

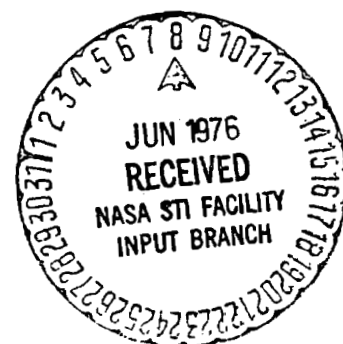
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CADMIUM MIGRATION IN AEROSPACE NICKEL CADMIUM CELLS

DR. PATRICK P. McDERMOTT

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**Dr. Patrick D. McDermott
Coppin State College
Baltimore, Maryland**

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ABSTRACT

The effects of temperature, the nature of separator material, charge and discharge, carbonate contamination, and the mode of storage are studied with respect to the migration of active material from the negative toward the positive plate. A theoretical model is proposed which takes into account the solubility of cadmium in various concentrations of hydroxide and carbonate at different temperatures, the generation of the cadmate ion, $\text{Cd}(\text{OH})_3^-$, during discharge, the migration of the cadmate ion and particulate $\text{Cd}(\text{OH})_2$ due to electrophoretic effects and the movement of electrolyte in and out of the negative plate and, finally, the recrystallization of cadmate ion in the separator as $\text{Cd}(\text{OH})_2$. Application of the theoretical model to observations of cadmium migration in cycled cells is also discussed.

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CADMIUM MIGRATION IN AEROSPACE NICKEL-CADMIUM CELLS

INTRODUCTION

In recent years, the sintered electrode, sealed nickel cadmium cell has proved to be a useful and reliable rechargeable power source for aerospace applications. Although much has been learned about the operation of the cell since its development during World War II, there is still much that is unknown. Much of the research and development has been aimed at increasing cell performance capacity and life, but the approach has been, in large measure, a trial and error methodology. This has resulted from the fact that the fundamental processes of the sealed nickel cadmium system are so complex and not yet adequately explained. Although bits and pieces of problem have been solved there is still some doubt as to the nature of the charge/discharge reactions in the positive and negative electrodes, the mechanism of oxygen recombination, distribution of electrolyte and the morphology of the active material with aging.

Depending on how a cell is constructed and cycled, there are certain factors which seem to limit the performance and life of the cell with aging. These would include among others: negative fading, cadmium migration, positive plate expansion and deterioration, loss of electrolyte and separator dryout, undesirable pressure buildup, carbonate contamination, leaks and shorts.

Although some of the failure modes are readily observed and explained, others such as cadmium migration are not well understood in terms of the fundamental processes which govern the operation of the cell. It is one thing to design a seal which will not leak given a certain state of the art of available materials. It is another thing, however, to "cure" the cell of some undesirable characteristic when that factor may be under the influence of several unknown variables.

The object of this present study is to examine one of the more pronounced degradation mechanisms in the nickel-cadmium cell during certain applications, that is, the migration of active material from the negative electrode into or toward the separator area. The material deposited in the separator is generally a dark grey substance which under x-ray diffraction analysis appears to be primarily hexagonal $\text{Cd}(\text{OH})_2$, the discharged active material of the negative electrode.

It is not clear how this material is deposited in the separator. Although $\text{Cd}(\text{OH})_2$ has low solubility in the highly concentrated KOH electrolyte there may be more soluble species of cadmium hydroxide such as $\text{Cd}(\text{OH})_3^-$ and $\text{Cd}(\text{OH})_4^{2-}$ which are generated during the charge/discharge reaction in the negative electrode. Conceivably, these negative soluble ion would migrate out of the electrode under the influence of the electric field gradient between the electrodes and/or transported out of the electrode with the movement of electrolyte which itself migrates in and out of the electrode during charge and discharge. The separator matrix would provide a location for the recrystallization of $\text{Cd}(\text{OH})_2$ from the soluble ionic species.

Even in cells where there is not an appreciable amount of material deposited in the separator, there may be a phenomenon occurring which could also be classified as "cadmium migration", that is, the migration of active material toward the surface of the electrode which eventually blocks the pores near the surface and lowers the efficiency and capacity of the negative plate. This could occur, for example, in a teflonated plate, where the teflon shield hinders further passage into the separator area.

This report presents a discussion of circumstances in which cadmium migration seems to be enhanced and the possible mechanisms to explain the generation of a soluble cadmium species which is in turn transported toward the separator and deposited either in the separator or on the surface of the electrode.

FACTORS AFFECTING CADMIUM MIGRATION

It is difficult to point to any one factor as the cause of cadmium migration. There are, however, circumstances or conditions in which cadmium migration seems to be enhanced. These include the extent and nature of the cycle regime, the temperature, the extent of carbonate contamination, and the nature and condition of the separator. There is no attempt at this point to attribute a direct cause/effect relationship between these factors and cadmium migration, but merely to point out occasions where cadmium migration is found to occur more frequently or with greater intensity.

Cycle Regime

In tests conducted at the Naval Ammunition Depot, Crane, Indiana, it has been observed that cells in 90 minute orbits (60 minute charge, 30 minute discharge) and moderately low depths of discharge (15% - 25% DOD) exhibit substantial migration of active material into the separator area. It has also been shown

that temperature is a factor in that for a given number of life cycles, cells operated at lower temperatures have less migration than cells operated at higher temperatures.

Substantial migration was noted, for example, in a 20 ampere-hour (Ah) cell (cell 494, pack 12E, NAD-Crane) at 20°C, 15% DOD, with only 2,522 cycles, less than 6 months of life cycling.

Severe migration and shorting was observed in a cell which had reached 9,987 cycles at 25°C and 15% DOD (cell 1-27, pack 28C, NAD-Crane).

In a near-earth orbit cell analyzed at the Goddard Space Flight Center (cell S/N 588, A-2 Flight Lot) there was significant deterioration of the separator material due to cadmium migration. This was surprising since the total test time was approximately 450 days of which over 70% was at temperatures of 15°C or below.

In contrast to the near-earth orbit tests, it has been found that those cells which have been cycled in a synchronous orbit regime have exhibited considerably less cadmium migration even after 9 or 10 eclipse seasons at very high depths of discharge (up to 80%). This author reported earlier that there is significant deterioration of the positive plates in the more rigorous synchronous orbit tests.¹ There does not, however, seem to be quite as much stress on the negative plate as appears to take place in near-earth orbit. (Sync. Packs 1-12, NAD-Crane).

One could interpret these results as an indication that cadmium migration is related to the number of cycles the cell has undergone since, in general, the total number of cycles in synchronous orbit is lower than that of near-earth orbit when one considers the normal life-time of a cell.

Temperature

The temperature of cycling seems to have an effect on the degree of cadmium migration. In contrast to those near-earth orbit cells cited above (which lasted less than 10,000 cycles at higher temperatures), cells at 0°C were able to sustain a much higher cycle life. A 12 Ah cell cycled at 0°C (Pack 101B, NAD-Crane) showed heavy migration but was able to complete 38,237 cycles. Another cell (Pack 16B, C-2, NAD-Crane), completed 50,727 life cycles. At higher temperatures there is also a more severe degradation of the separator material itself.

Physical inspection of synchronous orbit test cells shows some possible temperature dependence although the results are difficult to interpret since there is less overall migration from the negative electrode and more flaking and blistering of the positive electrode which itself tends to deposit materials in the separator.

Storage Mode

Figure 1 shows separator materials from cells which were subjected to different modes of storage over an 18 month period. These cells were 20 Ah Gultan cells with Pellon 2505 nylon separators. The first set of cells were shorted during this period. The second set subjected to a continuous C/40 trickle charge and the third set was subjected to a random sequence of charging and discharging.

The random storage test was set up to simulate conditions when the battery was utilized in a spacecraft during ground testing (integration). During the random test, the battery was left in open circuit for perhaps 40% of the time, usually often being trickle charged all day or after being cycled a couple of times during the day. During the weekends, the battery was always left in open circuit.

It is apparent from the photograph that the shorted and trickle-charged cells experienced little or no cadmium migration while the random storage test experienced severe migration. The implications of this test will be discussed later in this report.

Carbonate Contamination

The degree of carbonate contamination seems to have some effect on the amount of cadmium migration experience by a cell during cycling. Barney et. al.² studied the effect of carbonate on the performance of sealed nickel-cadmium cells. It was shown that carbonate in sealed cells lowered discharge voltage, raised charging voltages, decreased charge acceptance, increased cell pressures on overcharge, and lowered cycle life.

In reference to reduced cycle life, the authors noted that this was due to cadmium migration through the separator.

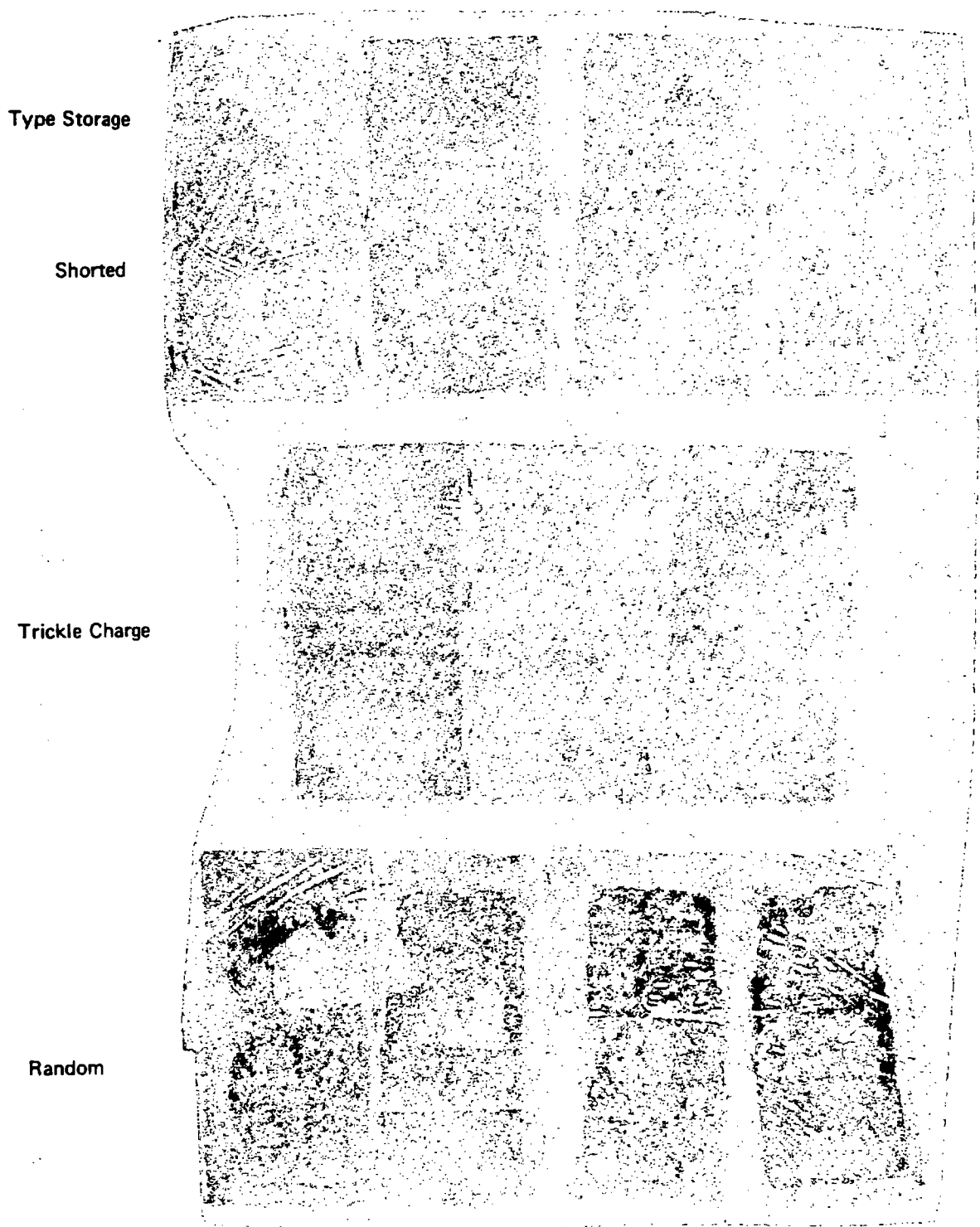


Figure 1. Photograph of separators after 18 months in storage mode tests (20 Ah cells).

Carbonates shortened repetitive cycle life of cells. Cells failed earlier as carbonate levels were increased. Failure occurred by shorting. Shorting probably occurred as a result of cadmium migration. Cells submitted to tear-down analysis showed greater penetration of separator at the higher carbonate levels.³

Type and Condition of Separator

At the 1972 Goddard Space Flight Center Workshop, T. Hennigan reported on the results of a series of tests on different separator materials which showed varying degrees of cadmium migration depending on the type of material (nylon and polypropylene) and the degree of electrolyte retention observed for the different separators.⁴

The test parameters were as follows. Non woven nylon and polypropylene separator materials were selected and given to a cell manufacturer for fabrication of sealed 6 Ah NiCad cells. The cells were cycled at NAD-Crane at 20°C and 25% DOD in a 90 minute orbit with recharge limited to 103 to 110%. Every 1500 cycles, cells were removed for analysis.

After 6000 cycles, the cells showed dramatically different degrees of migration. The nylon separators showed some migration but this seemed to be limited to the side facing the negative plate whereas the polypropylenes showed migration all the way through so that both sides of the separator were darkened. The one exception to this, however, was a Hercules polypropylene material, a micro-fiber type of material, which demonstrated significant migration on the side facing the negative electrode but had almost no cadmium on the side facing the positive. The material also showed a much higher wetting capacity than the other polypropylenes.

Further tests on the cycled cells indicated that the cells with nylon and the Hercules material were able to hold their charge much longer on open circuit stand than the cells with the polypropylene separator. Presumably, in these cells, the cadmium migration was so extensive that it provided an easier path for the plates to discharge.

Although no proof was offered that polypropylene separators increased cadmium migration, the data did suggest that separators which had less electrolyte retention capability were found to have cadmium migration all through the separator whereas "wetter" separators were able to stop or at least retard the migration to the area adjacent to the negative electrode. The correlation between separator wettability and overall electrolyte distribution will be discussed later in this report.

A THEORETICAL MODEL TO EXPLAIN CADMIUM MIGRATION

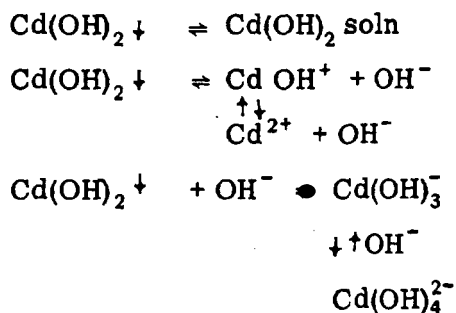
Figure 2 shows diagrammatically how cadmium migration could occur as a three step process. First, negative ions of cadmium must be generated in or on the surface of the negative plate. These might be $\text{Cd}(\text{OH})_3^-$ and $\text{Cd}(\text{OH})_2^-$ or possibly $\text{Cd}(\text{CO}_3)_2^{2-}$ and $\text{Cd}(\text{CO}_3)_3^{4-}$ in a heavily contaminated cells. In the second step, these negative ions would be transported into the separator through either the electrophoretic effect of negative ions moving in an electric field or through simple convection, that is, the physical displacement of ions (and possibly a non-ionic species of cadmium) as electrolyte moves out of the plate during discharge.

Finally, the ionic species must be precipitated as an insoluble species of cadmium on the surface of the electrode or, in the separator region.

Our investigations have shown that the insoluble material in separators we have examined is primarily hexagonal β $\text{Cd}(\text{OH})_2$, the discharged material of the negative electrode. Although our X-ray diffraction analysis has shown this to be the case, it is possible that the β $\text{Cd}(\text{OH})_2$ in the separator is not identical to that in the plate. We have observed that the dark residue removed from the separator does not readily dissolve in the ammonium acetate-ammonium hydroxide extraction solution which is used routinely to dissolve the discharged $\text{Cd}(\text{OH})_2$ from the negative plate for chemical analysis. This suggests possibly a different crystal morphology which is not detectable through x-ray diffraction. The chemical species is, however, $\text{Cd}(\text{OH})_2$.

Solubility of Cadmium in Alkaline Solution

According to Ryan et al.⁵ solid cadmium hydroxide can go into solution through the following processes.



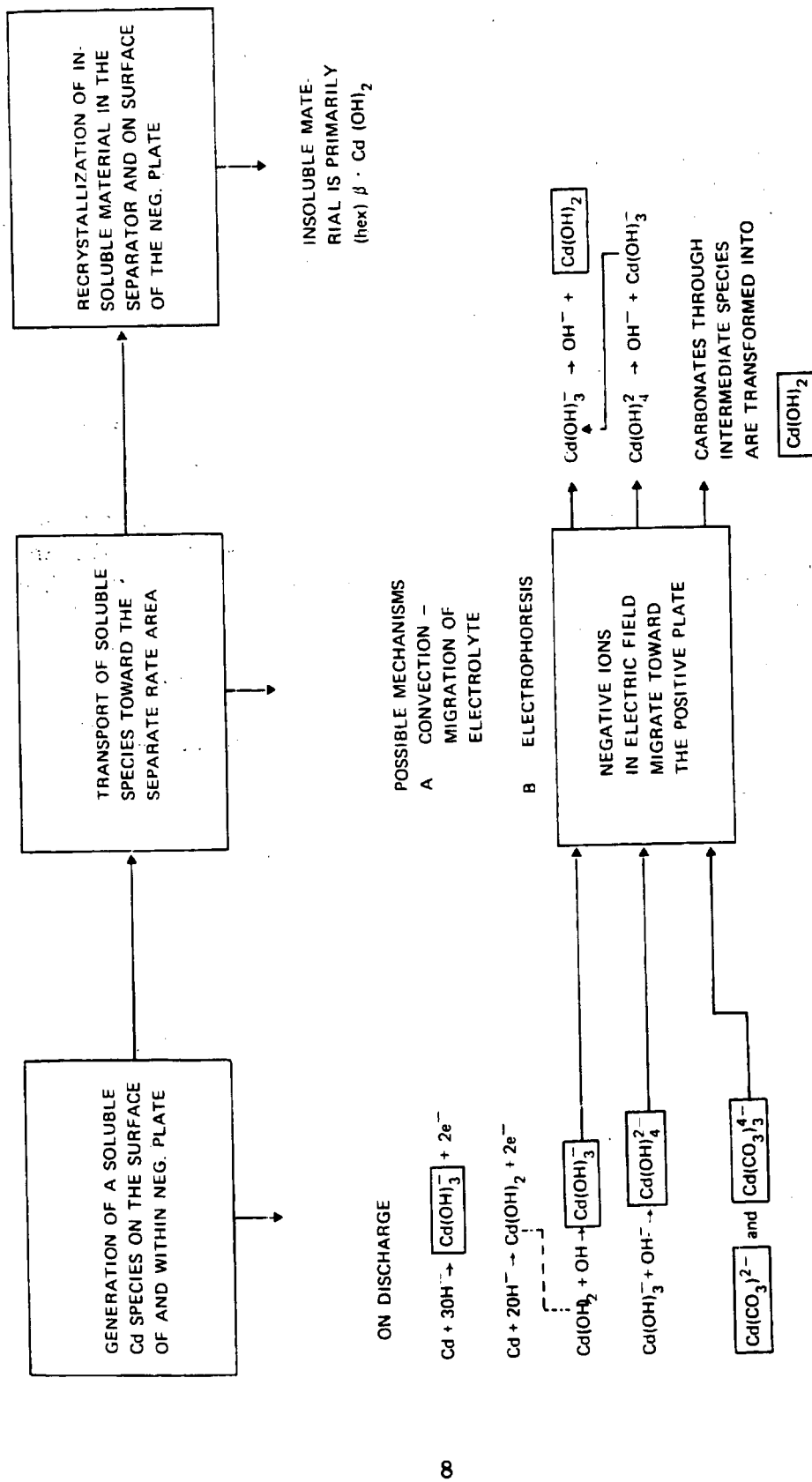
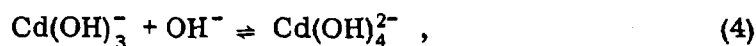
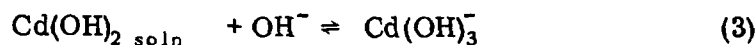
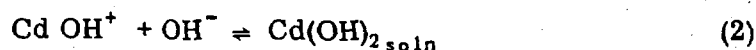


Figure 2. Diagram of theoretical model.

Assuming that the following reactions occur,



Ryan et al. calculated that equations (1) and (2) above predominate in hydroxide concentrations less than 0.5 M and equations (3) and (4) predominate in solutions greater than 0.5 M.

Halpert⁶ has shown that a cell charged with 31% KOH will actually cycle at a lower concentration of electrolyte and that the electrolyte will vary in concentration during charge and discharge. He calculated that there is a net increase of water during precharge without any alteration in the amount of OH⁻ which results in a 25% decrease in electrolyte concentration during a nominal precharge. During precharge, the following reactions occur at the positive and negative electrodes.

<u>Electrode</u>	<u>Reaction</u>
Positive	$4\text{OH}^- \rightarrow \text{O}_2 \uparrow + 2\text{H}_2\text{O} + 4\text{e}^-$
Negative	$\text{Cd(OH)}_2 + 4\text{e}^- \rightarrow 2\text{Cd} + 4\text{OH}^-$

For every mole of O₂ vented from the cell during precharge, there are 4 moles of OH⁻ consumed at the positive and 4 moles of OH⁻ generated at the negative with a net increase of 2 moles of water which accounts for the decrease in electrolyte concentration.

Further decreases of concentration are experienced as the cell undergoes charging. During charge, there is again a net increase of water with no change in the amount of OH⁻. The electrode reactions are as follows.

<u>Electrode</u>	<u>Reaction</u>
Positive	$2\text{Ni(OH)}_2 + 2\text{OH}^- \rightarrow 2\text{NiOOH} + 2\text{H}_2\text{O} + 2\text{e}^-$
Negative	$\text{Cd(OH)}_2 + 2\text{e}^- \rightarrow \text{Cd}^0 + 2\text{OH}^-$
Net	$2\text{Ni(OH)}_2 + \text{Cd(OH)}_2 \rightarrow 2\text{NiOOH} + \text{Cd}^0 + 2\text{H}_2\text{O}$

During overcharge there is no net change in electrolyte concentration since the oxygen generated at the positive is recombined at the negative with no net change in the amount of H₂O or OH⁻.

Figure 3 shows the calculated change in electrolyte concentrations as a function of depth of discharge for cells which were originally contained 31% KOH and were subjected to a nominal precharge.⁷ The shift in electrolyte concentration range from 23% at full charge to 28.5% at full discharge.

Table 1 shows the solubility of Cd(OH)₂ at 25°C for a range of KOH concentrations.⁸ For a cell operating in the range suggested above (23% to 28.5% KOH), the change in molarity would be approximately 5 M/L to 6.6 M/L KOH and the change in solubility of Cd(OH)₂ would be from 0.85 × 10⁻⁴ M/L to 1.3 × 10⁻⁴ M/L.

Table 1
Electrolyte Concentration and Cd(OH)₂ Solubility

% KOH	Moles/Liter	Solubility of Cd(OH) ₂ (M/L × 10 ⁴)
20	4.238	.75
22	4.740	.80
24	5.261	.90
26	5.792	1.05
28	6.342	1.25
30	6.908	1.38
32	7.488	1.50

The soluble species of cadmium in this range would be primarily Cd(OH)₄²⁻ with a small amount of Cd(OH)₃⁻. Ryan et al.⁹ proved empirically that the soluble cadmium concentration could be predicted by the following equation.

$$[\text{Cd}]_{\text{total}} = 3.0 \times 10^{-9} [\text{OH}^-]^{-1} + 1.0 \times 10^{-6} + 1.2 \times 10^{-6} [\text{OH}^-] + 3.1 \times 10^{-6} [\text{OH}^-]^2$$

The four terms in this equation correspond to the relative concentrations of the cadmium species [CdOH⁺], [Cd(OH)₂] soln, [Cd(OH)₃⁻] and [Cd(OH)₄²⁻]. If we were to choose a value for electrolyte concentration in a typical cell, [OH⁻] = 6 M/L, the above equation would yield the following partial concentrations for the various cadmium species.

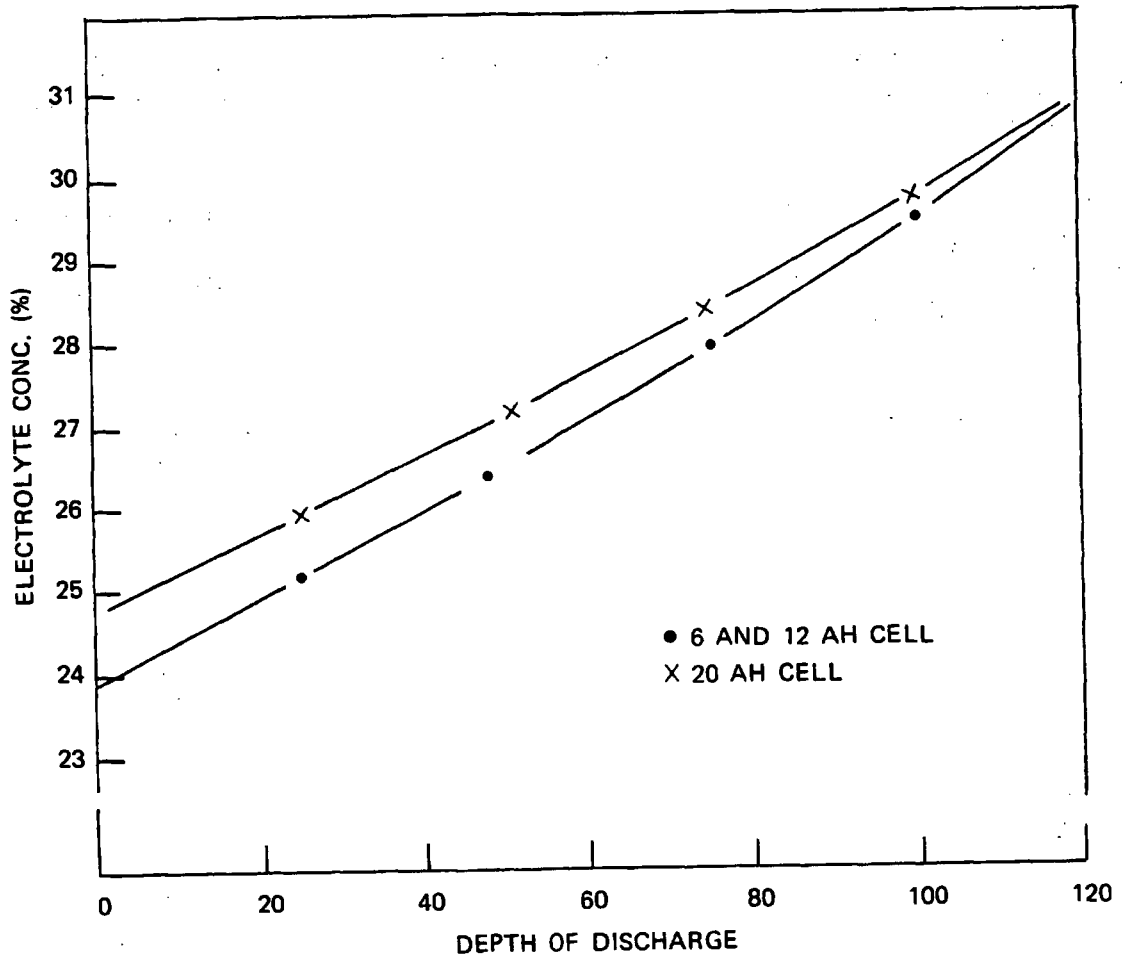


Figure 3. Electrolyte Concentration Vs. Depth of Discharge.

$$[\text{CdOH}^+] = 5.0 \times 10^{-10} \text{ M/L}$$

$$[\text{Cd}(\text{OH})_2]_{\text{soln}} = 1.0 \times 10^{-6} \text{ M/L}$$

$$[\text{Cd}(\text{OH})_3^-] = 7.2 \times 10^{-6} \text{ M/L}$$

$$[\text{Cd}(\text{OH})_4^{2-}] = 1.1 \times 10^{-4} \text{ M/L}$$

It is obvious that the $\text{Cd}(\text{OH})_4^{2-}$ species will predominate at higher $[\text{OH}^-]$ concentrations since its concentration depends on the square of the hydroxide concentration.

Lake and Goodings have shown through polarographic studies that the solubility of cadmium is strongly dependent on temperature and the concentration of hydroxide and/or carbonate.¹⁰ Figure 4 shows the results of their work as regards the solubility of cadmium with respect to hydroxide.

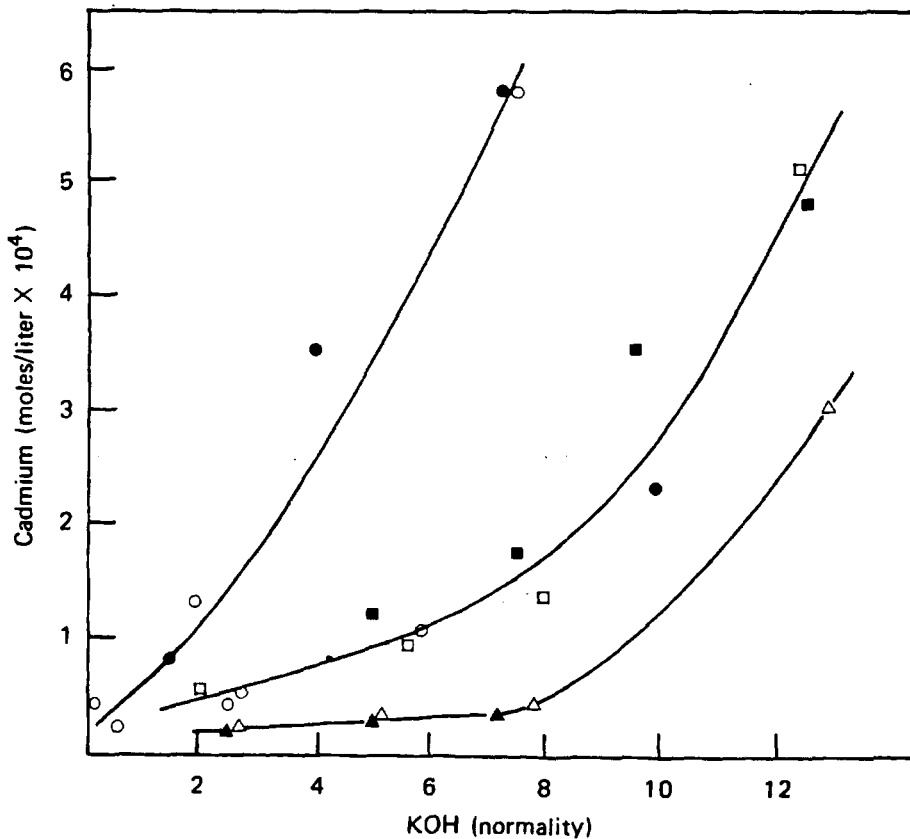


Figure 4. Concentration of Cadmium in Potassium Hydroxide Solution

If we were to choose again a typical value for electrolyte concentration, $[\text{OH}^-] = 6 \text{ M/L}$, we would find that the soluble cadmium would be approximately

$$\begin{aligned} 0.3 \times 10^{-4} \text{ M/L at } 0^\circ\text{C} \\ 1.1 \times 10^{-4} \text{ M/L at } 25^\circ\text{C} \\ 4.3 \times 10^{-4} \text{ M/L at } 50^\circ\text{C} \end{aligned}$$

At 50°C , in other words, there would be approximately 4 times as much cadmium in solution as there would be at 25°C and more than 10 times as much as there would be at 0°C .

One might also observe that at 0°C there is very little change in cadmium solubility as the KOH increase from 5 M/L to 6.6 M/L but at 50°C the cadmium solubility jumps from $3.5 \times 10^{-4} \text{ M/L}$ to $5.0 \times 10^{-4} \text{ M/L}$.

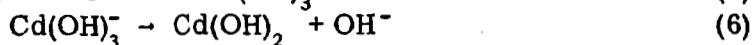
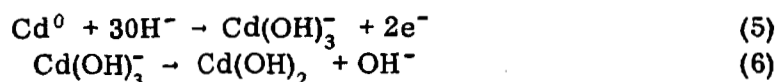
Lake and Goodings found that the solubility of cadmium is even more strongly dependent on temperature and concentration in the case of cadmium in pure carbonate but this dependency seems to decrease with mixtures of carbonate and hydroxide. They also found that the cadmium which exists which in solution with concentrated hydroxide and carbonate are in the form of complex ions $\text{Cd}(\text{CO}_3)_2^{4-}$ and $\text{Cd}(\text{OH})_4^{2-}$ (in support of Ryan et al.). The hydroxide-cadmium complex is the more stable of the two.

Generation of the Soluble Cadmate Ion in the Negative Plate

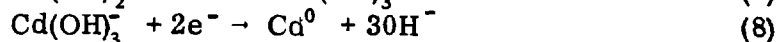
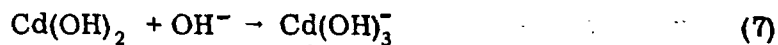
It is clear from the above discussion that a small but finite amount of soluble cadmate ion (either $\text{Cd}(\text{OH})_3^-$ or $\text{Cd}(\text{OH})_4^{2-}$) will be present in alkaline solutions containing $\text{Cd}(\text{OH})_2$, the discharged material of the negative electrode, and that the solubility is dependent on temperature and KOH concentration.

There may be however, a more abundant source of cadmate ion. According to more recent theories of electrode oxidation and reduction, $\text{Cd}(\text{OH})_3^-$ is produced as an intermediate during both charge and discharge.^{11, 12, 13} The so called "dissolution-precipitation" mechanism may be represented by the following equations.

Discharge:



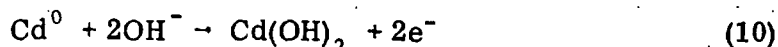
Charge:



Okinaka¹¹ using a rotating ring-disk electrode as well as a stationary electrode showed results which supported the mechanism that the anodic oxidation of Cd to Cd(OH)₂ in the active potential range proceeds entirely through the dissolution-precipitation sequence, while the cathodic reduction of Cd(OH)₂ takes place both through the solution phase and by a direct solid-state mechanism. This latter solid-state reaction would occur as follows.



Will and Hess¹³ believe that the solid state reaction also occurs during discharge.



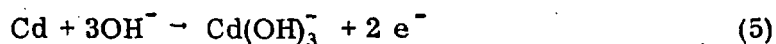
It is not clear which of the above reaction predominate during charge/discharge although there is some evidence to indicate that one or the other may predominate depending on the conditions of cycling.

Crystal Growth in the Negative Plate

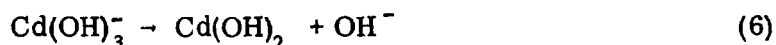
Several of the above authors have attempted to relate Cd(OH)₂ crystal morphology with the effects of temperature and cycling utilizing both the dissolution-precipitation and the solid-state mechanisms. Crystal growth is an important factor which may be related to negative plate loss of capacity and the redistribution of cadmium in the negative plate with aging. It may also for our purposes be an indication of the generation and persistence of the cadmate ion which is responsible for cadmium migration.

Okinaka and Whitehurst¹⁴ using light and electron microscopic examination and BET surface area measurements showed that the cadmium hydroxide crystals formed at lower discharge rates and at higher temperatures are larger in size and are difficult to reduce during subsequent charges. Their results can be accounted for qualitatively on the basis of the dissolution-precipitation mechanism alone during both the charge and discharge.

The dissolution-precipitation mechanism for the discharge reaction (eqs. (5) and (6)) predicts that $\text{Cd}(\text{OH})_3^-$ crystals will be larger when formed at lower discharge rates. The reason is as follows. At lower discharge rates, the reaction



proceeds slowly and thus the formation of $\text{Cd}(\text{OH})_3^-$ is slow. This causes the precipitation reaction



to occur more slowly with the $\text{Cd}(\text{OH})_2$ crystal precipitated from a more dilute and hence less supersaturated solution of $\text{Cd}(\text{OH})_3^-$. As a general rule, crystals formed from more dilute solutions tend to be larger than those in highly saturated solutions.¹⁵

The dissolution-precipitation mechanism will also explain why larger $\text{Cd}(\text{OH})_3^-$ crystals will form at higher temperatures. Here again, the solution will be more dilute since at higher temperatures the $\text{Cd}(\text{OH})_3^-$ is more soluble and, therefore, the solution will be less supersaturated with respect to $\text{Cd}(\text{OH})_3^-$.

The converse of the above reasoning should also hold, that is, smaller crystals will be precipitated from solution if there is a fast discharge and/or lower temperatures. If reaction (5) occurs rapidly there will be a fast build up of $\text{Cd}(\text{OH})_3^-$ and hence a more dense, highly supersaturated solution with the resulting rapid precipitation of small crystals. Also lower temperature would tend to lead to more saturation since the $\text{Cd}(\text{OH})_3^-$ is less soluble.

Using the same type of reasoning one could argue that a low rate charge especially at low temperature would tend to dissolve larger crystals. Large crystals, it was found, lead to a decrease in electrode efficiency and capacity.

In order to keep crystal structure small in the negative electrode Okinaka and Whitehurst suggest the following practical steps.

- 1) Use fast-rate, low temperature forming cycles.
- 2) Do not allow cells to discharge slowly. Avoid, for example open circuit stand with a charged cell since the slow self discharge would lead to large crystal growth.
- 3) Store cells at low temperature.

Will and Hess studied crystal growth by simulating a single pore using a cadmium chip of millimeter dimensions covered with an electrolyte film of micron thickness. Their studies supported the following mechanism.

On discharge, the solid state and the dissolution-precipitation mechanisms occur simultaneously, both contributing to the measured capacity and the dissolution-precipitation mechanism leading to the formation of large crystals.

On charging the rate and duration of charging is significant in determining the predominance of one or the other reaction mechanisms. On short, high rate charges the solid state reaction would predominate and would leave any large crystals in the electrode intact. Prolonged, low-rate charges would favor the dissolution-precipitation reaction and would therefore lead to the dissolution of the larger crystals.

According to Will and Hess cadmate ions could be expected to diffuse and, during discharge, to migrate toward the counter electrode. Once the ions left the surface of the electrode it was observed that very long charging times were required to electrodeposit them back onto the test electrode.

It would appear from the above discussions that large crystals are formed during a slow discharge and that large crystals are dissolved during a slow charge.

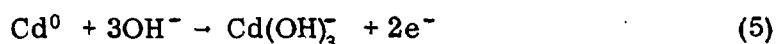
Cadmiate Ion Concentration as a Function of Temperature, Hydroxide Concentration and Charge/Discharge Rates

In a previous section, it was observed that cadmate concentration increases with an increase in temperature and/or an increase in hydroxide concentration. Increasing either the temperature or the hydroxide concentration would lead to increased cadmate ion solubility and thus to a decrease in the saturation of the solution. (It is important here to keep clear the distinction between concentration and saturation. A less saturated solution at higher temperature will contain more cadmate ions per ml. than a more saturated solution at a lower temperature).

The cadmate ion concentration could also be correlated to the cycle rates through arguments similar to those made above in the discussion concerning crystal growth.

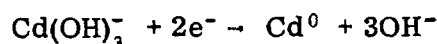
During a high rate charge or discharge, there would be very little cadmate ion generated if in fact the solid state mechanism proposed above was the predominate reaction. The charged and uncharged cadmium would be formed without an intermediate species.

During a slow charge or discharge, however the evidence seems to indicate that the dissolution-precipitation mechanism is the predominate reaction. During discharge, the rate of the total reaction would be determined by the rate of the dissolution reaction (5).



At lower discharge rates, the dissolution reaction would occur slowly leading to a lower accumulation of $\text{Cd}(\text{OH})_3^-$ and thus a less saturated solution with respect to the cadmate ion. The concentration of the cadmate ion would however be significant.

During charge, however, the opposite would seem to be the case. The reverse dissolution reaction



would remove cadmate ions continuously from the solution and thus lead to a less concentrated solution with respect to the cadmate ion.

In summary, the factors which have been suggested as increasing cadmate ion concentration would be:

- (1) An increase in temperature.
- (2) An increase in hydroxide concentration.
- (3) A slow rate of discharge.

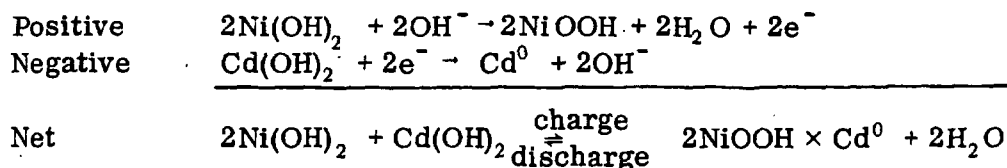
Mobility of the Cadmate Ion and Particulate $\text{Cd}(\text{OH})_2$

Once the cadmate ion has been formed, it could be moved toward the separator area by one of two mechanisms, convection or electrophoresis.

In convection the cadmate ion (or any particulate $\text{Cd}(\text{OH})_2$ which is not firmly attached to the substrate) would be "washed" out of the negative plate as the electrolyte moved back and forth during charge and discharge.

During cycling there are several factors which lead to a redistribution of electrolyte volume and concentration.

During the charge/discharge reaction there is a net gain/loss of 2 moles of H_2O for every mole of cadmium which is oxidized or reduced.



As was noted earlier this lead to a net decrease in electrolyte concentration during charging and an increase during discharge. Likewise, the total electrolyte volume would increase during charge and decrease during discharge.

Along with the change in electrolyte volume during charge and discharge there would be a significant change in the void volume of the negative plate due to the change in density of the active material. Cadmium metal (charged species) has a density of 8.64 g/cc whereas cadmium hydroxide (discharged species) has a density of 4.76 g/cc.

In a 6 Ah cell, the change in volume from charged to discharge cadmium would be approximately 2 cc, calculated as follows. Assuming that 1 Faraday of charge is equivalent to 26.8 Ah and that 2 Faradays are generated per mole of active material transformed (see eq. (5)), the amount of active material transformed during a total discharge would be 0.115 moles.

$$6\text{Ah} \left(\frac{\text{Faraday}}{26.8\text{Ah}} \right) \left(\frac{1 \text{ mole Cd transformed}}{2 \text{ Faraday}} \right) = 0.115 \text{ moles}$$

The total volume change could then be found by multiplying 0.115 times the difference in volume/mole between the charged and the discharged cadmium.

$$0.115 \text{ moles} \left(\overbrace{\left(\frac{\text{cc}}{4.76 \text{ gm}} \right) \frac{146.4 \text{ gm}}{\text{mole}}}_{\text{Volume/mole of Cd(OH)}_2} - \overbrace{\left(\frac{\text{cc}}{8.64 \text{ gm}} \right) \frac{112.4 \text{ gm}}{\text{mole}}}_{\text{Volume/mole of Cd}^0} \right) = 2.05 \text{ cc}$$

Thus, in a 6 Ah cell, the change in volume from charged to discharged cadmium would be equivalent to approximately 2 cc of void space. In other words, the growth in the cadmium species with discharge would subtract 2 cc of void space from the negative electrode.

If that space had been occupied by electrolyte, we would imagine that 2 cc of electrolyte would be displaced or "squeezed" out of the negative electrode during a total discharge. Considering that a cell is initially charged with 3 cc of electrolyte/Ah capacity or approximately 18 cc for a 6 Ah cell, this 2 cc of electrolyte displaced would represent significant shift in the electrolyte distribution during a total discharge.

As regards the negative plate itself, the change in void volume would be significant. Milner and Thomas¹⁸ calculated that a uniform layer of $\text{Cd}(\text{OH})_2$ on the nickel sinter would have a thickness of about 0.7μ , while the thickness of metallic cadmium would be about 0.3μ . Correspondingly, the porosity of the plate increases a reduction of the hydroxide to the metal, going from about 50% to about 67%.

If one began with an 80% porous plaque, it would be reasonable to assume, as shown in Figure 5, that there is a change in void volume in the negative plate of approximately 30% with total discharge.

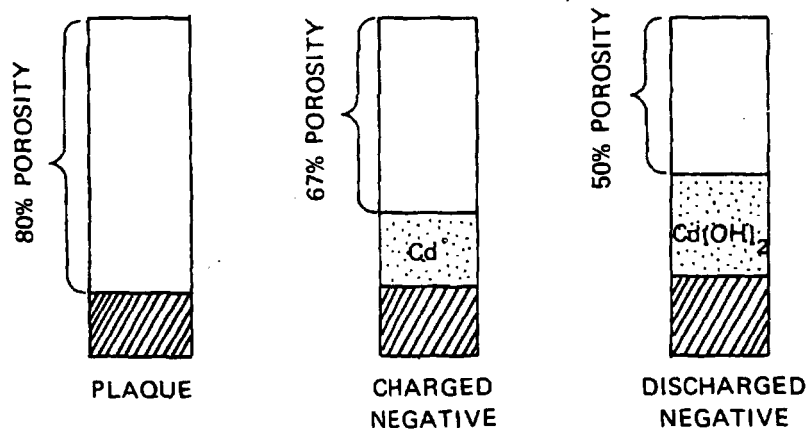


Figure 5. Illustration of Void Volume in a Typical Cell

According to the proposed convection model, the soluble cadmate ion (and, possibly, insoluble particles of cadmium hydroxide) would be carried out of the negative electrode with the outward flow of electrolyte.

Movement of Cadmium Species through Electrophoresis

S. W. Mayer at the Fall Meeting of the Electrochemical Society, 1974, presented data which indicated $\text{Cd}(\text{OH})_2$ will migrate in an electric field.¹⁹ His assumption was that $\text{Cd}(\text{OH})_2$ particles acquire a net negative charge in the KOH electrolyte (possibly arising from preferential absorption of OH^- ions as compared to absorption of K^+ ions), and that they then migrated in the electric field set up between the positive and negative plates. This would be consistent with the observation that the cadmium deposits in the separator are concentrated closer to the negative plate and seem to migrate deeper into the separator (toward the positive) with cycling.

The data and results of his study are shown in Table 2. A constant potential gradient was applied, by means of stainless steel electrodes, to a rotating suspension of $\text{Cd}(\text{OH})_2$ in KOH electrolyte (13.9% $\text{Cd}(\text{OH})_2$ in 34% KOH with K_2CO_3 concentration ranging from 0.8% to 9.0%). The weight of the cadmium hydroxide migrating in 6 minutes to one 2.0 cm diameter electrode in a collection cell was determined and tabulated.

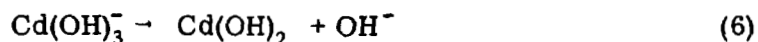
Weight of $\text{Cd}(\text{OH})_2$ Migrating	K_2CO_3 in Solution	Mobilities in cm/sec per volt/cm
31.0 mg	0.8%	0.08
60.9 mg	3.1%	0.11
98.8 mg	6.2%	0.14
181.4 mg	9.0%	0.18

Table 2 shows not only a considerable migration of $\text{Cd}(\text{OH})_2$, but a dramatic increase with the increase of K_2CO_3 in solution. This suggests that the $\text{Cd}(\text{OH})_2$ particles acquire a higher negative charge due to stronger preferential absorption for the doubly charged carbonate anion than for the singly charged hydroxyl ion.

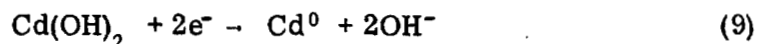
Deposit of Cadmium in the Separator and/or on the Surface of the Negative Electrode

From the above discussions it is suggested that cadmium in two different forms, particulate insoluble $\text{Cd}(\text{OH})_2$ or soluble cadmate ion $\text{Cd}(\text{OH})_3^-$ or $\text{Cd}(\text{OH})_2^{2-}$ can be deposited in the separator or on the negative plate surface by two mechanisms, convection and/or electrophoresis.

In the case of the soluble ion, deposition would occur by the precipitation reaches:



Once deposited in the separator area, it would be difficult to remove the insoluble cadmium since the material would not be electrical contact with the negative electrode. Neither the solid state reaction

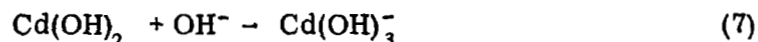


nor the dissolution reaction



could readily occur since electrons are not available via the conductive substrate of the negative plate.

The only way the residue in the separator could be removed is by slow dissolution through the reverse dissolution reaction.



Since the Cd(OH)_3^- would not be continuously removed by the reaction symbolized in Eq. (6), reaction (7) would occur very slowly. Even if this reaction did occur, the electric field would be such that the soluble ion would be driven further into the separator toward the positive plate.

What has been said about the material deposited in the separator area could also be applied to the surface of the negative plate with cycling. Active material which has migrated from the interior of the negative plate would be deposited on the surface with poor electrical contact to the conductive surface of the nickel sinter.

CORRELATION OF EXPERIMENTAL OBSERVATION WITH THE THEORETICAL MODEL

Cycle Regime

As was mentioned previously, the cells in near-earth orbit showed considerably more cadmium migration than those in synchronous orbit. These two cycle regimes differ in several important respects.

Relatively speaking, the near earth orbit cells have a higher charge rate and a lower discharge rate than the synchronous orbit cells. For example, a near-earth regime of 15% DOD (60 minute charge, 30 minute discharge) would experience a 0.15 charge and a 0.3 discharge (neglecting overcharge). A synchronous regime, on the other hand, would experience a very moderate charge, 0.5C, for example, with a discharge at the 72 minute maximum of 0.66C, more than twice the rate of near earth orbit.

The two regimes also differ in the number of cycles which are normally required for space applications with the near-earth orbit requiring many more cycles during its life time.

In the discussion on crystal growth, it was observed that large crystals would grow in the negative plate when the cell is subjected to a slow discharge and that these crystals would not likely be broken down unless the cell were subjected to a slow charge. These conditions may also apply to cadmium migration. That is, a slow discharge, enhancing large crystal growth would also produce more cadmate ion since the dissolution-precipitation reaction would be preferred over the solid state mechanism. According to this reasoning, the near-earth orbit discharge would produce more cadmate ion than the synchronous discharge.

Furthermore, during the slower charge of the synchronous orbit, time would be allowed for the dissolution of crystals which may have formed on or near the electrode surface. The faster near-earth charge would bypass this dissolution since the solid state reaction would be preferred. During subsequent cycles, the crystals would tend to grow large (and perhaps migrate into the separator area) without the benefit of dissolution.

The growth of large crystals and the migration of the active material may well account for the so-called memory effect and negative fading in near-earth orbit regimes. Furthermore, the restoring effect of reconditioning (fast discharge to 100% DOD with a subsequent low-rate charge) may be attributable to the breakdown of these larger crystals.

Cadmium migration may also be related to the number of cycles a cell must undergo since the convection mechanism suggested above would be operable during every discharge. (The electrophoretic effect would be present at all times during both synchronous and near-earth orbit since the cells are not generally allowed to go below 1 volt). Since the near-earth orbit cells are generally subjected to many more discharges than the synchronous orbit cells, it would be reasonable to expect more cadmium migration.

Temperature

It was also suggested in the discussions on cycle regimes that there was a possible correlation between increase in temperature and the increase in cadmium migration. Given the temperature dependence of cadmium hydroxide solubility, especially above 25°C, it would be reasonable to assume that if the cadmium hydroxide is more soluble, it will migrate under the influence of convection and electrophoresis, and thus enhance the degree of cadmium migration.

Carbonate Contamination

There seems to be a definite correlation of cadmium migration with amount of carbonate in the electrolyte (see Barney, et al., ref. 2). It is not clear from the work of Lake and Gooding (ref. 10) how carbonate, when mixed with hydroxide, affects the solubility of the cadmium species, but it does seem clear from the work of Mayer (ref. 19) that the increase in carbonate enhances the electrophoretic mobility of the cadmium species. Thus, if electrolyte is contaminated with carbonate, it would be reasonable to assume that the migration of both soluble and insoluble particulate cadmium hydroxide would be substantially increased due to the electrophoretic effect.

Type and Condition of Separator

In comparing nylon and polypropylene separators it was found that the cadmium migration was more severe, or at least more penetrating, in those separators with lower wettability characteristics. It would seem intuitively that the opposite should be the case. That is, the "wetter" separators should provide an easier path for the soluble and/or insoluble particulate cadmium hydroxide to penetrate the separator and migrate toward the positive plate.

Exploring however, our theoretical model, it may well be that the "wetter" nylon separators force the recrystallization of the soluble species near or on the surface of the negative electrode whereas the "drier" separators allow the soluble (and perhaps insoluble) species to pass further into the separator prior to recrystallization. The teflon barrier could also act as this recrystallization site which may account for its effectiveness in retarding cadmium migration.

There may be another factor at work here. In the starved cell condition, nylon with its enhanced wettability seems to compete better with the electrodes for its share of electrolyte than does polypropylene. If the separator does not compete well with the electrode, then the capillary action of the pores in the plate will act to hold most of the electrolyte in the plates.

According to the model suggested above, cadmium migration is aided by the dissolution-precipitation reaction and by the convection of electrolyte which is "squeezed" out when the negative electrode is discharged. Both of these effects depend on an abundance of electrolyte. If the nylon separator is competing with the negative electrode for electrolyte, then, the negative electrode may be functioning in a more starved condition and these two effects may be retarded. Thus a nylon separator would show less migration.

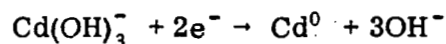
Storage Mode Tests

Figure 6 shows a summary interpretation of the storage mode tests using the theoretical model. During these tests, it was observed that the random storage mode showed extensive cadmium migration, whereas the shorted or trickle charge mode showed little or no migration.

During random storage the cells were subjected to frequent cycling and large periods of open circuit stand. During open circuit stand, the cell would be subject to a very slow discharge (self-discharge) which according to the theory would enhance large crystal growth and cadmium migration. Furthermore, during cycling, the cell would experience the convection mechanism on discharge which would increase the movement of electrolyte and hence the movement of the cadmium out of the negative plate. Since the cell is never discharged, the soluble (and particulate) cadmium species would be subject to the effects of electrophoresis.

In the started cell, relative to the other storage cells, there would be a maximum amount of $\text{Cd}(\text{OH})_2$ present in the electrode (minus the precharge Cd^0) but there would be no mechanism for moving the soluble cadmium toward the positive plate. There would be no electric field (hence no electrophoresis) since the cell is discharged. Also, there would be no convection since the cell undergoes no cycling. Furthermore, there would not be the generation of $\text{Cd}(\text{OH})_3^-$ which accompanies discharge via the dissolution-precipitation reaction. Hence, no cadmium migration.

Finally in the trickle charge cell, several factors would combine to retard cadmium migration. First of all, there would be a minimum amount of $\text{Cd}(\text{OH})_2$ present since the electrode is fully charged. There would be some $\text{Cd}(\text{OH})_3^-$ generated through the oxygen recombination self discharge, but this could be readily be oxidized to cadmium metal through the reaction



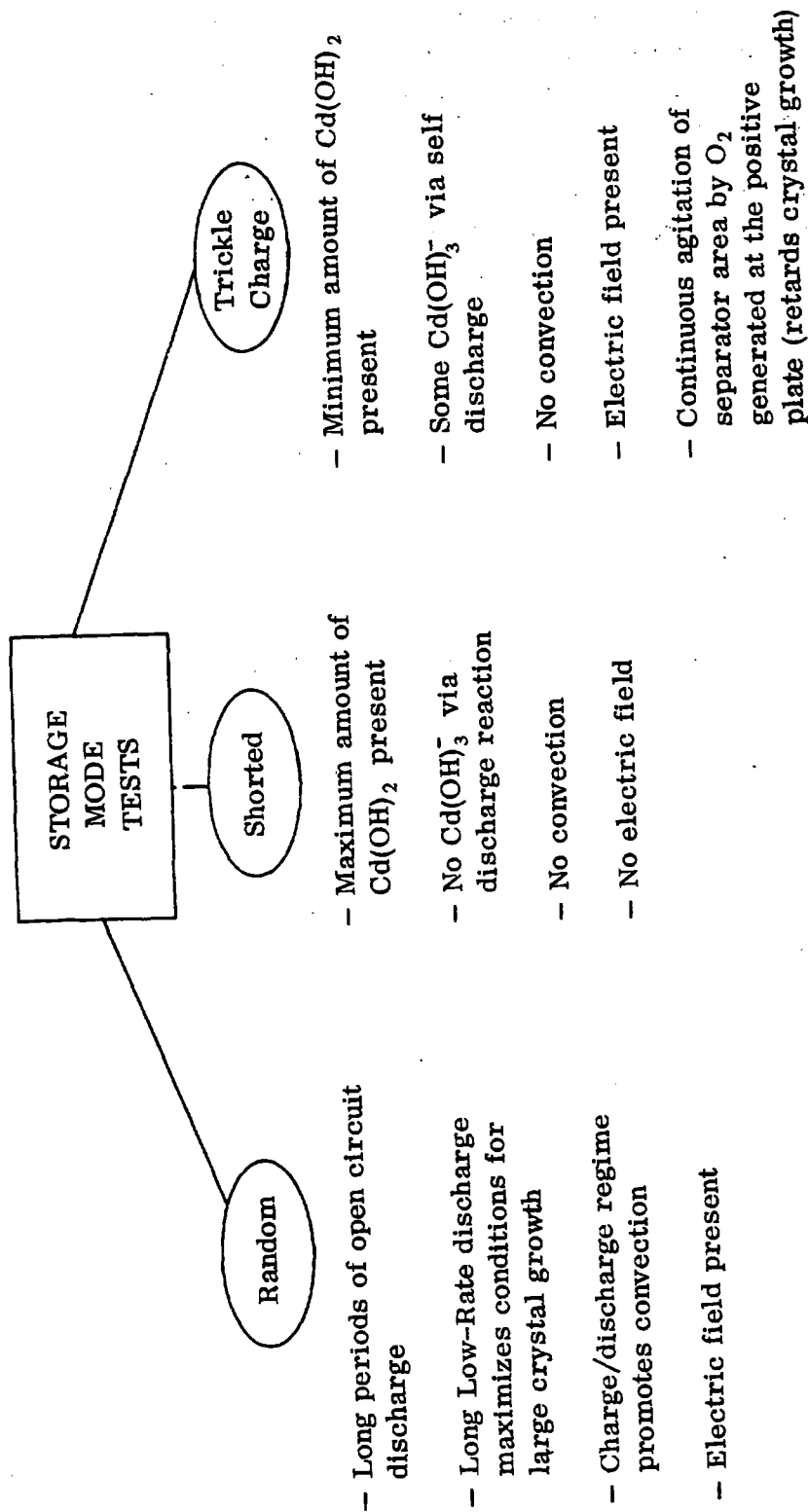


Figure 6. Factors Involved in Storage Mode Test

There would be little or no forced convection since the electrode is maintained in a charged condition. Electrophoresis would be possible since the cell is charged, but in the absence of significant amounts of $\text{Cd}(\text{OH})_2$ and cadmate ion, there would be little material which could be subject to migration.

Finally, the physical agitation of the electrolyte in the separator area due to the oxygen gasing at the positive plate could provide enough agitation in the solution to prevent any significant recrystallization in the separator area.

SUMMARY

A study has been made of various factors which seem to contribute to or enhance the migration of active material from the negative plate toward the positive electrode. These factors would include the type of charge/discharge regime, the temperature of cycling, carbonate contamination, the type of separator used and the mode in which the cells were stored.

A theoretical model was proposed in order to explain how these factors might be related to cadmium migration. According to the model, a soluble cadmate ion is generated in the negative electrode via the dissolution-precipitation reaction mechanism and its solubility is enhanced by temperature and hydroxide concentration.

The soluble cadmate ion (and perhaps insoluble particulate $\text{Cd}(\text{OH})_2$) may be propelled to the surface of the negative electrode and, hence, into the separator area through two mechanisms, the convection of electrolyte and electrophoresis. The soluble ion, once it has reached the separator area, would recrystallize as insoluble $\text{Cd}(\text{OH})_2$.

Finally an attempt was made to relate the theoretical model to the various factors which seem to contribute to migration.

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