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NEGATIVE TO POSITIVE MATERIAL RATIO
AND PRECHARGE LEVELS

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CONTENTS

ABSTRACT

A review is made of the factors affecting the choices of negative-to-positive materials ratio and negative precharge in nickel-cadmium cells. The effects of these variables on performance is given, and the different methods for setting precharge are evaluated. The effects of special operating requirements on the design are also discussed.

KEY WORDS

Aerospace Batteries

Batteries

Cadmium Electrode

Negative-Positive Ratio

Nickel-Cadmium Cells

Precharge

Secondary Batteries

Introduction

The advantages of operating the nickel-cadmium battery with capacity limited by the positive electrode and with a negative-to-positive capacity ratio greater than 1.0 was recognized very early in the development of this system, going back to Jungner; some of the Jungner designs were negative limited, however (1). Cells with sintered electrodes made in 1948 by Fleischer (2) typically had negative-to-positive ratios of 1.5 to 2.2 and today the range is about 1.2 to 2.0.

Reaction of oxygen with charged cadmium had been observed by Estelle in 1909, (3) but was rediscovered in 1933 by Lange and coworkers (4), then demonstrated again much later in 1954, by Hersch (5). Rublee had established the principle in 1939 that a surplus of uncharged negative can avoid hydrogen generation during charge (6); this concept was later applied to the nickel-cadmium system in 1952 by Neumann and Gottesmann (7 and 8) and in 1952 by the French company, Bureau Technique Gautrat (9). The basic idea is that if the negative electrode always has a surplus of uncharged material (cadmium hydroxide) then it will not evolve hydrogen during charge. Oxygen is produced during charge at the positive electrode and reacts with charged cadmium, thus keeping the negative electrode from getting fully charged. Limiting the amount of electrolyte in sealed cells favors the transfer and recombination of oxygen. Vented cells by contrast permit both positive and negative electrodes to become fully charged, generating both oxygen and hydrogen during overcharge.

Basic Considerations

One of the common reasons for choosing a particular negative/positive ratio is to assure that the cells will always be negative limited. There are some plausible arguments why negative limited discharge would be acceptable at times, and these should be considered in the light of specific applications. Rigid insistence that cells always be positive limited will probably force the negative/positive ratio to be higher than presently used in aerospace applications. Positive and negative capacities used for calculating the ratio are determined by flooded tests, which use a large excess of electrolyte.

Nickel-cadmium cells can be limited by either the positive or negative electrode during charge, and also by either electrode during discharge, as shown in Table 1. System #1 is by far the most common, with the positive electrode limiting during both charge and discharge. During charge, oxygen evolves from the positive electrode and recombines on the negative electrode, a process referred to as the oxygen cycle. System #1 degrades into System #2 as the negative electrode wears out and loses capacity, or as the positive electrode capacity increases due to corrosion or low temperature operation. System #2 also uses the oxygen cycle and has sometimes been used in commercial cells so that on accidental reversal oxygen will evolve from the negative. System #3 is an experimental one using negative electrodes with high hydrogen overvoltage to minimize hydrogen gassing. The oxygen cycle is operative in this system. System #3 degrades to System #4 since the self discharge of the nickel electrode is greater than that of the cadmium electrode. Energy density is low with Systems #3 and #4.

The acknowledged superiorty of System #1 is attested to by the fact that this is the concept around which current nickel-cadmium technology is based. The fact that this system often degrades to System #2 raises the question of how acceptable this can be. As is often the case with many issues, sometimes it is acceptable, and sometimes it is not. Arguments for and against

TABLE 1: ELECTRODE LIMITING DESIGN APPROACHES

	POSITIVE ELECTRODE LIMITING		NEGATIVE ELECTRODE LIMITING		SYSTEM OPERATION	COMMENT
	DURING CHARGE	DURING DISCHARGE	DURING CHARGE	DURING DISCHARGE		
SYSTEM #1	✓	✓			Oxygen cycle during charge. Hydrogen evolves during discharge reversal.	Conventional aerospace and industrial practice.
SYSTEM #2	✓			✓	Oxygen cycle during charge. Oxygen evolves during discharge reversal.	System #1 often degrades to System #2.
SYSTEM #3			✓	✓	Charge is stopped before H_2 gassing occurs. Oxygen evolves during discharge reversal.	Negative-limited design studied by JPL/NASA. Oxygen cycle inoperative.
SYSTEM #4		✓	✓		Charge is stopped before H_2 gassing occurs. Hydrogen evolves during discharge reversal.	System #3 often degrades to System #4.

permitting degradation to negative-limited discharge (System #2) are given in Tables 2 and 3, respectively.

Methods of Adjusting State of Charge

Adjustment of state of charge is often called "setting the precharge", after Grieger (10). Precharge refers to the excess of negative in the charged state, over and above that of the positive electrode. Properly designed nickel-cadmium cells will have both an excess of uncharged negative and an excess of charged negative.

There are at least ten basic approaches to adjusting state of charge (Table 4), which may have one or more variations. These approaches fall into either of two categories, depending on whether both electrodes are fully charged or fully discharged before making the adjustment. Approaches are also possible in which cells are assembled and sealed with electrodes that have unequal states of charge. Though such approaches might have possibilities for industrial batteries, they have not been considered here because they do not lend themselves well to good control and predictable performance.

When both electrodes are fully discharged at the beginning of precharge adjustment, the process will generally require either venting oxygen gas or adding hydrogen gas (Table 4). It doesn't matter from which electrode the oxygen is derived, as long as a known amount is removed from the cell. Precharge methods that start with both electrodes discharged have an advantage in that all of the adjustment results in a direct increase in precharge.
The addition of hydrogen as an adjustment method is included for completeness, but generally would be considered only for cells with hydrogen recombination electrodes.

TABLE 2: ARGUMENTS FOR PERMITTING NEGATIVE-LIMITED DISCHARGE

ITEM	ARGUMENT
Capacity	The capacity of the nickel electrode is greatest at low temperature, but this is seldom desired. Permitting negative-limited operation under such conditions meets capacity requirements and saves weight.
Reversal	Accidental reversal is safer, for oxygen is evolved and will be recombined during the next charge.
Capacity Divergence	Typically, batteries are operating at usually less than 40% DOD, and operation at full capacity is not a practical requirement. Therefore, cell design should not be penalized with unrealistic restrictions relating to behavior at the end of a complete discharge, such as capacity divergence or insistence on positive-limiting.
Experience	Many of the cells used to date have operated negative-limited at times without harm.

TABLE 3: ARGUMENTS AGAINST PERMITTING NEGATIVE-LIMITED DISCHARGE

ITEM	ARGUMENT
Capacity Divergence	Degradation of the negative electrode is unpredictable and non-uniform, leading to uncertainties in battery capability during operation. Therefore, there will be capacity divergence with operating life, and battery capability at any time will be uncertain.
Degradation	Complete discharges on the negative electrode are a big stress and will degrade the negative electrode faster as a result.
Hydrogen Generation	A full discharge of the negative electrode depletes all the reserve of undischarged cadmium, causing a risk of hydrogen generation at the beginning of charge.
Voltage Depression	Cadmium electrodes suffer voltage depression with cycling, due to formation of a cadmium-nickel compound. Operating with little or no negative reserve accentuates this problem.
Operating Complexity	Permitting both positive and negative-limited discharges complicates operation unnecessarily.
Reversal	If the positive electrodes were always limiting, there could be less chance for reversal because capacity would be greater and the cells would probably be better matched.
Capacity	Cells that are sometimes negative-limited will have lower capacity at those times than they would if they were positive-limited.
Experience	Most of the experience with sealed nickel-cadmium cells is with positive-limited design. Designing to permit negative-limited operation will require suitable test programs to verify that this is acceptable.

TABLE 4: SUMMARY OF PRECHARGE ADJUSTMENT APPROACHES

INITIAL STATE	GAS VENTED/ADDED	ITEM	ADJUSTMENT METHOD	EFFECT OF ADJUSTMENT	MAJOR SOURCES OF UNCERTAINTY
Both Electrodes Discharged	Vent O_2	1	Charge positive vs. negative and vent O_2	Increase excess charged cadmium (precharge)	o Uncertain amount of cadmium left when negative is discharged o Errors in volume of O_2 vented, or H_2 added
	Vent O_2	2	Charge negative vs. case and vent O_2		
	Vent O_2	3	Charge positive vs. negative part way, then discharge positive vs. case and vent O_2		
	Add H_2	4	Add H_2 in cells with recombination electrodes		
	--	5	No adjustment. Seal with electrodes discharged	Depends on inherent excess charged cadmium in discharged electrodes	o Variable excess of charged cadmium
Both Electrodes Charged	Vent H_2	6	Discharge positive vs. negative and vent H_2	Increase discharged cadmium reserve Precharge equals total negative excess less discharged reserve	o Uncertain amount of negative reserve o Uncertain amount of $Cd(OH)_2$ when negative is fully charged o Errors in volume of H_2 vented, or O_2 added
	Vent H_2	7	Discharge negative vs. case and vent H_2		
	Vent H_2	8	Discharge positive vs. negative part way, then charge positive vs. case and vent H_2		
	Add O_2	9	Add O_2 in cells		
	--	10	Charge with excess electrolyte. Remove excess electrolyte and seal.	Increase discharged cadmium reserve. Depend on efficiency difference between flooded and starved	o Uncertain difference in efficiency between flooded and starved

When both electrodes are fully charged at the beginning of precharge adjustment, the process will generally require either venting of hydrogen gas or the addition of oxygen gas. With these methods (items 5 to 10, Table 4), there is not an exact correspondence between the state-of-charge adjustment and the amount of precharge, for the adjustment increases the reserve of discharged cadmium. One must first know the amount of total negative excess, and the difference between the total excess and the adjustment will be the precharge. Though only scant data are available on accuracy, one would expect that this is the least accurate of the two basic approaches because the error in the difference of two numbers is equal to the sum of the errors of the two numbers. Addition of oxygen gas, item 9 of Table 4, is sometimes used to correct an error made in precharge adjustment by one of the oxygen venting methods.

The precharge adjust method that is mostly used for aerospace cells is item 1 of Table 4, in which oxygen is vented during charge, for which one gram of oxygen corresponds to 3.346 ampere-hours of precharge on the negative. There are several important variations of this method.

1. The cell is fully charged at the C/10 rate while temporarily sealed with a valve. The valve is then opened and the charge continued at the C rate for 12 to 20 minutes, following which the cell is sealed. This method was common during the 1960's but gives imprecise results because the oxygen recombination rate is variable from lot to lot and from cell to cell.
2. The cell is fully charged at about the C/10 rate, building up a positive pressure of oxygen in the cell. The charge rate is then increased to approximately the C/3 rate, the valve is opened and the oxygen is

collected by the displacement of water. When a predetermined volume of oxygen is collected, the valve is closed and the charging stopped.

3. The free volume is determined on a sample cell after normal electrolyte addition, either by topping off with water and obtaining a weight change or by connecting to a known volume of pressured gas and observing the pressure change. The cell to be adjusted is fully charged at approximately the C/10 rate, building up a positive pressure in the cell, and then the charge rate is increased to approximately C/3. The cell is vented approximately one to four times at known pressures until a predetermined amount of oxygen is released.
4. A method of adjusting precharge suggested by Turner (11) is to vent oxygen until pressure reduces to a predetermined value. This is based on the fact that recombination is faster at high levels of precharge. No use has been made of this method, however, not only because precharge would vary from cell to cell, but also because the recombination rate is very sensitive to electrolyte quantity and other variables.

All hydrogen venting methods start with both electrodes charged and set the state of charge by converting some of the excess charged cadmium to discharged cadmium. Of the several hydrogen venting methods listed in Table 4, there are two that deserve special comment, for they have been used commercailly. In the method of item 7, Table 4, both electrodes are fully charged in the cell following which a short discharge may or may not be added to minimize oxygen evolution from the nickel positive electrode. Using the steel case as the counter electrode, the negative electrode is discharged a predetermined amount. Hydrogen gas is generated at the case and vented from the cell. Use of the case as an electrode requires that the case liner be porous to permit ion transport; use of such a porous liner causes the resistance of electrodes to case to be less than for cell designs with non-porous liners. This method is used by Eagle-Picher, Inc. (12). Obviously, this method of adjusting state-of-charge cannot be used on cells with only one insulated terminal.

In the method of item 6, Table 4, both electrodes are fully charged in the cell, and then they are discharged together. The nickel electrode is permitted to overdischarge a predetermined amount, venting hydrogen gas. This method is used in Russia (13) and has been used experimentally to adjust precharge (19). Two factors which must be taken into account with this method are 1) reversal of the nickel electrode discharges it well below the usual discharge state, and 2) while at the hydrogen evolution potential, the nickel surface is activated and on subsequent charging some nickel is converted to nickelous hydroxide, increasing the capacity of the nickel electrode (13).

Two of the methods listed in Table 4 for setting precharge deserve special comment because no venting or addition of gasses is involved. The first one, item 5, is simply to take the fully discharged electrodes, put them in a cell, fill with electrolyte and seal. (Alternative one: perform discharge at low temperature; alternative two: short out positives after discharge, prior to cell assembly.) This method depends on two principles: 1) There always will be some undischarged metallic cadmium in a discharged negative electrode; when the cell is cycled, part of this cadmium is converted to electrochemically active cadmium; 2) A nickel electrode can be fully discharged in excess electrolyte especially at reduced temperature, to a greater degree than under starved cell conditions. Although industrial nickel-cadmium cells have been made this way, this method is not well suited for aerospace use because the amount of precharge provided is too variable, depending on differences in discharge utilization.

A second method which does not involve addition or venting of gasses is shown as item 10 of Table 4. Both electrodes are fully charged in the cell when flooded with electrolyte. After the excess electrolyte has been removed and the cell sealed, an excess of uncharged negative results because the positive electrode cannot be charged to as high a state of charge in the sealed, semi-starved condition as it would in the flooded state. The excess of uncharged negative is relatively small, however, although it can be increased by doing the adjustment at low temperature and by controlling the previous cycling history.

Uncertainty Problems in Setting Precharge

Setting precharge uniformly and predictably is important for sealed nickel-cadmium cells. Some of the major sources of uncertainty in setting precharge by the various methods are cited in Table 4. A basic problem is that it is necessary to establish a state of charge reference point, which is for the electrodes to be either charged or discharged. However, full charge and full discharge are only concepts that are not practicable to obtain, and conventional procedures give results that are variable.

With the oxygen venting methods, an important source or error is the uncertain amount of cadmium left when the negative electrode is discharged; for the hydrogen venting methods the problem is just the opposite; that is, an uncertain amount of discharged negative reserve when the negative electrode is fully charged. Where gasses are vented or added, there is the need to properly ascertain that the desired amounts of gas have been transferred.

Hydrogen venting methods have an added problem in that the adjustment increases the reserve of discharged cadmium. It is necessary to know the amount of total negative excess, for the precharge will be the difference between the total negative excess and the adjustment. Thus, setting precharge this way requires knowing two numbers accurately and taking their difference, a procedure that could lead to important errors.

Work at SAFT, France (14) showed that precharge gave inconsistent results when performed on plates immediately after capacity determination in flooded electrolyte. Uniform results were obtained if one or more preliminary cycles were conducted first. Table 5 gives a comparison between one preliminary cycle and five preliminary cycles, comparing also the effects of discharge to 1.0 volt, 0.0 volt, or reversal. One cycle shows a slightly higher precharge and less dispersion than five cycles; one cycle is preferred partly because it shows the least dispersion, and partly to save manufacturing time and effort. Data are not available for the effect of zero cycles, but this is reported to be the least desirable method. Reversal gave the greatest amount of electrochemically determined precharge.

In setting precharge by the oxygen venting method, the cells are charged from the fully discharged state. When the cells approach full charge, oxygen is evolved at a near-constant rate. There is a dispersion of data, however, due to differences in the state of charge among the cells and due to different oxygen recombination rates among the cells. This dispersion (Figures 1 and 2) helps explain the difficulty of getting reproducible results with the older method of setting precharge by overcharging for a predetermined period of time.

TABLE 5: EFFECT OF PRELIMINARY CYCLES ON ELECTROCHEMICALLY MEASURED PRECHARGE

Ref. 14

	Precharge* - Ampere Hours		
	Test A Short Circuit After Discharge To 1.0 V In Formation	Test B Positive Reversal In Formation	Test C Discharge To 0.0 V In Formation
Theoretical	8.7	8.7	8.7
Measured After 0 Cycles***	---	---	---
Measured After 1 Cycle**	5.4	6.5	5.5
Measured After 5 Cycles**	5.0	6.0	3.5

*Mean positive capacity = 31.6 AH
Mean negative capacity = 52.6 AH

**After formation, plates are washed, dried, assembled, and electrolyte added. Then up to five cycles were added before precharge was set.

***Inconsistent results from 0 cycles based on prior SAFT work.

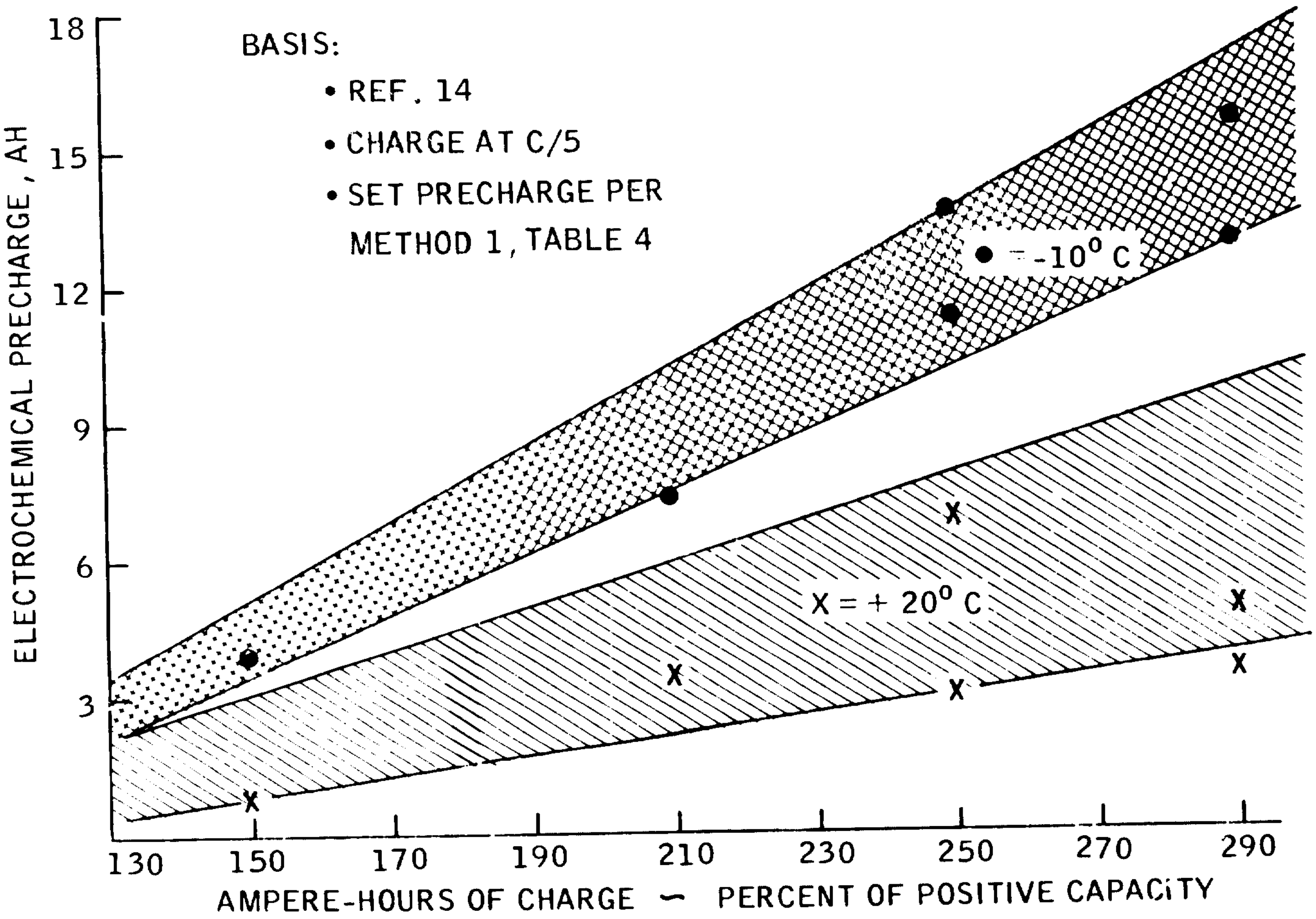

Figure 1. Effect of Temperature on Available Precharge

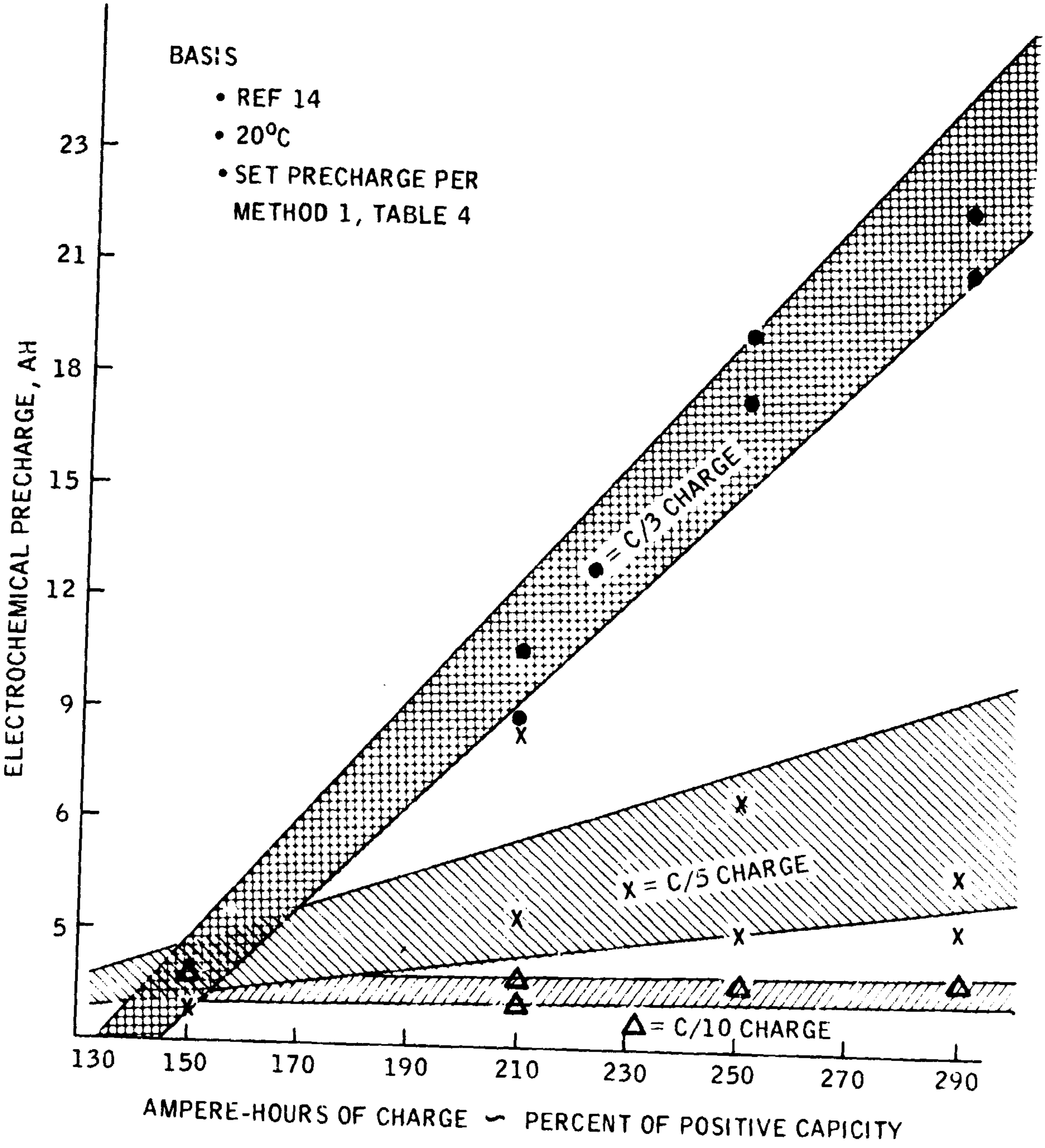

Figure 2. Effect of Charge Rate on Available Recharge

Setting precharge is more efficient at low temperature than at higher temperature, for the rate of oxygen recombination is lower then (Figure 1). High charge rates are also more efficient (Figure 2) because the fraction of gas which recombines is small. If the charge rate is too low (e.g., C/10, Figure 2), or if the negative electrode combines oxygen very rapidly, or if auxiliary recombination electrodes are used, then insufficient oxygen pressure will be developed for venting. On such cells, the oxygen recombination rate can be reduced by operating at very low temperatues such as -20°C (15 and 16) or by performing overcharge and oxygen venting in the flooded condition (15).

Another important source of uncertainty in setting precharge is the practice used sometimes of adjusting precharge on an individual cell basis to balance cells. When cells with insufficient negative/positive ratios are used to meet requirements for especially low temperature, such as -10°C, then the cells operate negative-limited. Capacity is uneven, but capacity matching can be improved by selective adjustment of precharge. This is considered to be a questionable practice. It is much preferred to meet low temperature requirements by an increased negative/positive ratio.

Effects of Precharge Adjustment on Electrolyte Concentration

When precharge is adjusted by oxygen venting, water is produced by the following overall reaction:

$$Cd(OH)_2 \rightarrow \tfrac{1}{2}O_2 + Cd + H_2O.$$

When precharge is adjusted by hydrogen addition, water is produced by the following overall reaction:

$$Cd(OH)_2 + H_2 \rightarrow Cd + 2H_2O.$$

When precharge is adjusted by hydrogen venting, water is consumed by the following overall reaction:

$$Cd + 2H_2O \rightarrow Cd(OH)_2 + H_2.$$

When precharge is adjusted by oxygen addition, water is consumed by the following overall reaction:

$$Cd + H_2O + \tfrac{1}{2}O_2 \rightarrow Cd(OH)_2.$$

Thus, when the state-of-charge adjustment is based on conversion of discharged cadmium into charged cadmium, water is produced which dilutes the electrolyte. When the adjustment converts charged cadmium into discharged cadmium, water is consumed, which makes the electrolyte more concentrated. Furthermore, it is seen that processes involving the venting or addition of hydrogen produce or consume twice as much water as oxygen does. Halpert showed (17) for cells with negative/positive ratio of 1.5 and precharge equal to 45% of excess negative capacity, established by oxygen venting, that precharge would reduce electrolyte concentration by 0.8%. Thus, setting precharge by addition of oxygen would increase concentration 0.8%, setting it by venting hydrogen would increase it 1.6%, and setting it by adding hydrogen would decrease electrolyte concentration by 1.6%. These changes must be taken into account during manufacture.

More significant than the electrolyte concentration changes due to precharge adjustment are the concentration changes due to charge or discharge. If the electrodes are put into the cell in the discharged state, then the water generated during charge will dilute the electrolyte from 31% to approximately 22.9% (17). Where precharge is set using flooded cells in order to reduce oxygen recombination, then it is necessary to know the amount of electrolyte in both the flooded and starved states in order to predetermine the proper initial concentration of electrolyte. Manufacturers sometimes do not make allowance for these effects.

Effect of Charged Cadmium Reserve (Precharge) on Performance

In the early 1960's, setting the reserve of charged cadmium, or precharge, was commonly done with oxygen recombination occurring simultaneously. As a consequence, quantitative data was often not available on the amount of precharge used, and at times quality control problems arose. In general, precharge levels were well below half of the excess negative capacity. During the late 1960's, there was some thought that the precharge should approach all the excess negative available, especially for cells with auxiliary recombination electrodes (15a). Tests conducted to determine the optimum precharge for cells with recombination electrodes showed that limiting recombination current on the cadmium electrode by means of a resistor was better than going to very high precharge (approaching 100 percent) to reduce fading.

Since fading is associated primarily with reduced utilization of metallic cadmium, increasing the precharge increases the metallic cadmium available and reduces the effects of fading. This was demonstrated in an early study (15) whereby precharge adjustment significantly increased cycle life (Figure 3). In that test, the rapid fading of the negative was accelerated by the use of oxygen recombination electrodes which, possibly due to increased discharge current density, reduced the reserve of charged cadmium present. This problem was minimized by limiting recombination current on the cadmium electrode with a sufficiently large resistor. Except for the fact that some hydrogen could be generated during charge, it was found that precharge to 50 percent of the positive electrode capacity (100 percent of excess negative

REF 15

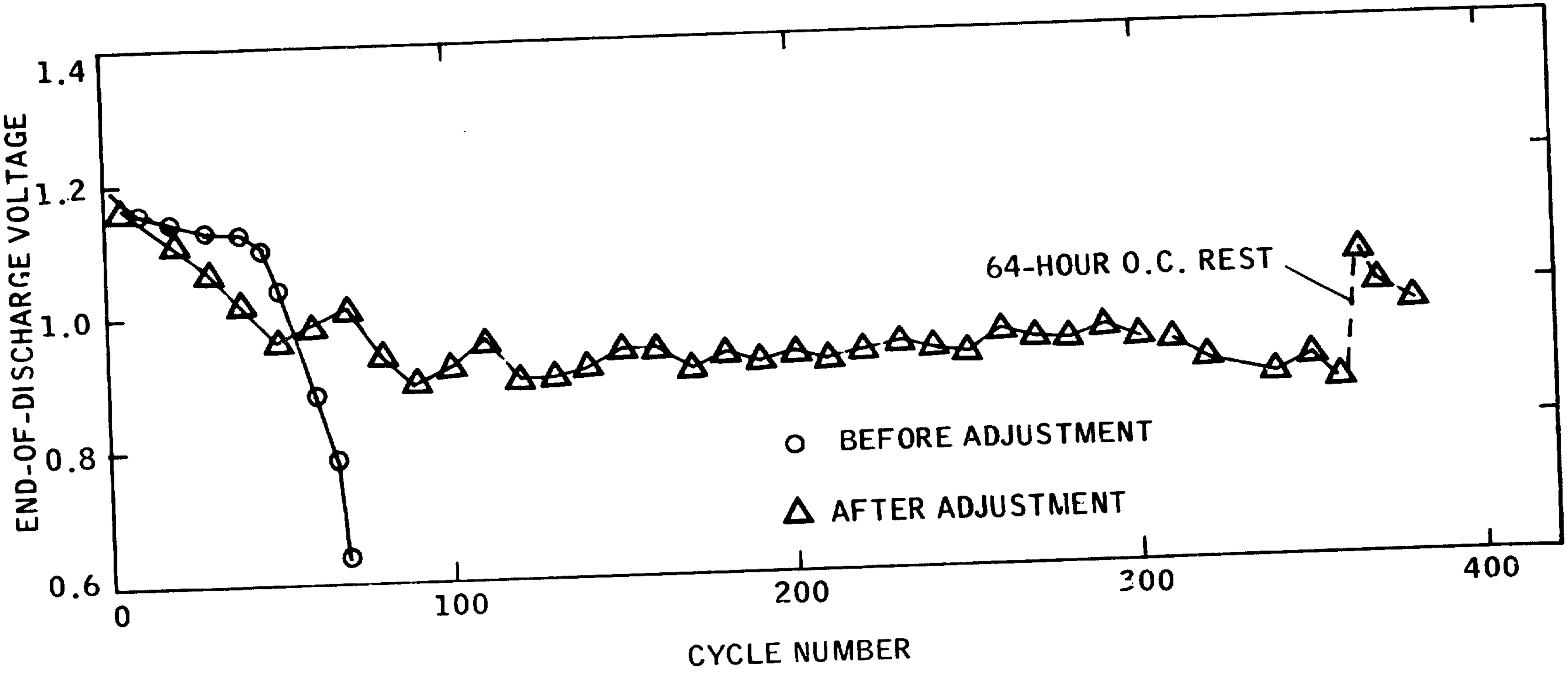

Figure 3. Effect of Adjusting Negative State-of-Charge on Cycle Life at 25° C, 75% DOD

capacity) was best, giving the least capacity degradation during cycling (18). Since such high precharge levels are unsatisfactory because hydrogen is generated during charge, the recommended precharge for cells with 1.50 negative to positive ratio was 42.5 percent of the positive capacity (85 percent of excess negative capacity). A further recommendation was for a minimum design negative-to-positive ratio of 1.75. This would provide more ampere hours of negative precharge and give better cell performance, especially at deep depths of discharge. These 1969 recommendations were made for nickel-cadmium cells with recombination electrodes; the recommendations were never adopted, however, partly because the performance problems were solved by use of a resistor to limit recombination current, and partly because cells with recombination electrodes have not since been popular, and also because this imposes an added weight penalty on cells.

An insufficient reserve of discharged cadmium in a cell will result in an abnormal voltage increase during charge, producing hydrogen gas in the cell. This insufficiency can occur either because the negative-to-positive ratio is too low, because the precharge is set too high, or because of negative plate fading. In tests on 20 ampere-hour cells from the OAO program, it was found that cells which had normal characteristics when new could exhibit such problems with cycling (19). A good test to disclose these problems is overcharge at the C/20 rate at 0^{o}C for 48 hours; insufficient discharged cadmium reserve will result in high voltages, and may even cause hydrogen generation. For example, during overcharge tests at C/20 and 0^{o}C, cell #424 had gradually increased in voltage from 1.472 initially to 1.576 after 5,642 cycles. Test results after 5,668 cycles are shown in Figure 4. Following the overcharge, the cell precharge was intentionally reduced by three ampere-hours, using a reverse charge to vent hydrogen. Reducing the precharge

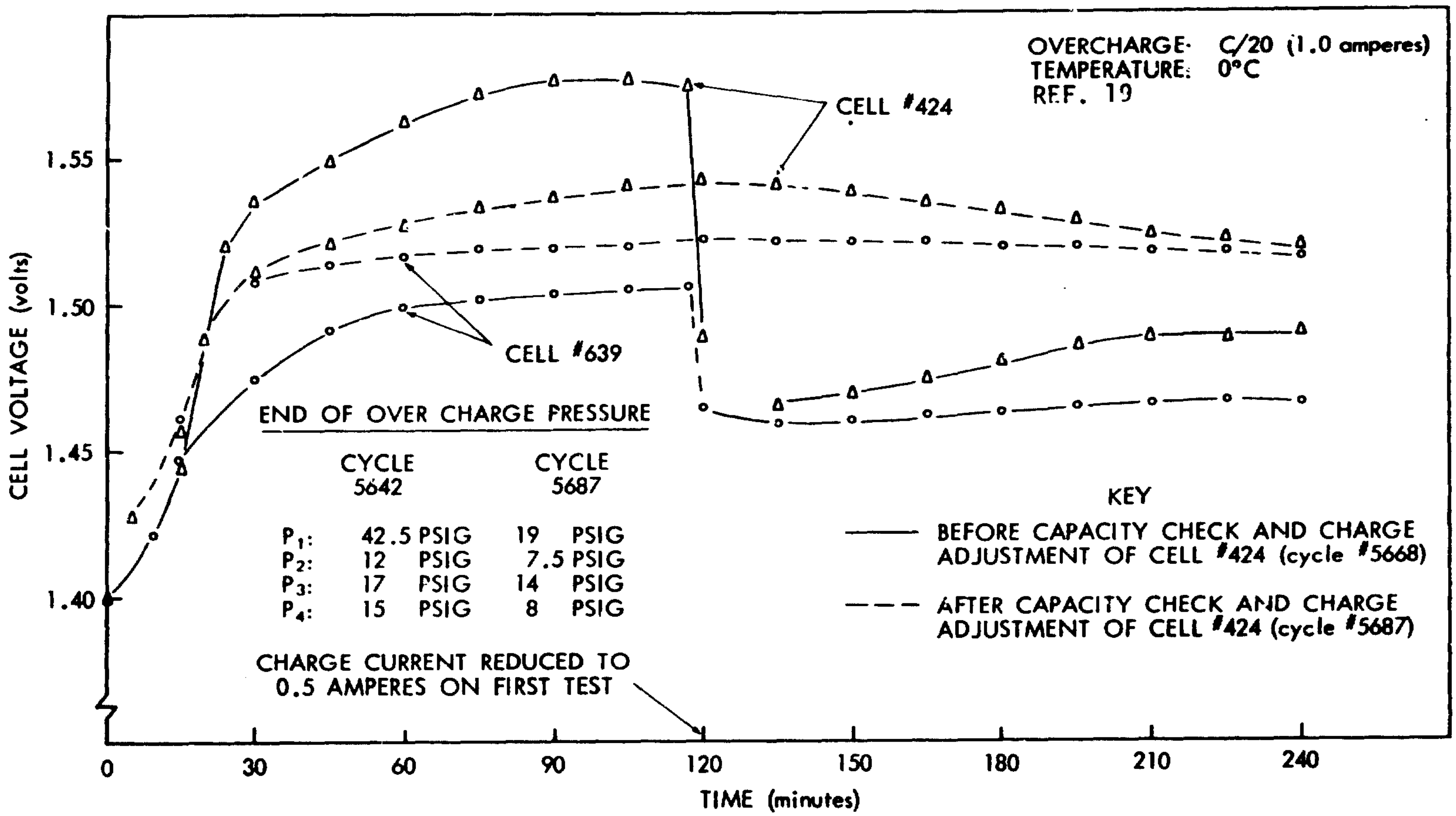

Figure 4: Voltage Profile During Overcharge Test

caused the overcharge voltage to decrease, as shown in Figure 4, the lowered voltage being similar to voltages shown by the other cells.

Precharge measurements on seven OAO cells, using oxygen recombination, gave values ranging from 1.0 to 6.1 ampere-hours (19). Cell capacities after 5,687 cycles were 23 ampere-hours, though initially this could approach 30 ampere-hours. Negative-to-positive capacity ratio on the cells when new ranged from 1.22 to 1.39. Thus, for some cells, most of the excess negative capacity could have been in the form of precharge.

All the OAO test cells exceeded 1.51 volts during overcharge. This is considered a high voltage and cannot be due primarily to high precharge because all cells did not have excessive precharge. Therefore, this is probably due to the combination of low negative-to-positive capacity ratio and fading, though drying out of electrolyte may have contributed to the high voltage.

Experience with the OAO cells has shown several important things.

1. Cells with normal operating characteristics when new can become deficient in discharged cadmium with extended cycling.
2. When relatively low negative-to-positive ratios are used (1.22 to 1.39 for OAO), it is especially important that the precharge adjustment during manufacturing be very precise.

One of the best studies available on precharge was conducted by Font (14). The study was confined to the initial effects of variables with cycling up to 30 days. Cells used in this study were made by the SAFT vacuum impregnation process, with mean capacities of 32.1 AH for the positive electrode and 56.3 AH for the negative electrode giving an average negative/positive ratio of 1.75.

After formation, prior to setting precharge by evolution of oxygen, it is found that the negative electrodes contain some charged cadmium even though the electrodes have apparently been fully discharged. This can be determined only by chemical analysis. Font found that this amounted to from 12 to 29 percent of the excess negative capacity on cells with negative/positive ratio of 1.75. (If the negative/positive ratio had been 1.5, then this would have amounted to from 16 to 37 percent of the excess negative capacity.) Furthermore, Font (14) and Dunlop (20 and 21) showed that with cycling, chemical cadmium was converted to electrochemical cadmium and vice versa. Thus, the total precharge, chemical plus electrochemical cadmium, is the important parameter, not just that precharge which is put in by evolution of either oxygen or hydrogen. This finding helps explain why manufacturers sometimes put in no precharge in their commercial sealed nickel-cadmium cells, and still have them operate all right.

Table 6 summarizes the results of Font's precharge analysis. Precharge was put in by the oxygen venting method, which, combined with the precharge already in the cells after formation, produced what is called total precharge. The cells were then analyzed showing that the precharge measured electrochemically is less than what was put in by oxygen venting. Total precharge was still the same, however. After 30 cycles, the total precharge was only slightly higher, but the distribution had changed so that most of the precharge was in the electrochemical form. Further cycling or cycling in a different manner might partition the electrochemical and chemical forms differently. It should be noted that the distinctions in precharge types made here are not always observed. Unless precharge information is clearly defined, it can be confusing.

TABLE 6: PRECHARGE ANALYSIS AT BEGINNING OF LIFE

Ref. 14		AH PRECHARGE ON 56.3 AH NEGATIVE ELECTRODES		
		TEST SERIES E (LOW PRECHARGE)	TEST SERIES F (MEDIUM PRECHARGE)	TEST SERIES G (HIGH PRECHARGE)
Measurements at Precharge Adjustment	Chemical Analysis After Formation	3 to 7	3 to 7	3 to 7
	Precharge Input by Venting Technique	4	10	16
	Total Precharge	7 to 11	13 to 17	19 to 23
Measured Precharge Before Cycling	Electrochemical	1.8	4.8	10.0
	Chemical Analysis	10.9	10.5	8.8
	Total Precharge	12.7	15.3	18.8
Measured Precharge After 30 Cycles (Charge C/10 for 11 hours, discharge C/2 for 1 hour, at 15^{o}c)	Electrochemical	8.6	14.0	20.0
	Chemical Analysis	3.4	3.0	2.1
	Total Precharge	12.0	17.0	22.1

Data are given in Ref. 14 on another set of precharge tests, some of which have been reduced and are shown in Table 7. This test compared cells with zero, 10, and 18 ampere hours adjustment. Cells with no precharge adjustment had the least capacity and the highest pressure. The decrease in pressure with increased precharge (Tables 7 and 8) is a well known phenomenon (11), a esult of the increased surface area of metallic cadmium required for oxygen recombination. However, it is not clear why the capacity was lower on the cells with no precharge. It is likely that these cells became negative-limited as a result of no precharge adjustment, similar to the negative electrode problems reported in Ref. 15 with insufficient precharge. The fact that the capacity at 40°C was nearly the same for the three groups (17 to 18 AH) supports the idea of negative-limited operation, as does the fact that the group with no precharge had a higher voltage on the voltage recovery test (1.23 V compared with 1.20 V for the other two groups). One reason precharge is used is to avoid such negative-limited conditions.

Another effect of low precharge levels is a low end of charge voltage, as seen in Tables 7 and 8. This is caused by low polarization on the cadmium electrode due to the large surplus of $Cd(OH)_2$. There is an opposite effect at the beginning of charge, with high voltage associated with low precharge; this is due to the low number of cadmium sites available to start the crystallization of cadmium.

One aspect of precharge that has received very little attention is the precharge distribution from plate to plate after the cells have been cycled and equilibrated. This could be sensitive to electrolyte distribution, with different current density on different plates. Significant plate-to-plate differences could affect cell life and could influence the choice of precharge level.

TABLE 7: EFFECT OF PRECHARGE ON ACCEPTANCE TEST PERFORMANCE

Derived from Ref. 14

	AVERAGE OF TEST GROUP P00 (No precharge adjustment)	AVERAGE OF TEST GROUP P10 (10 AH adjustment)	AVERAGE OF TEST GROUP P18 (18 AH adjustment)
Capacity (AH) C/2 discharge to 1.0 V, 21°C	22.60	27.32	27.32
Voltage Recovery (volts) 1.0 ohm for 12 hours, short for 2 hours, charge 10 minutes at C/10, open circuit 24 hours	1.232	1.200	1.199
Overcharge Voltage (volts) C/10 for 16 hours, 21°C	1.410	1.419	1.420
Overcharge Pressure (mbars) C/10 for 16 hours, 21°C	824	163	50

TABLE 8: EFFECT OF PRECHARGE ON CELL CAPACITY, PRESSURE & VOLTAGE

Ref. 14

	TEST SERIES E (Low* Precharge)	TEST SERIES F (Medium* Precharge)	TEST SERIES G (High* Precharge)
Capacity C_i after 30 cycles at $15^{o}C$ to 50% DOD - ampere-hours	25.7	27.3	28.0
Capacity C_s after reconditioning on C_i test - ampere-hours	24.1	25.7	26.4
Pressure at end of 11.0 hours C/10 charge, cycle no. 2 - atm. abs.	1.07	1.00	0.88
Pressure at end of 11.0 hours C/10 charge, cycle no. 29 - atm. abs.	1.05	0.99	0.83
Voltage at end of 11.0 hours C/10 charge, cycle no. 2	1.421	1.424	1.424
Voltage at end of 11.0 hours C/10 charge, cycle no. 29	1.414	1.416	1.420

*See Table 6.

Too much precharge can be just as bad or even worse than too little precharge, for this comes at the expense of overcharge protection; that is, excess discharged cadmium. For example, COMSAT tests (22) showed that some 20 AH cells made in 1969 had 12 to 18 AH of precharge, and from zero to seven AH excess discharged cadmium, giving little to no overcharge protection. Table 9 gives a qualitative summary of the effects of precharge level.

Effect of Discharged Cadmium Reserve on Performance

The amount of excess discharged cadmium is seldom stated as a design parameter but is readily obtained knowing the negative/positive capacity ratio and the precharge level. Since precharge is practically always less than half of the negative excess, the negative/positive ratio is the measured parameter which most closely determines the amount of excess discharged cadmium. The discharged cadmium reserve is so important that it should be identified in specifications and analyses.

Excess dishcarged cadmium is essential to avoid hydrogen generation during charge. Because of the importance of avoiding hydrogen, it is customary to design for a large safety factor in the amount of excess discharged cadmium. Charge rate and operating temperature have important effects on hydrogen generation, and thus strongly affect the amount of excess discharged cadmium needed.

The least amount of excess discharged cadmium needed is for applications where temperatures do not vary much and where charge rates are low. Some commercial sealed nickel-cadmium cells intended for low rates use a negative-to-positive ratio of only 1.2. Where operating conditions include high rate charging or low temperature, then a greater amount of excess discharged cadmium is needed. For example, the ISIS spacecraft cells had a negative-to-

TABLE 9: QUALITATIVE EFFECTS OF PRECHARGE LEVEL

	LITTLE PRECHARGE*	MUCH PRECHARGE*
Oxygen Pressure	High	Low
Capacity	Low	High
Cell Beginning-of-Charge Voltage	High	Los
End-of-Charge Voltage**	Low	High
Voltage Recovery Following Short	High	Low

*Precharge obtained at the expense of discharged cadmium reserve.

**High end-of-charge voltage is caused by the reduced amount of discharged cadmium reserve which can occur at high precharge levels.

positive ratio of approximately 2.0 in order to operate at -5°C continuously at the C/10 charge rate; also, Bell Telephone Laboratory 23 AH cells designed for a temperature range of -20°F to +140°F and continuous C/20 charge rate had a negative-to-positive capacity ratio of 2.0.

Low temperature operation is especially significant for two reasons. First, hydrogen gassing occurs more readily; and second, the positive electrode capacity is greater at low temperature. Both of these conditions require additional excess discharged cadmium.

Three other factors must be considered, all of which take away oxygen from the negative electrode and thereby require that it have additional excess discharged cadmium. These are:

1. Free Oxygen. Oxygen fills the free volume of the cell, especially at the end of charge when it can reach high levels of pressure. Small cells usually have a higher gas volume relative to the amount of electrode material; therefore, this consideration is most important for small cells and for cells that can be operated at high internal pressure. One cm^3 of oxygen at one atmosphere will require 4.39×10^{-3} ampere-hour of additional negative electrode capacity (23). Designing for 20 cm^3 and five atmospheres would require 0.44 ampere-hour additional negative electrode capacity.
2. Positive Electrode Corrosion. Corrosion of the positive electrode occurs during cycling. The amount varies with the cell design, the kind of usage, and the operating temperature. Capacity increases of more than 10 percent have been observed, though such large changes are less common today than previously. For example, cells tested for various synchronous orbit storage modes (22) increased positive electrode capacity

at least five percent in two years. A ten percent increase during cycling is not uncommon. As Seiger pointed out (24), there is a three ampere-hour increase in the negative state of charge for each ampere-hour increase in the positive electrode due to corrosion.

3. Separator Oxidation. Nylon separator material slowly oxidizes in nickel-cadmium cells, especially at high temperature. Lin (12) analyzed the effect of ten percent oxidation of 13 grams nylon separator in 24 ampere-hour cells containing 10 to 13 ampere-hours of excess discharged cadmium. This much oxidation would consume 10 ampere-hours of excess discharged cadmium, virtually eliminating overcharge protection.

One of the attributes of cells with little excess of discharged active material is a high end-of-charge voltage. Sometimes voltages greater than 1.50 volts are observed on new cells; for example, in COMSAT tests (12) cells with 1.54 volts at 0°C with C/20 charge were identified by analysis to have very little overcharge protection. This is probably caused by increased polarization of the cadmium electrode due to a relatively small safety margin.

Low voltages are also observed near the end of discharge on cells that have insufficient excess discharged active material. A cell acceptance test considered worthwhile is to require that cells shall be positive-limited at -5°C with a C/2 discharge.

In summary, it is seen that practically all the changes that occur during the life of a cell will reduce the excess discharged cadmium. It is necessary to anticipate these changes to be certain there is sufficient reserve for the life of the cell. Table 10 gives a summary of the qualitative effects of discharge cadmium reserve level.

TABLE 10: QUALITATIVE EFFECTS OF DISCHARGED CADMIUM RESERVE LEVEL

	LITTLE DISCHARGE RESERVE*	MUCH DISCHARGE RESERVE*
Cell End-of-Charge Voltage	High	Low
Cell End-of-Charge Voltage	Low	High
Tolerance to High Charge Rate	Low	High
Tolerance to Low Temperature Charge	Low	High
Tolerance to Effects of Separator Degradation	Low	High
Tolerance to Corrosion of Nickel Positive	Low	High

*Discharge reserve obtained at expense of precharge.

Design Considerations

Table 11 summarizes some of the experience on values used for negative-to-positive ratio and precharge. A wide range of values is found for both of these parameters, showing that within the industry there is a wide divergence of opinion on what are the best values to use for design. The NASA cell specification is suggested as a good reference point with which other designs can be compared; this prescribes a negative-to-positive ratio of 1.50 minimum, and precharge equal to 45 percent of the excess negative.

Figure 4 shows calculations of parametric relationships between precharge and negative/positive ratio. Selected data from Table 11 are included for reference, and a judgement is made defining the zone of acceptable design.

Table 12 summarizes qualitatively the effect of requirements on precharge and negative/positive ratio. The NASA specification (1.50 negative/positive ratio, precharge = 45 percent of negative excess) is again taken as the reference for "typical" aerospace requirements. Departures from this reference are acceptable where requirements are especially lenient or severe.

TABLE 11: EXPERIENCE SUMMARY ON NEGATIVE/POSITIVE RATIO AND PRECHARGE

NUMBER	ITEM	NEGATIVE/POSITIVE RATIO	PRECHARGE
1	Contract NAS 5-11547, March 1970, Characterization of Recombination and Control Electrodes for Spacecraft Nickel-Cadmium Cells	1.75 minimum recommended	---
2	NASA Spec 74-1500, Specification for the Manufacture of Aerospace Nickel-Cadmium Storage Cells, January 1974	1.50 minimum	45 ±5% of excess negative
3	OAO-A-2 Flight Batteries, per NASA report X-761-71-228, Summary of Test Results on Spare Nickel-Cadmium Cells from OAO-A-2 Flight Batteries, April 1971	1.22 to 1.39	2.8 to 17.4% of excess, calculated assuming average positive capacity = 27 AH, average negative/positive ratio = 1.3
4	AFAPL-TR-75-64, Development of Nickel Alkaline Batteries for Aerospace Lightweight Secondary Power, June 1975 (Spectrolab)	1.45 to 1.50	41.5% of excess negative
5	Goddard Spec S-615-P-17, May 1968, Procurement Specification for Nickel-Cadmium Cells, ISIS "B"	1.7 minimum, NOTE: Precharge was in addition to this value	---
6	Ref. 3413 - Final Report, COMSAT CSC-SS-282, Improved Nickel-Cadmium Cells for a Communications Satellite at Synchronous Orbit (SAFT, 1972)	1.75	Electrochemical: 7.4% to 41% Electrochemical + Chemical: 52% to 78%
7	Gould Long Life Design	1.7	Electrochemical + Chemical = 30%, assume chemical = 7%, then electrochemical = 23%
8	Union Carbide Commercial Low Rate Design	1.2	---
9	Union Carbide Commercial High Rate Design	1.4	---
10	Eagle Picher Cells for S-3 Spacecraft (6-month life requirement)	1.3	50%

TABLE 11 (Continued)

NUMBER	ITEM	NEGATIVE/POSITIVE RATIO	PRECHARGE
11	Gulton Cells, 1960-1970	1.30 to 1.35 (occasionally 1.20 or less)	---
12	SAFT America	1.55 to 1.60	30% to 40% of excess negative
13	Eagle Picher Cells for NATO-3 Spacecraft (synchronous orbit)	1.35	25% of excess negative
14	Motorola Commercial	1.40	50% of excess negative
15	Marathon Long Life Design	2.0	25% of excess negative
16	Chloride Commercial	1.35	33% of excess negative
17	G.E. Aerospace, Close Earth	1.50 minimum	0.33 to 0.50, depending on amount of negative and positive excess
18	G.E. Aerospace, Synchronous Orbit	1.50 minimum	0.15 to 0.5, depending on amount of negative and positive excess
19	Developmental IUE Cells	1.88	32% of excess negative
20	G.E. Cells for NRL	1.6	50% of excess negative
21	SAFT France 1972 Technology	1.50 minimum	25% of excess negative
22	Japanese Cells for Shinsei and Denpa Spacecraft	1.50 to 1.7	---
23	IUE 6AH Cell Design	1.85	42.6% of excess negative
24	IUE 12AH Cell Design	1.85	41.6% of excess negative

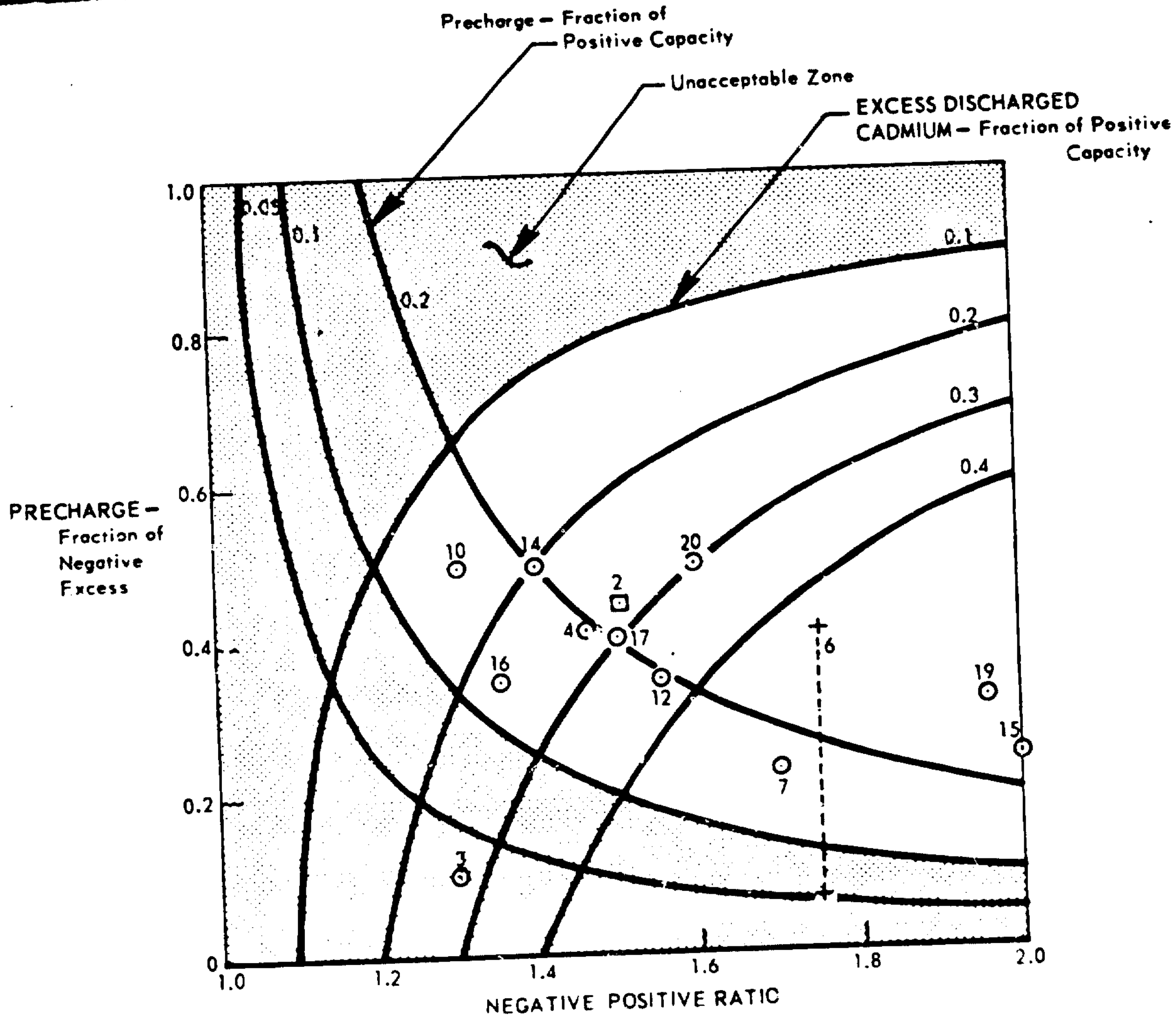
Precharge – Fraction of Positive Capacity
Unacceptable Zone
EXCESS DISCHARGED CADMIUM – Fraction of Positive Capacity
PRECHARGE – Fraction of Negative Excess
NEGATIVE POSITIVE RATIO
1.0
0.8
0.6
0.4
0.2
0
1.0
1.2
1.4
1.6
1.8
2.0
0.05
0.1
0.2
0.1
0.2
0.3
0.4
10
14
20
2
4
17
16
12
6
19
15
7
3

Figure 4

TABLE 12: FACTORS AFFECTING PRECHARGE AND NEGATIVE/POSITIVE RATIO

FACTOR	PRECHARGE CHANGE O.K. RELATIVE TO 45% OF NEGATIVE EXCESS			NEGATIVE/POSITIVE RATIO CHANGE O.K. RELATIVE TO 1.5 RATIO			COMMENT
	NO CHANGE	INCREASE	DECREASE	NO CHANGE	INCREASE	DECREASE	
Temperature limited to 10°C to 20°C			X			X	Least degradation occurs at optimum temperature range
Temperature above 30°C		X			X		High temperature more efficient, but more degradation
Temperature below 0°C	X				X		Poor negative efficiency at low temperature
Rapid temperature changes	X				X		Change from hot to cold reduces efficiency
Charge rate greater than about C/3	X				X		Hydrogen generation risk with fast charge
Overcharge rate greater than about C/16	X				X		More reserve needed for high rates
Synchronous Orbits, DOD 60%	X			X			Synchronous is worse than close Earth because of slow charge and deep DOD
Synchronous Orbits, DOD 60%		X			X		Deep discharge leaves little reserve
Close Earth Orbits			X	X			Fading less important at low DOD
Large amount of cadmium present in discharged negatives before setting precharge			X	X			Chemical cadmium will convert to electrochemical with cycling
Capability to set precharge precisely			X	X			Poor QC caused many of the prior precharge problems
Negative designed for low fading			X			X	Precharge provides some reserve for fading
Operation less than one year			X			X	Little degradation in one year
Operation more than four years	X				X		More negative to compensate for degradation
High free volume	X				X		Important for small cells
High cell pressure	X				X		Important for small cells
Separator oxidation significant			X		X		Changing only one parameter may suffice
Positive electrode oxidation significant			X		X		Changing only one parameter may suffice
Long storage periods in open circuit	X				X		Overcharge protection reduces in storage or in random integration testing

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