Journal of Power Sources, 48 (1994) 55–67

Technical trends in industrial lead/acid batteries in Japan

Masashi Iwata and Yahachiro Tagawa

Engineering Department, Japan Storage Battery Co., Ltd., Corporate R&D Center, Nishinosho, Kisshoin, Minami-ku, Kyoto (Japan)

Abstract

Although there have been only a few major technological changes in stationary lead/acid batteries in the past, some rapid and remarkable developments have occurred recently. The latter have included the introduction of catalyst plugs and valve-regulated lead/acid batteries (VRBs). Catalyst plugs have been used to avoid water addition with stationary lead/acid batteries. By virtue of their advantages (i.e., the elements retain electrolyte and equalizing charging and water addition are unnecessary), VRBs are being developed up to a maximum capacity of 3000 Ah. These designs have now captured about 50% of the stationary lead/acid battery market. The VRB technology has excellent characteristics, such as plate construction that can accommode grid growth, explosion-resistant plugs, good discharge characteristics, and minimal electrolyte stratification. In addition, by utilizing the benefits of VRBs, horizontal and multistoried systems can be assembled, though in early stages of development the construction was only for interchangeability with flooded-electrolyte type batteries.

Introduction

The technology of the sealed lead/acid battery began with small-sized batteries and then expanded into the field of stationary batteries, automotive batteries and traction batteries. In Japan, 'sealing' in stationary batteries has been steadily improved from the catalyst-plug to the VRB type. Such designs will be used more and more in the future.

Stationary lead/acid batteries

Sealed battery with catalyst plugs

The first sealed stationary battery was introduced in 1975 with catalyst plugs. The function of the plugs is to reduce the oxygen and hydrogen gases that are generated during overcharging to water with the help of a palladium catalyst. These plugs are positioned on the cover and convert flooded-electrolyte batteries into 'sealed' units. An example of the construction of a catalyst plug is given in Fig. 1. A battery fitted with such plugs is shown in Fig. 2. The specifications of catalyst plugs adopted in Japan are as follows:

Elsevier Sequoia
SSDI 0378-7753(93)01857-E

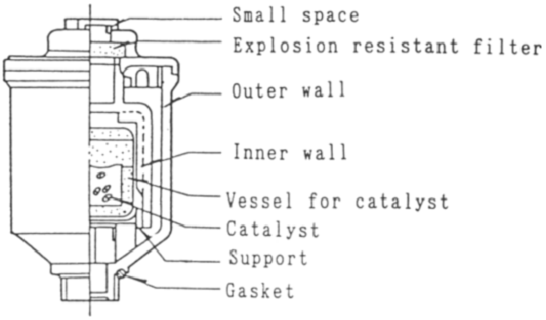

Fig. 1. Construction of catalyst plug.

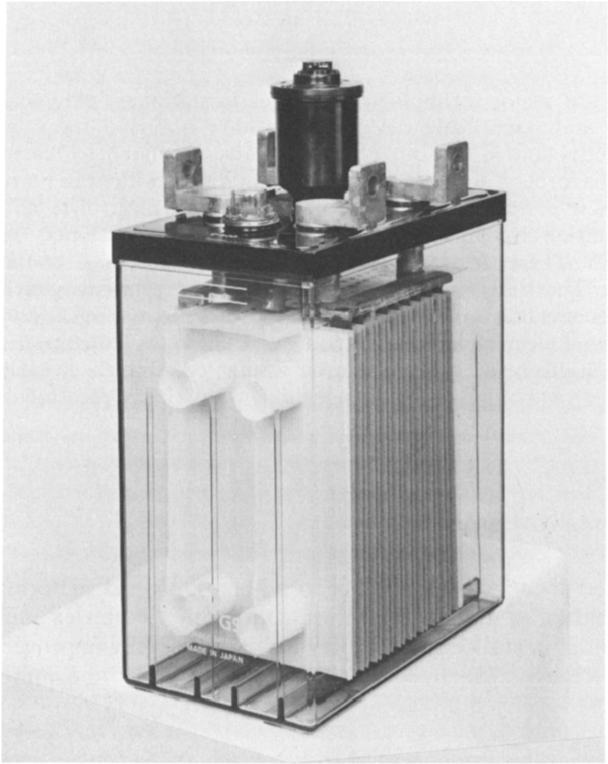

Fig. 2. Battery with catalyst plugs (CS type).

● life	5 years
● lowest service temperature	-5 °C
● maximum overcharged current	less than 0.05*C* A (*C* is the rated capacity)
● equalizing charge	2.25 V/cell for 48 h
	2.30 V/cell for 24 h
	2.40 V/cell for 8 h

The following problems are experienced when catalyst plugs are used: (i) an equalizing charge is required; (ii) as the life span of the plugs is shorter than that of the battery, exchanges of catalyst plugs are required; and (iii) not available lower than −5 °C.

Although plugs provide the advantage of eliminating water addition, the function is not sufficient to make the battery fully 'maintenance free'.

Valve-regulated lead/acid batteries

Characteristics and essentials

Valve-regulated batteries (HSE type and MSE types) have been developed in order to eliminate maintenance. The main functions are: (i) equalizing charge is not required; (ii) floating charge voltage is 2.23 V/cell; (iii) water addition is not required, and (iv) ambient temperature in service: −15 to about 45 °C.

Furthermore, as VRBs can be positioned horizontally, it is easier to check the floating charge voltage in order to control the batteries. Life expectancy is, at 25 °C, 5 years for the HSE type and 7 to about 9 years for the MSE batteries. The essentials of the HSE and MSE designs are listed in Table 1. In order to accommodate the requirements for various applications such as telephone, CVCF, control and communications systems, a wide range of battery capacities (viz., 30 to 9000 Ah) has been prepared. In addition, flame-resistant acrylonitrile/butadiene/styrene (ABS) plastic (UL94-V0) can be used for the container. MSE type batteries are presented in Fig. 3.

Construction

Separators

These consist of glass-fibre paper. The fibres are <1 μm in diameter and have a porosity of 93%. The separators are made from porous material with a very high degree of water containability.

Positive plates

Positive plate grids become corroded in service. Valve-regulated batteries have lead–calcium alloy grids, that tend to elongate with corrosion. From the results of field trials, the growth can be calculated by the following formula:

$$\text{Growth (\%)} = Kt^2 \qquad (1)$$

where K is the rate constant of growth; t is the period of time in service (days). The parameter K is influenced by both the temperature and the floating-charge voltage; the relationship is shown in Fig. 4. Temperature has a stronger influence than voltage. It is desirable to keep the temperature low in order to obtain reliable service from MSE type batteries. Because the growth is caused by corrosion of the positive grids, the development of a low-corrosion battery grid alloy is necessary.

Figure 5 shows the development of grid growth with time for the plates that yielded the data given in Fig. 4. The floating-charge voltage for the MSE type of battery is 2.23 V/cell. In this case, for a life of 15 years, the growth of the plates is about 10%. Thus, the horizontal space between the plates and the container has to be 10%. The plates have to have flexible feet in order to absorb the growth so that the resulting force is not directly placed upon the seal between the container and the cover. A design for absorbing positive-plate growth is given in Fig. 6.

TABLE 1

Essentials of HSE- and MSE-type batteries

Assembled battery type	Cell type	Nominal capacity (Ah)		Cell outer dimension (mm)				Weight (kg)
		10-h rate	1-h rate	TH	CH	W	L	
	HSE-30-12	30	18	217	190	128	363	22
	HSE-40-12	40	24					
	HSE-50-12	50	30					
	HSE-60-6	60	36					
	HSE-80-6	80	48					
	HSE-100-6	100	60	217	190	128	345	22
	MSE-50-12	50	32	217	190	128	363	22
	MSE-100-6	100	65	217	190	128	345	22
MSEX-150	MSE-150	150	97	362	330	170	106	13
MSEX-200	MSE-200	200	130	362	330	170	106	16
MSEX-300	MSE-300	300	195	362	330	170	150	24
MSEX-400		400	260					31
MSEX-500	MSE-500	500	325	362	330	171	241	38
MSEX-600		600	390					48
MSEX-700		700	455					54
MSEX-800		800	520					62
MSEX-900		900	585					72
MSEX-1000	MSE-1000	1000	650	362	330	171	471	72
MSEX-1200		1200	780					92
MSEX-1500	MSE-1500	1500	975	372	340	337	476	110
MSEX-2000	MSE-2000	2000	1300	372	340	337	476	146
MSEX-3000	MSE-3000	3000	1950	372	340	340	696	220
MSEX-4000		4000	2600					292
MSEX-5000		5000	3250					366
MSEX-6000		6000	3900					440
MSEX-7000		7000	4550					512
MSEX-8000		8000	5200					586
MSEX-9000		9000	5850					660

Vent plugs

The typical design of vent plug is presented in Fig. 7. The plug has a safety valve. Its function is to release the internal gas when the pressure increases above 0.2 kg cm^{-2}, and to prevent the entry of external gases. The vent plug is also explosion resistant. The microporosity of the alumina filter imparts explosion resistance. Also, the inclusion of a very small space (1 mm) above the filter has caused remarkable progress in explosion-resistance characteristics; an example of such characteristics is given in Fig. 8.

Performance characteristics

Discharge characteristics

The discharge characteristics of a MSE-type battery are shown in Fig. 9. The rated capacity is defined at the 10-h and 1-h rates. The discharge characteristics at both the low and high rates are excellent. The volumetric energy density at the

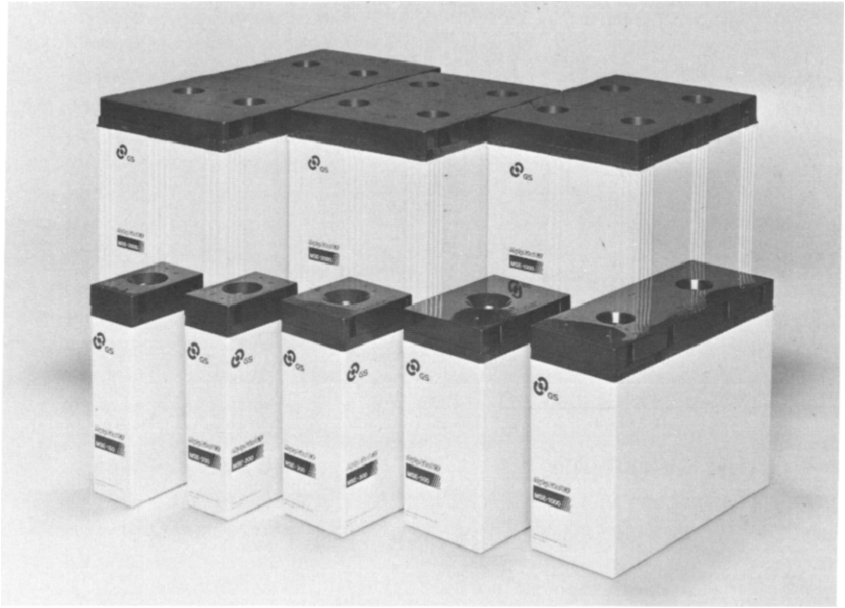

Fig. 3. MSE-type battery.

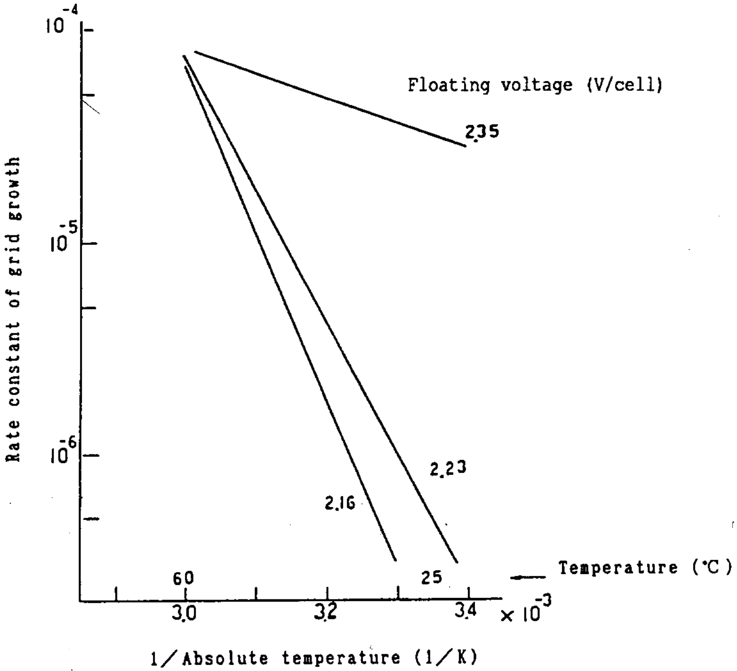

Fig. 4. Relationship between temperature and rate constant of grid growth.

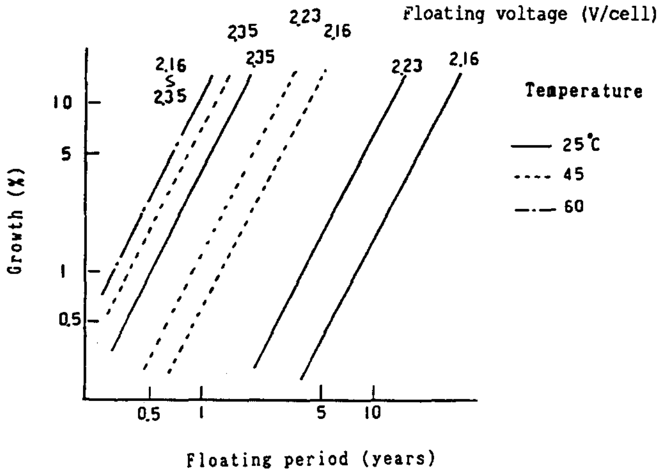

Fig. 5. Grid growth as a function of time.

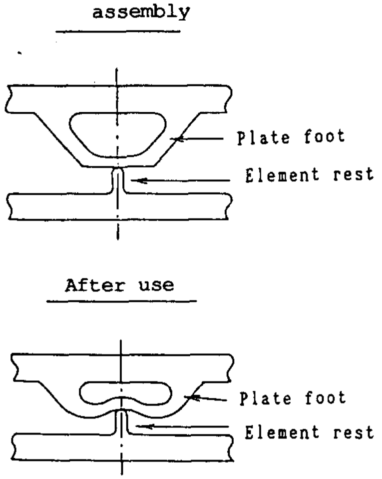

Fig. 6. Construction for absorbing positive-grid growth.

10-h rate is 67 Wh l^{-1}. This value is 1.4 times better than that for a HS-500(E) battery with catalyst plugs, viz., 47 Wh l^{-1}.

Charge characteristics

The relationship between overcharge current, terminal voltage and gas-recombination efficiency are shown in Fig. 10. The overcharge characteristics consist of the following three ranges:

(i) low-current range, where oxygen gas generated from the positive plates is totally absorbed;

(ii) high-current range, where oxygen gas generated from the positive plates is not completely absorbed, and hydrogen gas is generated from the negative plates, and

(iii) an intermediate range between (i) and (ii).

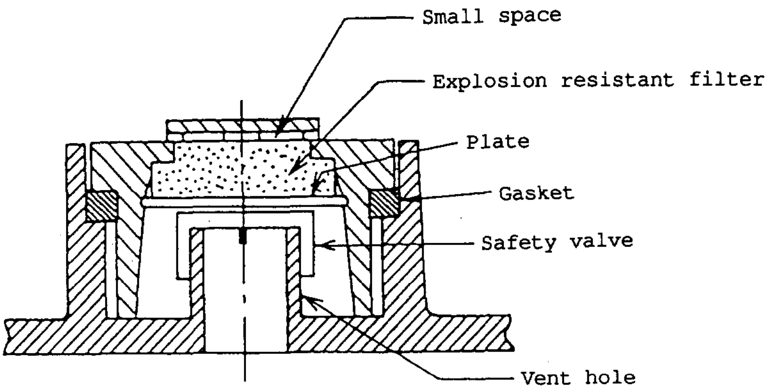

Fig. 7. Construction of vent plug.

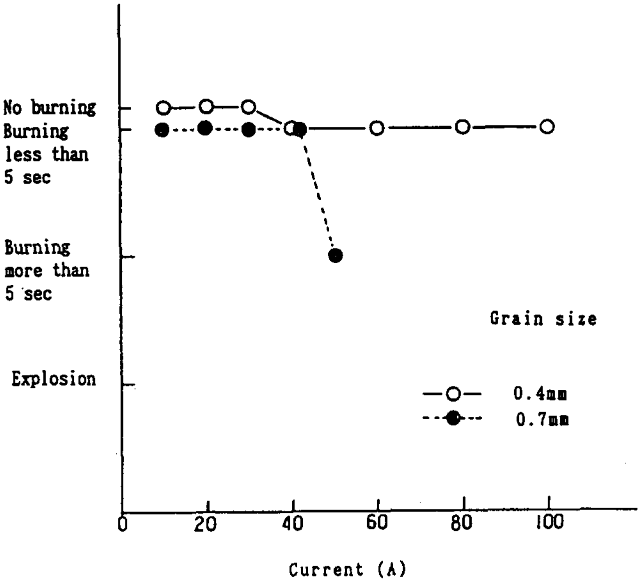

Fig. 8. Explosion resistance characteristics.

As shown in Fig. 10, the gas-recombination efficiency is 100% in range (i). In this case, the floating charge is not operative in range (i). Normally, the floating charge is set in range (i) at 2.23 V/cell.

Electrolyte stratification

Retainer-type, sealed batteries absorb and keep the electrolyte in the separators and the plates. The electrolyte is semi-fixed and is, therefore, unlikely to become stratified. Once stratified, however, it is more difficult to be made uniform over the height of the cell. This is a weak point of this design of battery. In order to hinder electrolyte stratification, a small amount of silica is added to make the electrolyte more viscous. The degree of stratification is evaluated by the following criteria:

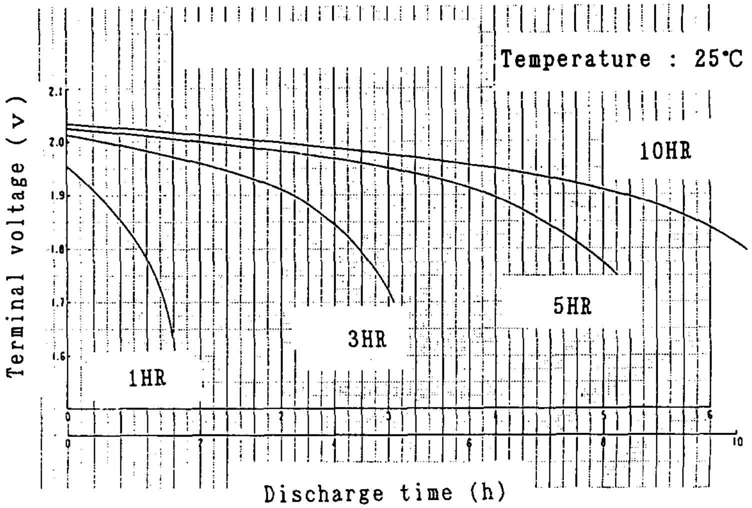

Fig. 9. Discharge characteristics of a MSE-type of battery.

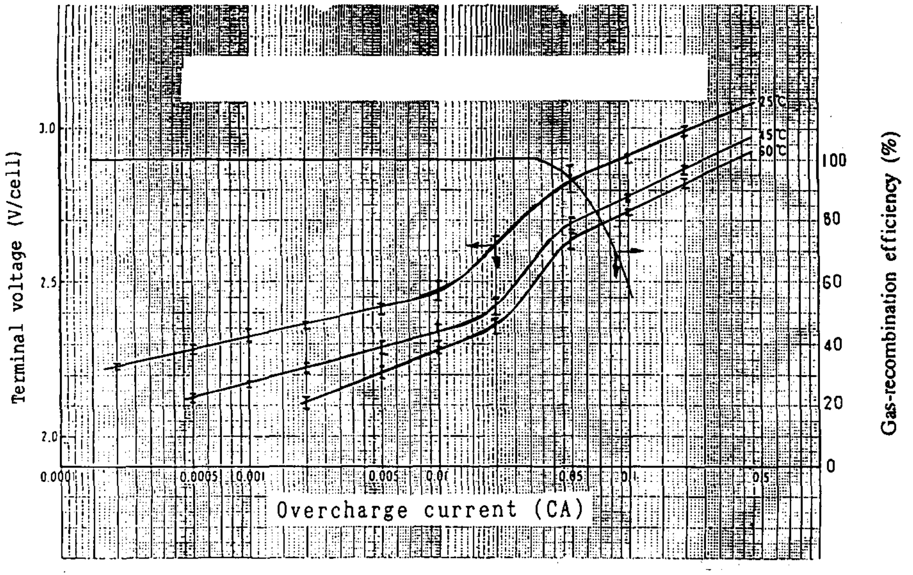

Fig. 10. Charge characteristics and gas-recombination efficiency of a MSE-type of battery.

(i) discharge 0.1C A (final voltage = 1.8 V/cell);

(ii) charge 2.30 V/cell (max. 0.1*C* A) for 48 h.

With these conditions, the relation between capacity and electrolyte concentrations in the upper and lower zones during charging and discharging is as shown in Fig. 11. In conventional retainer-type batteries, 20% of capacity is lost after 30 cycles, but in MSE-type batteries the decline in capacity is negligible.

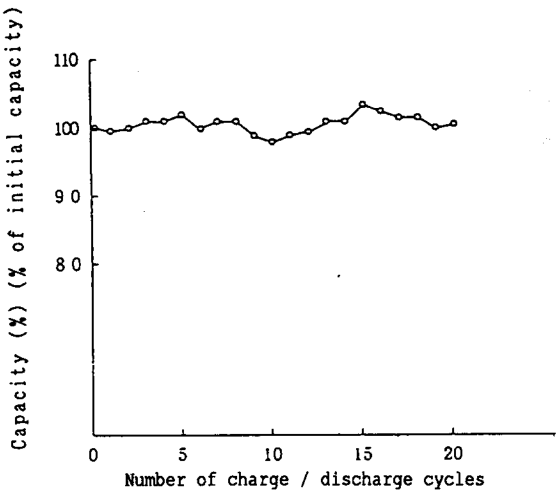

Fig. 11. Results of electrolyte stratification test conducted at 25 °C.

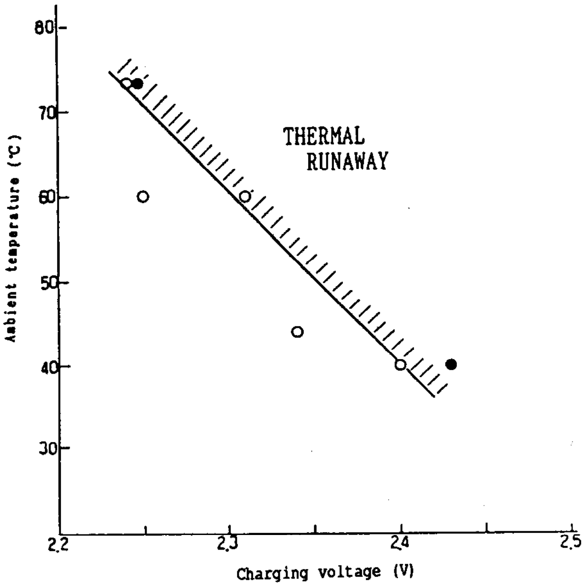

Fig. 12. Results of thermal runaway test. Inner temperature of cell: (○) <80 °C; (●) >80 °C.

Thermal runaway

The upper limit condition for thermal runaway in MSE-type batteries has been studied by taking the charging voltage and the ambient temperature as control parameters. The condition for thermal runaway should be defined as a rapid rise in battery temperature. In practice, the batteries temperature become greater than the heat resistance of the container, viz., 90 °C. Therefore, the condition for thermal runaway is taken as a temperature of >80 °C. The results from a thermal runaway test for

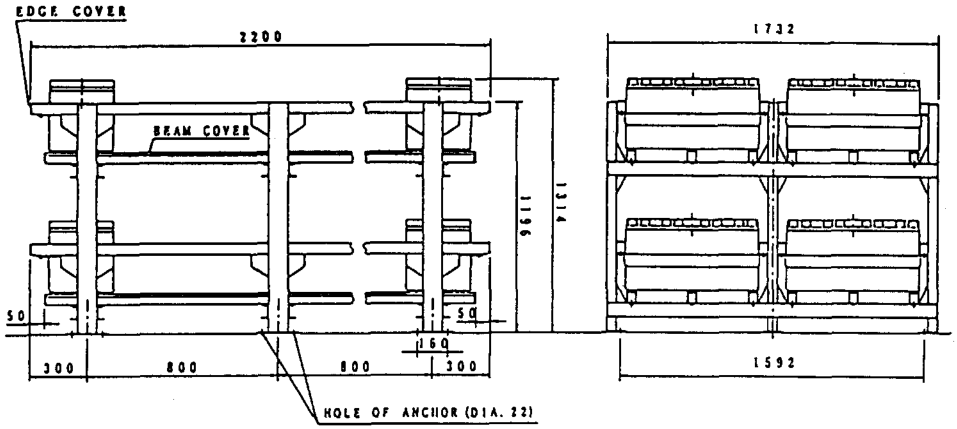

Fig. 13. Rack systems for MSE-300 batteries.

a MSE-3000 battery, which has the poorest value of radiation, are presented in Fig. 12. It can be seen that the higher the charging voltage, the higher is the ambient temperature and the easier it is for thermal runaway to occur. In case of a normal float voltage of 2.23 V/cell, the heat generation is small and thermal runaway will not take place at ambient temperatures less than 76 °C.

New trials with battery assemblies

Batteries have been generally installed on earthquake-proof racks. The racks are designed to endure an 1*G* of earthquake vibration. Examples of racks for assemblies of 24 MSE-3000 batteries are shown in Fig. 13.

As the electrolyte of the MSE type of battery is non-fluid, the units can be installed horizontally. By virtue of this advantage, we have developed a new type of battery assembly for NTT. This is as follows. Batteries using polypropylene containers are installed in channel steel frames that reinforce the containers. By connecting upper and lower units and left and right units, a set of batteries is assembled. Figure 14 shows a 3000 Ah unit and the assembled battery units are shown schematically in Fig. 15. The units are connected upper and lower on each side by using nuts and bolts. The upper and lower terminals of each cell are connected in series in the units with connecting plates. Six cells on each top and bottom step are connected side-by-side to give uniform pressure. An actual example of such a battery assembly is shown in Fig. 16. The maximum number of steps that can be used practically is 4, and it has been confirmed that the frame can endure 1.2*G*.

Summary

With the adoption of valve-regulated batteries by NTT, sealing of batteries has been promoted for a wide range of stationary applications, such as CVCF, communication, controlling, etc. The VRBs have several advantages including no need for an equalizing charge and the addition of water. On the other hand, they have disadvantages for example, it is not possible to measure the specific gravity of the electrolyte nor to view the inside of the batteries; these features are available with flooded-electrolyte batteries. Thus, it is necessary to develop effective methods for measuring how close

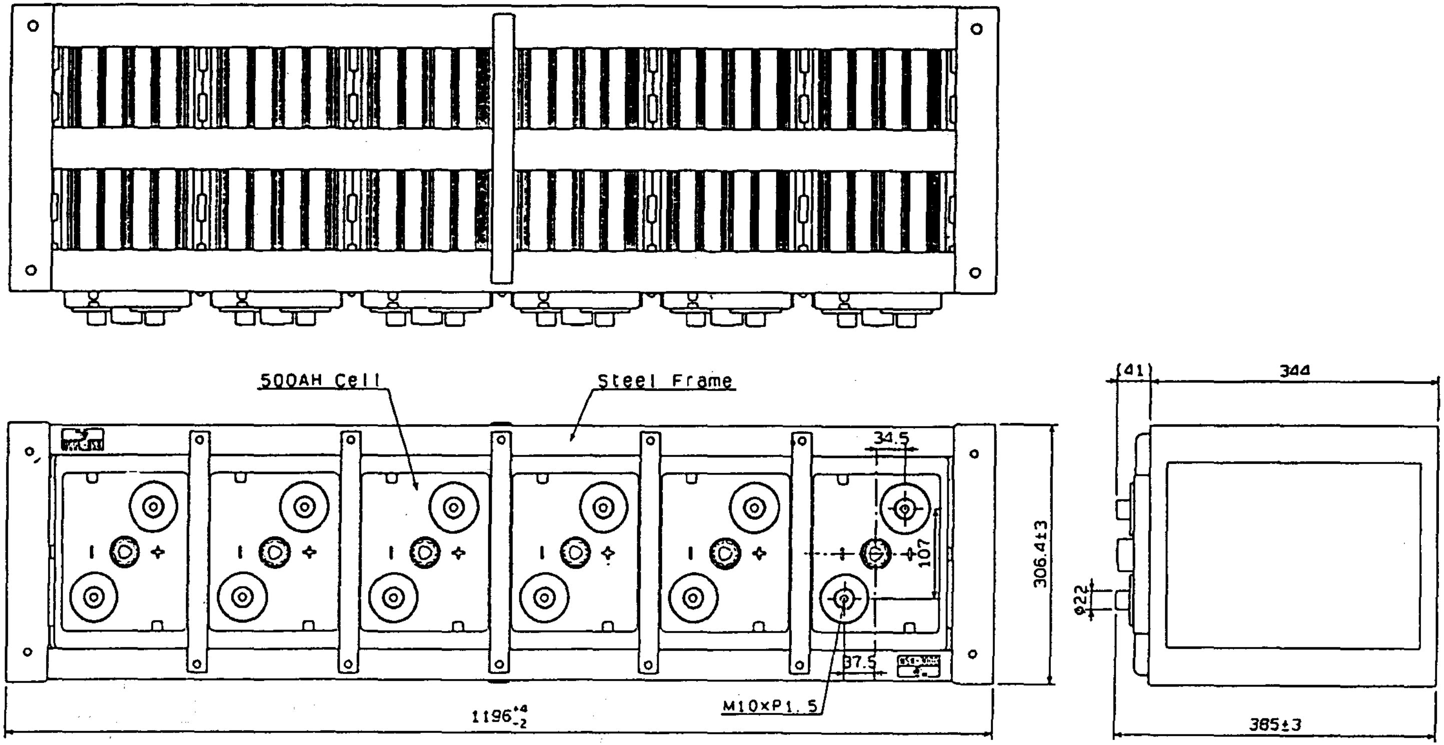

Fig. 14. Construction of unit batteries (3000 Ah).

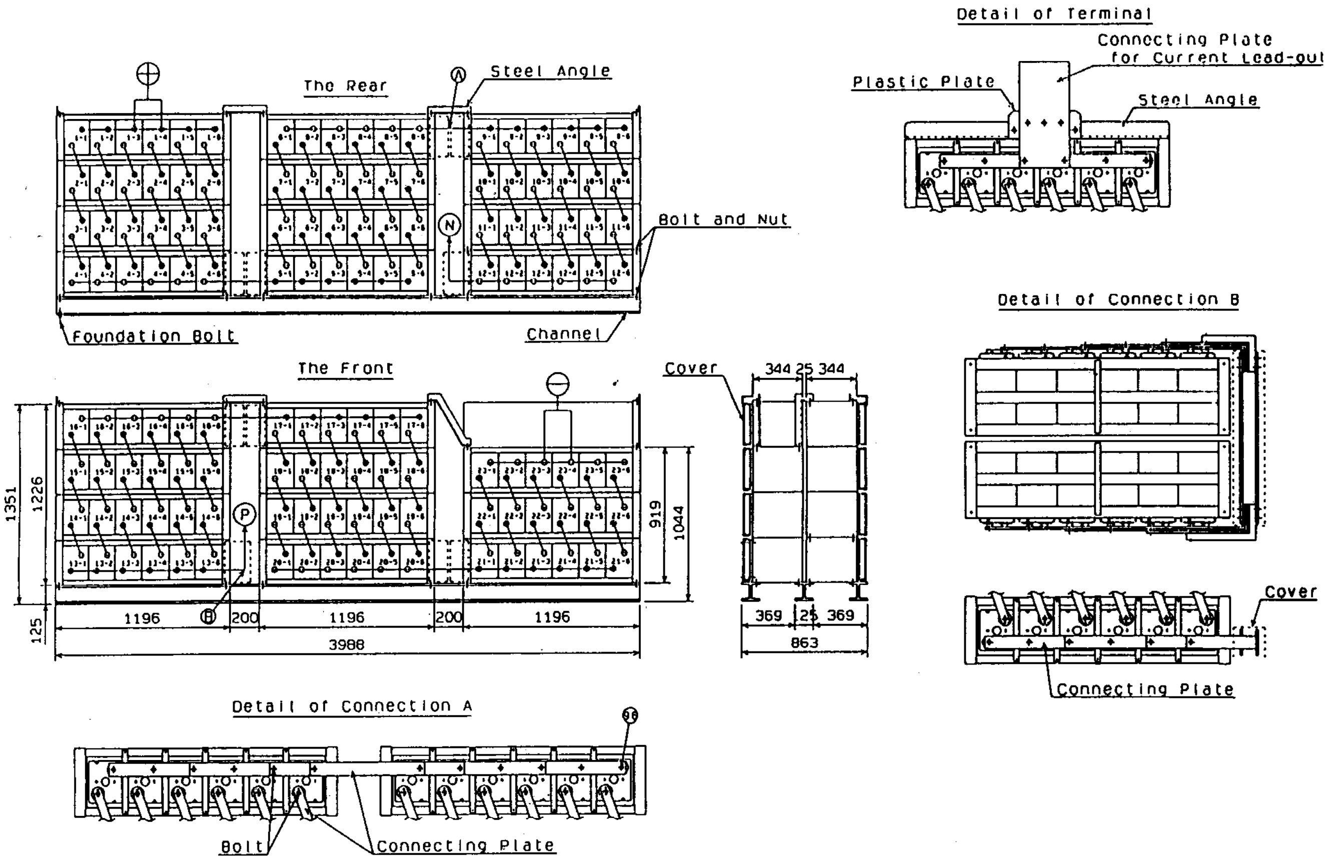

Fig. 15. Assembled unit of 23 batteries (3000 Ah).

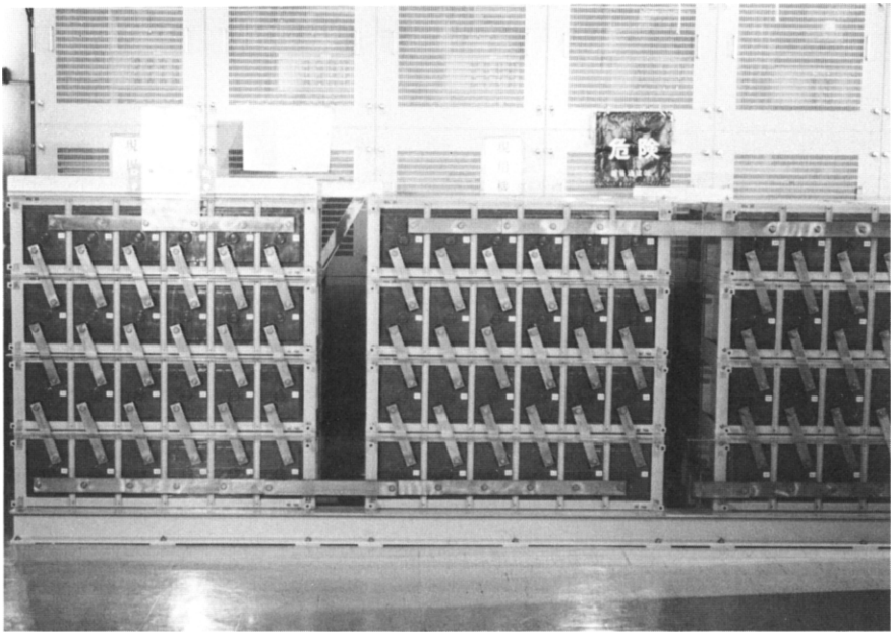

Fig. 16. Practical example of a unit of 23 batteries (3000 Ah).

a battery is coming to the end of its life. For VRBs to be used widely and steadily for stationary batteries with good reliability, it is essential to find precise methods for determining battery state-of-health.

References

1 A.G. Cannone, D.O. Feder and R.V. Biagetti, *Bell Syst. Tech. J.*, (1970) 1279.