Valve-regulated lead/acid batteries

D.A.J. Rand [a], L.S. Holden [b], G.J. May [c], R.H. Newnham [d], K. Peters [e]

[a] CSIRO, Division of Minerals, PO Box 124, Port Melbourne, Vic. 3207, Australia
[b] Technology C&D Charter Power Systems, Inc., 3043 Walton Road, Plymouth Meeting, PA 19462-0239, USA
[c] Hawker Batteries Group, Lathkill Street, Market Harborough, Leics. LE16 9EZ, UK
[d] CSIRO, Division of Minerals, PO Box 124, Port Melbourne, Vic. 3207, Australia
[e] Battery Design and Manufacturing Services, Glen Bank, Broadoak Park, Worsley, Manchester M28 4NS, UK

Abstract

Given the growing importance of valve-regulated lead/acid technology in many existing and emerging market areas, an expert panel was assembled at the Sixth Asian Battery Conference to answer questions from delegates on various technical and operational aspects of such batteries. Key issues included: advantages and disadvantages; performance and reliability; thermal runaway; and failure modes. The interaction between the audience and the panel was both vigorous and informative. Overwhelmingly, it was agreed that valve-regulated technology has come of age and offers a dynamic solution to many of the world's energy-storage requirements and opportunities.

Keywords: Lead/acid batteries; Valve-regulated lead/acid batteries; Thermal runaway; Mass balance; Failure mode

1. Question: What are the performance deficiencies of valve-regulated lead/acid batteries and what are the future prospects for improvement?

K. PETERS

Valve-regulated lead/acid (VRLA) batteries in which the electrolyte is absorbed in compressed, glass-mat separators have several characteristics that are an improvement on those of the traditional flooded-electrolyte design. For example, the high-power capability is generally better and, invariably, the batteries have improved vibration resistance. With respect to performance deficiencies, it is widely accepted that the cycle life is shorter and the low-rate performance is somewhat inferior.

The above views are not totally correct. For example, VRLA designs of automotive batteries will usually have a better cycling performance than the equivalent maintenance-free versions with excess electrolyte, and it is also possible to produce designs with improved low-rate capacities. The performance deficiencies highlighted by the question probably refer to a comparison of VRLA batteries with deep-cycling industrial batteries, or more specifically, with batteries for use in electric vehicles where weight is also critical.

These deficiencies are due to several factors that are not yet fully understood. Nevertheless, there have been recent improvements in the cycling performance, and it is likely that

this will continue by better control of certain key parameters, namely, compression, grid growth, designs to minimize stratification, and battery management. Given optimum control of these four parameters, the limiting failure mode will most probably be grid corrosion. In this case, battery technologies can more easily design for life. Consequently, valve-regulated, heavy duty, industrial batteries capable of 1000 deep cycles will be possible. Indeed, with a tightly compressed element that holds the positive plate together, weight for weight, it is likely that VRLA designs will be superior, particularly if alloys with improved corrosion resistance are used.

The shortfall in capacity when these designs are discharged at low rates is due to acid limitation. In some cases, this limitation can be overcome by design changes but, again, the improvement depends upon the application.

The most appropriate comment with respect to VRLA batteries is that they are a different product — one that enables lead/acid batteries to be fitted where they could not be used before. In many applications, such as in distributed-power systems and office-compatible equipment, this greater freedom of use and location makes up for the deficiencies and has effectively revolutionized the stationary-battery market. Once the apparent performance deficiencies have been overcome, these benefits are likely to be attractive to other markets.

2. Question: What are the life expectancy and failure modes of valve-regulated lead/acid batteries?

L.S. HOLDEN

From the outset, it should be understood that the failure modes of VRLA batteries are not necessarily generic, nor should it be taken that all such batteries fail for the same reasons — especially when failure is judged to be premature.

In about 1983, C&D started to make VRLA batteries, the Liberty LS series. During the period between 1983 to 1992, about one million units entered the market place and, for the most part, field experience was good. The technology was very similar to that of Chloride's Powersafe® battery. The Liberty LS batteries used calcium–lead–tin positives, AGM separators, and lead–tin top-lead.

The problems experienced were, in the main, traceable either to manufacturing defects (such as poor post seals and bad burns), or to application abuse (such as very high temperature cabinets in Florida and poorly-regulated charging systems).

Warranty was typically one-year free and nine-years pro rata. This was for a product with a life that the engineers defined as five years at 2.26 V/cell at 25 °C, but which usually achieved about seven years in the laboratory and more widespread results on accelerated testing. Excellent records show that warranty returns were less than 1% of sales for ten years in the market.

The same basic design characteristics were employed in the Liberty 1000 battery that was introduced in 1992. An automated assembly line was introduced, however, in order to minimize human error wherever possible. As a result, production capability was increased.
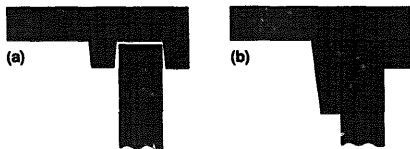
At the end of normal life, the Liberty LS or Liberty 1000 batteries suffered from corroded positive grids, together with an appreciable amount of grid growth. Separator dry-out was not a problem.

In 1990, C&D decided that it was time to expand its VRLA activities. At that time, the company was manufacturing a large-size gelled-electrolyte product, but it was thought that AGM technology was more appropriate for the high-quality market. The company considered that it was well informed about both the market and the existing competitors. Since there was good appreciation of the many problems in the large-size product market, the already substantial programme of competitor evaluation was focused and intensified. Many problems were indeed discovered and it was decided to aim for a design that would have none of the observed weaknesses — even if that meant a delayed entry into the market. The end result was the C&D Liberty 2000 product range. This is unique in many ways, most of which were born out of the elimination of other competitors' failure modes. The following are some examples.

(i) Many jar-to-cover leaks were found. Thus, it was decided to introduce a tongue-and-groove adhesive seal, instead of a heat seal (Fig. 1). This design gives a seal path that is about three times longer.

(ii) Many post-seal leaks were observed. Consequently, it was decided to introduce a unique seal that was based on a design that had proved very successful in flooded-electrolyte product for over 20 years (Fig. 2). This is a composite bushing of rubber and lead–tin alloy which is glued into the cover and a weld that is made by a computer-controlled, automated, proprietary machine. Also shown in Fig. 2 is the highly reliable, low-pressure, umbrella value (0.8–1.0 psi) which was adopted because it was found that higher-pressure Bunsen values caused problems of bulge, jar-to-cover leaks and sticking.

(iii) Many of the post-seal leaks were exacerbated by stress. Hence, an element suspension system was developed (Fig. 3). A sturdy, injection-moulded, polypropylene component fits on to the bottom of the element via lugs on the grids (Fig. 3(a)). There is a pocket moulded into the part that coincides with the positive, and this allows for growth. When the cell is in service in the horizontal position, the

Fig. 1. Jar-to-cover seals: (a) normal (motive-power type) heat seal, and (b) Liberty 2000 tongue-and-groove glue seal.
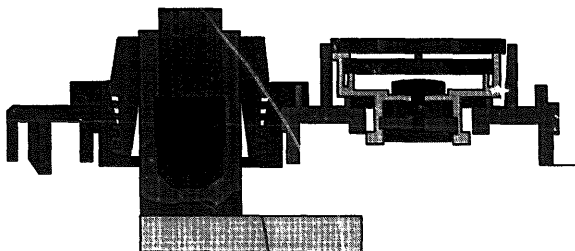

Fig. 2. Post-seal and safety-valve/flash-arrester assembly in Liberty 2000 battery.
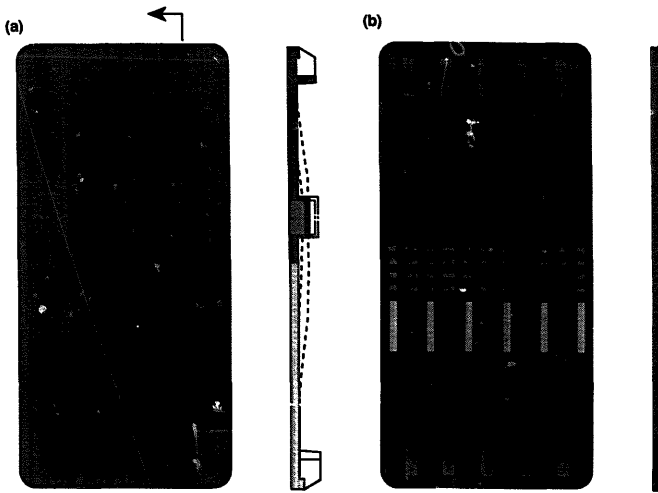
Fig. 3. (a) Schematic of effect of grid growth on bottom support. (b) Moss shield and top support.

element is supported by this component. A moss shield (that also serves as a top support (see Fig. 3(b)) compliments the bottom support. Again, it fits over the lugs prior to burning and, in the horizontal position, provides a support at the (traditional) top of the element. The net result is that, in the horizontal position, the whole weight of the element is suspended on the top and bottom supports. Thus, all the stress is
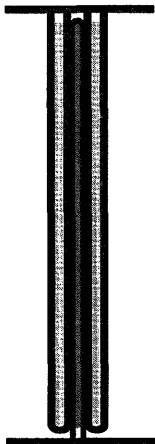

Fig. 4. Plate wrapping in Liberty 2000 battery.

removed from the post seals and the jar-to-cover seal, yet there is allowance for growth into the pockets.

(iv) Misplaced and damaged AGM separators were common. Accordingly, an alternating C-wrap approach was adopted, rather than the conventional U-wrap approach of other manufacturers (Fig. 4). This removes any possibility of shorts.

(v) In some instances, blocks of cells had become stuck together by the combined action of heat and expansion. By employing a ribbed box and a steel shim spacer assembly, it was possible to prevent the centre cells from becoming as much as 11 °C hotter than the end cells and, hence, the concomitant adverse effect on battery life was eliminated (Fig. 5).

(vi) Notice was taken of the research by Vaccaro of Bell Laboratories on the transmission of oxygen and moisture through plastics. As a result, a poly(vinyl chloride) jar and cover were introduced.

(vii) An extensive programme of accelerated life testing was undertaken. This resulted in the development of the 6 mm positive grid with its unique six-segment design for growth control. In Fig. 6, the outside dotted line shows the growth pattern for conventional, motive-power grids. The inside dotted lines indicate the reduced growth enjoyed by six-segment grids.

(viii) An abundance of severe problems was traced to poor jar-formation. The problems included heavily sulfated plates, remarkable variation in specific gravity and free acid, enormous variation in capacity, and poor and widely differing levels of compression.
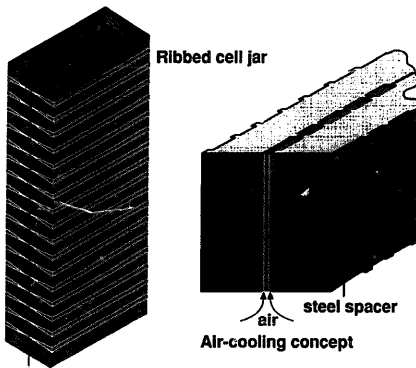
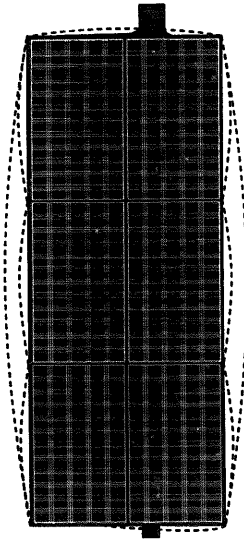Fig. 5. Liberty 2000 battery: cell-jar design and air-cooling concept.

Fig. 6. Schematic of grid growth with new six-segment grid design.

The outcome of this research and development was three-fold. First, C&D pledged itself to tank-formed plates. Second, C&D ensured measured and controlled compression during manufacture. Third, C&D invented the unique pressure-plate system. There were a number of other less significant obser-vations, all of which were taken into account in the final design of the Liberty 2000 product (Fig. 7).

Liberty 2000 batteries have now been in service for over three years. Admittedly, these are early days, but experience
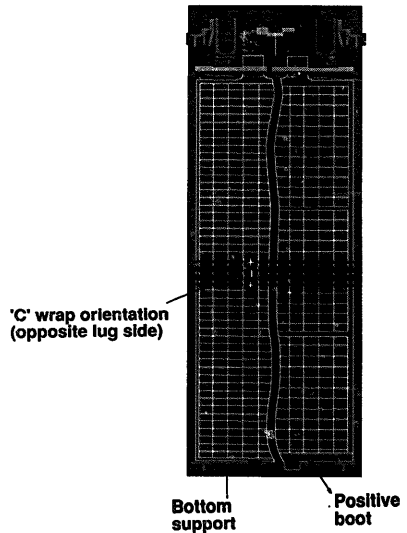

Fig. 7. Schematic of cell assembly in Liberty 2000 battery.

to date has been almost perfect. There have been a few plant-related problems, a few handling problems, but no known instances of capacity falling below 80% in the field. C&D feel confident that the approach adopted has produced a bat-tery that will, in all likelihood, provide 15 to 20 years of service. Accelerated life tests predict that grid corrosion will be the eventual cause of failure.

In summary, failure modes in VRLA batteries are not con-fined to certain mysterious mechanisms that are inherent in all types of VRLA technology. The detailed documented evidence in the C&D archives suggests strongly that failure modes are associated more closely with the design and vin-tage of the product, rather than with the fact that the cells happen to be valve-regulated technology. When it comes to life expectancy, generalizations should not be made about VRLA batteries. Instead, the claims of the manufacturer should be assessed against the design and process parameters built into the product.

3. Question: What causes thermal runaway in valve-regulated lead/acid cells?

G.J. MAY

In stand-by batteries on float, elevated temperatures will shorten life and, in extreme cases, overheating can lead to an unstable thermal runaway. The process occurs in stages until a final runaway situation arises.

If a battery is in an environment with above-normal temperatures at a constant voltage, the current flow will increase. Cells will tend to become drier as water is lost and the oxygen recombination becomes more efficient and, thereby, generates more heat. If the heat generated cannot be readily dissipated, the battery temperature will rise and the float current and heat input will increase still further.

The gassing levels can fall because the oxygen-recombination reaction further depolarizes the negative plates and hydrogen evolution is reduced. This has an additional effect in making heat dissipation more difficult, because hydrogen has a very high thermal capacity and an additional route for heat loss is effectively limited. The current then increases further to a level where the recombination reaction cannot take place sufficiently fast and the cell once again gases freely. At this stage, gassing has little effect in reducing the temperature because currents are already too high. Electrolyte drying increases the cell resistaɪ. ⹁ and ohmic heating is increased.

The battery case wiɪi generally soften and expand under the internal pressure, but there is also a risk of: (i) fire or explosion because of high temperatures; (ii) ignition sources if connectors or other components are ruptured; and (iii) release of potentially explosive mixtures of hydrogen and oxygen.

The usual result of thermal runaway is softening and gross distortion of the battery case. Dry-out eventually increases the cell resistance to a point where the current drops to lower levels and the temperature then falls but, by then, the battery is permanently damaged. Explosion and fire are rare occurrences but, nonetheless, are risks in severe cases. The use of flame-retardant vents is important in ensuring that external ignition of hydrogen and oxygen does not penetrate the battery and lead to an internal explosion.

4. Question: How can thermal runaway be avoided?

G.J. MAY

Thermal runaway can be avoided by a common-sense approach to battery-installation design. Simple convective cooling, with a spacing of 6 to 12 mm between cells, is sufficient to ensure temperature rises are reduced. The battery should be at the lower part of an enclosure so that cool ambient air is drawn across the battery, rather than air that has been heated by electrical or electronic equipment. The battery can be actively cooled by fans or by phase-change materials.

The float voltage can be temperature-compensated and a current limit can be applied. A battery-monitoring system can be used to apply further controls to the charging system if the temperature becomes excessive. Lastly, multiple parallel strings should be avoided as cell/string imbalances become a greater problem.

In practice, thermal runaway is a rare occurrence and can ⹂ ɪvoided by good engineering practice without excessive cost.

5. Question: What is the extent and effect of water loss on the performance of valve-regulated lead/acid batteries, particularly those used in deep-cycling applications?

R.H. NEWNHAM

Valve-regulated lead/acid (VRLA) batteries are used around the world in a variety of applications. This is due mainly to the low-maintenance requirements of the technology, i.e., the batteries do not require the addition of water. There are two types of VRLA technology. One type has the acid contained in sheets of absorptive-glass microfibre (AGM) that are wedged between the plates and also act as separators. The other type has the acid immobilized in a gel. This is achieved by the addition of small amounts of fine silicon dioxide particles to the electrolyte.

The performance of lead/acid batteries can degrade due to a variety of reasons. Not all the failure modes, however, occur in both valve-regulated and flooded-electrolyte designs. Fig. 8 shows the relationship between battery design and failure modes. The phenomena at the bottom-left of Fig. 8 occur only in valve-regulated units, whereas those at the top-right afflict only flooded-electrolyte designs. The failure modes that appear in the middle (overlap) region are common to both types of batteries.

The failure of VRLA batteries due to water loss is arguably the most controversial of all the failure mechanisms. It has attracted much discussion, but little detailed, unequivocal, experimental evidence has been published on this issue. Water loss from VRLA batteries can occur by two separate mechanisms. The first, and most obvious, process is gas evolution. This mode of water loss (WL_{gev}) occurs when oxygen and hydrogen, produced during battery charging, escape from the battery through either the pressure-release valve or through small imperfections in the battery case, e.g., leaking post seals and/or case-lid welds. Water is also lost by corrosion of the positive grid during battery charging (WL_{corr}). The corrosion process requires oxygen atoms which are only available from the water of the electrolyte. Hence, the production of lead dioxide consumes water according to:
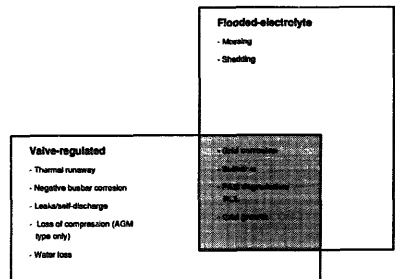

Fig. 8. Failure modes of lead/acid batteries.

$$Pb + 2H_2O \Rightarrow PbO_2 + 2H_2 \qquad (1)$$

Both the mechanisms of water loss (i.e., WL_{gev} and WL_{corr}) must be considered when attempting to quantify the effect on battery performance. More specifically, a decrease in performance occurs when the sum of WL_{gev} and WL_{corr} exceed a critical value (WL_{crit}).

Measurements have been made of both the rate of WL_{gev} (termed RWL_{gev}) and the WL_{crit} for both commercial and CSIRO-designed, gelled-electrolyte batteries operated under remote-area power-supply (RAPS) duty experienced in the field and simulated in the laboratory. This duty involves repeated deep-cycling of the batteries. In addition, calculations have been made of the amount of water required to corrode both 50% (WL_{corr50}) and 75% (WL_{corr75}) of the positive-grid material in the CSIRO batteries. From this information, it is possible to predict the period for which the gelled-electrolyte batteries can operate before their capacity is affected by water loss.

In order to evaluate the RWL_{gev} for the two battery designs, water loss from the units was monitored by recording the weight changes that occurred during operation under simulated RAPS conditions [1] at both 25 and 45 °C. The first battery type was manufactured by Johnson Controls Inc. (termed JCI battery: 6 V; 143 Ah, C_5/5 rate), whereas the second was designed and built by CSIRO (2 V; 135 Ah, C_5/ 5 rate). The results are given in Fig. 9 and Table 1. The CSIRO batteries have a RWL_{gev} of 0.02 and 0.03 ml/Ah/ cell/year at 25 and 45 °C, respectively. The corresponding values for the JCI batteries are 0.06 and 0.19 ml/Ah/cell/ year.

A bank of JCI batteries has been installed in a RAPS system located on a small island off the south coast of Australia. The facility is powered by both wind and diesel generators and contains a sine-wave power-conditioning unit. The battery bank comprises 40, 6 V batteries arranged in two parallel strings to provide a system voltage of 120 V. The island experiences mild temperatures (10 to 25 °C). Over a two-year monitoring period, an RWL_{gev} value of 0.07 ml/Ah/ cell/year has been experienced (see Table 1). Interestingly, this is very similar to that recorded for the same batteries operated at 25 °C under simulated RAPS conditions in the laboratory (viz., 0.06 ml/Ah/cell/year).

In the past, the water lost from flooded-electrolyte batteries due to the corrosion of positive-grid material has not been considered significant; it is negligible compared with that consumed during charging. By contrast, the relationship between WL_{gev} and WL_{corr} is critical for VRLA batteries that have a limited supply of water and rely on efficient recombination of oxygen to minimize water loss. Hence, it is important to know the amount of water that is available for corrosion processes in VRLA batteries.

Non-antimonial, flooded-electrolyte batteries used in stand-by applications can typically experience between 40 to 65% corrosion of the positive grid by the end of life, e.g., 10 to 20 years [2]. Using this as a basis, the amount of water
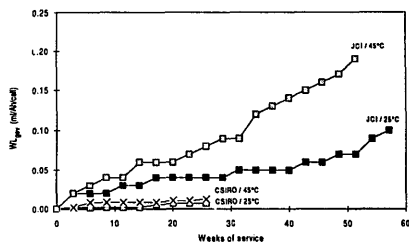
Fig. 9. Water loss (WL_{gev}) from gelled-electrolyte batteries under simulated RAPS service.

Table 1
Rates of water loss by gas evolution (RWL_{gev}) from gelled-electrolyte batteries

Duty	Battery	Temperature (°C)	RWL_{gev} (ml/Ah/cell/year)
Simulated	CSIRO	25	0.02
RAPS	CSIRO	45	0.03
	JCI	25	0.06
	JCI	45	0.19
Field	JCI	10–25	0.07

required to corrode both 50 and 75% of the positive-grid material in the CSIRO batteries, i.e., WL_{corr50} and WL_{corr75}, was calculated to be 1.8 and 2.7 ml/Ah/cell, respectively.

In order to measure the critical water loss (WL_{crit}) of the gelled-electrolyte batteries, the units were operated under a C_5/5 regime with a top-of-charge cell voltage of 2.8 V until the capacity of the battery fell below 75% of the initial value. It was considered that a high top-of-charge voltage would result in fast and efficient loss of water from the battery, but would minimize the concomitant corrosion through the promotion of poor recombination efficiency. The efficacy of this dry-out procedure was verified by tear-down procedures and subsequent scanning electron microscopic examination. No significant differences were detected in the thickness of the corrosion layers on positive grids removed from new and dried-out batteries. The effect of water loss on battery capacity for the CSIRO and the JCI units is shown in Fig. 10(a) and (b), respectively. The capacity of both batteries fell below 75% of the initial value when ~3.5 ml/Ah/cell had been lost. Hence, the WL_{crit} for both batteries is 3.5 ml/Ah/ cell.

In summary, it has been established that the JCI and CSIRO batteries can tolerate a water loss of 3.5 ml/Ah/cell before their performance is affected significantly. In addition, it has been calculated that the amount of water required to corrode 75% of the grid lead in the CSIRO battery (WL_{corr75}, a level considered to represent severe corrosion) is 2.7 ml/Ah/cell. Thus, 0.7 ml/Ah/cell is available for water loss by gas evolution.

Table 2
Summary of water loss data

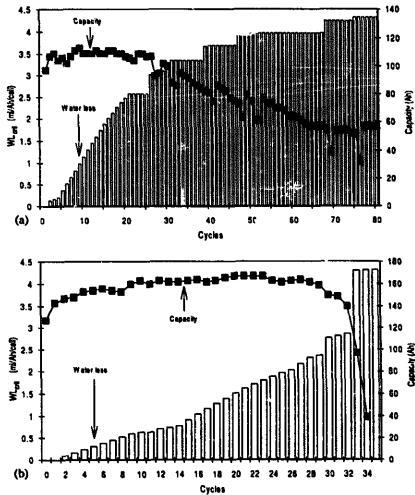| Duty	Battery	Temperature (°C)	RWL_{rev} (ml/Ah/cell/year)	WL_{crit} (ml/Ah/cell)	Years to reach WL_{crit}
Simulated RAPS	CSIRO	25	0.02	3.5	40
	CSIRO	45	0.03	3.5	27
	JCI	25	0.06	3.5	13
	JCI	45	0.19	3.5	4
Field	JCI	10–25	0.07	3.5	11

Fig. 10. Capacity and related critical water loss (WL_{crit}) for (a) CSIRO battery, and (b) JCI battery.

It has also been demonstrated that when operated under RAPS duty, the CSIRO battery has a rate of water loss of 0.02 and 0.03 ml/Ah/cell/year at 25 and 45 °C, respectively. Thus, it is easy to deduce that it would take approximately 40 and 27 years, respectively, for the corresponding batteries to lose 0.7 ml/Ah/cell, i.e., to reach a critical state. If it is assumed that the JCI battery has the same value of WL_{corr75} as that of the CSIRO battery, lifetimes of 13 and 4 years at 25 and 45 °C, respectively, can be expected before water loss limits battery performance.

The RAPS schedule used in these experiments is an accelerated regime and causes most batteries to fail within the first 12 months of operation. Further, it has been estimated that it would take 11 years for a set of JCI batteries to reach the WL_{crit} in an actual RAPS field site (see Table 2). Hence, it is considered extremely likely that the above batteries would fail due to other deterioration mechanisms, under either simulated or actual RAPS duty, before WL_{crit} is reached.

Another area that needs to be considered is the influence of increases in acid specific gravity (due to water loss) on the corrosion processes within the battery. After a water loss of 3.5 ml/Ah/cell (WL_{crit}), from the CSIRO battery, the acid specific gravity is estimated to have risen from 1.260 to 1.320. From independent corrosion experiments, it has been demonstrated that such an increase in specific gravity would increase the corrosion rate by ~20%. Given that the average specific gravity during operation of the battery must be lower than 1.320, and that the battery is capable of delivering ~1100 cycles to 100% depth-of-discharge whilst experiencing only 22% corrosion of the positive-grid material, then an increase in corrosion of only 20% would not decrease significantly the cycle life of the battery.

In conclusion, it should be made clear that these results do not suggest that the batteries evaluated in this study will last for decades under RAPS duty. Rather, it has been demonstrated that failure mechanisms other than water loss will cause the demise of the batteries. Moreover, this will occur well before water loss (due either to corrosion or to gas evolution) exerts any influence on battery performance, provided that appropriate charging regimes are used. Finally, the information is specific to the battery types described here and may not be relevant to all designs of valve-regulated batteries.

References

[1] W.G.A. Baldsing, R.D. Bramley, R.H. Newnham and C. Power, Lead/acid batteries for remote-area energy storage, *ERDC Project No. 1525, Final Rep.*, Feb. 1993, CSIRO Division of Mineral Products, Post Melbourne, *Communication MPC/M-379*, 1993.

[2] W.B. Brecht, *Batteries Int., 20* (1994) 40