# CHAPTER 3

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# CHAPTER .3

## LEAD-ACID BATTERIES

In this chapter the solar photovoltaic system designer can obtain a brief summary of the electrochemical reactions in an operating lead-acid battery, various construction types, operating characteristics, design and operating procedures controlling life of the battery, and maintenance and safety procedures.

## CELL DESIGN AND THEORY

In a lead-acid cell the active materials are lead dioxide ($PbO_2$) in the positive plate, sponge lead (Pb) in the negative plate, and a solution of sulfuric acid ($H_2SO_4$) in water as the electrolyte. The chemical reaction during discharge and recharge is normally written:

$$PbO_2 + Pb + 2H_2SO_4 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} 2PbSO_4 + 2H_2O$$
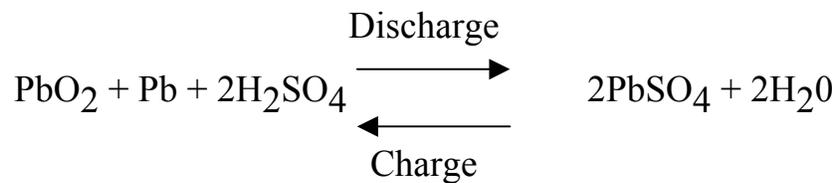
This reaction gives the ideal proportions by weight of the reactants to deliver capacity at a very low discharge rate when the amounts of $PbO_2$, lead and sulfuric acid would be simultaneously depleted to zero. In actual practice the reactions during discharge are not carried to completion, and the theoretical capacity 26.805 Ah per chemical equivalent of reactant is never delivered.

Life is limited normally by the positive plate which is least efficient. An excess of negative active material (Pb) is designed into the negative plate to extend wet life and cycle life. An excess of sulfuric acid is ,also present in the electrolyte in most cells to maintain proper acidity for long life.

As discharge continues, cell internal resistance increases and the cell voltage falls to an unusable value before more than 30-40 percent of the limiting positive active material is converted from $PbO_2$ to $PbSO_4$.

In each cell the manufacturer attempts to reduce excess or reserve active materials to control cost. In many applications the cell designer has a goal of maximum energy output per unit weight and per unit volume of total cell. Consequently, some cell designs may become acid limited if the discharge rate is at an amperage below the anticipated cell design range.

LEAD-ACID BATTERY CONSTRUCTION TYPES

Lead-acid battery types which are now commercially available are classified by type of positive plate:
- Manchex
- Tubular positive plate
- Pasted flat plate

The alloy used in the positive plate grid varies and is responsible for the following sub-types: (1) lead-antimony; (2) lead-calcium; and (3) pure lead (other alloys are also used, such as tin, cadmium, and rare earths). Lead-antimony cells are recommended for applications requiring very long life under cycling regimes discharging to depths greater than 20% of their rated capacity. Lead-calcium and pure lead cells are recommended for float and shallow cycling service where average discharge depth is less than 20%. Pure lead alloy cell types are used when very low charged stand loss is a requirement in the application and occasional deep cycles are expected. Negative plates in all lead-acid cells are the flat pasted type.

Manchex Type

The Manchex type is shown in Figure 3-1. The grid is cast with low antimony lead alloy. The button or rosette is a pure lead ribbon which is serrated and rolled into a spiral form. These in turn are pressed or wedged into the holes of the grid. The surface of the buttons is oxidized to $PbO_2$ for the positive active material.

The grid is quite heavy and therefore gives long life, particularly in standby type service with moderate cycling such as railroad signal and utility application. A life of 25 years is normal for utility operation.
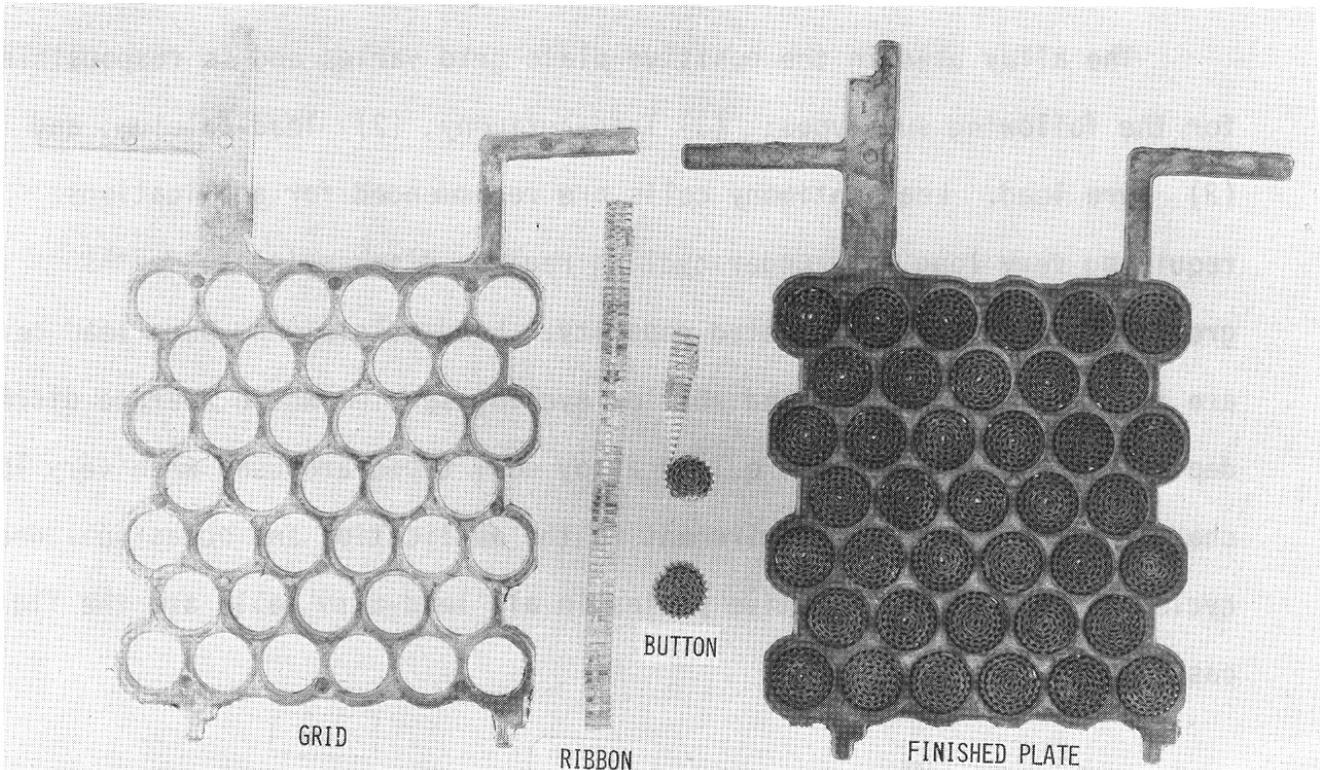
Figure 3-1 - Manchex Type

Tubular Positive Type

This plate construction is shown in Figure 3-2. The grid, which is the current conducting member, is a series of low antimony lead spines.  Woven or porous plastic or glass material is used for the tubing which is centered on each spine. Then the active material is added and the ends are sealed.

This type of battery is generally used in lift truck and material handling applications where deep cycling routines require an average discharge depth of 70 to 80 percent of the 6-hour rated capacity and recharge within an 8-hour period. Battery life is about six years in a lift truck application requiring an 80% depth discharge each working

day 250 days per year or 1500 cycles. Tubular positive batteries are also used for on-the-road diesel starting. In Europe they have wide use in utility switch gear. In 20% depth, shallow cycling regimes 4,000 or cycles can be obtained when multi-cycles per day are performed.

The tubu1ar positive battery gives exce11ent discharge performance from diesel starting rates to the 24-hour rate. It has excellent high charging characteristics, good standby life, and is a very versatile cell type.

Tubular batteries are normally produced in one plate thickness. Variations in capacity are obtained by increasing the number of tubes per plate and/or by varying the tube (or plate) height.

TUBES  SPINES  BOTTOM BAR  FINISHED PLATE
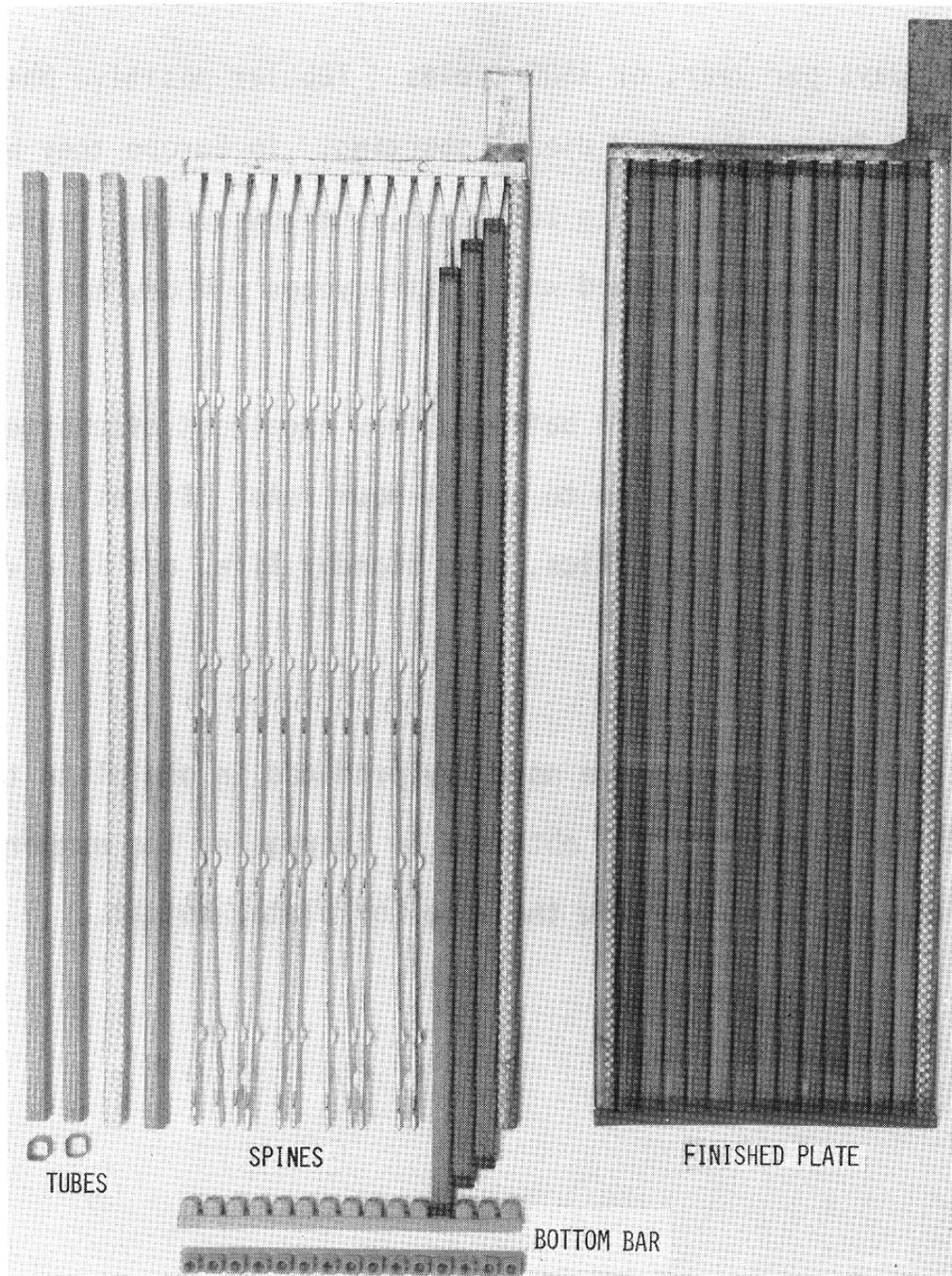
Figure 3-2 - Tubular Positive Type

Flat Pasted Plate Type

A typical pasted plate construction is shown in Figure 3-3. The lattice grid is cast with pure lead, lead-calcium or lead-antimony depending on the size of the plate and the application.

Active material is applied as a wet paste and the plate is then cured, dried and formed.

When used in repetitive deep cycle operation. such as fork lift truck handling. glass mats and a perforated plastic retainer are wrapped around the positive plate to minimize the loss of positive active material and to obtain good cycle life. This wrap performs the same function as the retainer tube of tubular positive plates.



| GRID | PARTIALLY WRAPPED PLATE | FINISHED PLATE |
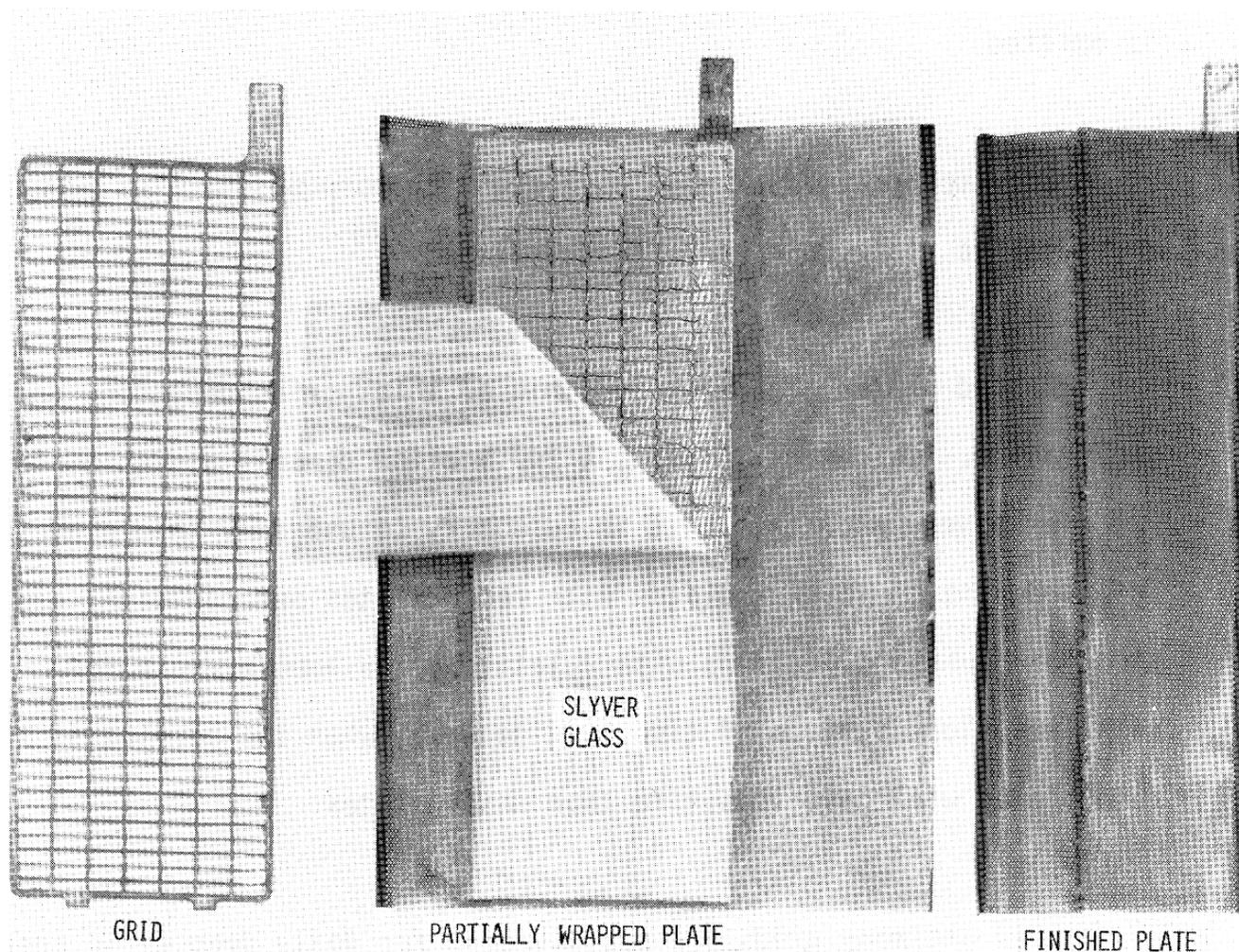
Figure 3-3 - Flat Pasted Plate

During the last stages of charge, oxygen gas is formed at the surface of positive plates. The agitation of gas bubbles streaming from the surface of exposed grid and active material tends to erode the active

material which is shed through the glass retainer and settles into the sediment space at the bottom of each cell.

In light cycle or in float service this positive active material shedding is not the major failure mechanism. In these applications the glass mat retainer is lighter, thinner, and the perforated outer wrap is omitted.

Both designs depend upon a ribbed microporous separator adjacent the negative plate to achieve longest life.

Pasted plates are made with thin or thick grids depending on the application. In general, when the application demands a high ampere rate for a very short time, it is customary to use many thin plates in a container. Thicker plates with fewer plates per container are used for those applications with relatively low ampere drain for relatively long periods of time. In general, when the service is similar, thin plates will give less life than thick plates.

Lead-antimony grids are usually used for daily deep cycle operation. Grids with a lead-calcium alloy or pure lead can also be cycled; but repetitive cycles are restricted to a depth less than 20% of capacity plus infrequent operations with a discharge depth as high as 50-60% of the 6-hour to 8-hour rated capacity.

The real advantage to cells with lead-calcium and pure lead positive grids is in standby operation when long periods of float are expected between power outages and discharge cycles. In general, pure lead designs offer better cycle life than lead-calcium, but poorer mechanical strength of the plates. During these periods the cells are maintained at a constant charge voltage, and the charge current required to maintain lead-calcium and pure lead positive grid cells at voltage is much lower than the lead-antimony grid. A reduction in float charge current reduces water loss and the maintenance cost of adding water to battery cells

LEAD-ACID CELL DISCHARGE CHARACTERISTICS

In the lead-acid system the average voltage during discharge, the capacity delivered, and the energy output are dependent upon the discharge current. A typical example is given in Figure 3-4.

[Figure and text continued on the following page]
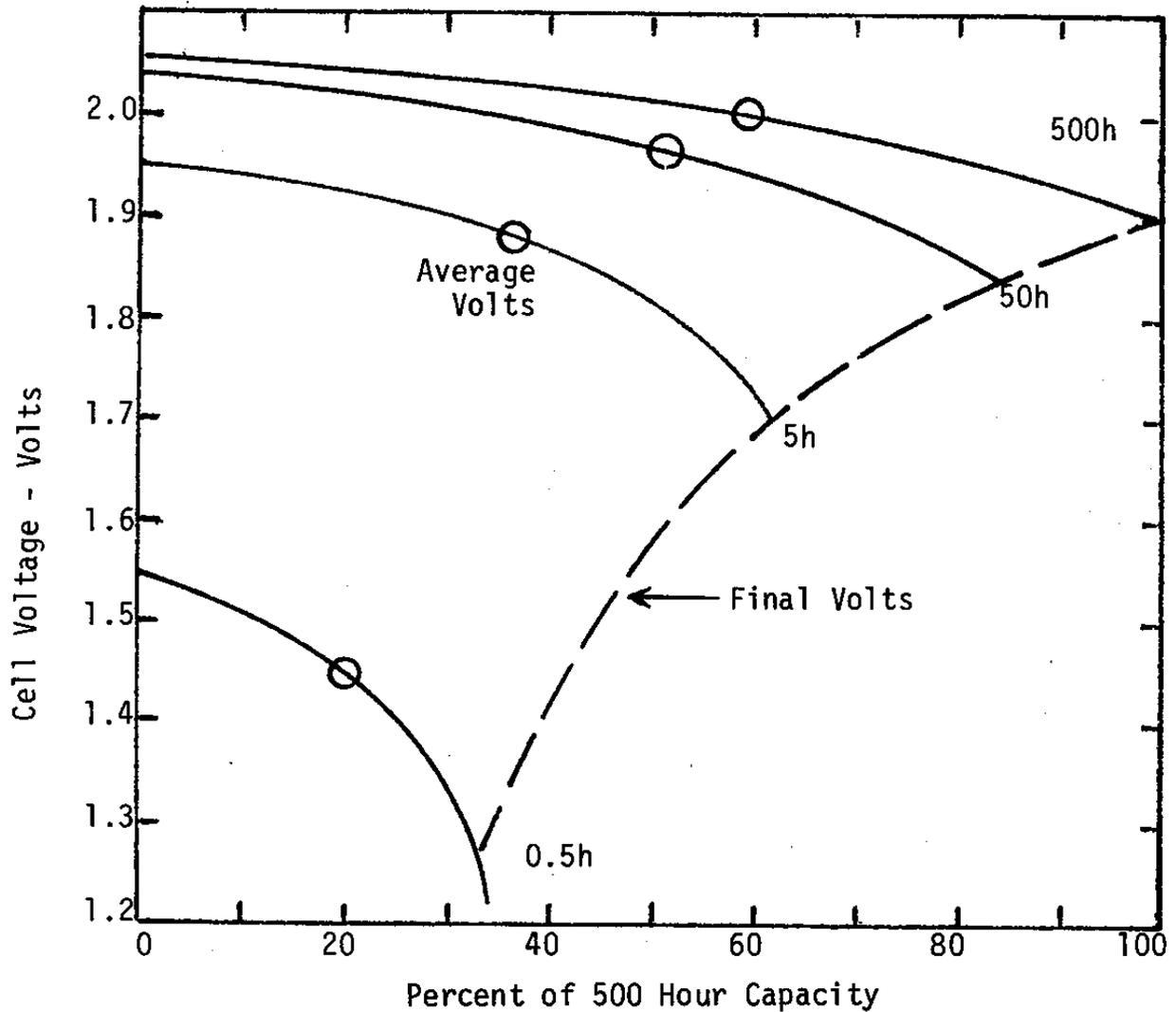
Figure 3-4 - Effect of Discharge Rate on Output at 25°C

Each cell type, size and design will vary from Figure 3-4 depending upon the cell design parameters such as the number and thickness of the plates, active material density, volume and specific gravity of the electrolyte, and the plate grid and separator system designs.

Useful capacity from a cell is normally defined in terms of discharge hours or ampere-hours to the 'knee' of the discharge curve or final voltage. Beyond this point, little capacity is available. As shown in Figure 3-4, the knee does vary with the discharge rate and

represents the low voltage limit for the various rates. Energy output for each rate is the integral of cell power output (volts x amperes) between discharge time zero and the time corresponding to the knee of the discharge curve, or final voltage. Average discharge voltages can be calculated by dividing the energy output in watt-hours by the corresponding capacity in ampere-hours. As an approximation the average voltage is the voltage at 0.6 times the discharge time to the final voltage.

Discharges may be terminated at some voltage higher than the knee of the curve. This voltage is called the discharge end voltage. It may be dictated by the test equipment, photovoltaic system components, or by an arbitrary choice. This end voltage may be a constant independent of rate of discharge.

When the end voltage is higher than the final voltage, the cell size becomes larger, and the capacity not used becomes a reserve capacity which can extend cycle life.

In designing a battery for a particular photovoltaic system, the number of battery cells needed in series can be determined by dividing the lowest specified system voltage by the final voltage of the cell selected when discharged at the required system rate for that cell.

This minimum number of cells in series assures the battery discharge voltage will be at or above the specified minimum voltage in the system voltage window.

Figure 3-5 is one method of displaying cell performance characteristics. The product of a particular current in amperes and the corresponding discharge time in hours read from this plot gives the rated or experimental mean capacity at any rate covered by the curve. Times to other end voltages are often shown as a family of similar curves.

The corresponding initial, average and final voltages are plotted for each discharge time. The system designer can obtain from this single figure a good estimate of the discharge time, the discharge capacity and the energy output (product of average voltage and capacity) at any discharge rate covered by the data. Table 3-1 summarizes a typical set of characteristics calculated from the data of Figure 3-5.

TABLE 3-1

Cell Discharge Characteristics

| Discharge Time | Discharge Current | Discharge Capacity | Cell Initial Volts | Cell Average Volts | Cell Final Volts | Energy Output |
|---|---|---|---|---|---|---|
| h | A | Ah | V | V | V | Wh |
| 100 | 20 | 2000 | 2.09 | 1.99 | 1.80 | 3980 |
| 50 | 38 | 1900 | 2.08 | 1.97 | 1.78 | 3740 |
| 10 | 160 | 1600 | 2.05 | 1.95 | 1.75 | 3120 |
| 5 | 290 | 1450 | 1.89 | 1.92 | 1.70 | 2780 |
| 1 | 1000 | 1000 | 1.77 | 1.60 | 1.48 | 1600 |
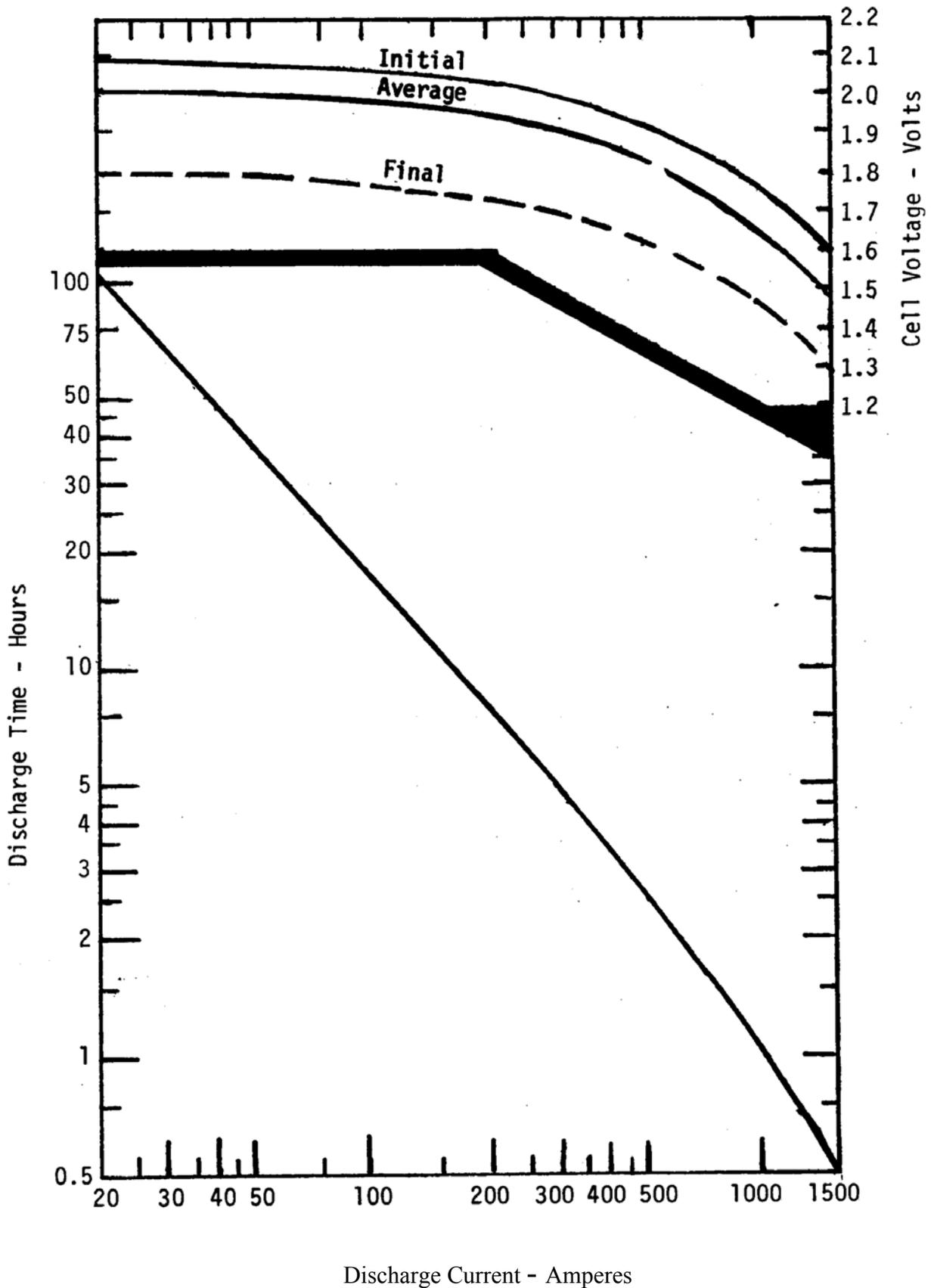
Discharge Current - Amperes

Figure 3-5 - Cell Discharge Characteristics

EFFECT OF SPECIFIC GRAVITY OF ELECTROLYTE AND OPERATING TEMPERATURE

Another design consideration is the specific gravity of the electrolyte. Discharge capacity in any single cycle increases with an increase in specific gravity. The amount of increase will depend upon the discharge rate, the active material density and the ratio of active material to acid electrolyte.

When specific gravity is increased, charge standlife and cycle 1ife will be decreased. Estimates of this loss can be made by the battery manufacturer for the particular battery under consideration.

The specific gravity increases during recharge and decreases during discharge. At low operating temperatures, the specific gravity can become so low that its freezing temperature is reached terminating the discharge prematurely and interfering with the subsequent charge. Freezing points are shown in Table 3-2 for various concentrations of acid electrolyte.

## TABLE 3-2

### Freezing Points of Sulfuric Acid Electrolyte

| Specific Gravity 25°C/25°C | at freezing temperature | Freezing Point °C | °F |
|---|---|---|---|
| 1 | 1.003 | 0 | 32 |
| 1.05 | 1.06 | -3 | 26 |
| 1.1 | 1.115 | -8 | 18 |
| 1.15 | 1.175 | -15 | 5 |
| 1.2 | 1.235 | -27 | -17 |
| 1.25 | 1.305 | -52 | -61 |
| 1.3 | 1.365 | -70 | -95 |
| 1.35 | 1.405 | -49 | -56 |

Before selecting cell capacity and the specific gravity of acid in the cell, the photovoltaic system designer must consider the effects of environment temperature on cell operating temperature. In some cases the low voltage limit at the end of the deepest discharge may be established just above that voltage corresponding to an end of discharge specific gravity that could freeze.

Figure 3-6 shows the effect of operating temperature on discharge capacity for three electrolyte gravities in a lead-calcium battery selected for a solar photovoltaic system. At the 1,8 and 500 hour rates of discharge only the highest gravity acid can be used below -18°C (0°F) without danger of freezing.
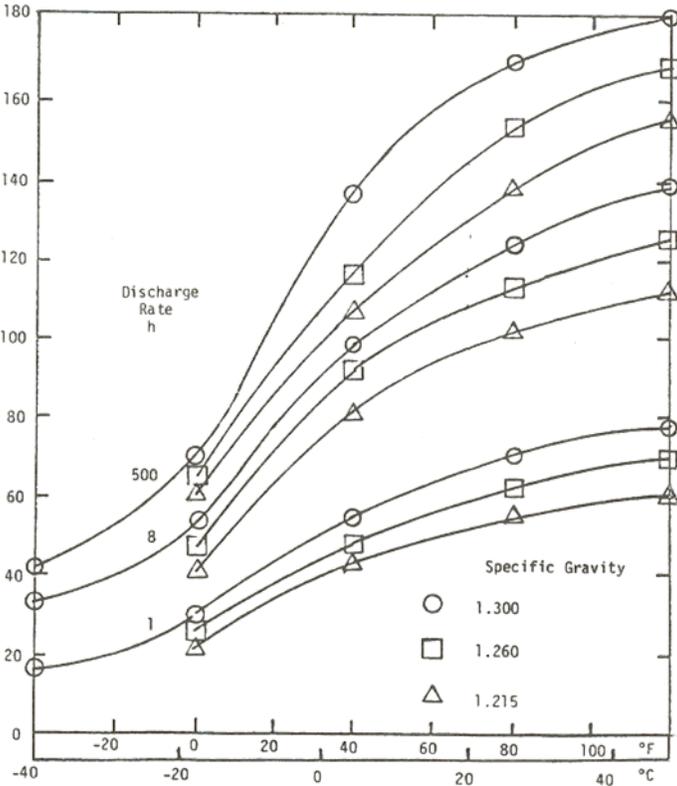


Figure 3-6 – Effect of Discharge Temperature Rate and Specific Gravity on Output Capacity
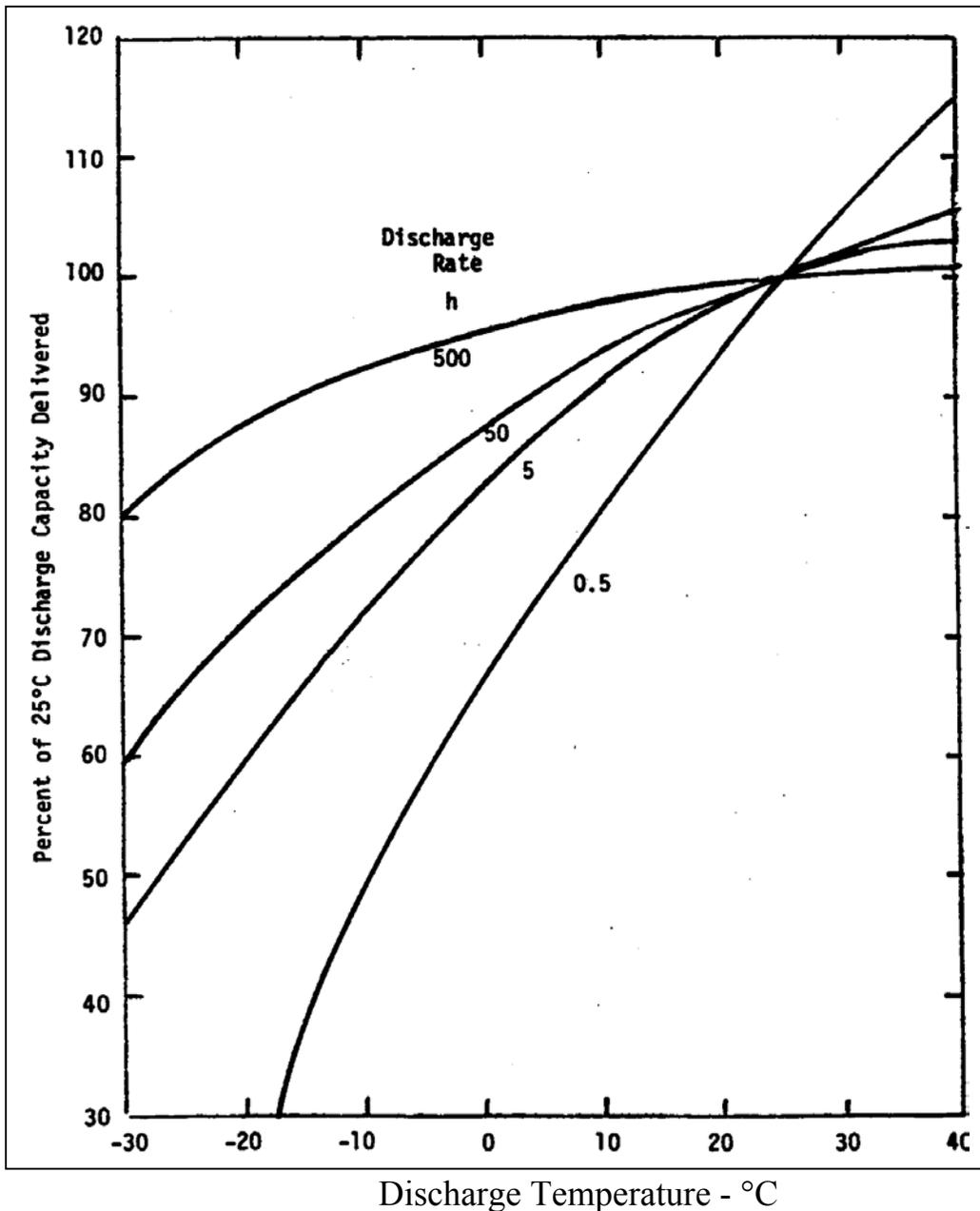
Figure 3-7 - Effect of Discharge Rate and Temperature on
25°C Discharge Capacity

For any particular specific gravity, the interaction of cell electrolyte temperature and discharge rate on output capacity is shown in Figure 3-7. The loss in capacity is particularly severe at high current rates of discharge and low temperature. At high temperatures, the gain in capacity is highest at the highest current rates of discharge.

METHODS OF CHARGING LEAD-ACID BATTERIES

Proper recharging between discharges is an important key to obtaining optimum life from any lead-acid battery.

Some of the rules for proper charging are given below and apply to all types of lead-acid batteries:

(1)     The charge current at the start of recharge can be any va1ue that does not produce an average ce11 vo1tage in the battery string greater than the gassing voltage. High recharge rates are less efficient.  However $I^2R$ losses in the battery and cabling must be considered to prevent overheating.  This is generally not a major factor in renewable energy systems unless a large generator is part of the system.

(2)     During the recharge and until 100 percent of the previous discharge capacity has been returned, the ampere rate should be controlled to maintain the gassing voltage, or lower, but as close to the gassing voltage as possible to minimize charge time.

(3)     When 100 percent of the discharged capacity has been returned under the above voltage control, the charge rate will have normally decayed to the charge "finishing" rate.   Finish the charge at a constant current 00 higher than this rate, normally 5A/100 Ah at the 5-hour rated capacity.

To achieve these rules there are a number of practices for charging lead-acid batteries.

These charging methods are commonly given the following names:

(1)     Constant current - one current rate

(2)     Constant current - multiple decreasing current steps

(3)     Constant potential

(4)     Modified constant potential with constant initial current

(5)     modified constant potential with a constant finish rate

(6)     modified constant potential with a constant start and finish rate

(7)     taper charge (ferroresonant type chargers)

(8)     Charging thit photovoltaics which is a variable constant current. Various algorithms

In normal industrial field application, the charging methods are numbers 4,6 and 7. Number 4 charging is found in on-the-road vehicles, utility, telephone, and uninterruptible power system applications. The charge circuit has a current limit and this value is maintained until a predetermined voltage is reached. Then the voltage is maintained constant until the battery is called on to discharge. Decisions must be made regarding the current limit and the constant voltage value. This is influenced by the time interval when the battery is at the constant voltage and in a 100 percent state-of-charge. For this "float" type operation with the battery always on charge, a low charge current is desirable to minimize overcharge, grid corrosion associated with overcharge, water loss by electrolysis of the electrolyte, and maintenance to replace this water. To achieve a

full recharge with a low constant potential requires the proper selection of the starting current and this selection should be made in consultation with the battery manufacturer.

Charging method number 6 is common for deep cycling batteries for fork lift trucks used in material handling.  Each work shift requires a discharge at the 6-hour rate to a depth of 80 percent of the 6-hour rated capacity, and the recharge is normally completed in an 8-hour period.  The charger is set for the constant potential of 2.39 volts per cell (the gassing voltage) and the starting current is limited to 16-20 amperes per 100 Ah of the rated 6-hour ampere-hour capacity.  This initial current is maintained constant until the average cell voltage in the battery reaches 2.39 volts.  The current decays at constant voltage to the finishing rate of 4.5-5 A per 100 Ah which is then maintained to the end of charge.  Total charge time is controlled by a timer.  The time of charge is selected to assure a recharge input capacity of a predetermined percent of the previous output - normally 110 to 120 percent, or 10-20 percent overcharge.  The 8-hour charging time can be reduced by increasing the initial current limit rate.

Charging method number 7 is a modification of method 6 to reduce equipment cost. The initial rate is limited, but the taper of voltage and current is such that the 2.39 volts per cell at 25°C is exceeded prior to the 100 percent return of the discharge ampere hours.

This method does result in gassing at the critical point of recharge, and cell temperature is increased. The degree of gassing and temperature rise is a variable depending upon the charger design, and battery life can be degraded from excessive battery temperature and overcharge gassing.

End of charge is often controlled by a fixed voltage rather than a fixed current. Therefore, when a new battery has a high counter EMF, this final charge rate is low, and the battery often does not receive sufficient charge within the time period allotted to maintain the optimum charged state. During the latter part of life when the counter EMF is low, the charging rate is higher than the normal finishing rate, so the battery receives excessive charge which degrades life. Thus the taper charger does degrade battery life but usually has less controls, and parts and is therefore a less expensive circuit.

For photovoltaic battery systems designed for optimum life, charging control and regulation circuits should produce a pattern of voltage and current equivalent to the best industrial circuits. Modified constant potential charging methods 4 and 6 are preferred. Optimum control to maximize life and energy output from the battery is best achieved when the depth of discharge and the time for recharge is predetermined and repetitious, a condition not always possible in solar PV applications.

Method 8- Most photovoltaic systems are designed for 5 days (or more) of autonomy (essentially sunless days). As a result, charge rates of 3.5 amperes per 100 AH of capacity are common. The batteries are charged at maximum available current until they are nearlyy charged and reach the gassing level. At this time the various algorithms are employed to limit charging. The specific methodology and set points varry with the charge controller manufacturer. It is recommended to pick a charge controller that can be optimized for the type and chemistry of the battery and the anticipated operating temperature range.

Selection of the battery voltage at top-of-charge and the number of cells in a series string is critical to successful operation and maximum life.

The photovoltaic system has a voltage window, a voltage range from the lowest to the highest limits acceptable to meet operating requirements. The number of cells in series in the battery subsystem times the average cell discharge end voltage must be greater than the lower voltage window limit.

Where this number of cells in series is used to set the upper voltage limit in the window, the calculation may show the upper voltage limit is not sufficiently high to charge the battery in the allotted time. A compromise must then be made.

A key rule is that the cell gassing voltage should not be exceeded except during the finishing step of charge. The gassing voltage is the voltage at which the predominant reaction consuming charge current is electrolysis of water in the electrolyte with evolution of oxygen at the positive plates and hydrogen at the negative plates. Gassing voltage decreases with increasing electrolyte temperature. See Table 3-3 Note: Electrolyte temperature is not the same as ambient room temperature until after an extended exposure of the battery to ambient conditions. In PV systems the electrolyte temperature is usually close to (neglecting termal time lags) room temperature due to relatively low charge and discharge rates represented by many days of autonomy.

Table 3-3

Correction Factors for Cell Gassing Voltage

| Electrolyte Temperature | | Cell Gassing Voltage | Correction Factor |
|---|---|---|---|
| °C | °F | Volts | Volts |
| ---------- | --------- | ---------- | --------- |
| 50 | 122 | 2.300 | -0.090 |
| 40 | 104 | 2.330 | -0.060 |
| 30 | 86 | 2.365 | -0.025 |
| 25 | 77 | 2.390 | 0 |
| 20 | 68 | 2.415 | +.025 |
| 10 | 50 | 2.470 | +.080 |
| 0 | 32 | 2.540 | +.150 |
| -10 | 14 | 2.650 | +.260 |
| -20 | -4 | 2.970 | +.508 |

When designing the system for 25°C operation, the constant charge potential for the battery subsystem would be 2.39 volts times the number of cells in series. If system temperature exceeds 25°C, the cells will gas and life of the subsystem will be decreased. If system temperature falls below 25°C, charge acceptance will be decreased requiring a longer charge time to sustain the same state-of-charge.

Charging controls and regulator circuits must therefore include a temperature compensation feature to correct the constant charge voltage to the 25°C equivalent using the correction factors shown in Table 3-3. Without the temperature compensating circuit, a battery charge circuit adjusted to 2.39 volts per cell at 25°C ambient would charge the battery at 0°C at an actual voltage of 2.24 volts per cell. To compensate +0.150 volts per cell must be added to the charge voltage as required by Table 3-3 to

achieve charge conditions equivalent to those at 25°C. Otherwise the lower actual voltage would substantially increase charge time or would prevent the desired state-of-charge from ever being reached.

For most lead-acid battery subsystems it is necessary that they be charged by voltage regulator circuits properly compensated for changes in operating temperature.

The number of cells in series is obtained by dividing the maximum system charge voltage by the maximum charge voltage in volts per cell specified by the cell manufacturer.

This maximum voltage is normally 2.60 - 2.65 volts per cell and is the maximum voltage the cell is allowed to reach during the finishing step of charge.

Table 3-4 gives an example of the calculation of the number of cells in series for a system voltage window and the voltage control during each charge step

TABLE 3-4

Battery Subsystem Voltage Ys. System Window
(200 - 300 Volts) -

| System Design Parameter | Unit | Value |
|---|---|---|
| Array Voltage Regulator Upper Limit | Volts | 300 (1) |
| Cell Charge Voltage Limit | Volts Per Cell | 2.60 |
| Number of Cells in Series String | Each | 115 |
| Cell Final Discharge Voltage Limit (5-h Discharge Rate) | Volts Per Cell | 1.70 |
| Battery Cut-out Setting | Volts | 200 |

This charging method has three steps and a dual voltage control:

| Step | Mode | Voltage control |
|------|------|-----------------|
| 1 | Initial Constant Current | 2.39 Volts Per Cell |
| 2 | Current Tapers to Finishing Rate | same |
| 3 | Finishing Rate Constant Current | 2.60 Volts Per Cell |

STRATIFICATION OF ELECTROLYTE IN CELLS

Stratification of acid electrolyte into levels of varying specific gravity can limit charge acceptance, discharge output and life unless understood and controlled during the charge process.

During a recharge, the oxidation of $PbSO_4$ to $PbO_2$ at the positive plates and the reduction of $PbSO_4$ to Pb at the negative plates forms sulfuric acid of higher concentration in the pores of the positive plates.
This higher density acid settles to the bottom of the cell giving higher specific gravity acid near the bottom of the plates and lower specific gravity acid near the top of the plates. This stratification accumulates during non-gassing periods of charge.  During gassing periods of charge partial stirring is accomplished by gas bubbles formed at and rising along the surfaces of the plates and in the separator system.

During discharge, acid in the pores of the positives and near their surface is diluted; however, concentration gradients set up by longer charge periods are seldom compensated entirely during shorter discharge periods.

Diffusion processes to eliminate these concentration gradients are very slow, so stratification during repetitious cycling can become progressively greater.  Two methods for stratification control are by deliberate gassing of the plates during overcharge at the finishing rate or by stirring of cell electrolyte by air-lift pumps.  The degree of success in eliminating stratification is a function of cell design the design of the air-lift pump accessory system, and cell operating procedures.

Overcharge at the finishing rate may be increased to obtain the required electrolyte circulation after deep discharges. Very large, tall cells may require air-lift pumps which use an outside air pressure source to operate one or more air-lift pumps to circulate dense acid from the bottom to the top of the cell.

Correct electrolyte circulation can increase the utilization of positive and negative active material, increase capacity and energy output and increase life. In most solar photovoltaic systems which use shallower cells, adequate circulation is achieved by judicious control of the percent of overcharge.  A battery or knowledgeable systems engineer should participate in the system design and in setting up the operating procedures.

# SELECTION OF CHARGE CURRENTS

Selection of charge currents for the initial high rate and final low rate charge periods is complicated by the following restraints:

- Completing the charge in the required time

- Remaining within the voltage limits

- Charging at rates which restore discharge capacity without excessive temperature rise

Initial charge currents allowed range up to 20-25 A per 100 Ah at the rated 5-h capacity. Final or finishing constant charge current ranges from 3-5 A per 100 Ah at the rated 5-h capacity. During the last hours of charge at the finishing rate, cell charge voltage increases with increasing finishing rate. A finishing rate of 5 A per 100 Ah end-of-charge voltage for newly produced cells can vary from 2.5 to 2.90 volts at 25°C depending upon the cell design and composition of the grids and the active materials. As battery life progresses the end-of-charge voltage for pure lead and lead-calcium cells remains essentially constant. For lead-antimony cells the end-of-charge voltage decays progressively during their cycle life to values as low as 2.4 volts after 2000 deep cycles.

This characteristic explains a common practice of designing the lead-antimony battery subsystem around the average end-of-charge voltage of 2.40 to 2.45 volts for normal charging rates. Table 3-5 shows the results of this practice during battery life

**TABLE 3-5**

Effect of Age of Lead-Antimony Battery on End-of-Charge Current and Voltage

| Relative Age | End-of-Charge Current at 2.60VPC A/100 Ah | End-of-Charge Voltage at 5A/100 Ah Finishing Rate Volts | Remarks |
|---|---|---|---|
| New | 0.50 to 0.75 | 2.90 | Low current prolongs time of charge |
| 25 | 1.50 to 2.00 | 2.75 | |
| 75 | 4.5 to 5.50 | 2.60 | Desirable state |
| 100 (End-of-Life) | 13.5 to 16.5 | 2.45 | Extreme gassing and higher cell temperature shortens cell life. |

The conditions of Table 3-5 are the result of high rates of self-discharge from a high antimony alloy in the positive grid and in the negative grid. As cell design changes decrease this local action self-discharge loss, the change of end-of-charge voltage with battery life wi11 decrease.

Table 3-6 illustrates the effects of depth of discharge, initial charge rate and the finishing rate on charge time for the case of a modified constant potential charge with an initial constant charge rate of 16 or 20 A per 100 Ah and a constant finishing rate of 2.5 or 5 A per 100 Ah of 5-h rated capacity.

Note: Reviewers in 2002 can not confirm the validity of the values in Table 3-5. These are being left in the document only for historic reasons. Use this data at your own risk.

# TABLE 3-6

### Effect of Discharge Depth, Initial Charge Rate at 2.39 VPC and Finishing Rate on Charge Time

| Depth of Discharge % | Initial Charge Rate A/100Ah | Finishing Rate A/100Ah | Charge Time Hours to Return | |
|---|---|---|---|---|
| | | | 100% | 105% |
| 60 | 20 | 5 | 4.0 | 5.0 |
| 80 | 20 | 5 | 5.0 | 6.0 |
| 60 | 16 | 5 | 4.5 | 5.5 |
| 80 | 16 | 5 | 5.8 | 6.8 |
| 60 | 20 | 2.5 | 4.0 | 6.0 |
| 80 | 20 | 2.5 | 5.0 | 7.3 |
| 60 | 16 | 2.5 | **4.5** | 6.5 |
| 80 | 16 | 2.5 | 5.8 | 8.0 |

In Table 3-6 the reduction in the finishing rate from 5 to 2.5 A per 100 Ah would reduce the charging voltage of the battery by 80 to 100 mv per cell and the rate of cell temperature rise during the finishing period.

The effect of initial charge rate and charging voltage on charge time is shown in Table 3-7 for the case of a modified constant potential charge where the end-of-charge current is governed by the preset potential.

**TABLE 3-7**

Effect of Initial Charge Current and Constant Potential on Charge
Time for 60 and 80% Depth of Discharge

| Depth of Discharge | Initial Charge Rate | Constant Potential | Charge Time Hours to Return | |
|---|---|---|---|---|
| % | A/100Ah | Volts at 25°C | 100% | 105% |
| 60 | 20 | 2.39 | 4.0 | 6.3 |
| 80 | 20 | 2.39 | 5.0 | 7.8 |
| 60 | 16 | 2.39 | 4.5 | 6.8 |
| 80 | 16 | 2.39 | 5.8 | 8.5 |
| 60 | 20 | 2.25 | 8.0 | 14.0 |
| 80 | 20 | 2.25 | 10.0 | 18.0 |
| 60 | 16 | 2.25 | 8.5 | 14.8 |
| 80 | 16 | 2.25 | 10.8 | 19.0 |

During repetitious cycling at 25°C and at depths of discharge as deep as 60 - 80%, a capacity return of 105 - 110% is normally required to maintain a given state-of-charge. Higher operating temperatures will require higher overcharge or a weekly equalization charge, or both.

Summarizing, to decrease charge time while maintaining a consistent state-of-charge, the following procedures should be used:

- Increase the initial charge current up to a maximum value of 25 A/100 Ah rated 5-h cell capacity.
- Use the highest setting of constant potential during the initial charge current period without exceeding the temperature compensated cell gassing voltage.

- Use three step charge with final finishing current controlled at 5A/100 Ah at the 5-hr rated cell capacity.

- Allow time for a prolonged equalization charge at some regular interval of accumulated discharge capacity.

EFFECT OF CELL DESIGN ON BATTERY LIFE

Battery life in years and cycles will depend upon the design features of cell components:

- Weight of lead and alloy composition in plate grids

- The dispersement of this lead in the grid structure

- The weight, density and composition of the active material in the positive and negative plates

- Electrolyte specific gravity

- Absence of impurities that could give interplate metallic shorts or excessive local action gassing of the plates

- Separator system and protection against shorting through accumulation of sediment

These design variables control the life and cell performance characteristics. For example, automobile starter-light-ignition (SLI) batteries give excellent initial cycle service but last for only 20-100 deep cycles. Newer on-the-road electric vehicle batteries are designed for somewhat longer deep cycle service (500-1100 cycles). Industrial motive power batteries are designed with cycle life as a major design requirement and can deliver 1500 to 2000 deep cycles. (Thick plate charge retaining batteries have excellent charged stand and low rate charge and discharge characteristics, but these cannot deliver or accept high power - Note: these charge retaining batteries are no longer readily available in 2002).

Technical assistance should be sought to obtain the most cost effective battery type which will meet the system needs.

## EFFECT OF OPERATING PARAMETERS ON BATTERY LIFE

Discharge capacity, power and energy requirements of the battery subsystem can be delivered by a variety of lead-acid batteries during early charge-discharge cycles of the battery's life. However, the sub-system cost per cycle can be decreased substantially in most applications by selecting a battery design with good charge stand capability, with a long operating life and with a capability for many repetitious charge-discharge cycles.

In some cases the battery design features which increase life tend to decrease the initial capacity, power and energy output, but the rate of decay of capacity with the number of cycles delivered can be significantly less. The photovoltaic system designer should therefore make certain that battery design features match the system operating and life requirements.

Operating parameters which influence battery life are depth of discharge, number of cycles required per year, and charging control.

- Increasing depth of discharge decreases cycle life
- Increasing the number of cycles performed per year decreases the wet life
- Excessive overcharging leads to increased positive grid corrosion active material shedding and shorter wet life.

Proper charging operations with good equipment maintains the desired state-of-charge with a minimum of overcharge and leads to optimum battery life.

Figure 3-8 is an example of the effect of discharge cycle depth and the number of cycles per year on battery life for one type of commercially available industrial battery.
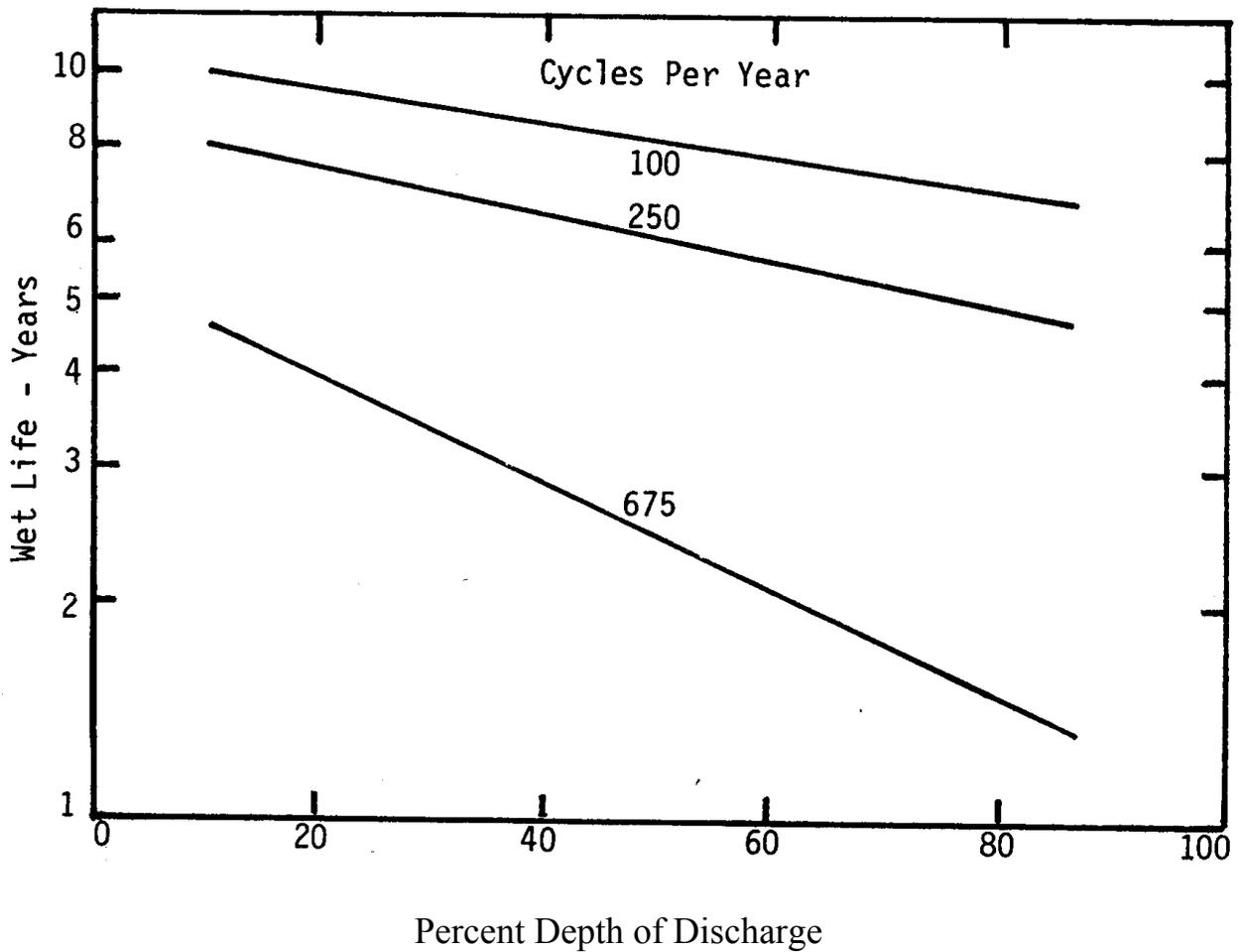


Figure 3-8    Effect of Depth of Discharge and Number of Cycles per Year on Wet Life, 250C.

Figure 3-9 is the more commonly published curve showing the relationship between the number of cycles to failure versus the discharge cycle depth. In most photovoltaic system operations no more than two cycles per day can be expected. One cycle per day is most common; however, assuming one cycle per day for a curve similar to Figure 3-9 can lead to false and high estimates of battery operating life in years. Battery life must therefore be verified by actual test.

ENVIRONMENTAL EFFECTS ON BATTERY LIFE

Operating temperature of the battery has a profound effect on operating characteristics and the life of a lead-acid battery.

Discharge capacity is increased at higher temperatures and decreased at lower temperatures. At higher temperatures, the fraction of theoretical capacity delivered during discharge increases. This increase in capacity per unit weight of active material decreases cycle life because more charge input and more discharge output is required for each cycle.

High temperature also increases local action or self-discharge The rate of chemical local action processes would be expected to double for each 10°C increase in operating temperature. One measure of local action is the current at a predetermined float voltage. See Figure 3-10.

Percent Depth of Discharge
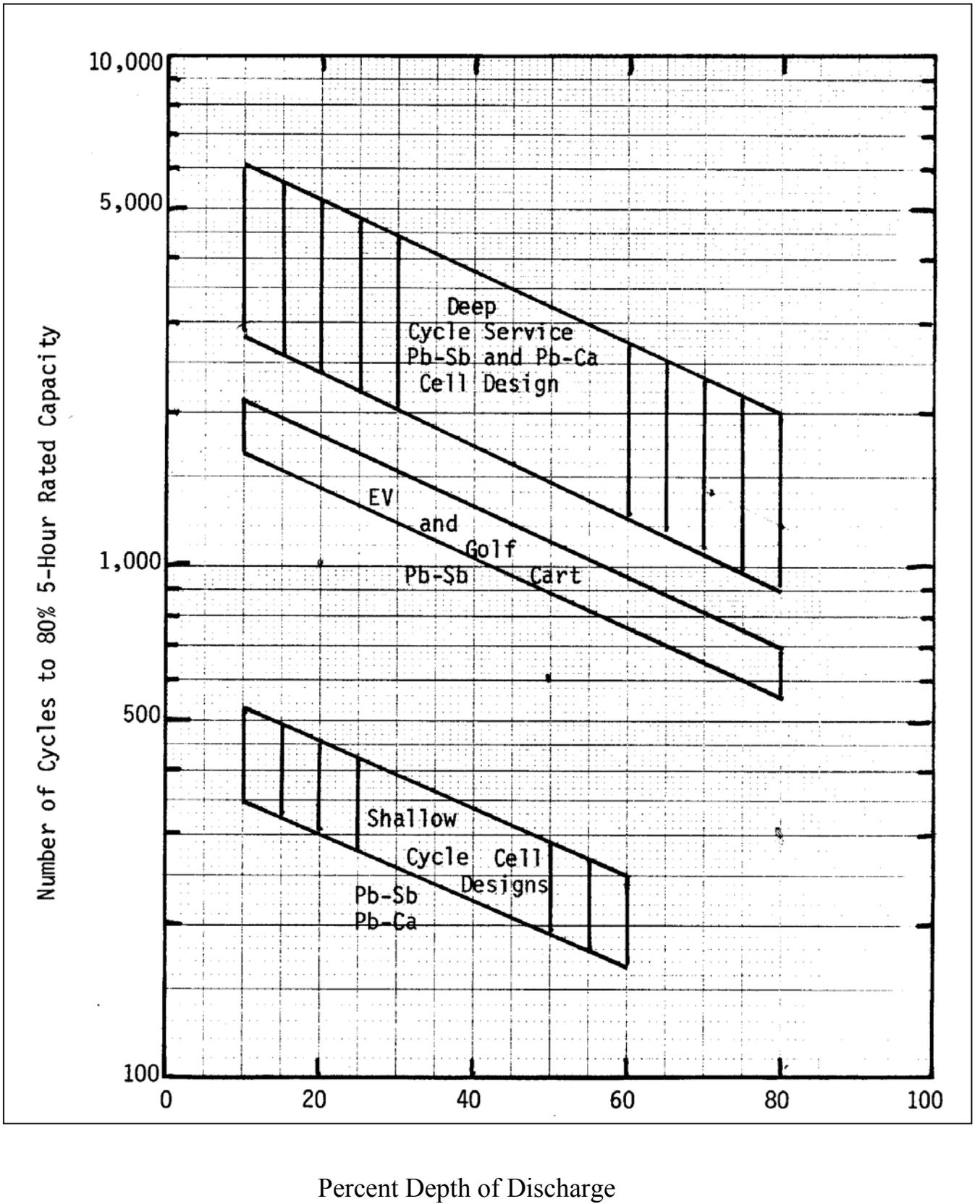
Figure 3-9    Effect of Cell Design and Discharge Depth on Estimated Cycle Life of Lead-Acid Cells at 25°C
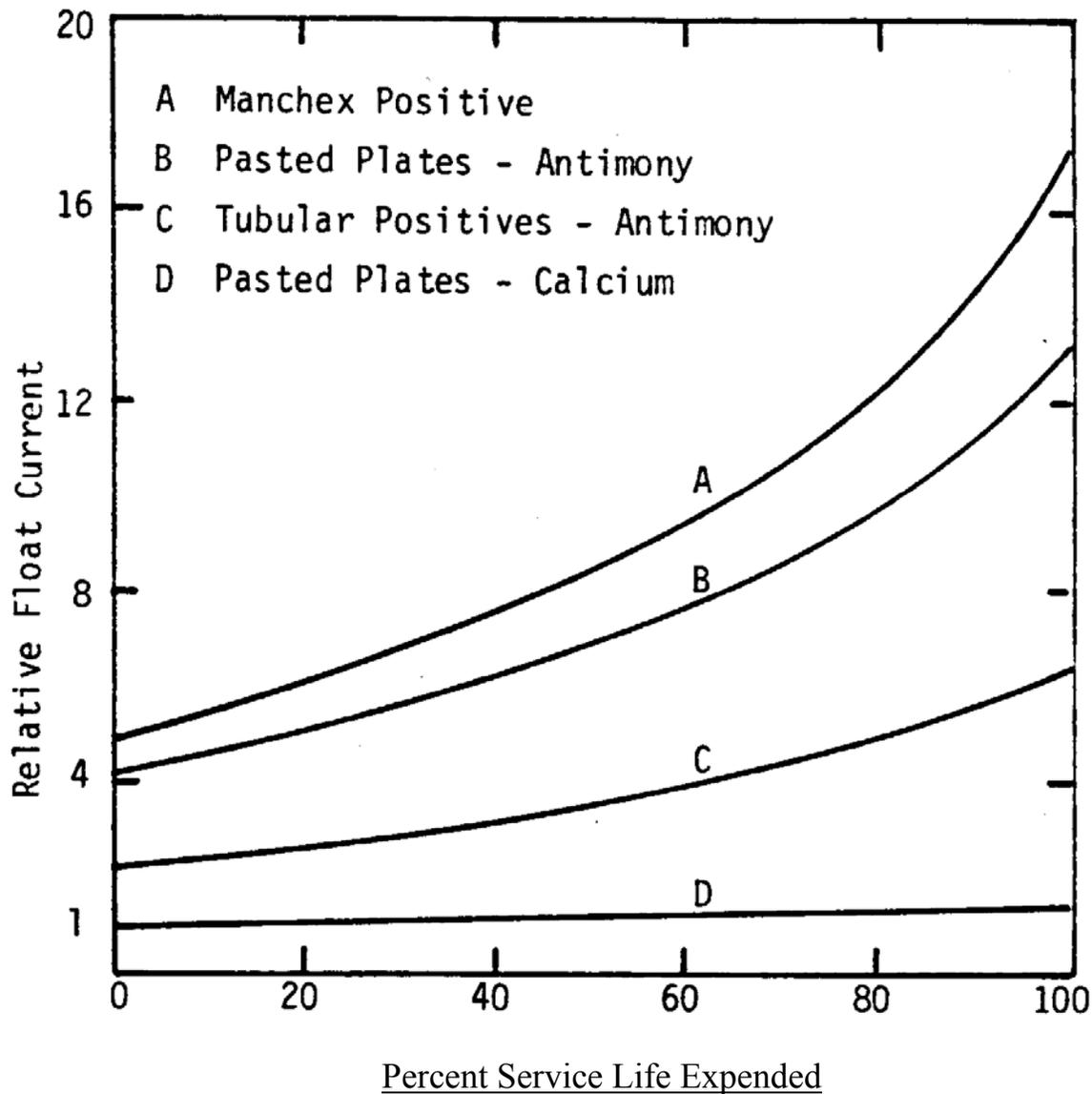
Figure 3-10 Relative Local Action of Cells of Different Construction

At higher float temperatures, float currents increase and give much reduced life. Eleven days float at 75OC are equivalent in life to 365 days at 25°C.

High operating temperature during cycle service requires higher charge input to restore discharge capacity and local action losses.  More of the charge input is consumed by the electrolysis reaction because *of* the reduction in the gassing voltage at the higher temperature.  Where 10 percent overcharge per cycle maintains state-at-charge at 25-35°C, 35-40% overcharge may be required to maintain state-of-charge at the higher 60-700C operating temperature

One attempt to relate operating temperature of cycling cells to cycle life limited by positive grid corrosion has shown cycle life at 49°C.  E.A. Wagner in unpublished data gives a derating factor of 0.7 to be applied to 25°C cycle life (3-6) for each 16°F (8.9°C) rise in cell operating temperature.

Shelf stand loss from local action is not a major concern in daily cycle service at normal temperatures.  At 80 percent depth of discharge in a daily cycle, the stand loss of capacity in a lead-antimony battery subsystem may approach 0.5 percent per day, which
is compensated by the daily recharge.

Figure 3-11 shows the typical effect of charged stand temperature on capacity loss rates for charge retaining batteries designed for this type of service.
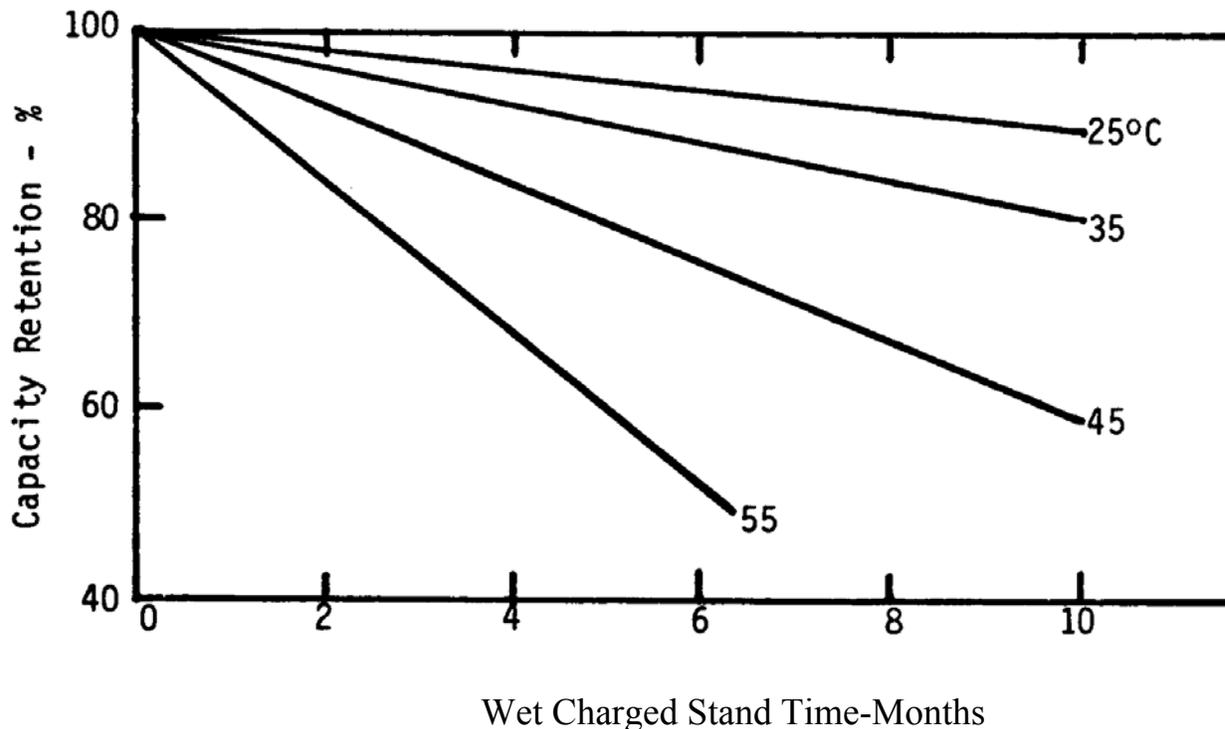


Figure 3-11  Effect of Cell Temperature on Capacity Loss During Charged Stand (Pure Lead Charge Retaining Cells)

When system power drains are very low for 30 days or longer without recharge, local action can add to capacity drain significantly. The battery must then be oversized to compensate for this loss. The battery type will determine the amount of excess capacity required.

For a high antimony lead-acid battery, a 130-150 Ah capacity may be required to deliver 100 Ah over a 30 day period to the load whereas for a lead-calcium or pure lead battery, only 102-104 Ah would be needed. This trade off must be considered

In general, therefore, solar photovoltaic systems must be designed to maintain nominal ambient temperatures on the battery subsystem by providing shade from direct sunlight and good air circulation over battery intercell and interrow connectors. Natural heat sinks such as the earth should be used whenever possible for remote solar PV installations to minimize the range of battery temperature excursions.

## MAINTENANCE OF LEAD-ACID BATTERIES

Battery subsystems for photovoltaic installations in remote locations must require low maintenance. The cost of maintenance can be prohibitive for remote systems in isolated areas where service personnel can visit the installation no more than once or twice a year.

Attended systems may have trained personnel available to perform maintenance. Battery designs with greater wet and cycle life, but which may also require greater maintenance, may be selected for these applications. A key step to long life is to properly train service personnel using service and operating instructions provided by the battery and photovoltaic system manufacturers.

Maintenance will normally consist of equalization charges, watering of battery cells, checks on individual cell voltage and specific gravity and cleaning the tops of cells of dust, dirt, acid spillage and spray.

## EQUALIZATION

During cycling, a high voltage battery having many cells in a series string can become unbalanced with certain cells limiting charge and discharge. Limiting cells receive more overcharge than other cells in the string have greater water consumption and thus require more maintenance.

The equalization charge has the function of balancing cells in the string at the top-at-charge.

Equalization charge simply extends the normal recharge for 3-6 hours at the finishing rate of 5 A per 100 Ah 5-h rated capacity, allowing the battery voltage to rise uncontrolled. Equalization charge should be continued until cell voltages and specific gravities rise to a constant acceptable value. See manufacturer1s maintenance instructions for details. Frequency of equalization charge is normally a function of the accumulative discharge output and will be specified by the manufacturer for each battery design and application.

## WATERING CELLS

During normal operation, water is lost from a battery as the result of evaporation and electrolysis into hydrogen and oxygen which escape into the atmosphere. Evaporation is a relatively small part of the loss except in very hot, dry climates. With a fully charged battery, electrolysis consumes water at a rate of 0.336 cc per Ah overcharge. A 500 Ah cell overcharged 10 percent can thus lose 16.8 cc, or about 0.3% of its water, each cycle.

Since replacing water can be a major maintenance cost, water loss can be reduced by controlling the amount of overcharge and by using hydrogen and oxygen recombining devices in each cell where possible.

Addition of water is best accomplished after recharge and before an equalization charge.
Add water to reach the high acid level line at top-of-charge. Gassing during charge will stir the water into the acid uniformly. Do <u>not</u> add water in <u>very cold weather </u>when it may freeze before mixing. Water added must be distilled water, demineralized
water, or local water which has been approved for use in batteries.

Automatic watering devices now in development and reliability testing can reduce maintenance labor costs further. Overfilling must be avoided as the resultant overflow of acid electrolyte will cause tray corrosion, ground paths, and loss of cell capacity.

A final check of specific gravity should be made after water is added to assure correct acid concentration at the top-of-charge helpful approximation is the equation:

Specific Gravity = Cell Open Circuit Voltage - 0.845

which permits electrical monitoring of specific gravity on an occasional basis.

## SAFETY PRECAUTIONS

Precautions must be routinely practiced to prevent explosions from ignition of the flammable gas mixture of hydrogen and oxygen formed during overcharge of lead-acid cells. The maximum rate of formation is 0.418 liters of hydrogen and 0.209 liters of oxygen per Ah overcharge at standard temperature and pressure. The gas mixture is explosive when hydrogen in air exceeds 4 percent by volume. Standard practice is to set warning devices to alarm at 20-25 percent of this lower explosive limit (LEL). Low cost hydrogen detectors are available commercially for this purpose (3-7).

With good air circulation around the battery, hydrogen accumulation is normally not a problem; however, if relatively large batteries are confined in small rooms, exhaust fans should be installed to vent the room constantly or be turned on automatically when hydrogen accumulation exceeds 20 percent LEL. Battery boxes should also be vented to the atmosphere. Sparks or flame can ignite these hydrogen atmospheres above
the LEL. To prevent ignition, electrical sources of arcs, sparks, or flame must be mounted in explosion-proof metal boxes. Battery cells similarly can be equipped with flame arrestors in the vents to prevent outside sparks from igniting explosive gases inside the cell cases. It is good practice to refrain from smoking, using open flames, or creating sparks in the vicinity of a battery.

Some types of batteries release small quantities of the toxic gases stibine and arsine.

These batteries have positive plates which contain in the grid alloy small quantities of the metals antimony and arsenic to harden the grid and to reduce the rate of corrosion of the grid during cycling. These alloying agents also substantially increase
the ability of the positive plate to cycle with good utilization of positive active material through a deep cycle life of 2000-3000 cycles. OSHA 1978 concentration limits for $SbH_3$ and $AsH_3$ are 0.1 PPM and 0.05 PPM respectively as the maximum allowable weighted average exposure for any 8-hour period. During continuous overcharge of such a battery, stibine ($SbH_3$) is released at an average rate of 0.05-0.l5mg per
1000 Ah rated 5-h capacity per ampere-hour of overcharge depending upon the overcharge rate and the alloy composition. The amount of arsine ($AsH_3$) released will
be less than one-tenth the amount of stibine. If these gases are allowed to accumulate in the battery room, toxic conditions can be created.

Ventilation is therefore doubly important. All tests indicate ventilation designed to maintain hydrogen below 20 percent LEL will also maintain stibine and arsine well below their toxic limits.

The system designer should consult the battery manufacturer's application or sales engineer to review and approve the battery box or room design, its ventilation, and safety features to promote good safety practice.

## SAFETY RULES TO AVOID CHEMICAL BURNS AND SHOCK HAZARDS

Severe burns can be caused by the sulfuric acid contained in lead-acid batteries.

- Do not get acid in eyes, on skin or on clothing. In case of contact, flush immediately and thoroughly with clean water. Obtain medical attention when eyes are affected.
- Wear a face shield, plastic or rubber apron and gloves when handling acid. Avoid spilling acid.
- Bicarbonate of soda solution (one pound to a gallon of water) will neutralize any acid accidentally spilled. Apply the solution until bubbling stops, then rinse with clear water.

  Batteries are electrically alive at all times!

- Keep the top of the battery clean and dry to prevent ground shorts and corrosion.
- Do not lay metallic objects on the battery; insulate all tools used in working on the battery to prevent short circuits. Also remove all jewelry before working on the battery.
- When lifting batteries, use completely insulated lifting tools to avoid risk of short circuits between cell terminals by lifting chains or hooks.
- Only personnel who have been trained in battery installation, charging and maintenance should be allowed to work on the battery subsystem.

References:

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3-4        H. Bode, Lead-Acid Batteries, John Wiley & Sons, Inc., New York, N.Y. 1977, p. 346.

3-5        N.J. Maskalick, Proceedings of the American Power Conference Volume 41, 1049 (1979).

3-6        E. A.. Wagner, Private Communication, July 1978.

3-7        Bacharach Instrument Company, 2300 Leghorn Street, Mountain View, CA. 94043