3e^{-0.1473X} \quad R^2 = 0.97 \\
\text{At } 2.55V: & \quad Y = 57.9e^{-0.1408X} \quad R^2 = 0.98 \\
\text{At } 2.60V: & \quad Y = 70.7e^{-0.1296X} \quad R^2 = 0.99 \\
\text{At } 2.65V: & \quad Y = 61.2e^{-0.1256X} \quad R^2 = 0.99 \\
\text{At } 2.70V: & \quad Y = 52.0e^{-0.1215X} \quad R^2 = 0.99
\end{align*}
\] (5.13) (5.14) (5.15) (5.16) (5.17) (5.18)

The \( O_2 \) reduction during OCV can be expressed by

\[ Pb + \frac{1}{2} O_2 + H_2SO_4 \rightarrow PbSO_4 + H_2O \] (5.19)
The rate of $O_2$ reduction would be:

$$R_{O_2} = \frac{dC_{O_2}}{dt} = -k_{O_2} \left[C_{O_2}\right]^n$$

(5.20)

where $\left[C_{O_2}\right]^n$ is the concentration of $O_2$ at time $t$ and $k_{O_2}$ is the rate constant.

If the reaction is a simple first order reaction and the kinetic parameter with $n = 1$, then,

$$C_{O_2}(t) = C_{O_2}^{\text{initial}} \exp(-k_{O_2} \cdot t)$$

(5.21)

The rate constant ($k$) for $O_2$ reduction can be obtained from the slope of the logarithmic graph of the $O_2$ concentration, log ($C_{O_2}$), as a function of time ($t$), were $C_{O_2}^{\text{initial}}$ is the oxygen concentration at $t=0$. Henn et al.\textsuperscript{28} restricted the time for the first order recombination reaction not to exceed 1 or 2 h. He ascribed the deviations from the first order reaction to plate structure modifications, which take place during the reactions, and to the slower diffusion through the negative mass, which decreases the rate. He also observed that at the same time, gas emission, due to self-discharge, can occur but at a much slower rate than the oxygen reduction and this would not influence results over the short period of time.

The $C_{O_2}^{\text{initial}}$ determined for equations (5.13 to 5.18) are not the $O_2$ concentration at $t=0$, since the testing was done sequential. The $C_{O_2}^{\text{initial}}$ could be determined from the equations by adjusting starting time of each OCV cycle to $t=0$. The important parameter is the rate constant $k$ for the OCV reactions. The $k$ values determined are similar to those observed during the OCV studies for the cycle tests after the 1\textsuperscript{st} and 2\textsuperscript{nd} charge step in figure 5.3 for tubular electrodes. Noticeably, the rate constants decreased slightly for each OCV after their respective float charge step. This implies that the rate of $Q_2$ recombination during the OCV improved slightly for subsequent testing steps due to more capillary channels in the AGM near the top of the cell being made available due to higher gassing rates and water loss, allowing more $O_2$ to access the negative electrode.
5.3.2. MCL batteries with flat plate electrodes

The characteristics of the $O_2$ concentration, cell pressure, and charge currents at various float charge voltages for cells made with positive flat plate electrodes are shown in figures 5.12 and 5.13.

Figure 5.12: Changes in cell pressure, oxygen concentration and current during various constant voltage float charge steps with intermediate OCV rest periods for a MCL VRLA cell made with positive flat plate electrodes.
Figure 5.13: Changes in the $O_2$ concentration and a linear curve fit for the respective OCV steps after each constant float voltage charge for a MCL VRLA cell made with positive flat plate electrodes. The charge current during various constant voltage float charge steps with intermediate rest periods is also shown.

The maximum $O_2$ concentrations at the various float charge voltages are shown in table 5.2.

Table 5.2: Comparison of charge voltage and maximum $O_2$ concentration for MCL VRLA cell made with flat positive electrode.

<table>
<thead>
<tr>
<th>Float Voltage (V)</th>
<th>% $O_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.45</td>
<td>54</td>
</tr>
<tr>
<td>2.50</td>
<td>86</td>
</tr>
<tr>
<td>2.55</td>
<td>84</td>
</tr>
<tr>
<td>2.60</td>
<td>70</td>
</tr>
<tr>
<td>2.65</td>
<td>56</td>
</tr>
<tr>
<td>2.70</td>
<td>49</td>
</tr>
</tbody>
</table>

It was not possible to obtain a similar float charge current as for the previous cells made with tubular electrodes. This was due to a noticeable increase in charge current, even after 18 h of charging at a relatively low voltage of 2.45 V. This increase in current can be mainly attributed to the $O_2$ recombination current (fig 5.13).
This increase in charge current during the constant voltage charge step is an indication of the recombination efficiency of the cell. This current increases considerably as the charge voltage is increased, and is related to the relative amount of O$_2$ present in the free space above the cell assembly. This can be seen by the fact that the % O$_2$ at the 2.65 and 2.70 V float voltages reaches a maximum of 56 and 49 % respectively, which was lower than the values observed at 2.50 and 2.55 V. This can be ascribed to an increase in the gassing rate at higher voltages which in turn increase the available capillary channels in the AGM separator between the negative and positive electrodes, allowing for more Q$_t$ to recombine, thereby increasing the observed charge current.

The current ($i$) observed during the charge step can be summarized as the sum of the cathode and anode currents:

$$i = \{i_{O_2\text{gas}} + i_{\text{other}}\}_{\text{Cathode}} + \{-i_{H_2\text{gas}} + i_{O_2(\text{Re.d})} - i_{\text{PbSO}_4(\text{Re.d})}\}_{\text{Anode}}$$

(5.22)

where $i_{O_2(\text{Re.d})}$ continued to increase and dominate the current due to the oxygen recombination, whilst $i_{\text{other}}$ is due to side reactions of positive grid corrosion and decomposition of organics. During the charging process, the reduction of oxygen according to equation (5.10) would suppress the overpotential of the hydrogen formation at the negative electrode (equation (5.9)), thereby keeping the negative electrode in a partial state of charge (PSoC). Hence, the dominant current would be the reduction of oxygen, followed by the reduction of PbSO$_4$. Only once the hydrogen overpotential of the negative electrode is reached, would the hydrogen begin to form significantly.

However, care must be taken in ensuring a correct material balance on the negative electrode. If excessive lead sulphate is formed on the negative electrode due to prolonged float charging and gassing, irreversible sulphation of the lead could lead to premature capacity loss during subsequent discharge cycles.

The recombination of O$_2$ for the cell with flat plate positive electrodes, which was taking place during the subsequent OCV steps between the various float charge
steps, obeyed a similar linear relationship with time as described previously for the cells that were capacity cycled (fig 5.7). The linear equations for this decrease in \( \text{O}_2 \) concentration for each successive OCV step (fig 5.13) are shown below. This linear equation corresponds to a zero order kinetic relationship, implying that there is no rate-limiting step of the \( \text{O}_2 \) recombining at the negative electrode with time. This is different to the results from the cell made with tubular positive electrodes where the OCV \( \text{O}_2 \) recombination is a first order rate relationship with time.

At 2.45V: \[ Y = -6.0815X + 159.4 \quad R^2 = 0.97 \] (5.23)
At 2.50V: \[ Y = -5.1704X + 383.64 \quad R^2 = 0.96 \] (5.24)
At 2.55V: \[ Y = -5.6245X + 646.79 \quad R^2 = 0.95 \] (5.25)
At 2.60V: \[ Y = -5.6016X + 870.46 \quad R^2 = 0.96 \] (5.26)
At 2.65V: \[ Y = -6.0619X + 1179.8 \quad R^2 = 0.96 \] (5.27)
At 2.70V: \[ Y = -6.287X + 1476.2 \quad R^2 = 0.95 \] (5.28)

The \( C_{\text{O}_2}^{\text{initial}} \) (Y-axis intercept) for each equation is not the \( \text{O}_2 \) concentration at \( t=0 \), since the testing was sequential. The \( C_{\text{O}_2}^{\text{initial}} \) could be determined from the equations by adjusting starting time of each OCV cycle to \( t=0 \). The important parameter determined, however, is the slope of the straight-lines, which can be related to a rate constant \( k \) for the \( \text{O}_2 \) recombination reaction during the OCV. As seen from these equations, the constants are similar to those observed during the OCV steps during the capacity cycle tests in figure 5.7.

The \( \text{O}_2 \) recombination, observed in these OCV studies, obeys rather a linear kinetic relationship over the short period of time with an average rate constant of 5.8 \% \( \text{O}_2 \)/h. This implies that during OCV, the decrease of the \( \text{O}_2 \) concentration in the free space above the cell assembly would be about 6\% per hour where the cell construction with a flat plate positive electrode promotes the efficiency of the oxygen recombination at the sponge lead negative electrode. The efficiency is further influenced by the increase in the gas / liquid interface area and the decrease of the diffusional path length of the gaseous oxygen from the positive to the negative electrode\textsuperscript{27}. 
Bodoardo et al\textsuperscript{27} and Henn et al\textsuperscript{28} relate the rate constant \( K_{\text{O}s} \) of \( O_2 \) recombining at the negative electrode during OCV to the measured rate constant \( K_O \) and a geometry factor (\( \Gamma \)) of the particular cell under test. They reported that for a complete cell, \( K_{\text{O}s} \) should be between 0.02 to 0.1 cm/h. This relationship is shown in equation 5.29.

\[
K_{O,\text{r}} = K_O \Gamma
\]  

(5.29)

where \( \Gamma = \frac{V}{S_n} \) and \( K_O \) is the measured rate constant in mole fraction of \( O_2 \)/h.

\( V \) = the free volume of the space above the cell assembly and \( S_n \) = the total surface area of the negative electrodes in the cell. For the MCL cells using flat plate positive electrodes, \( \Gamma = 0.345 \) cm, and the rate constant \( K_O \) for the OCV determined previously is approximately 6 %/h. This gives a rate constant \( K_{\text{O}s} = 0.021 \) cm/h, which is in agreement with the results reported in the literature. However, similar calculations for the MCL batteries made with tubular electrodes resulted in a rate constant \( K_{\text{O}s} = 0.00046 \) cm/h.

5.4. Summary

This investigation shows that the use of flat plate electrodes increases the ability for the \( O_2 \) to diffuse to the negative electrode, whereas the use of tubular electrodes reduces the diffusion. During OCV, the reaction of oxygen in the free space above the electrode assembly is limited to react with the lead near the top of the negative electrodes, which would result in lead sulphate forming on the top section of the electrodes. This can lead to the formation of inhomogeneous negative potentials to occur between electrodes and on the same electrode between the bottom and top sections or from the core of the active material to the surface.

The pressure decrease for the cells made with flat plate electrodes during the OCV steps was significantly high, where pressures of 100 kPa below normal atmospheric pressure was observed (fig 5.12). This rapid change in pressure was due to the fast recombination of the \( O_2 \) in the free space above the cell assembly. Similarly, pockets of \( O_2 \) gas that were still trapped in the separator could easily diffuse through to the negative electrode and recombine thereby reducing the pressure in the cell. Instead,
the pressure decrease for cells made with tubular electrodes was considerably less, implying a less efficient recombination of the O\textsubscript{2} at the negative electrode.

The technical feasibility of a working MCL VRLA battery without any special external or internal gas recombination components has been shown to have an effective O\textsubscript{2} recombination cycle. The overcharge voltage and internal pressure of a cell are not simply related to the charge rate, but seem to be influenced by the structural factors such as the type of electrode and the distribution of the electrolyte and transport properties of oxygen through the separator.

Both battery types (tubular and flat plate) have their advantages and disadvantages. The tubular battery has the advantage to maintain electrode structural integrity longer in deep discharge cycle applications and harsher environments, whereas a battery made with a positive flat plate electrode would experience positive active material shedding much sooner. The results have shown that the flat plate battery would have a better O\textsubscript{2} recombination efficiency with a lower water loss in service application than a tubular battery. However, excessive and long float charge applications of such batteries can lead to the under-charging of the negative electrode, which then in subsequent discharge applications can lead to premature capacity loss.

The MCL batteries made with the tubular positive electrodes did have some degree of O\textsubscript{2} recombination occurring during typical testing sequences of capacity cycles and float charge applications. However, the comparative water loss to the batteries with the flat plate electrodes would be higher, requiring the addition of water during periodic service intervals.
6. Accelerated life-cycle testing of VRLA MCL batteries
6.1. Background

One of the tests that a battery is subjected to is a capacity life-cycle sequence. There are many specifications for life-cycle testing of batteries and they are often related to their particular use, where a simulation of the real-life application is performed. With the development of the flat plate positive electrode VRLA MCL battery, it was important to ensure that the expected capacity could be obtained through many cycles at elevated temperatures and at least be comparative in performance to similar competitor’s batteries that are commercially available.

Many field-trials of MCL batteries in the mining industry have shown that batteries that contain positive tubular electrodes require significant amount of maintenance in terms of filling the cells periodically with water. This introduces a number of problems in terms of following the correct service procedure, especially in terms of using the correct purity levels of water. It was necessary to develop a MCL VRLA battery with sufficient life-cycle capabilities that would not require the service of water replenishment.

The literature and previous work (section 5) has shown that the use of positive flat plate electrodes with the use of Pb-Ca alloys as grids reduces the consumption of water significantly\textsuperscript{75, 76 & 81}. It was therefore necessary to compare the life-cycle capabilities of the MCL VRLA batteries to those of competitor’s batteries made with similar flat plate electrodes only. The life cycle testing of MCL VRLA batteries made with tubular electrodes was not tested due to the high rate of water loss experienced, where they would need to periodically replenish the water. The batteries subjected to the following test sequence were not serviced in the sense of replenishing the lost water during the testing sequence, which was a requirement from the battery manufacturer.

Life-cycle testing cannot be carried out quickly and can become time consuming and expensive. As mentioned previously, the life expectancy of a MCL battery is 2 years
with about 700 cycles at 56 % DoD, assuming a working temperature of 25°C (section 1.4). It was therefore necessary to develop an accelerated testing sequence that would give a reasonable indication of the life cycle durability of the battery over shorter periods of time, but can be considered as a fair reflection of the life expectancy of the battery under normal applications.

One important component that must function consistently during accelerated life-cycle testing is the pressure release valve used to regulate the internal pressure of the cell. The purpose of measuring the release pressure and the reliability of a VRLA release valve was to evaluate its opening and closing consistency during a typical capacity life-cycle application.

The requirement by the manufacturer was that the valves would open and close at repeatable constant pressures. This would ensure that minimal gas is lost during the battery’s application but also to ensure that the rubber material used would not age prematurely and fail during excessive exposure to sulphuric acid. This was carried out by evaluating the release valve independent of the other components of the battery by blowing air through a highly concentrated acid solution allowing small amounts of spray to form on the rubber valve, as described in section 2.4.1.

6.2. Pressure release valve

The evaluation of the pressure release valves used in the VRLA MCL batteries for two valves are shown in figures 6.1 to 6.4.
Figure 6.1: The opening and closing release pressure of valve A tested for 14 days.

Figure 6.2: The opening and closing pressure of valve A for the first 40 h.

Figure 6.3: The opening and closing release pressure of valve B tested for 14 days.
The results show that consistent opening and closing of the valve was observed for the 14-days of evaluation. The opening and closing cycle would correspond to almost one year of application in a battery, where a typical charge and discharge cycle would correspond to a 24 h shift. An important characteristic of the valve was its ability to close after the pressure had decreased to a certain value. This can be seen in figure 6.2 and 6.4, where the valve would maintain the internal pressure of almost 10 kPa during the 1 h rest period.

However, the results for valve B were slightly different. The maximum release pressure of below 40 kPa was similar for the two valves evaluated, except for a short period after 2 days of testing where the pressure increased above 40 kPa for valve B, but decreased again to below 40 kPa for the rest of the 14-day test. Valve B, however, showed a lower closing pressure than valve A. This was especially evident during the 1 h rest period as shown in figure 6.2 and 6.4. The differences might not be significant over short periods of time and in particular in the application of a MCL battery. An important aspect of the study was the safety aspect of the valve opening consistently at a specified pressure. The slight difference in the closing pressure might influence the long-term recombination efficiency, where the valve that closed at a lower pressure, would cause more oxygen and hydrogen to escape, thereby having a higher water loss. This would only be critical in applications where many cells are connected in a typical UPS system where inconsistent water loss between cells would cause cells to capacity-cycle relatively different to each other.

Figure 6.4: The opening and closing pressure of valve B for the first 40 h.
The rubber vent caps used for the pressure release valve were subsequently modified in order to increase the release pressure to about 100 kPa as shown in the results of the previous study (section 5).

6.3. Life-cycle testing of MCL batteries.

The following accelerated electrochemical life cycle testing of VRLA MCL batteries made with positive flat plate electrodes was carried out at elevated temperatures and higher discharge currents. An acceleration factor (F), which relates to the higher testing temperatures, can be used to give some indication of the expected life cycle capabilities of the battery in real life applications.\(^{97}\)

The acceleration factor (F) is given by

\[
\ln F = k(T - 25^\circ C) \tag{6.1}
\]

where F is the ratio of life cycle at 25°C to the cycle life at the test temperature (T). The coefficient (k) is determined for particular battery types and can be assumed to have a value of about 0.02 for small flooded batteries with antimony grids\(^{97}\). No factor for VRLA type batteries was reported in the literature, but it can be assumed to be slightly higher due to the effect of temperature on the \(O_2\) recombination efficiency and the fact that the battery is working in an acid starved environment. For the following study, a coefficient (k) of 0.03 was assumed.

The graph in figure 6.5 show the first three life cycle units for one of the batteries evaluated. They were capacity cycled to 35 % for 40 cycles followed by a 1 A discharge test at 40°C.
Figure 6.5: An example of 3 life cycle units for the accelerated tests done on a MCL battery with flat plate positive electrodes.

The following table summarizes the 1 A capacity results, obtained after every 40 life cycle units for the MCL batteries made with flat plate positive electrodes. Results were compared to similar competitor batteries made with flat plate positive electrodes.

Table 6.1: Life cycles for MCL batteries (1 unit = 40 cycles)

<table>
<thead>
<tr>
<th>Battery name</th>
<th>Life Cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unit 0</td>
</tr>
<tr>
<td></td>
<td>Cap (Ah)</td>
</tr>
<tr>
<td>Willard 1</td>
<td>17.3</td>
</tr>
<tr>
<td></td>
<td>13.7</td>
</tr>
<tr>
<td>Willard 2</td>
<td>17.2</td>
</tr>
<tr>
<td></td>
<td>13.9</td>
</tr>
<tr>
<td>Comp 1</td>
<td>15.9</td>
</tr>
<tr>
<td></td>
<td>11.5</td>
</tr>
<tr>
<td>Comp 2</td>
<td>15.7</td>
</tr>
<tr>
<td></td>
<td>12.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Battery name</th>
<th>Life Cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unit 6</td>
</tr>
<tr>
<td></td>
<td>Cap (Ah)</td>
</tr>
<tr>
<td>Willard 1</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td>10.3</td>
</tr>
<tr>
<td>Willard 2</td>
<td>9.9</td>
</tr>
<tr>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Comp 1</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Comp 2</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>
An important parameter in VRLA type batteries is their water loss characteristics during a life cycle test. These results are shown in figure 6.6, and indicate that about 50 % of the total water is lost during the first 80-100 cycles. This can be explained by the fact that new batteries could be considered as flooded systems, where little or no $O_2$ recombination takes place. As the battery continues to cycle, and water is lost, the glass mat separator becomes porous, allowing for $O_2$ to migrate through to the negative electrode to recombine. The results show that the relative loss in water for the competitors batteries were lower than the two Willard batteries, implying that they might have had less water during the initial stages of testing.

![Graphical representation of accumulative water loss during life cycle at 40°C for the MCL batteries.](image)

**Figure 6.6:** Graphical representation of accumulative water loss during life cycle at 40°C for the MCL batteries.

The 1 A capacity tests after every 40 cycles showed that the Willard 1 battery could achieve 440 cycles at 35 % DoD before a capacity of below 50 % of the rated capacity was reached. These results are shown graphically in figure 6.7.
Using a coefficient \((k)\) of 0.03, an acceleration factor \((F)\) at 40°C would be 1.57. The Willard 1 battery achieved a total of 440 cycles, which would correspond to about 691 cycles at 25°C. This is close to the expected life cycle of 700 for a battery used in the miner’s helmet lighting application\(^{41}\).

### 6.4. Failure analysis of the MCL batteries tested.

An important aspect of evaluating the life cycle ability of a battery is to determine the reasons for failure. This was done by carefully cutting the housing of the failed battery open and to visually inspect the various components in order to determine the reasons for failure. By doing this, the weakest component that contributed to the failure can be determined and in-turn would help the manufacturer to modify and improve the particular component in order to increase the performance of the battery. The dissection of each battery will be discussed individually with comments to support the failure mode observed in capacity loss.

#### Failure Analysis of the Willard 2 Battery

The battery had a 5-plate configuration (2 positive and 3 negative). The Willard VRLA MCL battery achieved 320 cycles before the cycle testing was stopped due to the fact that the 1 A discharge capacity at 40°C was 7.7 Ah (below 50 % of rated capacity).
After cutting the battery open and qualitatively analysing the electrodes and active material, the following was observed, which could account for the loss in capacity.

1. One of the main reasons for capacity loss in VRLA batteries is their excessive water loss and drying of the glass matt separator. However, the glass matt separators in the cells were not dry. Both cells of the battery showed sufficient electrolyte in their active material and separators. The reasons for the capacity loss could not have been due to excessive gassing and subsequent loss of water.

2. The reasons for loss in capacity for this battery could be mainly attributed to:
   a. Positive active material shedding
   b. Negative grid-strap corrosion
   c. Negative active material sulphation

The following pictures support the suggested failure modes.

**Figure 6.8:** Corroded lug-strap inter-phase at the –ve electrodes.

**Figure 6.9:** Weak –ve lug-strap bond with cracking of the –ve active material due to excessive sulphation.
**Figure 6.10:** Cracking of –ve active material due to excessive sulphation

**Figure 6.11:** -ve strap-lug interface showing extensive corrosion along the boundary.

**Figure 6.12:** +ve active material shedding.  
**Figure 6.13:** +ve active material shedding.

**Figure 6.14:** +ve strap lug interface showing some corrosion extending along the boundary.
The corrosion at the positive strap-lug interface would have had little influence on the performance of the cell over the duration of the life cycle test. A weakness considered in many battery failures is the corrosion of the positive grid support for the electrode. In this case, however, the corrosion was concentrated at the surface of the grid with limited corrosion propagating along the grain boundary interface. However, due to the thickness of the electrodes, the grid maintained sufficient support during the testing and would not be one of the contributing factors for failure.

It must be remembered that the causes of capacity loss mentioned previously are often interrelated. For example, the failure of a negative plate due to lug/strap corrosion and active material sulphation could cause the positive plates to overcharge thereby increasing their active material shedding during the testing. Negative active material sulphation occurs due to insufficient recharging of the electrode. This can occur during the oxygen recombination cycle. If there is a poor strap-lug interface bond, the active material loses its required conductivity thereby increasing its sulphation. With the increase in the \( \text{O}_2 \) recombination during capacity cycling, more lead would convert to lead sulphate and not have sufficient current during recharge to convert back to the active lead. Insufficient recharge of the negative electrode would then occur due to a higher efficiency in the oxygen recombination, that shifts the negative potential to such low values that the plate cannot fully recharge.

This effect is also observed if an incorrect material balance during the design of the battery was used. An increase in sulphation results in excessive expansion of the active material causing it to loose adhesion to the grid support. This “cracking” of the negative active material is often referred to as the “Venetian blind effect”. This effect becomes accumulative and causes irreversible sulphation and would start to deteriorate other components in the cell, such as an increase in the positive active material shedding.

A weakness in many lead acid batteries is the use of different lead alloys for the grid and strap in the manufacturing process. The use of the different alloys for the lug (grid) and strap encourages increasing galvanic corrosion at the interface. This characteristic is not as common in flooded type batteries as in VRLA types. The strap and lug in flooded batteries are usually submerged under the electrolyte that reduces
the corrosiveness. In a non-flooded system such as in a VRLA, the exposure to low concentrated acid spray and oxygen would accelerate the interface corrosion.

**Failure Analysis of the Competitor 1 Battery**

The competitor battery had a 7-plate configuration (3 positive and 4 negative). The Competitor 1 battery achieved 320 cycles before the cycle testing was stopped due to the discharge capacity at 40°C only being 8.2 Ah (almost 50 % of rated capacity). Cutting the battery open and qualitatively analysing the various electrodes and active material showed the following failure analysis.

1. The separators were completely dried out. Both cells of the battery showed that their electrolyte had been lost due to excessive gassing, which can occur during overcharging with poor recombination characteristics. Figure 6.6 showed that the loss of water during the testing was relatively little when compared to the other batteries. This could be an indication that the battery had started off with limited electrolyte. The drying-out of the separators also showed that the recombination of oxygen was inefficient. The other components of the cells showed very little or no corrosion.
   a. The Positive Active Material was still firm with very little shedding.
   b. There was no detrimental negative or positive lug-strap corrosion.
   c. The negative active material showed no “Venetian blind effect” due to sulphating.

The following pictures indicate some of the observed characteristics of the various components analysed.
Failure Analysis of the Competitor 2 Battery

The competitor battery had a 7-plate configuration (3 positive and 4 negative). The Competitor 2 battery achieved 320 cycles before the cycle testing was stopped due to the discharge capacity at 40°C being 8.7 Ah (almost 50% of rated capacity). Cutting the battery open and qualitatively analysing the various electrodes and active material
showed that the failure mode was identical to those observed in the competitor battery 1. The main reason for failure was the drying-out of the glass-mat separator.

The following pictures indicate some of the observed characteristics of the two cells for competitor battery 2.

**Figure 6.19:** Separator removed from –ve active material. Separator stuck to active material.

**Figure 6.20:** Separator removed from +ve plate. No shedding of active material.

**Figure 6.21:** -ve lug-strap interface. Grid boundary can be seen with a poor bond. Lug penetrated only partially into strap.

**Figure 6.22:** +ve lug-strap interface. The grid tip can be seen with some corrosion into the lug.
Failure Analysis of the Willard 1 Battery

The battery had a 5-plate configuration (2 positive and 3 negative). The Willard K1 MCL battery achieved 440 cycles when the cycle testing was stopped due to the discharge capacity at 40°C achieving only 8.7 Ah (close to 50% of rated capacity). Cutting the battery open and qualitatively analysing the electrodes and active material showed the following analysis for failure.

1. The separators did not show any drying out. Both cells showed sufficient electrolyte remaining in their active material and separators. The reasons for the capacity loss could not have been due to excessive gassing and subsequent loss of water.

2. Possible reasons for loss in capacity could be due to:
   a. Positive active material shedding. Excessive shedding was observed on all the positive plates.
   b. Negative grid-strap corrosion. The lug/strap interface on the negative plates showed poor strength, with moth plates “falling off” when being removed from the cell.
   c. Negative active material sulphating. Large cracks in negative active material were observed.
   d. The grid/strap bond on the positive electrodes were corroded but still retained enough strength for the duration of the cycle test.

The following pictures indicate some of the observations, which could lead to capacity failure. The observations were very similar to those discussed previously for the failure analysis of Willard 2 battery.
Figure 6.23: -ve plate-strap showing excessive corrosion at lug/strap interface.

Figure 6.24: -ve plate-strap showing corrosion and poor lug/strap bonding.

Figure 6.25: Cracking in –ve plate active material.

Figure 6.26: Active material shedding on +ve electrodes.
6.4.1. Summary of life-cycle failure

The accelerated life cycle testing of MCL batteries showed that the Willard flat-plate battery could achieve 440 cycles at 35% DoD. This was performed at elevated temperature (40°C) and ensuring sufficient overcharging at a constant voltage (110% of rated capacity). The failure modes of the Willard batteries, when compared to the competitor batteries were considerably different. The failure modes highlighted the strength and weaknesses of the two batteries (Willard versus competitor) and can be summarized as follows:

**Competitor battery (1 and 2)**

Main contributing factors for loss in capacity:

1. Loss of water (electrolyte). Figure 6.6 summarizes the accumulative water loss of the batteries during the life cycle. The competitors’ batteries showed a lower initial water loss when compared to the Willard batteries. This could imply that the batteries started off with a lower amount of electrolyte, which was quickly depleted after the first few capacity life cycle units.

2. The electrode components showed little or no corrosion or shedding that would have affected capacity loss:
a. Positive grid corrosion was minimal. The +ve grid showed little corrosion for the duration of the test. Similarly, the grid strap interface showed very little corrosion, with the grid lugs still strongly imbedded in the strap.

b. Positive active material shedding. The PAM maintained its “grittiness” with very little shedding. Initial shedding is usually observed near the areas of contact with the separator.

c. Negative strap lug interface corrosion. On all cells investigated, the negative plates showed no corrosion at the strap lug interface of the negative cells. However, the lug depth penetration of the grids (lug) into the strap was poor.

d. No cracking or shedding of negative active material was observed, implying that limited sulphation had taken place.

**Willard Batteries (K1 and K2)**

Main contributing factors for loss in capacity:

1. Positive active material (PAM) shedding. The PAM was “sludge like” and easily separated itself from the grid support. The active material can be clearly seen on the area in contact with the separator, especially at the bottom of the plate. It must be remembered, that the PAM shedding could be due to the weaknesses of the negative plates that accelerated the shedding due to the electrode overcharging.

2. Negative strap lug interface corrosion. On all the cells investigated, the negative plates showed excessive corrosion at the strap-lug interface. This could be considered as the main reason for the sudden capacity loss in the K2 battery after 320 cycles.

3. Cracking or shedding of negative active material. As a compounding effect of the poor strap-lug interface, the active material showed large cracks (Venetian blind effect), which clearly reduced the active material utilization.

4. Loss of water (electrolyte). Figure 6.6 summarizes the accumulative water loss of the batteries during the life cycle. The batteries showed a large initial water loss that then levelled to a relatively low loss per life cycle unit after 200 cycles. This could imply that the batteries started off with an excess amount of electrolyte, but maintained a reasonable level of electrolyte up to the end of the
life cycle test, implying good recombination efficiency. This is definitely a good characteristic for the battery, since water loss is considered as one of the main causes of failure in VRLA batteries.

By combining the strengths and the weaknesses of the competitors and Willard’s batteries after the life cycle test, an improvement in the battery design and its performance can be achieved. The main contributing factor of failure, observed in the Willard batteries, motivated the following study to evaluate various strap alloys and their manufacturing processes.

6.5. Corrosion study of the strap and lug interface in MCL batteries.

The results from the life cycle study showed that the strap to lug interface for the negative electrodes was one of the weakest components, contributing to the failure of the batteries evaluated. Wagner\(^9\) had referred to such plate failures due to crevice corrosion that takes place when using Pb-Sb alloys for the strap. The crevice is made during poor welding, where a negative meniscus at the surface of the interface between the strap and lug occurs. Electrolyte is trapped in the crevice and encourages electrochemical reactions to take place causing a voltage drop that shifts the potential to a range where corrosion is accelerated. He recommended the use of non-Sb lead alloys with proper techniques in the casting of the strap. However, the flow characteristics of the molten Pb-Sb alloy during casting of the strap are considerably better than a Pb-Ca alloy\(^9\).

David Pregaman\(^9\) discusses the effects of variables in the cast-on-strap manufacturing process and the importance of a good strap to lug bond in lead acid batteries. The following study evaluates various strap alloys and their ease to weld to the lug of a grid and to maintain a good bond under accelerated corrosion conditions.

Table 6.2 summarizes the lead alloys and their composition used as strap alloy. The grid (lug) was made from the CAP alloy.
Table 6.2: The Pb-alloy composition specification used for the study.

<table>
<thead>
<tr>
<th>Alloy Type</th>
<th>% Sn</th>
<th>% Sb</th>
<th>% As</th>
<th>% Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>3HT</td>
<td>0.20-0.25</td>
<td>3.70-4.00</td>
<td>0.10-0.15</td>
<td>-</td>
</tr>
<tr>
<td>5HT</td>
<td>0.28-0.32</td>
<td>4.50-5.00</td>
<td>0.25-0.30</td>
<td>-</td>
</tr>
<tr>
<td>A75</td>
<td>0.10-0.15</td>
<td>2.50-3.00</td>
<td>0.10-0.15</td>
<td>-</td>
</tr>
<tr>
<td>CAP</td>
<td>0.55-0.80</td>
<td>0.0001</td>
<td>0.001</td>
<td>0.03-0.056</td>
</tr>
<tr>
<td>CAP/5HT</td>
<td>A 1:1 mixture was prepared of the above two alloys</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

After exposing the assembled samples to an accelerated electrochemical corrosion test, cross-sections of the strap and lug interface were evaluated by using an optical microscope.
6.5.1. Corrosion characteristics of the 3HT strap alloy

Figure 6.29 a-c summarize the observed corrosion characteristics of using the 3HT alloy as the strap.

![Microscope pictures of 3HT strap alloy and CAP lug alloy.](image.png)

The pictures show that a good interface bond between the two alloys was obtained with some inter-grain corrosion that is typical of CAP alloys on the surface of the lug. Slight galvanic type corrosion that extended along the beginning of the strap lug interface was observed. A negative meniscus of the strap alloy at the surface of the strap-lug interface for some of the samples was observed.
6.5.2. Corrosion characteristics of the 5HT strap alloy

Figure 6.30 a-c summarize the observed corrosion characteristics of using the 5HT alloy as the strap.

The pictures show that a good interface bond between the two alloy types was obtained with a good (positive) surface meniscus at the interface. Some inter-grain corrosion was observed on the surface of the lug alloy (fig 6.30 c), but no strap-lug interface corrosion was observed with a good bond between the two alloy types.
6.5.3. Corrosion characteristics of the A75 strap alloy

Figure 6.31 a-c summarize the observed corrosion characteristics of using the A75 alloy as the strap.

The pictures show the interface between the two alloys with a lot of corrosion along the interface. The A75 alloy used for the strap gave poor casting properties where large cavities were observed due to the negative meniscus effect on the surface at the interface. The areas can lead to excessive corrosion that penetrates along the interface region. Even though on some samples, the surface meniscus was flush with the lug (positive), corrosion was still observed moving along the interface boundary (fig 6.31 b).
6.5.4. Corrosion characteristics of the CAP strap alloy

Figure 6.32 a-d summarize the observed corrosion characteristics of using the CAP alloy as the strap.

![Figure 6.32 a-d: Microscope pictures of CAP alloy for both the strap and lug.](image)

The pictures show that the use of CAP alloy for the strap gave a good bond and mix of the lug and strap components. The use of the same alloy for both strap and lug gave an indistinguishable interface. However, a poor interface negative meniscus at the surface of the lug-strap interface was observed. These areas are small cavities that allow dilute acid to accumulate and thereby accelerate grain corrosion along the interface.
6.5.5. Corrosion characteristics of the CAP/5HT strap alloy

Figure 6.33 a-d summarize the observed corrosion characteristics of using the CAP/5HT alloy mixture as the strap.

![Microscope pictures of CAP/5HT strap alloy and CAP lug alloy.](image)

The samples showed a poor strap to lug bond. Excessive corrosion had occurred at the interface (6.33 a). The strap alloy showed an unusual grain type structure of large typical Ca-Pb alloy grains intermixed with the “fishbone” type structure of a Sb-Pb alloy. The strap alloy showed a high level of inter-grain corrosion with poor bonding ability to the lug alloy.
6.5.6. Summary of strap alloys

The 5HT alloy as strap showed the least amount of interface corrosion with all strap-lugs having a good positive meniscus and was recommended for the use as strap alloy. The positive meniscus is an important parameter to consider in the casting process and indicates if good “wetting” and “flowing” of the strap alloy around the lug during manufacturing had occurred.

The use of the CAP alloy as the strap showed no interface corrosion with a good mixing of the lug and strap. However, the negative meniscus observed on most samples at the interface surface showed that poorer alloy flowing had occurred during the manufacture. Improvement in the manufacturing process can be achieved which would ensure a better wetting of the strap to lug. However, the alloy is more difficult to work with and would be more expensive than the antimony alloys.

The A75 alloy showed a poor negative meniscus at the interface with a lot of interface corrosion. The 3HT alloy showed slight interface corrosion and a poor (negative) surface meniscus at the interface. The use of the mixed 5HT and CAP alloy as strap did not prove to be successful. The aim was to obtain an alloy that had the flow characteristics of the 5HT alloy and lower galvanic corrosion properties at the interface by using a Pb-Ca alloy. However, the resulting alloy had a different structure and showed poorer welding properties than expected.
CHAPTER 7.

7. Continuous monitoring of the state of health of batteries.

7.1. Background.

A method was investigated that would monitor certain internal physical characteristics of a lead-acid battery on a continuous basis, thereby giving some indication of its State of Health (SoH) over its service life. The proposed system would incorporate the internal physical characteristics that are unique to VRLA type batteries (to a lesser degree in flooded type batteries) with that of common remote monitoring parameters such as cell or battery voltage, current and temperature.

The cell of a VRLA battery is assembled in such a way that the internal components exert a certain amount of pressure on the container’s cell wall. A considerable amount of expansion and contraction occurs during the discharge and charge cycle of a lead acid cell. The conversion of lead and lead oxide to lead sulphate during the discharge cycle could cause approximately 2-3% expansion of the active material. The cell in a VRLA system is assembled in a compressed state where the state of compression of the AGM separator is an important factor in the O₂ recombination ability of the electrodes. The compressibility between the top and bottom section of a new assembled cell should be similar and during a capacity cycle should not vary significantly. The utilization of the active material that includes the electrode’s material and the sulphuric acid near the top of a cell should be similar to that of the bottom of the cell. This utilization can be considered as an important parameter that relates to the SoH of the cell.

As the cell ages due to electrolyte loss, acid stratification and active material shedding, a variation in the compression across a cell height becomes evident. The loss of electrolyte that occurs in glass matt separators usually occurs firstly at the top of the cells, thereby drying out the matt and active material near the top of a cell assembly. Active material shedding that occurs on the positive electrode in a cell usually occurs in the middle and bottom of the electrode, causing the shed material to accumulate near the bottom of the cell. Similarly, with the electrolyte stratification, with time and loss in water, the acid at the bottom of a cell would have a higher
specific density. The loss of water due to electrolysis would also contribute to an increase in the specific density of the electrolyte at the bottom of the cell thereby increasing the sulphation of the active material on the electrodes.

7.2. Testing the state of health of a MCL VRLA battery

The proposed monitoring of the SoH of a cell is by continuously measuring the changes in the compressibility of the assembled cell between the top and bottom part of a cell during its service lifetime. As the battery discharges and charges, a number of internal stress factors of the separator and electrodes would give a certain amount of pressure against the cell wall of the container\footnote{42}. Initially, there should be no difference between the top and bottom of the cell assembly. As the battery ages, the differences can then be measured and can be used as an indication of the SoH of the cell.

Figure 7.1 shows a MCL VRLA battery that contains two sets of strain gauges of different sizes fitted to each cell wall. The cells were individually tested under extreme capacity cycle conditions and the temperature, cell voltage and voltage change between the top and bottom strain gauges amplified through a strain gauge amplifier and recorded on a portable data logger. The difference in strain exerted between the top and bottom parts of the cell assembly is normalized with respect to the strain difference experienced as a new cell.
Figure 7.1: Photograph of a MCL VRLA battery with strain gauges at the top and bottom of the cell walls.

Figure 7.2 shows the results of the discharge and charge voltage, the cell temperature and the discharge capacity during 41 cycles of testing the first MCL cell. Figure 7.3 shows the same discharge / charge profiles as in figure 7.2 with the % strain change between the top and bottom of the cell. The 5mm strain gauge was used for cell 1.
Figure 7.2: Discharge / charge voltage and temperature profiles and the respective cell capacities for the MCL cell (5 mm strain gauges).

Figure 7.3: Discharge / Charge voltage profiles and the % strain change experienced between the top and bottom of the cell walls (5 mm strain gauges).

The results show a relatively consistent charge and discharge voltage profile for the first 13 cycles with an average discharge capacity of just over 10 Ah, after which, the capacity starts to decrease for the next 28 cycles. The % strain change for the first 13 cycles showed a consistent repeatable cycle, where the small increases towards the end of the charge cycle are followed by a decrease and levelling off.
These repetitive “spikes” can be attributed to the increase in pressure in the cell during the gassing stage of the recharge cycle of the cell. Once the pressure increase has affected both the top and bottom parts of the cell and the oxygen recombination has started to become effective, the pressure difference would level off to a relatively constant value. After 13 capacity cycles, a factor such as the water loss of the cell had increased significantly and thereby influenced the cell assembly pressure. Differences in applied pressure between the top and bottom part of the cell can be seen, from the increases in “spikes” that occur during the recharge. A drop in the cells capacity was observed at the same time. Subsequent capacity cycling resulted in an even larger increase in the “spikes” during capacity cycling and an overall increase in % strain difference. The average strain difference with large “spikes” at the discharge cycle remains relatively consistent between 40-50 %. At this point, the separator at the top of the cell had sufficiently dried out and had lost its original cell compression contact with the container wall. The large subsequent “spikes” observed during recharge are due to the gassing and increase in pressure evident during the overcharging of the cell. The increase in “spike” during the recharge can also be attributed to the increase in acid concentration at the bottom of the cell and the reduction in the cavities of the separator that allow for similar expansion and contraction to be sensed at the top part of the cell. The decrease in capacity during cycling continued up to 41 cycles, where only 55 % of the initial capacity remained. The decrease can be ascribed to loss in electrolyte where noticeable drying of the AGM separator was observed. Other contributions to loss of capacity were positive active material shedding and electrolyte stratification.

It can therefore be seen that by continuously monitoring the applied pressure difference between the top and bottom of a VRLA battery, deterioration of the cell components with capacity cycle can be determined.

The results of the second cell with the 2 mm size strain gauges are shown with the discharge and charge voltage, cell temperature and the % strain change in figure 7.4. The respective discharge capacities for each capacity cycle are shown below the voltage profile graph.
Figure 7.4: Charge / Discharge voltage, cell temperature and the % strain change experienced between the top and bottom of the cell walls for cell 2 (2 mm strain gauges). The respective capacity after each discharge is indicated at the bottom of the voltage discharge graph in Ah.

Similar charge and discharge profiles were used as in the tests done for the previous cell. The cell, however, failed after 8 capacity cycles, when only 50 % of the first capacity was obtained. The cell failure was due to poor bonding of the strap lug interface of the negative plates, where excessive sulphation occurred on the negative electrodes. This resulted in excessive overcharging and a higher water loss. Even though the failure mode was different in the cell and can be ascribed to premature capacity loss due to poor assembling and manufacturing, the % strain change between the top and bottom of the cell still showed a characteristic change in the strain profile, where an increase in strain was observed after 6 capacity cycles. However, only after the 8th capacity cycles, was it evident that there was a problem in the cell, where the capacity started to decrease significantly. After the 9th and 10th capacity cycle, it was clear that the cell had failed.
7.3. Summary.

There was no significant difference in performance of the sensor between using the 5 mm or 2 mm strain gauges. The sensor with the 5 mm strain gauges seems to give a larger deviation with applied strain. This could be beneficial when one has to develop a software algorithm that would trigger at a certain strain deviation to indicate failure in the battery in a remote location. A larger deviation with applied strain can eliminate unnecessary background noise that could possibly trigger false alarms.

The above results show that as a cell ages with capacity cycling, a pre-emptive indication of the loss in capacity can be observed from the change in strain between the top and bottom sections of a compressed cell assembly. The two main criteria for observing a possible failure is the deviation of the average strain difference from the strain experienced of a new battery and the large “spikes” superimposed on the deviation.

This type of analysis becomes important in large banks of batteries where the capacity performance of individual cells cannot be simply monitored. However, their SoH in terms of available capacity is important for the functioning of the entire bank. A cell that loses its capacity, relative to the others, would cause the entire bank to work out of specification and decrease its overall usefulness.

Another important parameter to monitor would be the cell temperature. In the above examples, slight increases in cell temperature were observed during the charge cycle. However, once the cell started to lose its capacity, no significant deviations could be seen in the temperature profile. It would therefore not be possible to rely solely on the change in temperature of a cell to indicate its SoH. The unusual changes in temperature would only be a good indication that external environmental abuse had taken place thereby increasing the gassing rate of the cell. If the recharging currents were too high or the charge room temperature was too high for long periods of time, increases in water loss and aging of the battery would result, thereby reducing the effectiveness of the battery.
The measured parameters battery voltage, % strain change and temperature can be incorporated into a data-monitoring program that would trigger an alarm if certain criteria were met. These criteria would incorporate limits to the deviations of the strain or when a too high battery temperature occurs. This would be beneficial in a remote access battery bank such as telecommunication towers, where 200-300 cells are involved for the use in stand-by or supply applications. The continued monitoring of selected cells in the bank would allow for pre-emptive indications of possible cell and battery failure to occur that can trigger a response through a programmed set of algorithms via a remote modem. Corrective action can then occur through on-site technical support.
CHAPTER 8.

8. Conclusion.

This study shows the complexity of implementing a relatively new technology (20-30 years) such as the VRLA system into a small miners cap lamp (MCL) battery. The study highlighted the need for careful understanding of various manufacturing processes and the advantages and limitations of modifying them to suit a new type of cell design whose chemical and electrochemical behaviour is different to that of the previous technology. This is in particular true when comparing two types of cell designs such as the tubular and flat plate positive electrode. Special attention is usually given to the design and understanding of the positive electrode of a lead acid battery, which seems to be the limiting component when it comes to extended battery capacity cycle life. However, it was shown that lead acid batteries with a valve-regulated system can also have other components susceptible to corrosion and failure, such as the interface between the negative electrode grid and its strap. Various aspects of the VRLA MCL battery were investigated and the main findings are summarized in the following points:

1. The use of certain Pb-Ca alloys as grid material in positive electrode manufacture shows that the role of the Sn content and in particular the Sn to Ca ratio is an important factor to reduce its corrosion characteristics. The addition of small amounts of Ag to the alloy seems to reduce the corrosion characteristics, but would increase the cost of the alloy.

Another characteristic investigated was the age-hardening properties and the reduction of time required for hardening to take place of Pb-Ca alloys. This was achieved by using a heat-treating process of the alloy after casting. The study shows that it is beneficial for certain grids made with Pb-Ca alloys to heat-treat them for at least 8 h at 110°C in order to harden the grid sufficiently, so as to decrease the overall time of manufacturing. However, care must be taken not to unnecessary heat treat Pb-Sb alloys, where a reduction in its hardness property was observed after heat treatment. Care should also be taken in the handling of certain Pb-Ca grids that have been heat-treated. Their respective
britleness characteristics can be high and, when subjected to conditions of high stress during manufacturing or final cell assembly, can result in unnecessary grid failure. Over-age hardening did not seem to be a concern for the grids studied, which maintained their hardness character during the 100 days of study.

2. An improvement was achieved in terms of reducing the manufacture time of pickling tubular electrodes with a better understanding of the relationship between the physical and electrochemical characteristics of batteries using these positive tubular electrodes. The study shows that it is sufficient to soak (pickle) tubular electrodes for only 5 seconds before curing, mainly to reduce the loose dust on the surface of the electrode. This can be further automated and the manufacturing time further reduced, by using a continuous conveyor process of acid spraying and washing the filled electrodes, before curing. This process would considerably increase the production rate of electrodes ready for assembly in comparison to the existing batch process of tank dipping for a few hours, which is relatively slow. The study shows that the pickling and curing parameter influences the active material surface area and porosity of the final formed electrode and that the optimal surface area is obtained within the 15-60 minutes of soaking which is prior to applying the formation current.

3. The addition of red lead in the manufacturing of flat plate and tubular electrodes, used in MCL batteries, has certain cost implications. In addition, the formation used in the manufacturing process of batteries is the most time consuming step. The study investigated the use of red lead in making electrodes and the effect of reducing the formation time. The advantages of using positive flat plate instead of tubular electrodes, are the relatively lower cost in manufacture, a higher throughput due to automation, better oxygen recombination and better efficiency in terms of active material utilization. However, the use of tubular electrodes increases the life cycle capability of the battery.

The addition of red lead to enhance the formation efficiency must be approached with caution. However, with a careful material balance approach
and monitoring the cell temperature during formation, it was shown that a reduction in the time required for formation was possible. Flat plate electrodes require less material but need careful material balance within an automated process where each electrode made should be within specified parameters. Inconstancies such as plate thickness and active material usage can result in variations in battery performances.

The addition of small amounts of red lead (up to 25 %) to the active material for flat plate electrodes was shown to be beneficial. Adding more than 50 % caused the plate handling and paste preparation to become difficult, with active material not retaining its cured material texture. Improvement of the formation procedure was achieved by reducing the time required by half, for batteries made with both flat plate and tubular electrodes.

The possibility of reducing the red lead content of tubular electrodes showed that there was no benefit of using less than 75 % red lead for these electrodes. It would be better to continue to use 100 % red lead in the manufacture process, since there would be an extra step of adding 25 % grey oxide with limited benefit. The reduction of the pickling time used for tubular electrodes was shown to be beneficial. This would speed up the manufacturing time, but also reduce the detrimental effect of “over-sulphation” of the cured active material

4. The study shows the importance of measuring the porosity and surface area of cured and formed electrodes used in lead acid batteries. A practical and relatively cost-effective technique that relies on Archimedes’ principle was shown to be a viable method to determine the porosity of active material used in lead-acid batteries. The techniques’ results are comparative to the results obtained by Hg porosimetry and can be used in a factory laboratory for routine analysis.

After analysing a number of samples, received from a local manufacturer, made under different conditions, the results show that there is more variation in the porosity of the negative formed electrode with relatively little change in the
respective surface area. This implies that it is more important to monitor the porosity of the formed electrode, rather than its surface area.

Instead, the study shows that the surface area of the positive formed electrodes tend to vary more from sample to sample, when compared to their respective porosity. Hence, here it is then more important to monitor the surface area of such samples. The porosity and surface area of the cured material from the positive and negative electrodes showed only small variations within the manufacturing parameters investigated.

Many parameters influence the formation process of a lead-acid battery, such as the formation rate, temperature, acid concentration and current strengths. Varying the acid concentration between 1.10 and 1.28 SG, and keeping all other parameters constant, the study showed that significant differences in the surface area of the formed positive active material was observed. There were only slight changes in the respective porosity. There was no significant variation in the resulting porosity and surface area of the formed negative electrodes.

The study also showed that the glycerol displacement method can be used to evaluate the porosity of cured and formed positive tubular electrodes. Significant differences were observed in porosity of cured electrodes, made under varying conditions of dipping and curing, with relatively little change in the corresponding surface area. Similar characteristics of the tubular formed electrodes were observed, where significant changes in the respective surface area was observed with little change in corresponding porosity.

5. There was a noticeable difference in the oxygen recombination that was taking place in the VRLA MCL battery made with flat plate or tubular electrodes. Repetitive discharge / charge capacity cycling and the float charge test showed that the flat plate electrode had a lower maximum oxygen concentration during the charge steps than the corresponding battery made with tubular electrodes. As the pressure in the cell increases, diffusing more oxygen to the negative electrode, a large increase in the float recharge current was observed,
especially at the higher constant charge voltages. The rate of recombination of oxygen during the OCV step of the test sequence showed that the decrease in oxygen with time in a cell with flat plate electrodes was linear and was about 8 % $O_2$ /h, whereas the corresponding decrease in $O_2$ in a cell with tubular electrodes was exponential with time with a rate constant of about 0.14 h$^{-1}$. Hence, the $O_2$ recombination in a VRLA MCL battery with flat plate positive electrodes is considerably more efficient, and would result in a lower water loss during its service application.

Care must be taken for possible inhomogeneous recombination reactions to take place on the surface of the negative electrode. This is particular relevant to applications where long charge cycles are required. Uneven distribution of the acid and active material composition across an electrode surface can occur. However, this effect would not be critical in this type of application, when consistent charge and discharge capacity cycling is used in a typical mine application.

6. The life-cycle testing of VRLA MCL batteries with flat plate electrodes achieved 440 at 36 % DoD without any replenishment of water under an accelerated test at elevated temperatures. If one considers an acceleration factor due to the temperature effect, the battery would achieve almost 700 cycles under normal conditions. This is almost equivalent to two years in a typical mine application, which is the expected life of the MCL battery specified by the manufacturer.

The failure mode analysis of the MCL battery was predominantly due to grid and strap interface corrosion at the negative electrode. Various combinations of strap alloys with the grid were evaluated under simulated grid corrosion conditions. The results showed the importance of good manufacturing procedures, ensuring that good bond-strength is obtained and that the strap alloy should have good flow characteristics, typical of a Pb-Sb alloy.

7. A working model of a SoH sensor was built and tested in a VRLA MCL battery. The sensor can be incorporated into larger VRLA type batteries that are specifically built for standby power applications. It would monitor certain
characteristics of a VRLA battery on a continuous basis to give a pre-emptive indication of possible loss in capacity or failure. This sensor can be applied to a number of cells in a bank of batteries used in remote access power supply applications. The difference in strain pressure between the top and bottom section of a VRLA battery, together with temperature, cell voltage and current would be monitored on a continuous basis. A certain algorithm can be set up to trigger alarms that would indicate possible failure of a cell or battery, which would then require the necessary technical service.

VRLA MCL batteries made with flat plate positive electrodes are currently supplied to the South African mining houses for typical underground applications. After 1 – 2 years of successful trials with limited failure, the manufacturer will do further development in order to improve the performance and characteristics of the battery. This includes the development of smaller, lighter more compact batteries. Once the VRLA concept is shown to work successfully in the application of a MCL battery, the development of larger batteries with VRLA technology will be carried out to include applications such as stand-by power for telecommunication towers and 36 V SLI batteries.
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Appendix A:

Specifications of the level of impurities in Pb and other components used in the manufacturing of Pb-acid Batteries.

1. Recommended specifications for soft lead used in VRLA batteries\textsuperscript{101}.

<table>
<thead>
<tr>
<th>Element</th>
<th>Recommended levels for VRLA (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>10</td>
</tr>
<tr>
<td>As</td>
<td>1</td>
</tr>
<tr>
<td>Ba</td>
<td>10</td>
</tr>
<tr>
<td>Co</td>
<td>1</td>
</tr>
<tr>
<td>Cr</td>
<td>5</td>
</tr>
<tr>
<td>Cu</td>
<td>10</td>
</tr>
<tr>
<td>Fe</td>
<td>5</td>
</tr>
<tr>
<td>Mn</td>
<td>3</td>
</tr>
<tr>
<td>Mo</td>
<td>3</td>
</tr>
<tr>
<td>Ni</td>
<td>2</td>
</tr>
<tr>
<td>S</td>
<td>10</td>
</tr>
<tr>
<td>Sb</td>
<td>1</td>
</tr>
<tr>
<td>Se</td>
<td>1</td>
</tr>
<tr>
<td>Te</td>
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</tr>
<tr>
<td>V</td>
<td>4</td>
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</table>

2. Materials specifications for soft lead used by Willard Batteries\textsuperscript{102}.

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<thead>
<tr>
<th>Element</th>
<th>Maximum allowed (%)</th>
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<tbody>
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<tr>
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<td>-</td>
</tr>
<tr>
<td>Co</td>
<td>-</td>
</tr>
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<td>Cr</td>
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<td>Mn</td>
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<tr>
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<td>Ni</td>
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<td>S</td>
<td>-</td>
</tr>
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<td>Sb</td>
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<tr>
<td>Sn</td>
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</tr>
<tr>
<td>Cd</td>
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<tr>
<td>Th</td>
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3. Materials specifications for sulphuric acid used Willard Batteries\textsuperscript{103}.

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<thead>
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<th>Impurities</th>
<th>93.2% concentration Max Allowed (ppm)</th>
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<tr>
<td>Organic matter</td>
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</tr>
<tr>
<td>Fixed Residue</td>
<td>300</td>
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<tr>
<td>Sulphurous (SO\textsubscript{2})</td>
<td>20</td>
</tr>
<tr>
<td>NO\textsubscript{3}</td>
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<tr>
<td>NH\textsubscript{4}</td>
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<td>Cl</td>
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<tr>
<td>Te</td>
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4. Materials specifications for sodium sulphate used Willard Batteries\textsuperscript{103}.

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<td>Cu</td>
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<td>Fe</td>
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<td>Mn</td>
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<tr>
<td>Ca</td>
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<td>Sb</td>
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<td>Te</td>
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<tr>
<td>Mg</td>
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Appendix B:
XRD diffractograms of some of the common lead oxide / sulphate phases used in Pb-acid batteries.\(^{100}\)