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FEASIBILITY OF RECHARGING FAA IN-SERVICE DRY CELL BATTERIES

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AUGUST 1965

FEDERAL AVIATION AGENCY

Systems Research & Development Service

Washington, D.C.

FINAL REPORT

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DRY CELL BATTERIES

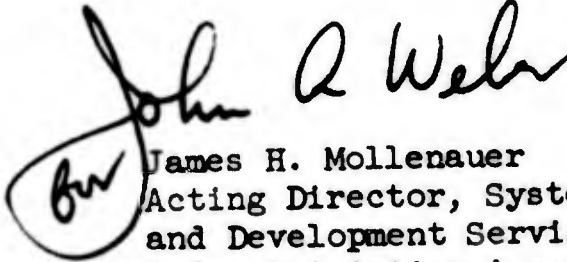
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AUGUST 1965

This report has been approved for general availability. It does not necessarily reflect FAA policy in all respects and it does not, in itself, constitute a standard, specification, or regulation.

A handwritten signature in cursive script, appearing to read "John Q. Weber", with a large, stylized flourish at the end.

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ABSTRACT

Inasmuch as the FAA uses a large number of dry cell batteries in test and radiological equipment, a considerable saving would be possible if the batteries could be economically recharged instead of discarded and replaced. The report explains the feasibility of recharging the presently used carbon-zinc batteries and also considers the use of other types which may have a better charge acceptance.

It was found that, although the carbon-zinc battery is listed as being a primary cell, i.e., not rechargeable, it actually has a limited recharge capability provided the charging is done soon after discharge. Since most of our batteries are for emergency use, the loss of capacity is due to self-discharge rather than actual use. Inasmuch as capacity lost by self-discharge cannot be replaced by charging, it is not recommended that a recharging program for carbon-zinc batteries be undertaken.

A number of other types of batteries are better adapted for standby application, such as radiological equipment, and are more rechargeable than the carbon-zinc type. However, except for alkaline manganese dioxide-zinc batteries the cost of these other types is so high that their use cannot be justified on an economic basis. Recommendations are made for the use of secondary manganese dioxide-zinc batteries at some locations.

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INTRODUCTION

A. Background.

1. The Federal Aviation Agency has a large number of radiological instruments located at various facilities throughout the country all powered by dry cell batteries, as well as a great number of flashlights and test instruments that also use dry cells. The radiological equipment, being for emergency use, must be available and capable of working at all times. Therefore, the present practice is to replace the dry cells on an annual basis regardless of how little the instrument may have been used during the year. This means an annual consumption of at least 38,000 batteries for radiological instruments alone. In most cases the only loss of battery capacity is that caused by self-discharge.

Recently, battery chargers have appeared on the market with manufacturer's claims that they will fully recharge any type of battery including carbon-zinc, alkaline, nickel cadmium and mercury, a minimum of 15 times. Since a capability such as this would result in a considerable saving to the Government, R&D effort was requested by IMS to determine the feasibility and cost of recharging dry cell batteries.

- B. Scope This report makes no attempt to evaluate any particular battery charging system. The information contained herein is not obtained from tests or experimentation by the FAA but is the result of a study of technical literature and the results of tests performed by others. It covers the capabilities of various types of dry cell batteries with respect to shelf-life, rechargeability, and cost, with some reference to the practical aspects of a recharging program.

DISCUSSION

A. Carbon-Zinc Cells

1. Description of Carbon-Zinc Cells

Carbon-zinc primary batteries of the dry Leclanche type are more widely used than any other type of dry cell because of the low cost and reliable performance. They have changed little in the fifty years prior to 1945. However, since then, through the use of spun paste and paper lined construction with improved mix and electrolyte, capacities have been increased and production techniques have been perfected with resulting cost reduction. Capacities are now in the order of fifty watt-hours per pound.

The electrochemical system of the carbon zinc battery uses a zinc anode, a manganese-dioxide cathode, and an electrolyte of ammonium chloride and zinc chloride. The rod in the center of a cylindrical cell is carbon and functions as a current collector. Powdered carbon is used in the depolarizing mix, usually in the form of acetylene black, to improve conductivity of the mix and to retain moisture.

2. Performance of Carbon Zinc Cells

The closed circuit or working voltage of a carbon zinc cell falls gradually as it is discharged, Figure 1. The service hours delivered are greater as the cutoff or end point voltage is lower.

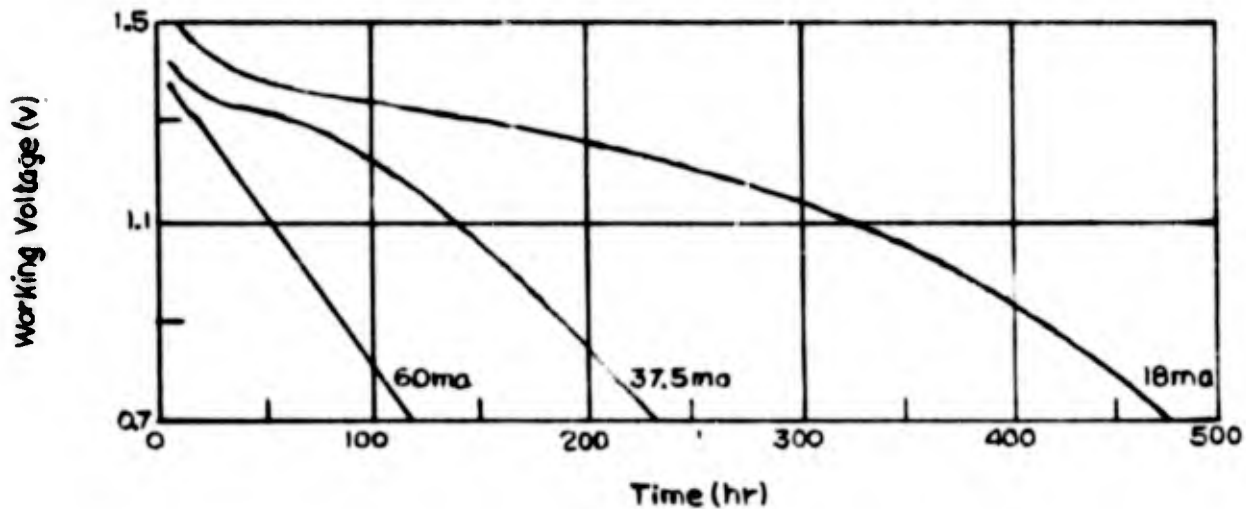


FIGURE 1 VOLTAGE-DISCHARGE CHARACTERISTICS OF CARBON-ZINC D-SIZE BATTERY DISCHARGED 4 HR PER DAY

It can be seen from the curves that lowering the cutoff voltage from 1.1 volts to .8 volts will greatly increase the capacity available. This should be done, if the equipment can tolerate it, to obtain most efficient use of the battery. The service capacity of the Leclanche type carbon zinc battery is not a fixed number of ampere hours because it depends on a number of conditions; the current drain, the operating schedule, and cutoff voltage. It is also effected by the operating temperature and storage conditions of the battery prior to use.

The chemical efficiency of a carbon zinc battery improves as current density decreases. For this reason as large a battery as possible should be used consistent with physical limitations. Over a certain range of current density, service life may be tripled by halving the current drain. However, this would not be true for applications where the battery gets very little use because self-discharge becomes an important factor. Performance is normally better when the service is intermittent. Continuous use is not necessarily inefficient if the current drain is very light.

3. Effect of Temperature

Carbon-zinc batteries are normally designed to operate at 70°F. The higher the battery temperature during discharge, the greater the energy output. However, high temperatures reduce shelf life, and prolonged exposure to temperatures above 125°F causes very rapid disintegration of the battery.

Shelf life is the period of time that a battery retains a given per cent of its original energy content.

The shelf life of a carbon-zinc battery stored at 90°F is about 1/3 that of one stored at 70°F. Low temperature storage is very beneficial to shelf life. From 40°F to 50°F is a good temperature range for storage purposes.

4. Rechargeability

It has been known for a long time that carbon-zinc dry cells can be recharged to a limited extent even though they are considered primary cells. This is not because the chemical reaction is reversible but because the charging current tends

to assist in the redispersion of the chemicals, an action which must take place in the depolarization process. Normal recuperation is accelerated by the charger and in so doing the total life of the battery is extended. However, this is contingent on recharging soon after discharge. The loss of capacity which is the result of self-discharge (shelf life) cannot be replaced by charging. Also, the capacity to a given cut-off voltage decreases with each cycle. The insoluble salts formed by diffusion occurring on stand seem to limit the charge acceptance.

Interest in the recharging of dry cells increases during periods of battery shortages such as in wartime. It is worth noting, however, that almost all of the charging installations developed during 1943-1946 have since been abandoned. The explanation usually given is that the poor and uncertain results did not justify the extra efforts required for collection, care in charging, testing, and redistribution of rejuvenated cells. A review of some of the methods used indicate that not enough attention was paid to the reactions occurring in the dry cell during the charging process. The constant current method can result in over charging unless the exact amounts of discharge and charge are known and carefully used. The cells were often allowed to run down too low before attempting the recharge. Constant potential charging will damage the cells if an excessively high voltage is used to obtain a rapid recharge.

5. Tests by the National Bureau of Standards

In recent tests made by the National Bureau of Standards it was found that from two to almost seven times normal capacity was obtained by introducing charge periods in between the discharge periods. Table 1 gives some of the data from the test. An explanation of the tests is given immediately below the Table.

	4 ohms discharge 4 hr/day		
	<u>1.20v</u>	<u>1.10v</u>	<u>1.00v</u>
Straight discharge	9.8	11.3	14.5
Discharge-charge cycle	47.9	66.5	97.2
Cycled cell performance factor	4.9	5.9	6.7
Discharge-charge-rest cycle	23.4	58.2	77.2
Cycled cell performance factor	2.4	5.2	5.3

Table 1. Capacity improvement from charging F size dry cells

Straight discharge - The cell is continuously discharged by a 4 ohm resistance for 4 hours each day until the cell voltage is reduced to 1.20 volts. Then the total number of hours of discharge time is recorded. The 4 hours per day discharge is then continued until the voltage is reduced to 1.10 volts and again the total discharge time in hours is recorded. The 4 hour discharge with 20 hours of rest per day is repeated until cell voltage reaches 1.00 volts and total discharge time is again recorded. No charging of the cell is included in this test.

Discharge-charge cycle - Here the cell is discharged for 4 hours per day as above, but instead of resting for the remainder of the day the cell is charged at an initial rate of 350-400MA at constant potential during this 20 hour period each day. Total discharge hours are recorded at the three cell voltages as in the above test.

Cycled cell performance factor - The factor is calculated by dividing the discharge-charge cycle time by the straight discharge time for each voltage.

Discharge-charge-rest cycle - In this test the charge time was reduced to 16 hours, immediately followed by a 4 hour rest period.

Some use of the over-voltage effect was possibly obtained since lower capacities resulted when the rest period was employed. Since some of the zinc on charging is deposited as trees or sponge in the paste layer, the loss of capacity on standing could also have been due to a reaction between the zinc trees and the $Mn O_2$ -C mix.

The decrease in the performance factor was not due to the shorter charging time since the final current was the same within a few milliamperes in each case. There was also not much voltage drop in the 4 hour rest period.

The favorable results obtained were largely due to the fact that charging took place soon after discharge and the fact that the charging was carefully controlled. Also, the cut-off voltage was not permitted to go below 1.0 volt per cell. In long term cycling such as covered in Table 1, the voltage of the cells decreases

rapidly after reaching about 0.95 volts. Recharging is not very effective for cells discharged to low voltages. Tests on cells discharged below 0.95 v indicated that little additional capacity can be obtained even with prolonged charging. The cells apparently did not accept the charge. Examination of such cells showed that the paste layer had partially dried out and large areas of the zinc were covered with a dry white film. The cathode mix was dry and hard. Microscopic examination of the mix did not reveal any significant amount of white salts or precipitates. It was evident from examining cells having various states of discharge that failure was due to the apparent dryness of both mix and paste. The cells did not gas during charging and were sealed so that little or no water could be lost by evaporation. No change of weight could be detected. It was concluded that there was a gradual transfer of water to the mix core and that it was absorbed by hydration of the lower valence manganese oxides or by greater dispersion of the Mn oxides and acetylene black. The latter effects could be due to the repeated charging and discharging processes.

Further tests were made by the Bureau of Standards in which variations were made in cell components and test conditions. The results and conclusions are given as follows:

1. Paper-lined cells are less suitable for charging than the pasted variety. Apparently, the zinc sponge penetrates the short distance through the paper very quickly and in large amounts, so that little gain in capacity is obtained by charging.
2. Artificial MnO_2 is more amenable to recharging than the natural MnO_2 types and is especially beneficial to the higher voltage end points.
3. Overcharge often produces a yellow-orange color in the paste and degrades its gel characteristics. The coloration is due to ferric chloride which results from dissolution of iron impurities in the MnO_2 ore. Apparently, the normally insoluble iron is dissolved by the increased acidity in the mix produced by the overcharging. The chlorine evolved may also assist in this process.
4. No perforation of the zinc case occurs when the fixed potential charger is used and charging is continued each time to low final current values. This insures that most of the zinc dissolved on discharge is plated back onto the zinc can.

5. A high voltage of about 1.75-1.80 persists for several hours after charging and could cause damage to lamp or electronic tube filaments. It can be decreased to safe values by aging the cells a few days or by a short discharge.
6. Dry cells with different degrees of use or past histories can best be charged in parallel. For a short period, the high-voltage cells charge the low-voltage ones, but this is not harmful. In series charging such cells, the good high voltage cells are overcharged and damaged while obtaining adequate charging of the poor low voltage cells. Charging of cells connected in series in a battery is satisfactory since they have been used as a group.

B. Characteristics of Other Cell Types

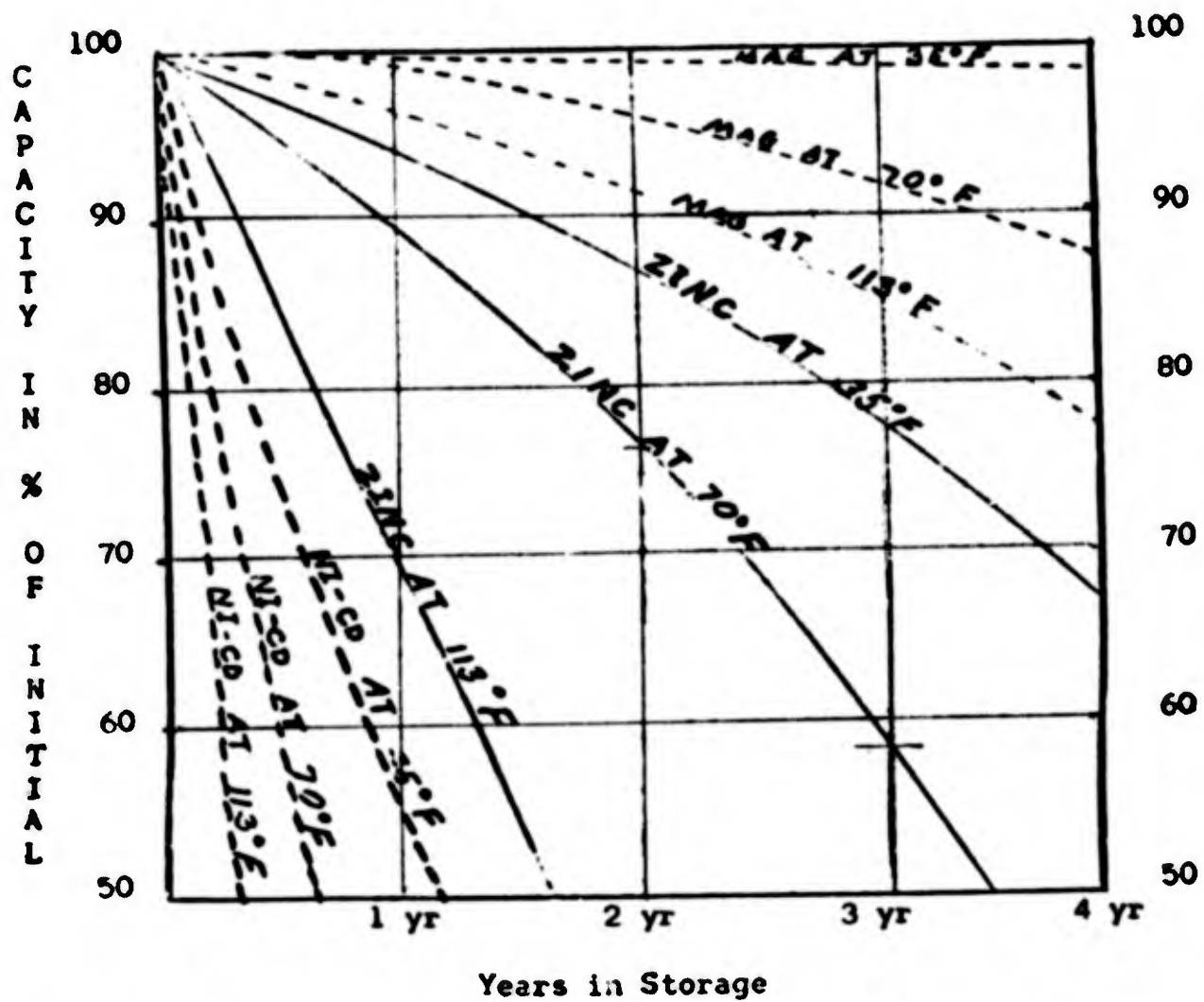
1. General

If secondary cells are used having silver, nickel, mercuric oxide, or manganese dioxide cathodes and cadmium, zinc, or magnesium anodes, recharging is much more feasible.

Following are the dry cell battery types utilizing combinations of the above materials.

- Nickel - Cadmium
- Silver - Cadmium
- Silver - Zinc
- Manganese dioxide - Magnesium
- Alkaline Manganese dioxide - Zinc
- Mercuric oxide - Zinc

Some of the above cells are more rechargeable than others and some have better shelf life than others. Figure 2 shows the differences at various temperatures of three types.



NOTE: These capacities are lower limits. 90% of the batteries will have greater capacities.

FIGURE 2 SHELF LIFE OF ZINC, MAGNESIUM AND NICKEL-CADMIUM BATTERIES MEASURED IN PERCENT OF INITIAL CAPACITY AT DIFFERENT AMBIENT TEMPERATURES

2. Nickel Cadmium

Nickel cadmium batteries do not show up well on the above graph, but due to the fact that they are completely rechargeable, they are often referred to as having indefinite shelf life.

The sealed sintered plate construction has had a big boost from military and space development contracts and consequently is fairly trouble free and in quantity production. This type of cell has a number of advantages:

- (1) It is ruggedly built and may be stored under all conditions and in temperatures ranging from -75° F to $+160^{\circ}$ F without damage.
- (2) It is leakage free, and consequently there is no loss of liquid or vapor.
- (3) It does not deteriorate physically regardless of the state of charge.
- (4) It can take a continuous overcharge at the 16 hour rate without damage to the cell.
- (5) It can take a rapid charge.

The case for nickel cadmium cells, however, is not entirely favorable. The disadvantages are as follows:

- (1) Poor capacity (on single discharge) compared to zinc and magnesium cells.
- (2) Difficult to determine state of charge.
- (3) Higher self-discharge rate than carbon zinc.
- (4) Cost at least 20 times as much as carbon zinc.
- (5) Requires charging before installation.
- (6) Subject to high replacement rate due to pilferage.

The self-discharge rate at 70° F is as follows:

- 20% loss of capacity in 1 month
- 40% loss of capacity in 3 months
- 60% loss of capacity in 6 months

3. Manganese dioxide - Magnesium

It can be seen from Figure 2 that Magnesium cells have very good shelf life, however, they are such a new type that they are not fully developed and are not readily available. When not in use a film develops on the magnesium anode which causes the cell to have a short delay (2 seconds) when the circuit is closed. This is followed by a surge to 1.8v which may last up to 30 minutes. Indications are that these objections will be overcome.

4. Alkaline Manganese dioxide - zinc

Manganese dioxide - zinc cells are made in both the primary and secondary types. These cells have good high and low temperature characteristics, 50 to 100% more energy than a carbon-zinc cell, and good shelf life. The main advantage of the manganese cell is its high efficiency under continuous and heavy duty high-drain conditions where the standard carbon-zinc cell is unsatisfactory. On light drains, or under intermittent-duty conditions the manganese cell loses some of its economic advantage over carbon-zinc. However, it has good charge retention characteristics and since its cycle life is increased by light load conditions it should be advantageous where most of the withdrawal of capacity is due to self-discharge. At 70° F the capacity loss due to self-discharge is approximately 0.2% per month. This is almost as good as the charge retention of magnesium cells. The cost is only a little more than three times that of carbon zinc.

5. Silver-Cadmium and Silver-Zinc

Silver-cadmium and silver-zinc batteries are quite similar to each other. They differ from the nickel cadmium battery primarily in that they use silver instead of nickel for the anode; and, in the silver-zinc battery, zinc instead of cadmium for the cathode. They are available in both the sealed and vented types. Silver-cadmium and silver-zinc batteries are ruggedly built and have the strength

to withstand severe shock, vibration and acceleration; have flat voltage curves, wide operating temperatures range (-20° F to 165° F for silver cadmium), long storage life, and their self-discharge rates are much lower than that of sealed nickel cadmium but also cost three to four times as much as nickel cadmium.

6. Mercuric oxide - zinc

Mercury batteries have been on the market for some 15 years. During most of this time they were made up as primary cells, but recently a rechargeable type has appeared. The new type utilizes a cathode mix of 20% silver oxide and 90% mercuric oxide, a zinc foil anode, and potassium hydroxide electrolyte. This battery will accept about 200 shallow cycles. Its cost per unit of capacity, as a rechargeable battery is not yet competitive with nickel cadmium cells. The primary cells have a capacity only a little above that of new type zinc batteries. They have a number of advantages over the zinc type, however, namely; long shelf-life (at 70° F, 95% of capacity at the end of two years), uniform discharge potential, high resistance to environmental conditions, very well suited to portable electronic equipment, particularly well suited to transistor applications requiring constant current, low drain, long service life. Mallory Company states that it is the best hot weather cell known.

As with the other non carbon-zinc types, the price is disproportionately high, being at least 10 times that of carbon -zinc.

See Figure 3 for the relative cost of the various types of dry cell batteries.

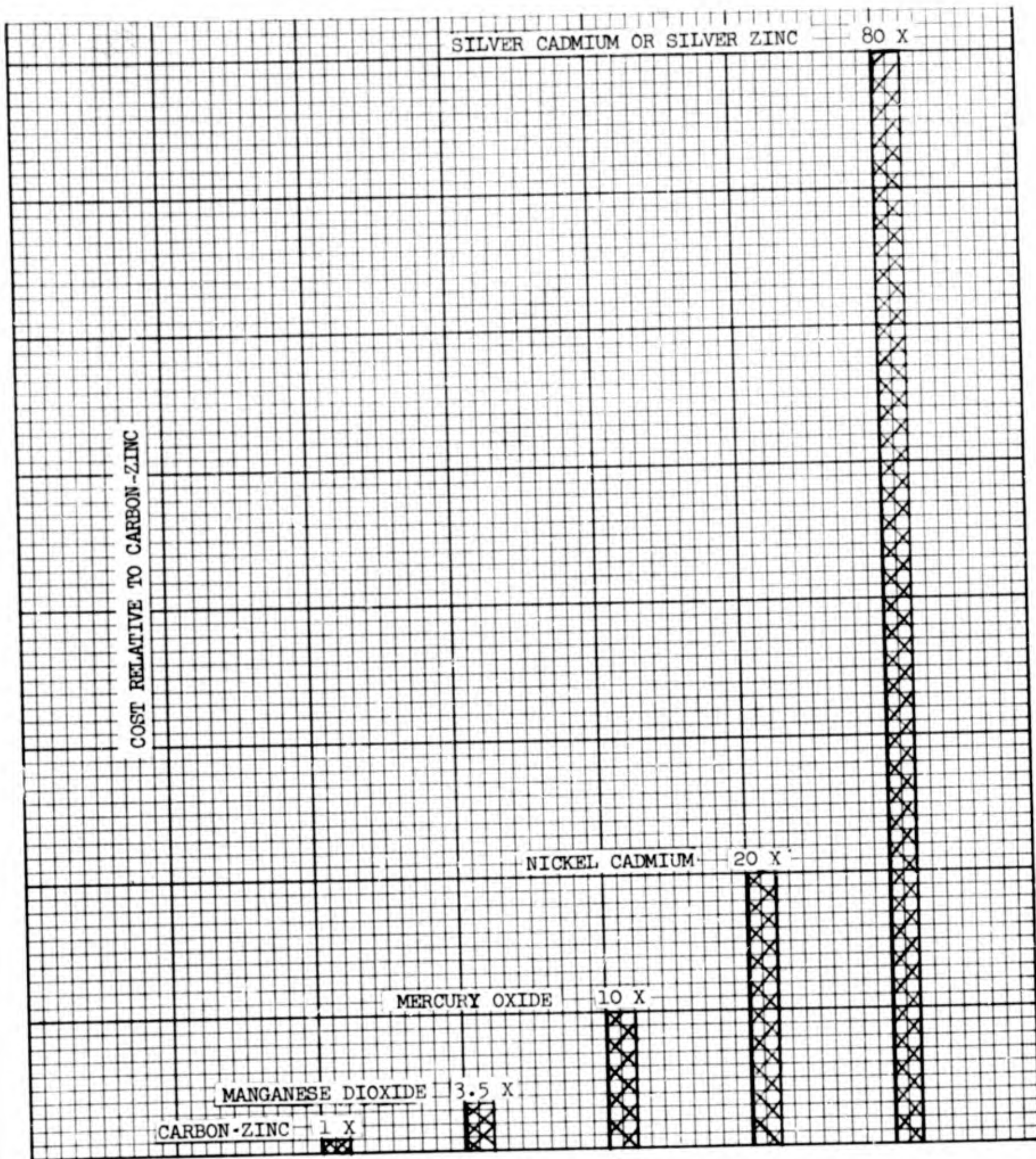


FIGURE 3 RELATIVE COST OF VARIOUS TYPES OF DRY CELL BATTERIES

CONCLUSIONS

A number of conclusions have been drawn in the Discussion section. These add up to the fact that there are a number of cell types that are more suitable for radiological equipment service than the carbon-zinc types now in use, but they are all so much higher priced that no saving is realized by their use. This is true even if the carbon-zinc batteries are discarded annually.

The benefits derived from charging carbon-zinc batteries are marginal unless the right conditions prevail and the charging is carried out in a careful and consistent manner. One of these conditions is that charging take place as soon as possible after discharge. This is not possible when the discharge is due to local action within the battery as is the case during stand periods. The advantage of charging carbon-zinc cells is greatest when the batteries have heavy or continuous use and least for cells having only intermittent or occasional use.

Magnesium cells offer almost unlimited shelf life and twice the capacity of zinc cells but their initial cost is high at the present time. When large scale production is achieved, the cost should be commensurate with zinc cells per operating hour. Even though the magnesium cells are not rechargeable a saving over zinc cells will be possible in the future through elimination of the need for refrigerated storage and the supply and handling costs.

While the mercury battery is well adapted for use in radiological equipment, its use would not be more economical than carbon-zinc batteries until the price differential is reduced and even then, recharging would be required.

The Silver-Cadmium and Silver-Zinc batteries also have characteristics which make them well adapted for use in radiological equipment but the cost is about 80 times that of carbon-zinc batteries.

Alkaline manganese dioxide-zinc batteries are readily available, have a little more capacity than the new paper lined carbon-zinc batteries, may be recharges 40-50 times if the discharge is shallow, and have a voltage

curve on discharge similar to that of carbon-zinc batteries. There is a difference of opinion in the reference material regarding the capacity advantage of the Alkaline Manganese cell over the carbon-zinc type. 50 to 100% more total energy is given in one reference, only a slight capacity advantage over the paper lined carbon-zinc is given in another. However, the principal difference for our application seemed to be the fact that self-discharge can be restored in the manganese dioxide-zinc cell and cannot in the carbon-zinc cell.

RECOMMENDATIONS

It is recommended that:

1. A recharging program for our carbon-zinc batteries not be undertaken.
2. Alkaline manganese dioxide-zinc batteries of the secondary type be used where collection and charging can be accomplished conveniently. These batteries should be recharged annually or after 6 watt hours of use (for D size) whichever comes first. Charging information is given in Appendix.

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APPENDIX

For best results, an alkaline manganese dioxide secondary battery should be recharged by applying the recommended charging current for a time long enough to replace 120 per cent of the ampere hours removed on the previous discharge. This figure is not critical. It may be varied between 100 and 150 per cent of the ampere hours removed without seriously reducing service life. Recommended charging circuits are available from battery manufacturers.

An alkaline manganese dioxide secondary battery should not be discharged completely. It should not be permitted to drop below a voltage value of 0.9 volts per cell. During deep discharge (below 0.9v per cell) a secondary electro-chemical reaction takes place which is not reversible and makes it impossible to recharge the battery. It is, therefore, desirable that the instrument using the battery contain some automatic provision against complete discharge of the battery. For applications where self-discharge is the main cause of discharge, annual recharging will prevent excessive discharge and the charge time can be calculated from the discharge curve data.

In order to keep the labor involved comparable to present procedures, it would be necessary to have an extra set of batteries charged and ready for use at the scheduled time for battery changeout. The batteries taken out of service would be charged and stored. At the end of the year, when the next change is due, the batteries that are to go into service are given a booster charge to insure full capacity.

A better procedure is possible especially if the batteries can be charged without removal from the instrument or meter. External jacks or terminals would be needed for connection to the charger. The instruments would be sent down to the charger room one at a time. In this way one set of batteries and one charger per facility would suffice. As given in RECOMMENDATIONS, rechargeable batteries and recharging procedures are not recommended for small or unattended facilities where the procedure cannot be carefully controlled.