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# Performance of flooded- and gelled-electrolyte lead/acid batteries under remote-area power-supply duty

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# Abstract

Both flooded-electrolyte and gelled-electrolyte lead/acid batteries have been operated under field and simulated remote-area power-supply (RAPS) service. Suitably designed batteries of the flat-plate, flooded-electrolyte variety provide the best performance under laboratory conditions. Good results can also be obtained from tubular-plate, flooded-electrolyte units, as well as from flat- and tubular-plate gelledelectrolyte types. Operation at elevated temperatures reduces the lifetime of both the gelled-electrolyte and the tubular-plate, flooded-electrolyte batteries. The principal failure modes of flooded-electrolyte batteries operated at moderate temperatures are degradation of the positive active-material (i.e., shedding, sulfation) and corrosion of the positive grid. At higher temperatures, grid corrosion becomes the dominant life-limiting factor. Similar debilitating processes are suffered by gelled-electrolyte batteries. The two best gelled-electrolyte designs identified in the laboratory study have been installed at RAPS sites and have provided 'trouble-free' service for over three years. Also, it has been demonstrated, in both the laboratory and the field, that water loss from gelled-electrolyte batteries does not cause premature failure unless the batteries are excessively overcharged. Thus, it has been confirmed that gelled-electrolyte technology is suitable for use in RAPS facilities, provided that adequate charge control is available. The evaluation programme has identified a set of design and performance specifications for RAPS batteries — the incorporation of these features will relieve many of the failure modes associated with RAPS batteries. In particular, suppression of positive-plate degradation by the application of significant plate-group compression has been identified as crucial for extending battery life under RAPS duty. The specifications have been used to design and construct a series of advanced gelled-electrolyte RAPS batteries. The units are superior to existing commercial gelled-electrolyte batteries when operated at 45 °C under simulated RAPS conditions. Finally, an operational strategy for use with batteries that are not prone to acid stratification has been identified. The procedure, termed the 'partialstate-of-charge profile', can provide a three-fold increase in the total energy available from a battery and can yield charging efficiencies of up to 99.5%.

Keywords: Remote-area power-supplies; Gelled-electrolyte batteries; Flooded-electrolyte batteries; Lead/acid batteries; Failure modes; Acid stratification; Partial-state-of-charge; Cycle-life performances; Premature capacity loss; Localized premature capacity loss; Plate-group compression

# 1. Introduction

Stand-alone power-supplies that supply power independent of the mains grid are commonly referred to as remotearea power-supply (RAPS) systems. The systems are used in many applications that include: (i) houses; (ii) community dwellings and services; (iii) telecommunications; (iv) water pumping; (v) emergency lighting; (vi) sign lighting; (vii) lighting beacons; (viii) cathodic protection; (ix) vaccine refrigerators, and (x) electric fences. Such systems can derive their power from both non-renewable and renewable energy sources. As the name suggests, RAPS systems are expected to operate reliably in isolated, harsh environments. Locations can vary from the cold of arctic regions to the intense heat of desert areas. Such facilities can also be employed in 'built-up' areas, where the cost of connection to the mains network is prohibitive and/or impracticable.

The use of RAPS systems has increased significantly over the last decade. This has been brought about by three developments. First, advances in technology have allowed much more sophisticated RAPS systems to be produced; these have resulted in refined control strategies, enhanced lifetimes and improved running efficiencies. Second, the use of renewable energy derived from hydro generators, wind generators or photovoltaic (PV) arrays assists efforts to minimize the greenhouse-gas emissions that are produced by the burning of fossil fuels. Third, the cost of fossil fuels has increased, while that of renewable energy technologies has fallen.

The design and componentry of RAPS systems are variable and are determined by several factors. These include: (i) energy demand; (ii) availability of renewable energy; (iii) cost of system maintenance; (iv) site accessibility, and (v) available finance. Either alternating current (a.c.) and/or direct current (d.c.) can be produced; the choice depends upon the quantity and quality of the power required. To supply continuous power, the RAPS facility must have either a diesel generator back-up or an energy-storage facility. The former option is not desirable as it often involves running the generator at low loads, which results in an increase in fuel consumption and extra maintenance requirements. For RAPS facilities based solely on renewable energy, a battery bank is essential in order to provide power during periods of low insolation, or low wind, or reduced water-flow.

Several different battery technologies have been employed as energy-storage mediums for RAPS systems; these include lead/acid, nickel/cadmium and nickel/iron batteries. The lead/acid battery, in particular, has gained widespread acceptance in RAPS applications and is the most efficient and cost-effective option for the vast majority of situations. Moreover, in most countries, there is an effective infrastructure for the distribution, service and recycling of lead/acid batteries. This situation is unlikely to change for many years to come, even though considerable efforts have been made during the past decade to bring other battery systems to commercialization.

Despite the maturity of the lead/acid technology, batteryrelated problems are still claimed to be responsible for many RAPS system failures. In order to improve the reliability of these facilities, CSIRO has embarked on a research programme designed to evaluate the lead/acid technologies that are available for use in RAPS applications and to develop batteries of enhanced performance. The strategy adopted has involved: (i) determination of the cycle lives of commercial batteries under simulated RAPS conditions; (ii) evaluation of promising technologies in selected field sites; (iii) identification of the subsequent failure modes by conducting autopsies, or 'tear-downs'; (iv) improvement of the parameters found to be important for RAPS duty; (v) application of the key features to develop 'advanced' RAPS batteries and evaluation of the performance of these units. The following paper summarizes the results obtained from both laboratory and field studies. It also presents design criteria for batteries that should increase significantly both the performance and the reliability of battery energy-storage systems in RAPS facilities. (Note, preliminary data describing the laboratory performance of several battery types has been reported previously [1,2].)

# 2. Simulated profiles

The performance of various types of lead/acid batteries has been examined in the laboratory under simulated RAPS schedules in order to identify and advance the most suitable technology for remote-area energy-storage facilities. Batteries produced in many parts of the world have been evaluated, together with prototype units that have been developed by CSIRO and are presently undergoing commercialization by Battery Energy South Pacific Pty. Ltd. in Sydney, Australia.

Three simulated schedules have been used in the laboratory studies. The first two regimes -- termed the '7-day' and '1day' profiles --- were formulated from insolation and load data recorded at RAPS sites around Australia [1-5]. The 7day profile cycles the batteries down to  $\sim 30\%$  state-ofcharge (SOC) over a period of 7 days, after which the battery is fully recharged. Under the 1-day schedule, the SOC of the batteries is decreased gradually to  $\sim 25\%$  and then returned to 100%, on a daily basis. With the latter schedule, the charge and discharge rates are generally twice those encountered in the 7-day profile. Before application of either the 7-day or 1day profile, the batteries were cycled to a constant  $C_5/5$ capacity at 25 °C. These capacities were then used as the basis for calculating the charge/discharge currents for the batteries, irrespective of the operating temperature. After every four weeks, the batteries were removed from the profile for determination of the  $C_5/5$  capacity. Batteries were considered to have failed when the capacity had decreased to below 75% of the initial value.

The third schedule, termed the 'partial-state-of-charge' (PSOC) profile, was designed to simulate continuous operation at less than full charge [6,7]. It involves cycling the battery between 40 and 70% SOC. This mode of operation is continued for two weeks (84 cycles), after which time the battery is fully recharged and its  $C_5/5$  capacity is measured. The procedure is repeated until the  $C_5/5$  capacity falls to below 75% of the initial value.

# 3. Performance of batteries under simulated RAPS duty

A range of flooded-electrolyte and gelled-electrolyte batteries was evaluated under simulated RAPS duty. Details of these batteries are given in Table 1. The selected batteries were operated at 25 °C (1-day, 7-day and PSOC schedules) and at 45 °C (1-day profile) in order to establish their resilience towards both deep-cycle operation and water loss under a given duty. The top-of-charge voltages (TOCVs) recommended by the manufacturers were used to regulate the charging of the batteries. These limits were temperature compensated when the batteries were operated above 25 °C. The TOCV for the gelled-electrolyte batteries at 25 °C was 2.35 V/cell for types (m) and (n), and 2.45 V/cell for types (o), (p) and (q). At an operating temperature of 45 °C, the TOCV was 2.30 V/cell for types (m) and (n), and 2.40 V/cell for types (0), (p) and (q). The TOCV for the floodedelectrolyte batteries was 2.55 and 2.46 V/cell at 25 and 45 °C, respectively.

# 3.1. 7-day profile

The electrical performance of the various battery designs evaluated under the 7-day RAPS regime at 25 °C is given in Fig. 1. This data is an update of that reported previously [2].

Table 1			
Description of batteries evaluated	under simulated	RAPS	profiles '

Code	Plate/electrolyte/capacity $(C_5/5)$ /voltage	Antimony content (wt.%)		Positive-plate thickness (mm)	Duty profile
		Positive	Negative		
a	FP/FE/39/12	5.6	5.4	2	7-day
b	FP/FE/46/12	1.6	4	2	7-day
с	FP/FE/165/6	4.8	4.1	3	7-day
d	FP/FE/42/12	0	3.8	5.5	7-day
e	FP/FE/115/6	1.6	1.6	6	1-day, 7-day, PSOC
f	TP/FE/205/6	8.5	n.d.		1-day, 7-day
g	TP/FE/165/6	9.5	7.2		l-day, 7-day
h	TP/FE/210/2	3.0	n.d.		l-day, 7-day
i	TP/FE/125/2	5.3	0		7-day
j	TP/FE/119/12	9.0	n.d.		l-day
k	TP/GE/85/2	0	0		7-day
1	FP/GE/25/12	0	0	2.5	7-day
m	FP/GE/143/6	0	0	3	1-day, 7-day, PSOC
n	FP/GE/110/12	0	0	3	1-day, 7-day
0	FP/GE/125/2	0	0	5.5	1-day
р	FP/GE/125/2	0	0	5.5	1-day
q	FP/GE/125/2	0	0	5.5	1-day

<sup>a</sup> FP = flat plate; TP = tubular plate; FE = flooded-electrolyte; GE = gelled-electrolyte; n.d. = not determined.



Fig. 1. Performance of batteries under the 7-day RAPS profile at 25 °C.

#### 3.1.1. Flooded-electrolyte batteries

Five designs of flat-plate, flooded-electrolyte batteries have been evaluated. Cycle life varied widely from unit to unit, e.g., 39 weeks for type (a) batteries (thin positive plates, 5.6 wt.% antimony) to almost 300 weeks for type (e) units (thick positive plates, 1.6 wt.% antimony). Also, a battery with thick positive plates made from pure-lead grids operated successfully for over 100 weeks (type (d)). These performances confirm the preliminary indications [2,4] that positiveplate thickness is at least as important as grid-antimony content, and that high-antimony positive grids are not required for long service-lives under RAPS conditions. The water consumption of the batteries was monitored throughout the testing period. In general, batteries with high levels of antimony in the positive grids consumed the most water. Also, the rate of water consumption of antimonial batteries increased with service life due to the progressive poisoning of the negative plates with antimony. The increase is especially relevant when water-maintenance requirements contribute significantly to system running costs, i.e., unforeseen visits to remote sites (e.g., on top of mountains) can markedly influence the economics of a particular system configuration. Consequently, it is recommended that floodedelectrolyte batteries for RAPS duty have a large electrolyte reservoir so as to maximize the time between water additions. Of course, it is recognized that this would add to the weight, volume and cost of a battery.

The most common failure mode of the flat-plate, floodedelectrolyte batteries operated under the 7-day RAPS schedule was degradation of the positive plates, i.e., the active material lacked cohesion and was poorly bonded to the grid. In many cases, the decrease in mechanical strength of the positive plate gave rise to active-material shedding. This, in turn, resulted in failure due to mossing and related short-circuits. The presence of separator envelopes around the positive plates was found to minimize shedding and to assist in maintaining electrical contact within the active material. As a consequence, it is suggested that positive plates be either wrapped both vertically and horizontally with glass-mat, or be encased in a complete separator envelope. The use of edge protection on the plates would further improve the immunity of batteries to short circuits. Also, a large sediment space at the bottom of the battery is desirable, as this allows the harmless accumulation of shed active material.

Another method for minimizing active-material shedding is to ensure that adequate compression is applied to the cell group. Such a strategy would also sustain electrical contact, both within the active material and at the positive-grid/ active-material interface. The effectiveness of compression in improving the performance of lead/acid batteries was first reported in the early 1980s [8-10] and received some further attention in the early 1990s [11,12]. Nevertheless, practical means for incorporating adequate compression into commercial batteries has not been forthcoming. More recently, there has emerged a renewed interest in using compression as a means to improve the performance of lead/acid batteries [13,14]. This has given rise to the development of separator systems and compression devices that allow up to 150 kPa to be accurately, reliably and uniformly applied to plate groups [15]. Given the failure modes observed above, it is suggested that the use of such plate-group compression would be highly suitable for RAPS batteries that have to withstand the harsh operating conditions that are often experienced in remote locations. That is, compression would offer significant protection against positive active-material degradation, shedding, and subsequent mossing.

Corrosion of the positive grid and related grid growth was the second major failure mechanism of batteries subjected to the 7-day RAPS profile. In many batteries, especially those with thin plates, little of the original grid material remained intact. Also, in several batteries, the top sections of the positive-grid frames had ruptured, moved upwards, and had come into contact with the negative busbar to form a short circuit. To avoid this occurrence, RAPS batteries should be designed to accommodate relatively large levels of grid growth and corrosion. This can be achieved by incorporating the following design features into the batteries: (i) strong, corrosion-resistant positive grids (through appropriate grid design and new alloys); (ii) collapsible bridges at the bottom of the plates; (iii) an appropriately designed positive-post configuration that allows movement of the post through the battery lid.

Irreversible sulfation of the positive and negative plates was a further degradation mechanism of batteries operated under 7-day RAPS cycling. This sulfation occurred to varying degrees in most batteries and, in several instances, contributed significantly to capacity loss.

The performance of four designs of tubular-plate, floodedelectrolyte batteries was evaluated (Table 1). These batteries employed positive-grid alloys with different antimony contents. A low-antimony battery (3 wt.% antimony; type (h); 240 weeks) purpose-built for RAPS applications out-performed two high-antimony units (8.5 and 9.5 wt.% antimony; types (f) and (g); 115 and 130 weeks) designed for use in motive-power applications (Fig. 1). Further, the water consumption of the low-antimony battery was approximately half that of the high-antimony units.

The primary failure mode of the tubular-plate batteries was the shedding of positive active-material from the extremities of the tubes. This was caused by either loose-fitting or ineffective end-caps or seals. As with the flat-plate batteries, the shedding resulted in secondary failure modes, namely, mossing and subsequent short-circuits. Significant corrosion of the positive spines also occurred, and it is likely that this also contributed to capacity loss.

In summary, a number of important design parameters for flooded-electrolyte RAPS batteries have been identified. The most important of these relate to the antimony content of the grid alloys and, for flat-plate designs, to the positive-plate thickness. The best performance under RAPS conditions is displayed by flat-plate or tubular-plate batteries with lowantimony positive grids (flat-plate  $\leq 2$  wt.% antimony; tubular-plate  $\leq 3$  wt.% antimony) and antimony-free negative plates. With flat-plate batteries, the use of thick positive plates has been demonstrated to be at least as important as the positive-grid antimony content in determining the service lives of batteries under RAPS duty. The elimination of shedding is also necessary to ensure battery longevity. Enveloped positive plates and/or edge strips, together with capacious mud spaces at the bottom of the battery case are recommended. Compression has also been identified as a means of minimizing the degradation of positive active-material that occurs under the rigours of RAPS duty. Finally, a large electrolyte reservoir is beneficial as this maximizes the interval between water additions. For tubular-plate batteries, improvements in tube/plug designs are required to avoid loss of active material.

#### 3.1.2. Gelled-electrolyte batteries

In general, both tubular- and flat-plate gelled-electrolyte batteries have been found to display good endurance under simulated RAPS conditions. The service lives of the betterperforming batteries (type (m)) exceeded those of all but two of the flooded-electrolyte units (type (e), flat-plate; type (h), tubular-plate (Fig. 1)). It is to be noted that these last two units were purpose-built for RAPS duty. The type (e) and type (h) batteries completed a service life of 300 and 240 weeks, respectively, whereas the cycle lives of the gelledelectrolyte units ranged from 110 weeks (type (n)) to 220 weeks (type (m)). (Note, the next best flat-plate and tubularplate flooded-electrolyte batteries lasted for only 120 weeks (type (c)) and 130 weeks (type (g)), respectively.)

The principal failure modes of the flat-plate, gelled-electrolyte batteries were similar to those observed for the flooded-electrolyte batteries, viz., degradation/softening of the positive active-material, grid corrosion, and sulfation of both the positive and negative active-material. By contrast, the loss of capacity in the tubular-plate design was related mainly to sulfation of the active material. It is important to note that shedding and related failure modes (i.e., mossing, short circuits) were not observed in any of the gelled-electrolyte batteries. This is because dislodged material is not free to move around the battery and is held next to the plate by the immobilized gel structure, whereas in flooded-electrolyte designs, convection currents within the electrolyte together with stirring caused by gas evolution during charging can distribute the loose material throughout the cell compartment. Nevertheless, it is advisable that future designs of gelledelectrolyte batteries be constructed with significant plategroup compression (similar to that recommended above for flooded-electrolyte designs) as this will minimize any capacity loss associated with positive active-material degradation. Water loss is not considered to have contributed significantly to the decrease in battery performance (see below).

Comparisons between the cycle lives of the best-performing flooded- and gelled-electrolyte batteries are complicated by differences in positive-plate geometry. The flooded-electrolyte (type (e)) and gelled-electrolyte (type (m)) designs employed positive plates of thickness 6 and 3 mm, respectively. Given that batteries with thick positive plates are more resistant to positive-grid corrosion and degradation of the positive active-material, it is obvious that gelled-electrolyte batteries with thick plates (i.e.,  $\geq 5 \text{ mm}$ ) will offer significant improvements in cycle life in comparison with thinner-plate versions.

Hones et al. [16] investigated the performance of floodedelectrolyte, gelled-electrolyte and absorptive glass-mat (AGM) lead/acid technologies under simulated RAPS conditions. The batteries were operated in the laboratory under the following three simulated schedules; (i) float; (ii) stand at 33% SOC, and (iii) cycling under a simulated solar schedule. The SOC throughout the simulated solar schedule and the method used to formulate it are akin to those of the 7-day profile used in the CSIRO study. Given that the regimes were developed independently, the observed similarity supports the practicality of the simulations and the strategies used to derive them. In the Hones study [16], flooded-electrolyte, lead/acid batteries were found to perform well under all three cycling conditions. Moreover, it was concluded that this technology was relatively simple to control and did not require any 'special' protection against overcharge. Nevertheless, water-maintenance requirements and acid stratification were seen as detracting from the efficacy of using this technology in photovoltaic-based RAPS systems. The performance of the gelled-electrolyte units was also shown to be acceptable under all the test conditions. By contrast, the capacity of the AGM counterparts deteriorated under both the standing and the simulated solar schedules.

In summary, the above findings indicate that gelled-electrolyte batteries with either tubular or flat plates can perform very well under RAPS applications at moderate temperatures. Further, the construction of gelled-electrolyte batteries with thick positive plates ( $\geq 5$  mm) is expected to enhance the performance of the batteries under RAPS service. Finally, it is considered that the incorporation of significant levels of plate-group compression would further improve the endurance of gelled-electrolyte batteries under RAPS duty.

# 3.2. 1-day profile

The cycle life of all battery types subjected to the 1-day RAPS profile at 25 and 45 °C is given in Figs. 2 and 3,



Fig. 2. Performance of batteries under the 1-day RAPS profile at 25 °C.



Fig. 3. Performance of batteries under the 1-day RAPS profile at 45 °C.

respectively. Comparison with the data given in Fig. 1 shows that the service lives of batteries operating under the 1-day schedule are less than those obtained under 7-day operation. This is because the former profile is a more strenuous charge/ discharge regime than the latter.

#### 3.2.1. Flooded-electrolyte batteries

There was little variation in the cycle lives of floodedelectrolyte batteries operated at 25 °C (Fig. 2). Lifetimes varied from 72 weeks for a low-antimony, tubular-plate unit (type (h)) to 90 weeks for both high-antimony, tubular-plate (type (f)) and low-antimony, flat-plate (type (e)) batteries. It is interesting to note that battery type (e) was also the best performer (300 weeks) under the 7-day profile.

The results from tests conducted at 45 °C are more difficult to interpret (Fig. 3). The flooded-electrolyte, flat-plate unit (type (e)) has operated for over 140 cycles and is still delivering excellent capacity. Surprisingly, the equivalent unit at 25 °C survived for only 90 weeks (Fig. 2). To date, no explanation has been found for the superior performance at 45 °C. By contrast, the cycle life of the type (g) tubular-plate battery at 45 °C (60 weeks) was some 20 weeks less than that at 25 °C (80 weeks).

Failure of the tubular-plate units at both 25 and 45 °C is due to active-material shedding, mossing and related short circuits. As with the 7-day tubular-plate units, this shedding was caused by inadequate sealing at both the top and bottom of the tubes. In some instances, the end-plugs had fallen out of the gauntlets. In addition, very little of the lead spines remained unoxidized in the tubular-plate battery operated at 45 °C. Clearly, this severe level of corrosion would curtail the life of the battery.

#### 3.2.2. Gelled-electrolyte batteries

The performance of the gelled-electrolyte batteries operated under the 1-day RAPS profile at 25 °C has been most promising (Fig. 2). The type (m) units provided lifetimes of ~60, 80 and 100 weeks, whereas a type (n) battery operated for 95 weeks. In general, this performance matches that of the best flooded-electrolyte designs (i.e., 72 to 90 weeks).

The behaviour of the gelled-electrolyte batteries at 45 °C was complicated by charging difficulties. It was found that the units were not being returned to a full SOC at the end of each 1-day cycle. Other researchers [17] have encountered similar problems with the charging of gelled-electrolyte and AGM lead/acid batteries at elevated temperatures. They concluded that charging was more difficult and, accordingly, recommended an increase in overcharge of 0.5% for each 1 °C rise in temperature above 25 °C. On extending the final charging period of the 1-day profile by 4 h (i.e., the 1-day or 24-h profile becomes a 28-h schedule), the capacities of the batteries tested at 45 °C increased to match those of the units operated at 25 °C.

The lifetime of the gelled-electrolyte batteries decreased markedly with increasing temperature. At 45 °C, battery types (m) and (n) lasted only 43 and 57 weeks, respectively, (Fig. 3). In general, this service is about 40% less than that recorded for the corresponding units at 25 °C (Fig. 2). By contrast, higher operating temperatures did not affect greatly the cycle life of the flooded-electrolyte units (indeed, in one case, cycling at an elevated temperature actually increased the cycle life, see above). At elevated temperatures, therefore, it would appear that the durability of the gelled-electrolyte units.

The failure of the gelled-electrolyte batteries under 1-day RAPS duty at 25 °C was mainly associated with: (i) breakdown of the integrity of the positive active-material; (ii) grid corrosion, and (iii) irreversible sulfation of both the positive and negative plates. As might be expected, positive-grid corrosion in the batteries operated at 45 °C was more severe than that in the lower temperature equivalents.

As mentioned above, the positive-plate thickness of the gelled-electrolyte batteries discussed to date is appreciably less than that of the flooded-electrolyte units. Hence, it is concluded that the use of thick positive plates in gelled-electrolyte technology would improve the resistance towards grid corrosion and render the batteries more suitable for high-temperature RAPS duty. Indeed, this design philosophy has been adopted in the construction of a series of advanced gelled-electrolyte batteries designed by CSIRO. Examples of the batteries are operating under the 1-day profile at both 25 and 45 °C (types (o), (p) and (q)). Their performance is described below in Section 5.

# 3.3. Partial-state-of-charge profile

It is well known that stratification of the electrolyte can occur in both flooded-electrolyte and AGM battery designs [18-24]. Stratification can result in an accumulation of lead sulfate in the bottom regions of the plates and can also accelerate positive-grid corrosion. If the stratification is not removed on a regular basis, the lead sulfate deposits become refractory and cannot be converted by normal charging procedures. Therefore, a decrease in battery capacity will eventuate.

RAPS batteries are often undercharged due to periods of low insolation or low wind, or to inappropriate system sizing. As a result, the batteries are especially vulnerable to stratification. In order to determine the extent of this problem, a flooded-electrolyte and a gelled-electrolyte battery were operated under PSOC conditions (see Section 2) that are designed to promote acid stratification [7]. The schedule cycles the batteries between 40 and 70% SOC for a period of two weeks (i.e., 84 cycles) and then a  $C_5/5$  capacity check is conducted. The procedure is repeated until the  $C_5/5$  capacity falls to below 75% of the initial value. The best gelledelectrolyte (type (m)) and flooded-electrolyte (type (e)) batteries, as identified under the 7-day and 1-day profiles, were chosen for evaluation. The results to date are presented in Fig. 4.

The flooded-electrolyte battery provided 1796 cycles under PSOC conditions before failure. This corresponded to a total energy delivery of 61 962 Ah. Under conventional operating conditions, the battery is expected to deliver  $\sim 1200$  cycles to 100% depth-of-discharge (DOD), or 138 000 Ah. Thus, PSOC cycling decreased battery performance.

The voltage at the end of both the charge period (TOCV; nominal 70% SOC) and the discharge period (EODV; nominal 40% SOC) during PSOC operation was recorded for both batteries. During a typical 2-week cycling period, the TOCV of the flooded-electrolyte battery increased by  $\sim 500$ mV whilst the EODV decreased by  $\sim 200$  mV. By contrast, the equivalent TOCV and EODV values for the gelled-electrolyte battery increased by 150 mV and decreased by 40 mV, respectively. (Note, full battery recharge at the end of each 2-week cycling period returned the TOCV and EODV of both batteries to the base levels.) Other workers have operated flooded-electrolyte batteries under PSOC conditions [20] and have observed the same trends in TOCV and EODV with cycling. The extent of the changes was attributed simply to the degree of acid stratification within the battery.

The specific gravity (sp. gr.) of the acid in the floodedelectrolyte batteries was measured regularly during the cycling period. Typically, a difference of 70 points between the sp. gr. of the acid at the top and the bottom of the battery developed during the 2-weekly cycling period between 40 and 70% SOC. Thus, PSOC operation does indeed result in the formation of significant electrolyte stratification. A full tear-down and analysis of the batteries revealed that the negative plates were in good condition and that failure originated from the positive plates. The active material at the bottom of the positive plates was in a poor condition - it had undergone significant expansion, was very soft, lacked cohesion, and was poorly bonded to the grid. Total loss of the material from the plate was only prevented by the presence of the separator envelopes. Analysis showed that there were minimal amounts of lead sulfate in either the positive or negative plates.

The failure of the battery has been explained [7] in terms of the uniform theory of premature capacity loss (PCL)



Fig. 4. Cycle life of batteries under PSOC duty.

Table 2 Total energy available from a gelled-electrolyte battery at different depthsof-discharge [7]

Depth-of- discharge (%)	Number of cycles	Total available energy (Ah)
10	6000	86000
20	3200	91500
40	1250	71500
60	900	77000
80	700	80000
100	500	71000

developed by Hollenkamp and co-workers at CSIRO [13,14]. The key phenomenon is the progressive expansion of positive active-material that occurs during the charge and discharge of lead/acid batteries. The Hollenkamp theory argues that the volume increase invokes a concomitant gradual decrease in electrical conductivity. Once a critical degree of expansion has been reached, the amount of positive activematerial available for reaction is limited by the electrical conductivity of the active mass. This leads to a decrease in capacity. The severity of this phenomenon is determined by several factors, one of which is the extent of active-material utilization [7]. It is known that the active-material utilization in stratified batteries is higher at the bottom of the plates than at the top. This is due to a preferential discharge that is driven by the accumulation of strong acid in the region. Hence, the deterioration of the battery is attributed to the occurrence of PCL that has occurred in a localized fashion, i.e., at the bottom of the plates. Such capacity loss is referred to as: 'localized PCL' [7].

The gelled-electrolyte battery has completed 6000 cycles and is still operating at 95% of its original capacity. This corresponds to a total energy delivery of 257 400 Ah. (Note, the decrease in capacity between cycles 2500 and 4000 was related to a problem with the cycling equipment. After the fault was rectified, the capacity of the battery increased to  $\sim 100\%$  of the original value.) The expected cycle life and associated energy delivery claimed by manufacturers of gelled-electrolyte batteries under conventional cycling conditions (i.e., a full recharge after each discharge) at varying DODs is given in Table 2 [7]. The energy delivery under PSOC duty (257 400 Ah) is over three times greater than that obtained under conventional cycling conditions to 60% DOD (i.e., 40% SOC), viz., 77 000 Ah. The remarkable increase in energy is not simply due to the moderate DOD of the PSOC profile (i.e., 60%), as decreasing the DOD from 100 to 20% under traditional operating conditions will afford only a 30% increase in energy delivery, i.e., 20 500 Ah (Table 1).

It is thought that the marked increase in energy available from the gelled-electrolyte batteries under PSOC duty is due to the reduction in the amount of overcharge that the battery receives. Using traditional charging procedures, the battery is overcharged during each charge/discharge cycle. Under PSOC conditions, however, the battery is only subjected to overcharging after every 84 cycles, or 3604 Ah of energy delivered. As a result, the battery operated under PSOC conditions receives an order of magnitude less overcharge and operates with a charge efficiency of over 99.5%. Such a reduction in overcharge reduces significantly the oxygen produced during charging, and thus moderates the rate of both positive-grid corrosion and disruption/degradation of the positive active-material [25].

In summary, flooded-electrolyte batteries have been shown to fail prematurely under PSOC conditions. The poor performance is attributed to acid stratification that results in increased acid concentration and, hence, increased activematerial utilization in the bottom parts of the positive plates. The losses in capacity are explained in terms of PCL. More specifically, it is recognized that PCL can occur in localized regions within the positive active-mass; the phenomenon is termed 'localized PCL'. Also, it has been demonstrated that the total energy available from batteries that are not susceptible to significant electrolyte stratification (e.g., gelled-electrolyte batteries) can be at least tripled through the use of PSOC operation. Such a strategy can also provide charging efficiencies as high as 99.5%. Partial-state-of-charging ameliorates the capacity losses that are associated with grid corrosion and overcharge processes.

#### 3.4. Water consumption of gelled-electrolyte batteries

The gelled-electrolyte technology does not require water maintenance during normal lifetime as a result of a recombination reaction during battery charging that reconverts oxygen to water at the negative plate. This process is not 100% efficient, however, and gasses from the battery are vented to the atmosphere via a pressure-relief valve. The net result is that some water is lost from the battery. As a consequence, valve-regulated batteries require more careful charging than flooded-electrolyte counterparts in order to avoid dry-out of the electrolyte. If charging is not regulated correctly, premature failure can occur. In order to establish the extent to which water loss can affect battery performance, the present study has included an investigation of electrolyte loss from gelled-electrolyte batteries under RAPS conditions.

Water loss (WL) from valve-regulated batteries can occur by two separate processes, namely, gas evolution ( $WL_{gev}$ ) and corrosion of the positive grid ( $WL_{corr}$ ) [26]. When the sum of these two parameters exceeds a critical value ( $WL_{crit}$ ) a decrease in performance occurs, i.e.,  $WL_{gev} + WL_{corr} >$  $WL_{crit}$ . Hence, it is important to consider both these parameters when quantifying the effect of WL on battery performance. In this study, values of  $WL_{crit}$  and the rate of  $WL_{gev}$ (termed  $RWL_{gev}$ ) have been established for both CSIRO (type (o)) and commercial (types (m) and (n)) gelledelectrolyte batteries operated under simulated RAPS conditions, viz., the 1-day schedule. This information, together with the amount of water ( $WL_{corr}$ ) calculated to corrode a significant proportion of the positive grid lead in the CSIRO

Table 3 Summary of water-loss data

Duty	Battery type	Temperature (°C)	<i>RWL</i> <sub>gev</sub> (ml/Ah/cell/year)	WL <sub>crit</sub> (ml/Ah/cell)	Years to reach $WL_{crit}$ (with $WL_{corr50}$ )
Simulated 1-day	CSIRO (o)	25	0.02	3.5	85 *
RAPS service	CSIRO (o)	45	0.03	3.5	57 <b>*</b>
	(m)	25	0.06	3.5	28 *
	(m)	45	0.19	3.5	9
	(n)	25	0.10	2.4	6
	(n)	45	0.35	2.4	2
Field service	(m)		0.07	3.5	24 ª
	(n)		0.07	2.4	9

<sup>a</sup> See note in text.

battery, allows a prediction to be made of the WL that must take place before the battery capacity is seriously reduced. The  $RWL_{gev}$  of the three gelled-electrolyte designs was established by monitoring battery weight during operation under RAPS conditions. A weight loss of 1 g was considered to equate to the escape of 1 ml of water.

When subjected to 1-day RAPS duty at 25 and 45 °C, the CSIRO battery design (type (0)) showed an  $RWL_{gev}$  of 0.02 and 0.03 ml/Ah/cell/year, respectively (see Table 3). The  $RWL_{gev}$  values for the commercial types (m) and (n) were 0.06 and 0.10 ml/Ah/cell/year at 25 °C, and 0.19 and 0.35 ml/Ah/cell/year at 45 °C. Also, types (m) and (n) recorded an average  $RWL_{gev}$  of 0.07 ml/Ah/cell/year over a 2-year operating period in the field (see below and Table 3).

Non-antimonial, flooded-electrolyte batteries used in stand-by applications can typically experience between 40 and 65% corrosion of the positive grid by the end-of-life, e.g., 10 to 20 years [27]. Using this as a basis, the amount of water required to corrode 50% of the positive-grid material in the CSIRO battery, i.e.,  $WL_{corr50}$ , has been calculated as 1.8 ml/Ah/cell.

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 TOCV of 2.8 V until the capacity of the battery remained below 75% of the initial value. It was considered that a high TOCV would result in fast, efficient water loss from the battery through the promotion of poor recombination efficiency, whilst keeping corrosion to a minimum. The efficacy of this process was verified by tear-down procedures and subsequent scanning electron microscopic (SEM) examination. No significant differences in the corrosion-layer thickness were detected between positive grids removed from new batteries and those subjected to the dryout procedure.

The total water loss that battery types (m), (n) and (o) can tolerate ( $WL_{crit}$ ) before their performance is affected significantly is 3.5, 2.4 and 3.5 ml/Ah/cell, respectively, see Table 3. If the amount of water required to corrode 50% of the grid lead in the CSIRO battery ( $WL_{corr50} = 1.8 \text{ ml/Ah/}$  cell) is subtracted from  $WL_{crit}$ , the remainder is available for WL by gas evolution ( $WL_{gev}$ ). When operated under RAPS

duty, the CSIRO battery has an  $RWL_{gev}$  of 0.02 and 0.03 ml/ Ah/cell/year at 25 and 45 °C, respectively, see Table 3. Hence, it is easy to calculate that it would take approximately 85 years at 25 °C, and 57 years at 45 °C, for the batteries to reach  $WL_{crit}$ . Since these cycle lives are not realistic, clearly other mechanisms cause battery failure well before WL becomes a life-determining factor. Furthermore, if it is assumed that battery types (m) and (n) have a similar values of  $WL_{corr50}$  to that of type (0), corresponding lifetimes of 28 and 6 years at 25 °C and 9 and 2 years at 45 °C can be expected before WL affects battery performance, see Table 3. Similarly, the type (m) and (n) batteries that are operating at the field sites promise a life of 24 and 9 years, respectively.

Given that the RAPS schedule used in the WL studies (1day profile) is an accelerated regime that results in most batteries failing within the first 12 months of operation, see Section 3.2, it is considered very likely that the above batteries would be subject to other deterioration mechanisms well before  $WL_{crit}$  is reached. If, however, a gelled-electrolyte battery is required to be especially resistant to overcharge and electrolyte dry-out due to continuous operation under hightemperature RAPS duty, it would be beneficial for the batteries to contain additional electrolyte compared with standard units. A greater amount of water would then be available for both  $WL_{corr}$  and  $WL_{gev}$ . Such a modification can be achieved by increasing the volume above the cell group and filling the additional space with gelled-electrolyte.

In conclusion, it should be emphasized that the authors do not assert that the batteries evaluated in this study will last for the periods calculated above for RAPS field service. Rather, the study has served to show that other failure mechanisms will cause the demise of the batteries well before WL (due to either corrosion or gas evolution) exerts an adverse effect on battery performance, provided that appropriate charging regimes are employed. Finally, the information is specific to the gelled-electrolyte batteries described above and may not be relevant for AGM designs.

# 4. Performance of batteries under field duty

The evaluation of batteries conducted in the laboratory under simulated RAPS duty has identified gelled-electrolyte



Fig. 5. Average temperatures of gelled-electrolyte batteries and battery room at French Island RAPS site between days 260 and 264.

batteries as promising candidates for use in RAPS field sites. The final test in proving the efficacy of this technology in such applications is to measure battery performance in actual RAPS facilities. Consequently, the best two gelled-electrolyte battery designs (types (m) and (n)) identified in the study have been placed in RAPS facilities in remote locations in Australia.

A battery bank of 40, type (m) batteries has been installed in a medium-sized RAPS system on French Island (situated 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 is configured to provide a system voltage of 120 V. The battery bank provided trouble-free service for three years, after which time monitoring at the site ceased.

A second RAPS system has been established in a house at Talbot in Victoria. Power is generated by a small photovoltaic array and diesel generator; the latter operates infrequently. The lead/acid battery bank consists of four, type (n) gelledelectrolyte batteries. The units have been in service now for five years and are still performing acceptably.

The WL from the batteries at both field sites was monitored for the first two years of duty. After an initial 'drying-out' period (one to two months) when the water consumption was high, water usage in the various modules of both battery packs ranged between 0.002 to 0.006 ml/Ah/cell/month. If the worst case is assumed, (i.e., 0.006 ml/Ah/cell/month), an  $RWL_{gev}$  of 0.07 ml/Ah/cell/year is obtained (Table 3). This value is similar to that recorded for equivalent batteries operated at 25 °C under simulated RAPS conditions in the laboratory, viz., 0.06 and 0.1 ml/Ah/cell/year (Table 3). This result supports the authenticity of the laboratory-testing regimes in respect to WL measurements. (Note, both RAPS sites experience temperatures between 10 and 25 °C with occasional extremes of zero or 35 °C.)

Valve-regulated lead/acid batteries are more susceptible to thermal runaway than traditional flooded-electrolyte batteries. This is because the recombination reaction produces significant heating effects. Also, by virtue of the sealed nature of valve-regulated lead/acid batteries, heat dissipation is not as efficient. In order to assess heating effects that can occur in gelled-electrolyte batteries during operation, temperature sensors were placed in every cell of two type (m) batteries installed at the French Island RAPS site. The tip of each sensor was put in contact with the top of a negative plate. The ambient temperature of the battery room was also recorded. Negligible variation in temperature from cell to cell was observed within a given battery. Also, the temperatures of both the battery room and the cells were found to follow a diurnal variation, i.e., increase during the day and decrease at night, see Fig. 5. Further, the change in the internal battery temperature was less than that observed for the battery room. In other words, the internal battery temperature was lower than that of the battery room during the day, and higher at night. This behaviour is attributed to the large thermal mass of the batteries. In addition, the insulating nature of the battery cases slows down any swings in temperature.

In summary, gelled-electrolyte batteries have performed well under actual RAPS conditions. Also, the rate of WL from the batteries has been minimal and should not affect the capacity of the battery before other failure mechanisms become active. Finally, both the combination of the minimal heating effects observed in batteries during field operation, and the promising performance of all the gelled-electrolyte batteries cycled at 45 °C under simulated RAPS duty (Fig. 3), suggest that the technology is resistant to thermal runaway, provided that a reasonable charging regime is available.

#### 5. Advanced gelled-electrolyte batteries

An important outcome of the present study is the development of an advanced gelled-electrolyte battery. The construction of this battery is based on many of the design features that have been identified in the laboratory studies as being beneficial for RAPS duty. The battery is especially well-suited to deep-cycle applications. The first prototype cells provided ~1100 cycles to 100% DOD ( $C_3/3$  rate). A second series of prototypes ('prototype II'), that include three cell designs, has been constructed. The cell types differ only in positive-grid composition.

The prototype II cells are currently operating under the 1day RAPS profile at both 25 and 45 °C. The results of the studies to date are given in Figs. 2 and 3. The batteries have operated trouble-free for ~65 weeks at both 25 and 45 °C and are delivering ~100% of their nominal capacity. The performance at high temperatures already exceeds that of commercial batteries (types (m) and (n)).

A prototype III battery is currently under construction. The design incorporates a pressure device and a new type of separator that will maintain a high level of plate-group compression throughout the life of the battery. Preliminary data show that this strategy markedly increases the cycle life relative to that of batteries constructed with traditional levels of compression.

#### 6. Design specifications for RAPS batteries

Batteries used for energy storage in RAPS systems are subjected to a vast range of conditions that varies from continual overcharge to extended periods of time in a discharged state. Temperature extremes are also common — battery banks can be subjected to the sweltering heat of deserts or the intense cold of the arctic. Reliable performance under such a wide range of operating conditions requires very detailed attention to battery design. One of the outcomes of the present study is the development of design and performance specifications for RAPS batteries. It is considered that the adoption of these specifications will minimize batteryrelated system failures and greatly improve the reliability of RAPS facilities. The specifications are outlined below.

# 6.1. Design and performance specifications for RAPS batteries

# 6.1.1. Battery type

Either flooded-electrolyte or gelled-electrolyte batteries with either tubular-plate or flat-plate positive-plates are recommended. (Note, another type of valve-regulated lead/acid battery is available, i.e., the AGM design, but it demands very precise charging on a regular basis. As this cannot always be provided in RAPS facilities, AGM batteries are not recommended for RAPS duty.)

#### 6.1.2. Battery container

The battery container should be constructed from fire-retardant material and be strong enough to resist significant deformation that may result from either grid growth or the application of significant compression to the cell group. A transparent material is preferred as this allows a useful examination of the physical state of the cells in the battery.

# 6.1.3. Plate-group configuration

Batteries should be able to accommodate relatively large levels of grid growth in both the vertical and horizontal planes. A collapsible bridge at the bottom of the plate group is recommended. The plate-group height in flooded-electrolyte batteries should be minimized so as to decrease the extent of electrolyte stratification.

#### 6.1.4. Sediment space

Flooded-electrolyte units should have sufficient sediment space to allow the build-up of shed material without the formation of short circuits. A space which is at least 10% of the height of the positive plate is recommended. No sediment space is required for gelled-electrolyte batteries.

#### 6.1.5. Grid composition

The antimony content of either the positive or the negative grids of flooded-electrolyte batteries should not exceed 2 wt.%. It is recommended that gelled-electrolyte batteries, in their current state of development, do not contain antimony in either the negative or positive grids.

# 6.1.6. Positive-plate thickness

For flooded-electrolyte, flat-plate batteries, the minimum thickness of the positive-plate should be 5 mm (pasted and formed). Gelled-electrolyte, flat-plate units of moderate capacity (<150 Ah,  $C_{10}/10$  rate) are, at present, manufactured with thin positive plates ( $\leq 3$  mm). Hence, the minimum thickness recommended for the positive plate is 3 mm. Future gelled-electrolyte battery designs should be constructed with thick positive plates ( $\sim 5$  mm).

#### 6.1.7. Protection of plate edges

The negative and positive plates of flooded-electrolyte batteries should have suitable edge protection to decrease the likelihood of internal short circuits (top, bottom and sides).

#### 6.1.8. Separation mode

For flooded-electrolyte batteries, the positive plates should be wrapped with glass-mat, both vertically and horizontally. Plates of opposite polarity should be further isolated by sheet separation. A total separator envelope around the positive plates is preferred. Gelled-electrolyte batteries should have their positive plates wrapped vertically with glass-mat, and should have sheet separation between the positive and negative plates. Alternatively, a layer of glass-mat may be bonded to the sheet separators. This absorbent material faces the positive plate, i.e., the ribbed side of the separator should be in contact with the negative plate (enveloped separation is not required with this technology as shedding of active material is minimal). If the battery is built with significant plategroup compression, it is suggested that the separators should be able to withstand twice the actual compression level applied at the time of manufacture.

### 6.1.9. Cycle life

The battery should be able to deliver at least 1200 discharge cycles at the  $C_5/5$  rate to 80% DOD. The discharges are to be performed at 25 °C. The battery will be deemed to have failed when its  $C_5/5$  capacity has dropped to 80% of the nominal value.

# 6.1.10. Self-discharge

The self-discharge of the battery at 25 °C should not exceed 3% of the rated  $C_5/5$  capacity per month.

# 6.1.11. Water maintenance

The minimum water replacement period for flooded-electrolyte batteries should be not less than 6 months. This can be achieved by utilizing a large electrolyte reserve and/or a low antimony content in the positive and negative grid alloys. Gelled-electrolyte batteries that are to be operated at constant high temperatures should also be manufactured with a large electrolyte volume. This design feature renders the battery especially resistant to overcharging and failure due to excessive WL.

# 7. Summary

Flat-plate, flooded-electrolyte batteries with thick, low antimonial positive plates are found to out-perform tubularplate, flooded-electrolyte and also flat-plate and tubular-plate, gelled-electrolyte batteries under RAPS conditions.

Positive-plate thickness is shown to be at least as important as the level of positive-grid antimony for good performance of flat-plate, flooded-electrolyte units under RAPS conditions.

Gelled-electrolyte batteries provide acceptable service lives under RAPS duty. Negligible deterioration in battery performance is expected due to water loss before normal failure modes (e.g., grid corrosion, positive active-material degradation) become dominant, provided adequate charge control is exercised.

The principal failure modes of the batteries under RAPS conditions at moderate temperature are degradation/sulfation of the active material and grid corrosion. At elevated temperatures, grid corrosion becomes the dominant failure mechanism.

A method of operation, called 'PSOC', provides at least a three-fold increase in the total energy available from batteries that are not susceptible to acid stratification. The operational strategy can also offer total charge efficiencies of close to 100%.

As a result of the research programme, a set of design and performance specifications for RAPS batteries has been identified. The design features should alleviate many of the failure modes observed under RAPS duty. Significant plate-group compression is identified as especially important in minimizing failures associated with positive active-material degradation and mossing.

Based on the outcomes of the research programme, a series of advanced gelled-electrolyte batteries for RAPS applications has been designed and constructed. The batteries are out-performing existing commercial equivalents under high-temperature simulated RAPS conditions.

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