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VRLA Refined™ lead — A must for VRLA batteries Specification and Performance

M.W. Stevenson[a], C.S. Lakshmi[a], J.E. Manders[*], L.T. Lam[b]

[a]Pasminco Limited, Level 7, Royal Domain Centre, 380 Street Kilda Road, GPO Box 1291K, Melbourne 3004, Australia

[b]CSIRO Novel Battery Technologies, Gate 7, 71 Normanby Road, Clayton, Vic. 3168, Australia

Abstract

VRLA Refined™ lead produced and marketed by Pasminco since 1997 is a very high purity lead with guaranteed low levels of the gassing elements but with optimum bismuth content that produces oxide of finer particle size, higher acid absorption and imparts outstanding electrical performance and endurance especially under conditions of deep cycling.

VRLA batteries suffer dry-out, self-discharge, negative plate capacity loss and poor cycle life unless special lead is used for the grids and active material.

This paper addresses the lead used for active material.

Keywords: VRLA Refined™ lead; VRLA batteries; Bismuth benefits; Lead specifications

1. The Specification

High purity lead is necessary for VRLA batteries but generic 99.99% is inadequate with national standards and the EN standard continuing to neglect to specify all critical gassing elements such as Te, Ni, Co, Se, Cr and V and continuing to allow excessive levels of Sb and As. Simply put, a 99.99% specification is not good enough.

More than 10 years of testing has shown that there are major benefits and no dis-benefits with the inclusion of Bi in soft lead for battery oxide production at optimum levels of 0.05–0.06% yet the Bi level is limited to 0.01% maximum.

This is understandable since these standards have been developed for a wide range of lead applications and hence are based on the total lead content rather than the requirements of the end-use.

With the continuing development of higher technology batteries and the increasing amount of lead consumed by batteries relative to other end-uses, it will be necessary into the future for standards committees to produce specifications or grades specific to battery applications if standards are to remain relevant.

Whilst many battery companies are now specifying some or all of the gassing elements to much more relevant levels and some manufacturers are now specifying bismuth inclusions it is alarming that there are large reputable battery companies who persist in specifying 99.99% lead with maximum Bi content at 0.005%. Thus, limiting the performance of their products.

A great deal of time and money was spent at Pasminco in development of routine test methods for all harmful elements and the VRLA Refined™ lead specification was based on the lowest practical level for these problem elements. Other elements such as Ag, Ba, Cu, and S which have not been shown to have a major impact on battery performance at low levels were specified at those levels appearing in national standards.

Some misunderstanding of this approach has occurred in some quarters with companies believing that these levels were present in the Pasminco lead.

These elements have been reviewed and the specification modified to include all elements at the lowest practical level for routine measurement (Table 1).

The specified levels are those that can be reproducibly measured day in day out in production ensuring each and every batch produced meets the specification.

Actual levels are far lower but at this stage cannot be measured feasibly on every batch.

2. Performance

VRLA Refined™ lead was developed with the assistance of CSIRO and most of the electrical performance results have been reported previously by officers of that Australian research body.

* Corresponding author.

E-mail address: mandersj@pasminco.com.au (J.E. Manders).

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Table 1
Specification-VRLA Refined^{TM} lead

Major element	
Bismuth (%)	0.05–0.06
Major deleterious elements[a]	
Tellurium	0.00003
Cobalt	0.0001
Nickel	0.0002
Antimony	0.0001
Arsenic	0.0001
Selenium	0.0001
Manganese	0.0003
Iron	0.0002
Chromium	0.0002
Barium	0.0005
Vanadium	0.0004
Molybdenum	0.0003
Other controlled elements[a]	
Silver	0.001
Copper	0.001
Tin	0.0005
Sulphur	0.0005
Cadmium	0.0005
Zinc	0.0005

[a] Maximum levels.

By far the most important feature of the bismuth inclusion is the significantly enhanced deep cycling achieved whereas low gassing, self discharge and high performance during float service are a result of the guaranteed high purity of the lead.

2.1. Deep cycling

Excellent deep cycling performance is clearly outlined in the results of the latest trials (Fig. 1) involving identical batteries produced with oxide from both high purity 99.99% lead and Pasminco's VRLA Refined^{TM} lead.

Trials 4 and 5 continue to cycle without failure.

2.2. Cycle life performance

The endurance when tested to IEC standards is shown in (Fig. 2) and to JIS standards (Fig. 3) for batteries produced in the same factory with the manufacturer's standard commercial product (using 99.99%) and with VRLA Refined^{TM} lead.

In Fig. 3 the VRLA Refined product and commercial product A were produced by the same manufacturer whereas commercial product B was the same model produced elsewhere.

All batteries exceed the minimum acceptable cycle life but the VRLA Refined^{TM} lead products are outstanding.

2.3. Capacity

Data obtained from Pasminco customers and from investigations in the CSIRO laboratories have shown conclusively that the presence of bismuth at the optimum level of 0.05–0.06% in lead oxide made from Pasminco's VRLA Refined^{TM} lead produces a significant increase in the initial capacity of VRLA batteries.

An example of this is shown during the first 10 cycles (Fig. 4) where clearly the VRLA Refined^{TM} lead product yields persistently a higher capacity. Moreover, whereas the Bi-free product requires over 10 cycles to reach maximum capacity the VRLA Refined^{TM} lead battery achieves maximum capacity in 2–3 cycles [1].

CSIRO showed further that the benefits of bismuth are more obvious when the capacity is plotted against compressive force [1].

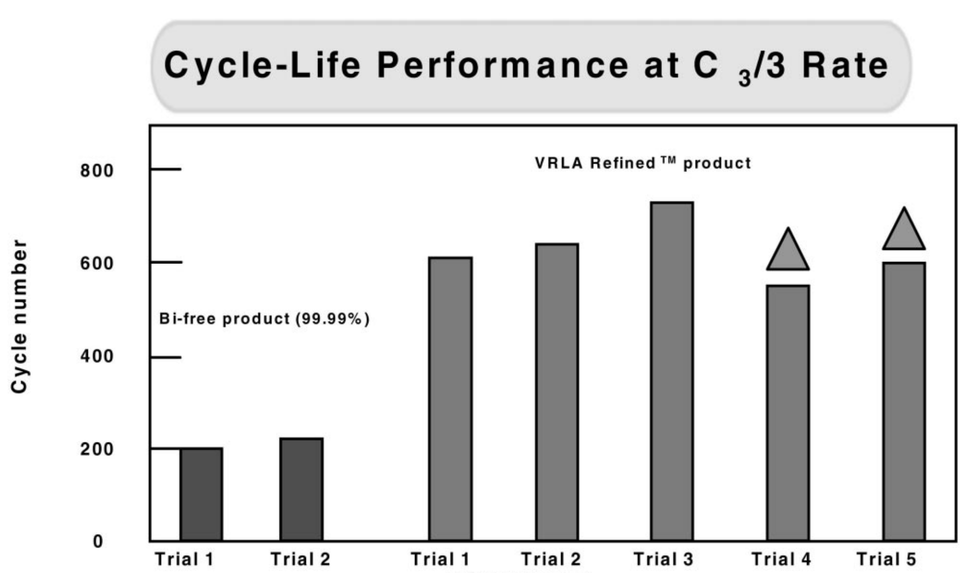

Fig. 1. Cycle-life performance at $C_3/3$ rate.

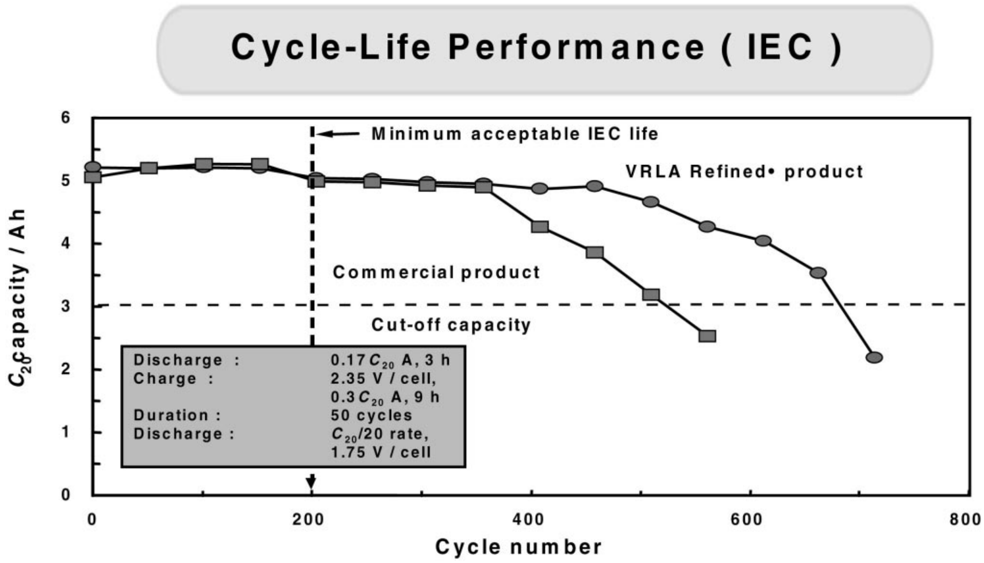

Fig. 2. Cycle-life performance (IEC).

2.4. Self-discharge and gassing

The change in voltage of three batteries, two with oxide from VRLA Refined™ lead and the other with oxide from 99.99% lead, is shown in (Fig. 5). After 216 days the self-discharge rate was 0.6 mV or 5.3 mA h per day for VRLA Refined™ lead product. By contrast both the voltage and the capacity of the standard commercial product (99.99%) decreased more rapidly to give a higher self-discharge rate of 1.2 mV or 18.6 mA h per day.

CSIRO [2] have shown that VRLA batteries produced with VRLA Refined™ lead "experience less water loss, better charging efficiency and lower rates of grid corrosion and self-discharge".

2.5. Float performance

Recent concern [3–6] has raised the possibility of "selective discharge" of negative plates during float service.

This prompted studies at CSIRO which have demonstrated [7] that VRLA batteries produced with VRLA Refined™ lead do not experience selective discharge of either the negative or positive plates during float service.

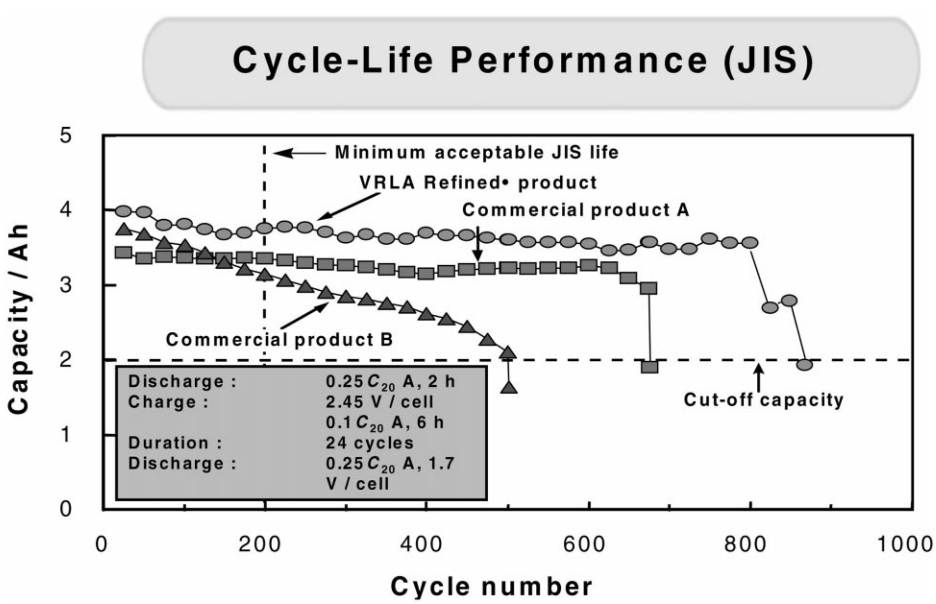

Fig. 3. Cycle-life performance (JIS).

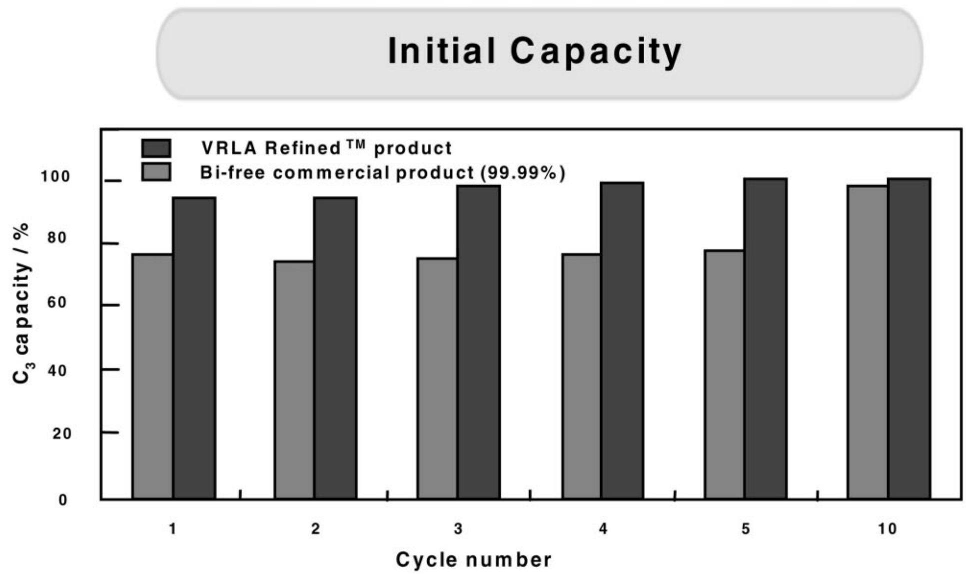

Fig. 4. Initial capacity.

More importantly, the batteries deliver lower float currents than existing commercial VRLA batteries, even at high temperatures (up to 55°C). This indicates that batteries produced with VRLA Refined™ lead will suffer less water loss and a much reduced risk of thermal runaway during service.

2.6. Summary of benefits

Benefits of VRLA Refined™ lead now identified and proven are:

- significant improvement in deep cycling performance at C_3 rates;
- significant improvement in cycle life when tested to IEC and JIS standards;
- very much less water loss, lower self discharge and better charging efficiency;
- significantly accelerates the cycling up to maximum capacity;
- batteries do not experience selective discharge of either the negative or positive plates during float service;
- batteries deliver significantly lower float currents than existing commercial VRLAs, even at high temperatures (up to 55°C) indicating batteries will suffer less water loss and provide more resistance to thermal runaway.

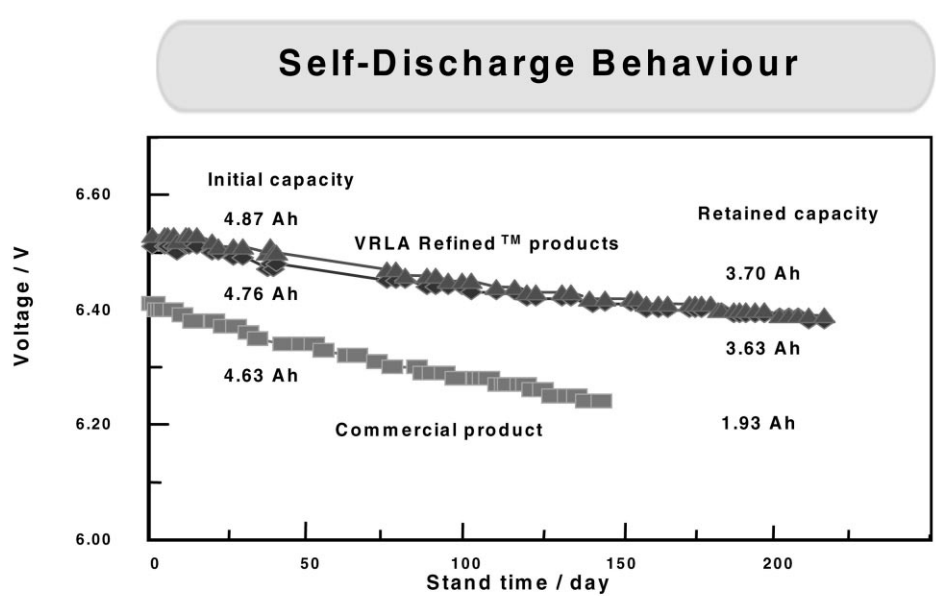

Fig. 5. Self-discharge behaviour.

3. Oxide properties

VRLA battery tests have consistently shown that when batteries use oxide produced from VRLA Refined^{TM} lead the total capacity is higher, the immediate capacity is higher and maximum capacity is obtained in fewer cycles. This indicates a higher reactivity associated with VRLA Refined^{TM} lead.

The reactivity of battery oxide is influenced by its fineness/surface area and hence a comparison has been made of those characteristics which will contribute to the reactivity, namely Brunauer, Emmett and Teller (BET) surface area, acid absorption and particle size distribution.

This comparison was carried out on oxide produced in the same plant and the same ball mill from 99.99% lead sourced from Canada, 99.99% lead sourced from China and Pasminco VRLA Refined^{TM} lead.

It was observed (Table 2) that both the acid absorption and the BET surface area are higher for the oxide produced from VRLA Refined^{TM} lead reflecting it's greater reactivity, but particle size distribution was similar.

Acid absorption is well known but BET surface area although often quoted is not always understood. BET surface area sometimes referred to as the internal surface or inner surface is determined by the BET gas adsorption method. It measures the surface area of both the internal pores and the external surface of the oxide by calculating the volume of gas required to cover the surfaces with a monolayer of gas. Nitrogen is usually used but krypton and helium can also be used.

SEM micrographs of the three oxides are shown in Fig. 6.

Oxide particle size is seen to be smaller and the lead particles to be finer and more widely distributed in the oxide produced from VRLA Refined^{TM} lead. This also correlates with anecdotal evidence from battery companies who find that plate curing takes place faster when using VRLA Refined^{TM} lead.

Further evidence of this increased reactivity was found during ageing tests on the three oxides under conditions of elevated temperatures and humidity.

The oxides were stored in shallow containers without lids and exposed to two test environments:

1. 22 ± 2°C and 50% humidity;
2. 32 ± 2°C and 90% humidity.

Samples were taken at regular intervals and the free lead contents measured. The change in free lead content is shown in Fig. 7.

Whilst under moderate conditions the free lead content of all oxides remained stable for a long period, all oxides suffered rapid reduction of free lead at the elevated conditions with the free lead in the oxide produced from the VRLA Refined^{TM} lead being oxidised most rapidly.

It should be mentioned here that the CSIRO studied [8] the influence of bismuth on the morphology of positive plate material and found that bismuth encourages the formation of needle-like crystals on the surface of the agglomerates. These crystals spread out and inter-weld to form ‘‘bridges’’ between the agglomerates and thereby consolidate the porous mass of the electrode. This influence of bismuth on morphology is considered to be responsible for the demonstrated improvements in capacity performance.

4. M.F. Refined^{TM} lead

Whilst this presentation mainly covers Pasminco's VRLA Refined^{TM} lead, a sister product M.F. Refined^{TM} lead was developed for flooded batteries and has been used commercially for some 4 years.

The benefits of this product have been reported previously but until recently all studies were carried out using book-mould cast grids.

Current work being carried out at CSIRO involves plates and batteries produced with expanded metal grids and as yet is relatively incomplete.

Some repeated reserve capacity cycling has been completed for batteries using plates which have experienced tribasic lead sulphate cure (3BS).

Expanded positive and negative grids were obtained from two large battery producers and two barton-pot oxides of high quality were used to produce paste for each type of grid. One contains bismuth and was manufactured from Pasminco's M.F. Refined^{TM} lead and the other was supplied from the USA and was manufactured from high purity 99.99% lead containing virtually no bismuth.

Cells produced from the resulting plates were evaluated under a repetitive reserve capacity test.

The cells were discharged to 1.75 V at 25 A and recharged at 2.5 A to an overcharge of 15%.

The procedure was repeated until the measured reserve capacity was equal to 50% of the maximum value.

Fig. 8 shows that the cells assembled with the grids pasted with the M.F. Refined^{TM} lead significantly outperformed those with plates containing low or no bismuth.

Table 2
Properties of lead oxide

Lead type	Free lead content (wt.%)	BET surface area (m^2/g)	Acid absorption, H_2SO_4 (mg) per g oxide	Particle size range (μm)
Pasminco VRLA (0.05% Bi)	29–33	1.76	298–333	0.1–100
China lead (0.005% Bi)	29–33	1.66	269–285	1–200
Canada lead (0.005% Bi)	29–33	1.64	270–282	0.1–100

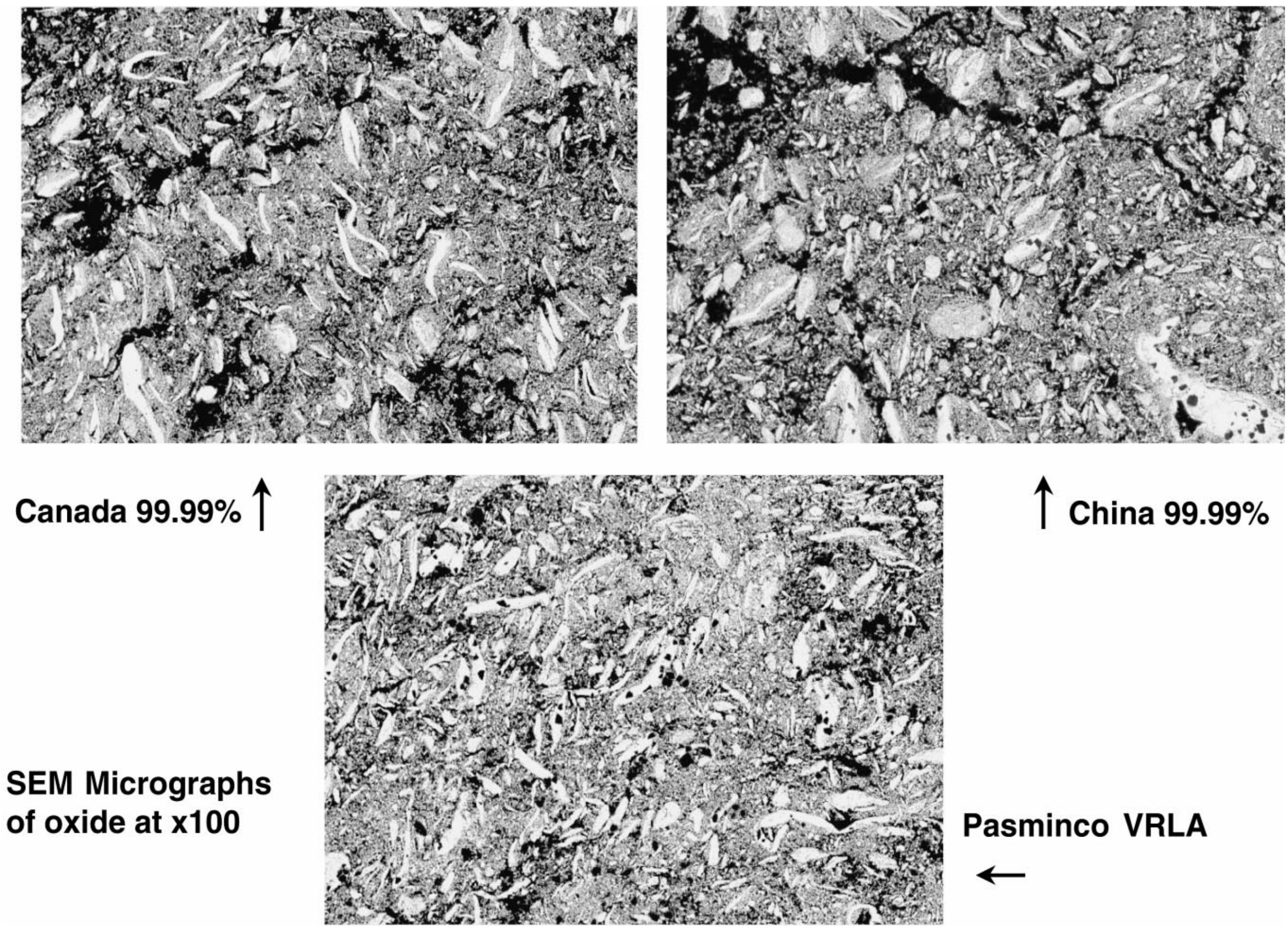

Fig. 6. SEM micrographs of the three oxides at 100×.

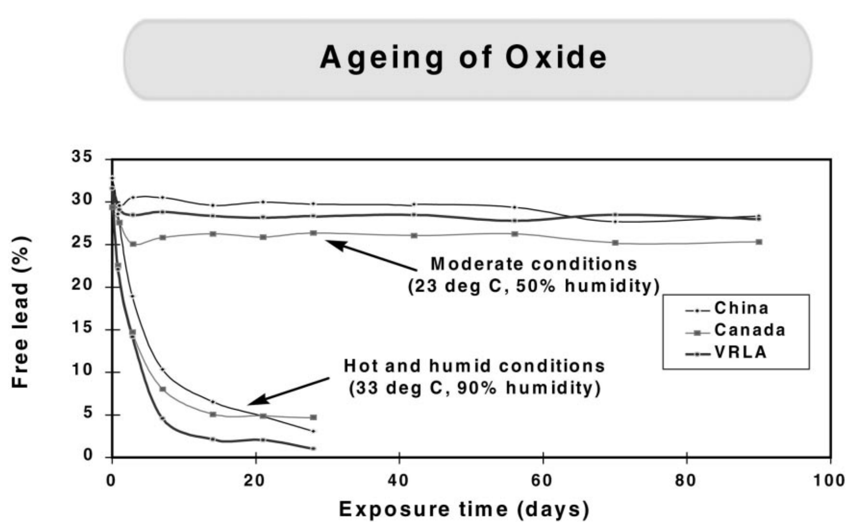

Fig. 7. Ageing of oxide.

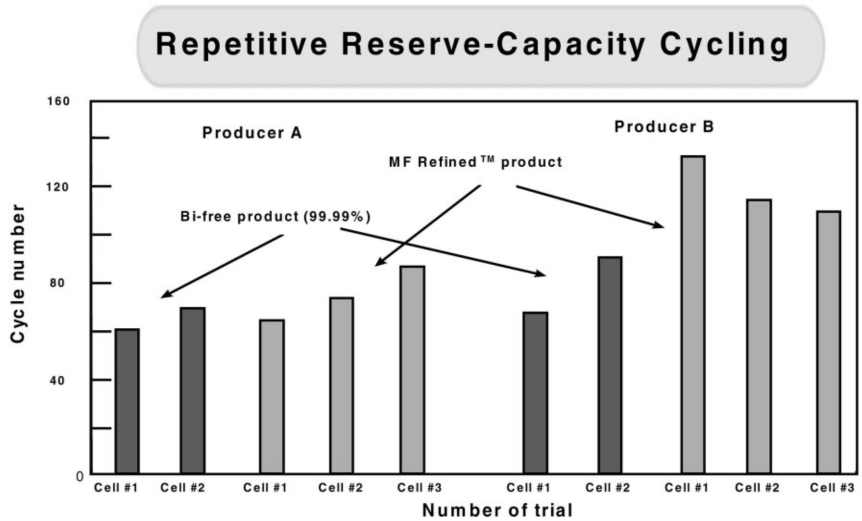

Fig. 8. Repetitive reserve capacity cycling.

It should be noted that there were thickness differences between the grids of producer A and producer B as well as significant differences between the level of tin in the alloys used for grid production.

5. Conclusion

VRLA batteries can suffer dry-out, self-discharge, negative plate capacity loss and poor cycle life unless special lead is used for the grids and active material. Generic 99.99% lead is inadequate for the active material of VRLA batteries.

Pasminco has, with CSIRO's valuable assistance, developed and continues to improve soft lead for the active material. This is now known as VRLA Refined^{TM} lead.

VRLA Refined^{TM} lead guarantees the minimum level measurable, in a smelter environment, for elements known to be detrimental to VRLA performance. It also contains the optimum level of bismuth which has been shown over 8 years of exhaustive testing to impart significant benefits and no dis-benefits.

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