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Goddard Space Flight Center

1970 NASA/GSFC BATTERY WORKSHOP

Greenbelt, Maryland
Monday, 16 November 1970

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Goddard Space Flight Center

1970 NASA/GSFC BATTERY WORKSHOP

Goddard Space Flight Center
Auditorium, Building 3
Greenbelt, Maryland

Monday, 16 November 1970

Session 1 Materials Processing and Chemical Analysis

Chairman: G. Halpert

Session 2 Cell Processing and Testing

Chairman: F. Ford

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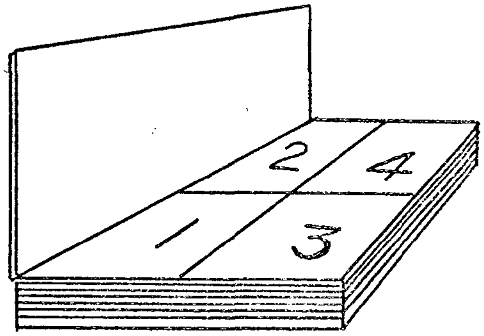

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FIGURE NO. 1

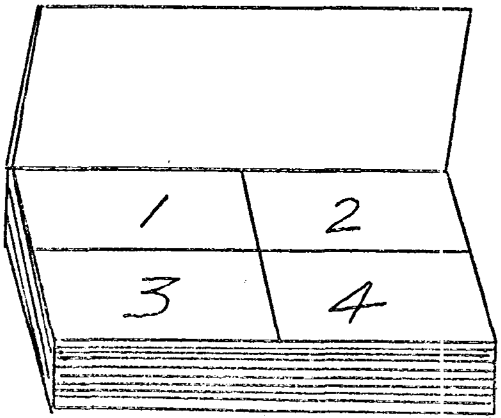

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FIGURE NO. 2

PROCEEDINGS

HALPERT: I would like to welcome you all here this morning.

The purpose of the program here today is to air some of our problems and present some of the test results that have been accumulated during the last couple of years. We hope that you all will take part whenever the situation presents itself. We have four sessions planned with a fifth session tentatively scheduled for Wednesday morning, if there is a special subject that we may want to carry over.

There are speakers who have already come forward and indicated they would like to talk. Each session chairman is responsible for the speakers in his group. I will introduce each of the chairmen so that if you want to be added to the speakers list, you can contact the chairman before the specific session of interest. I am sure he will be very happy to put you on the program.

I will be chairing the first session this morning on materials.

Floyd Ford will be chairing the afternoon session on cell production testing and precharge.

The third session tomorrow will be chaired by Tom Hennigan. It will be on the separators, seals and battery hardware.

The chairman of the fourth session on Tuesday afternoon will be Bill Billerbeck from Comsat. Bill's session will include new designs, devices and new applications.

As you can readily see and as in the past our program is recorded and is being taken down by a stenographer.

In order for the books to be published later on, we need the identification of everyone who wishes to question or comment on a subject. Will you please clearly give your last name and your affiliation and he will be glad to take down the information.

At a later time before you leave we will hope to have a listing of the speakers who have planned their presentations for today and tomorrow. If that doesn't come out, it certainly will come out with the booklet later on.

For any of you who did not return a brown card to me, I will have them available this afternoon.

I would like to have your full addresses including ZIP's and mail codes to make sure you get a copy of the minutes.

The area that we hope to cover during the workshop starts with -- if I can have the first slide.

(Slide.)

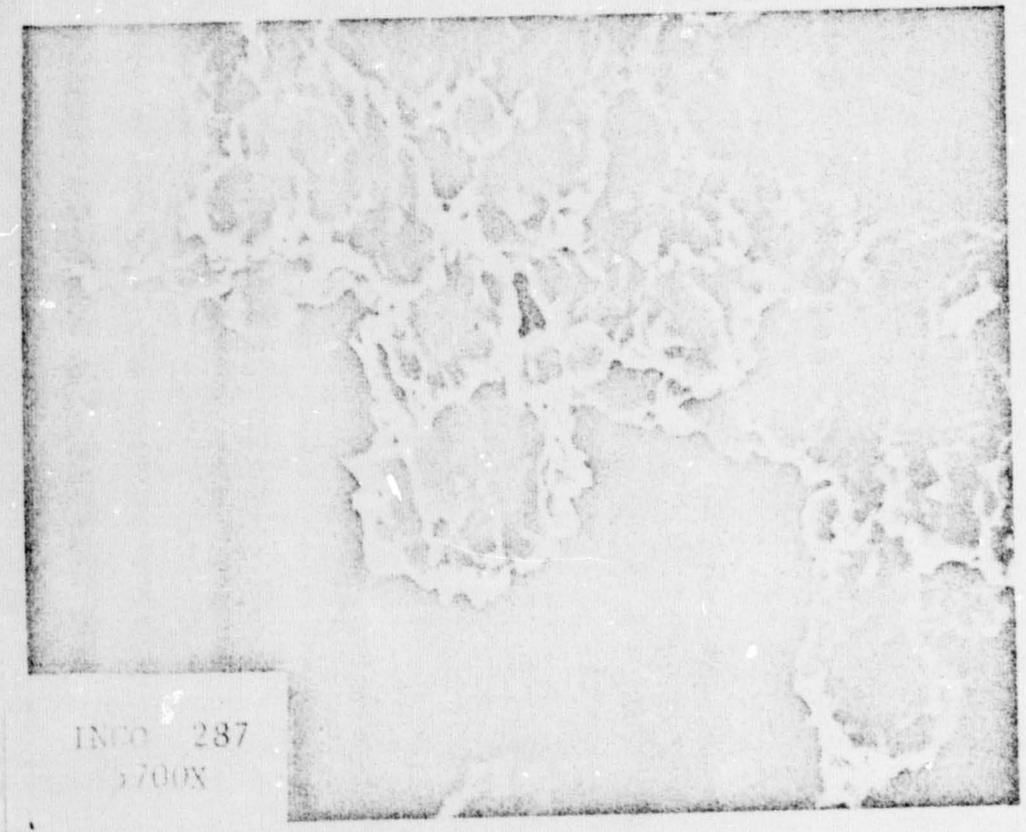
-- the nickel powder.

We see pictured a scanning electron photomicrograph of nickel powder .287 with 5700 "X" magnification. This powder is used in the manufacture of the porous plaque used as the basis for the nickel and cadmium plates. And this is it when the cell is all assembled and cased.

(Slide.)

This is an OGO battery ready for flight use. After battery assembly we can't really do much about it. So the problem areas exist between those two points.

It is appropriate at this time for us to put into perspective the major problems that must be solved for the aerospace battery. To describe the key issues that the power system designer must contend with now and in the future, we are fortunate to have with us Mr. Chuck MacKenzie, Chief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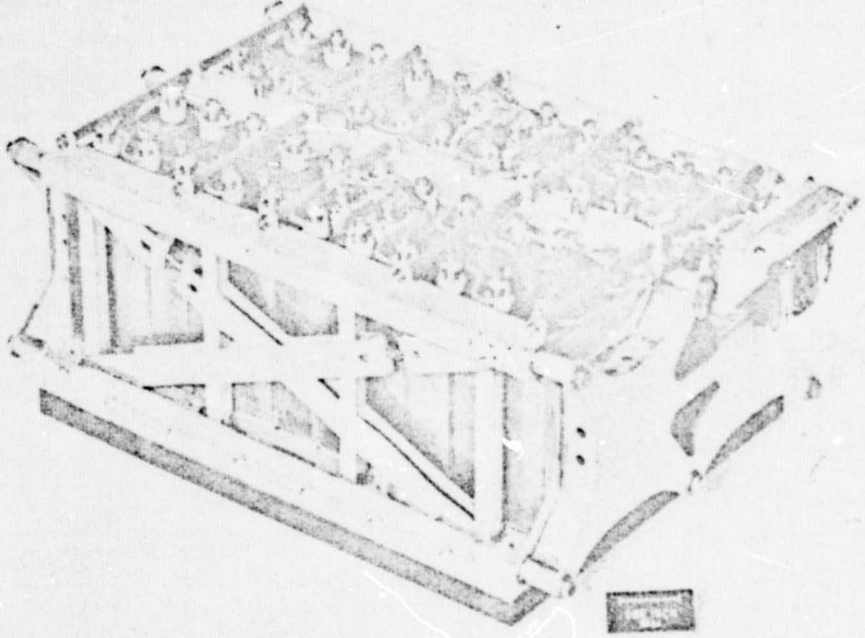

of the Space Power Technology Branch. Mr. MacKenzie has considerable experience in satellite power system design and operation. And at present he has the overall power responsibility for ever satellite at Goddard.

It is my pleasure to introduce Mr. Chuck MacKenzie.

XXXX MAC KENZIE: Thank you, Jerry. I would like to also extend the welcome of the Center to each and every one of you. We are very happy to have you here tackling what we in the power system area consider our most important component on the spacecraft.

I make the solar array people and the power conditioning people unhappy with that statement, but to us in the system design, the battery is the most important component we have, probably because it is the least understood component that we have.

We are still pushing in the general sense for a need for higher energy density on cells and a longer life. As I look over your agenda I notice that you are more nicad oriented than you are total battery oriented. But I do ask you to keep in mind the high energy density requirements. It hit us in the face again last week where somebody wants a five-to-one improvement on nicad weight with the same lifetime. And we will continue to get that.

I think you will have to look at your battery programs in a climate of short funds;and for the people who monitor these programs in a climate of short travel. This means you have one very important management function that must be far better than it has been in the past, the communication must be good. We must understand our terms and talk the same terms so we can communicate.

I look at the battery problem from a system engineering standpoint. I know just a little bit about batteries, a little bit about solar cells, a little bit about power conditioning, but I can put them together efficiently.

I am your principal user. And while you might not agree with me as to what I see the problems are, you have two things to think about:

First of all, am I right in my views of the problem? And if I am not, you have the duty to correct me. If I am right in my views of the problem you have to get us the answers.

To me there are three basic needs that we need from the battery people right now. We need a uniform product. We need one that we know. Now, the Crane Program has done us a world of good to give us an idea of how the battery operates and what we can do.

But I think from my standpoint, the first six or seven years of Crane data is only indicative of the battery because there are so doggone many failures due to process control and assembly and misfabrication that we cannot trust the data. We hope that your uniformity and your process control will improve to the extent that the data can be categorized and can be trusted for our predictions.

Second, we need some good parametric data. What we would like to see is an impossibility, but we would still like to see it. We would like to see the battery characterized as a transistor with as well defined parameters that we can pick up and use as a design just as we do with the transistor.

How we get this I don't know. I'm not even sure we can get it. But I think this is one area where I ask you to search all your in ingenious technical minds and try and help us solve this problem.

The third problem is that we need some reliability models and we need some accurate test extrapolations. We're looking at three, five, seven and in the future ten-year design lives.

The only component we have to meet these requirements right now is the nicad cell. But for a 10-year requirement we cannot put a cell on test for 10 years. So we have to know something about the reliability of the device and how we can get good test data in a short time that will predict the long life.

This is not an easy task. However, I do see the competence and the capability in this room to solve it. I have no fear that we will get the answers in the future. But we need them as fast as you can get them to us. I thank you all for coming. I hope your workshop will be productive.

Good luck to all of you.

(Applause.)

HALPERT: That is as close to a keynote address as I've heard here for t-e battery industry. I think we all have a mission to accomplish. Chuck has certainly given us the key to start. I hope we will continue on in light of what he has said.

SESSION 1

The first session is material assembly, plaque, plate, control and some of the basic operations in making the plates that go into a nickel cadmium cell.

We have as our first speaker this morning Richard Beauchamp of Bell Labs who has done a considerable amount of work at Bell in working out new processes of plate manufacture.

I would like to introduce Dick Beauchamp.

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BEAUCHAMP: I would like to give a review this morning of a paper that was presented at the fall meeting of the Electrochemical Society.

For those of you who were there I ask you to bear with me. For those who weren't, also bear with me. And I will begin my talk this morning by briefly describing some of the conventional impregnation processes used commercially. And then we will discuss the more rapid and direct electrochemical method.

The limitations of these processes as presently practiced will be shown before proceeding to describe the new electrochemical technique whereby the amount of active material introduced into a sintered nickel plaque is significantly higher than that obtained under normal operating conditions.

Numerous process parameters have been explored. And the optimum ranges of the variables will be selected. The effect of these parameters on crystal morphology will be demonstrated with electron photomicrographs. Also shown will be the uniform distribution of active material in the pores and the high surface area of the deposit. And then finally results of both open and sealed cells cycled under various conditions will also be presented.

If I may have the first slide, please.

(Slide.)

This shows a schematic of the commercial impregnatio process in which a sintered nickel plaque is filled with a saturated salt solution, cadmium nitrate, nickel nitrate, by immersion. And the hydroxides are precipitated by electrolytic, chemical or thermal conversion. And the plates are washed and dried and maybe given as many as five to eight cycles in order to achieve electrodes of high energy density.

The amount of material deposited in one cycle is dependent upon the solution concentration,and it is often necessary to repeat this step several times.

(Slide.)

Here we show a schematic of the electrochemical impregnation process which was first talked about by Edison and Candler.

In this case you start with a sintered nickel plaque again, but the battery active material, the hydroxides, are precipitated in situ in your saturated salt solutions by passing a cathodic current between the plaque and two suitable counterelectrodes.

The plaques are then washed and dried. And, if necessary, the process can be repeated to increase the loading.

(Slide.)

Here we show a graph of the theoretical electrode capacity in terms of ampere hours per cubic inch versus impregnation time.. And this represents the optimum conditions of loading using the electrochemical process at room temperature.

We use a four-molar solution of nickel nitrate at a current density of 2 amps per square inch. And you can see that we can achieve a loading of 1.2 grams nickel hydroxide per cc of plaque void which is equivalent to nearly a loading of five ampere hours per cubic inch. Here too the process can be recycled if a higher loading is desired.

When initial attempts were made to prepare cadmium electrodes by this process, we were less successful. Finally after renewed effort we were able to at least obtain the loading conditions as shown in the next slide.

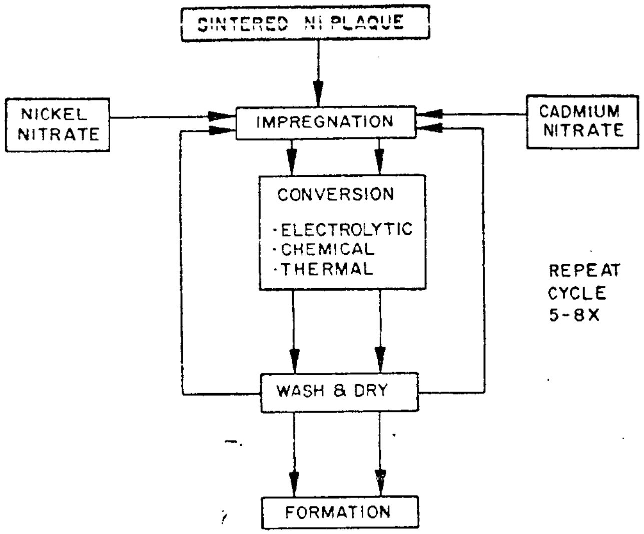
(Slide.)

This is also electrochemcially precipitated at room temperature. And it shows that the maximum loading obtained is about one gram of cadmium hydroxide per cc of plaque void.. Here again it is equivalent to about five ampere hours per cubic inch. In this case we've used a solution of two-molar cadmium nitrate at a current density of .125 amps per square inch.

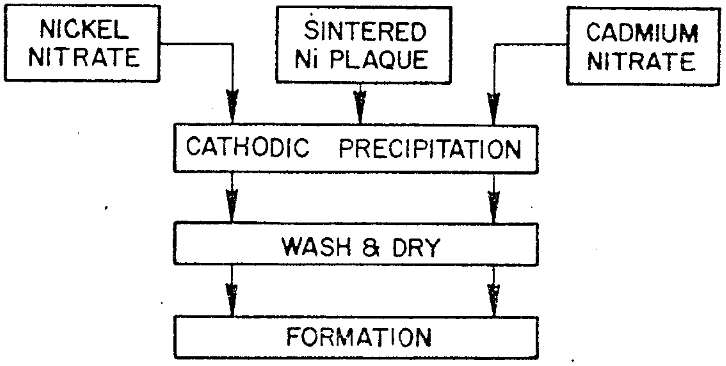
And to reach this loading requires an impregnation time of approximately 75 minutes.

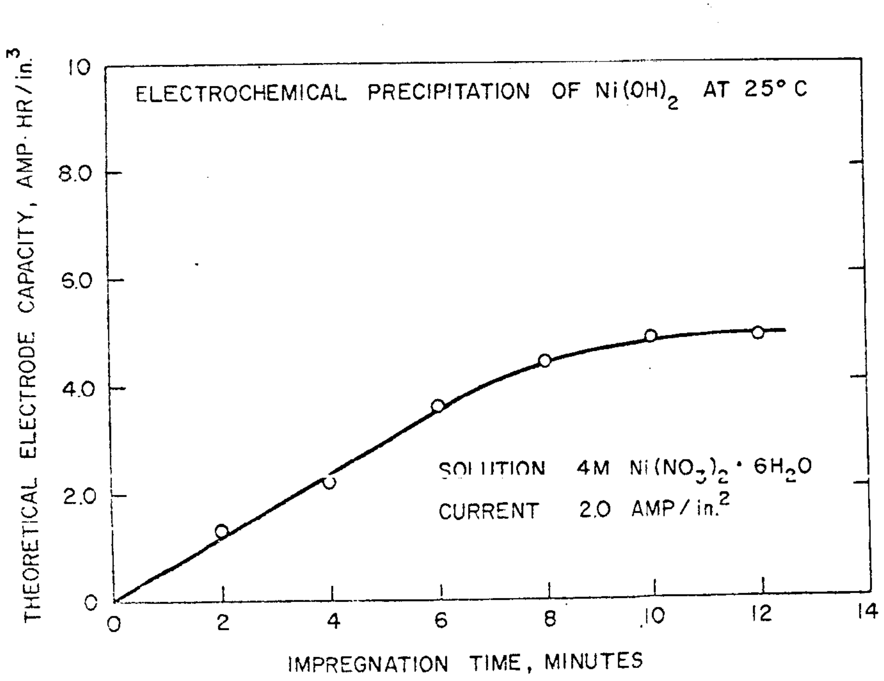
One of the problems we've found with the preparation of cadmium electrodes with this process was the effect of

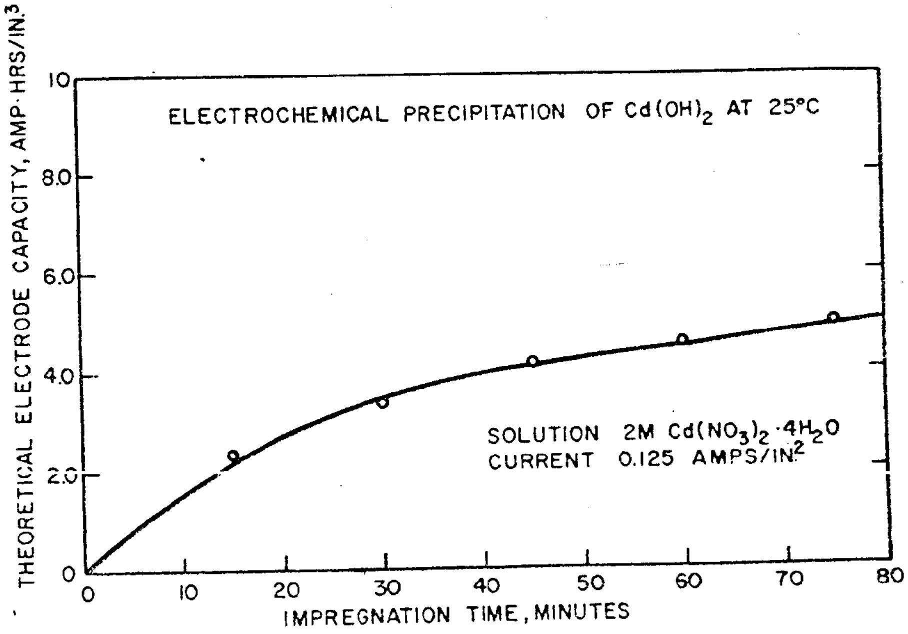
SCHEMATIC OF COMMERCIAL IMPREGNATION PROCESS



SCHEMATIC OF ELECTROCHEMICAL IMPREGNATION PROCESS







crystal size and the blockage of the pores which hindered subsequent precipitation. We did some initial attempts to decrease the size of the cadmium hydroxide. And we found that if we increased the temperature up to near the boiling point of the cadmium nitrite solution we did indeed decrease the crystal size as shown in the next slide.

(Slide.)

These are transmission electron photomicrographs, 10,000 "X" magnification. The cadmium hydroxide was deposited onto a planar nickel sheet in a boiling cadmium nitrate solution at different temperatures.

You can recognize the familiar hexagonal leaflets of cadmium hydroxide. And their size increases up to 75°C. However, at higher temperatures, and especially at temperatures approaching the boiling point, we have found that we precipitated a very small crystal size of a similar shape. And when the experiment was carried out using a porous nickel plaque instead of a planar nickel electrode, we did indeed find increased loading.

I would like to sum up the results of the initial work by showing you the next slide which is kind of hard to take. But if you look at it for a while, it starts to make a little sense.

(Slide.)

In this case we used a plaque 28 mils thick and about 75 percent porous. And the conditions were such that the current and time gave us a one ampere hour charge level in each case.

And I have plotted the capacity of the electrode in ampere hours per cubic inch after the plaque had been impregnated and formed. This represents the weight gain of the plaque material. And we looked at a current density of .25 to one amp per square inch and a solution concentration of .5 to 4 molar cadmium nitrate.

The purpose of this slide is only to show you that the range of conditions is not that sensitive to current and solution concentration. The best results were obtained at a solution concentration of from two to four molar cadmium nitrate at a current density of a half to one amp per square inch.

This represents the upper plateau of the diagram, this region here. Plaques prepared under these conditions were nearly identical in loading. Since this process is pH dependent, one of the conditions you would like to achieve is to insure that the pH of the solution during impregnation remains as constant as possible.

One of our initial difficulties was as impregnation proceeded, the pH of the solution dropped, and it was difficult to determine the effect at any one pH level.

(Slide.)

On the next slide we show that in the very beginning here we have plot of solution pH versus the concentration of sodium nitrite, but we've found with no nitrite that the initial pH fell from a value of 2.75 down to zero and in some cases less, depending on the impregnation. time.

So we looked for an additive which was compatible with the chemistry of the solution and yet did not induce impurities into the active material. In this case you can use either sodium or potassium nitrite. And the nitrites are oxidized to nitrates at the anodes. And what I would like to show here is that as you increase the concentration of sodium nitrite, the pH of the solution tends to stabilize until you get up to about .5 to .6 molar, in this case sodium nitrite.

And we found that the pH remained constant at least under these conditions using a two molar solution of cadmium nitrate at a current of a half an amp per square inch for 45 minutes.

Also as a side effect which we didn't discourage was a slight increase in capacity with increasing nitrite concentration

Now I've singled out some of the conditions which appeared to give us optimum loading. And in this case I have used a plaque 76 percent porous and 27 to 29 mils thick.

The plaques were cleaned initially in a dry hydrogen atmosphere prior to impregnation.

(Slide.)

And on the next slide it shows the results we can attain using a two-molar solution of cadmium nitrate and in this case 3/10th molar sodium nitrite at the boiling point of the solution which in this case is around 104°C.

We have plotted the theoretical electrode capacity versus impregnation time. And at a current of a half an amp per square inch we can attain a loading of 2.1 grams of active material for cc of void, which represents a loading density of approximately 9.7 ampere hours per cubic inch.

The theoretical electrode capacity was based on an electron, a two-electron,transfer. After the plaques had been impregnated they were washed and dried and then cycled and then brushed and washed and dried again. So we've tried to eliminate a material that did deposit on the surface.

When the same techniques were applied to the preparation of thepositive electrode, similar results were obtained. In this case the calculation of theoretical capacity based on weight gain was a one-electron transfer in the charge and discharge of the positive active material, as shown on the next slide.

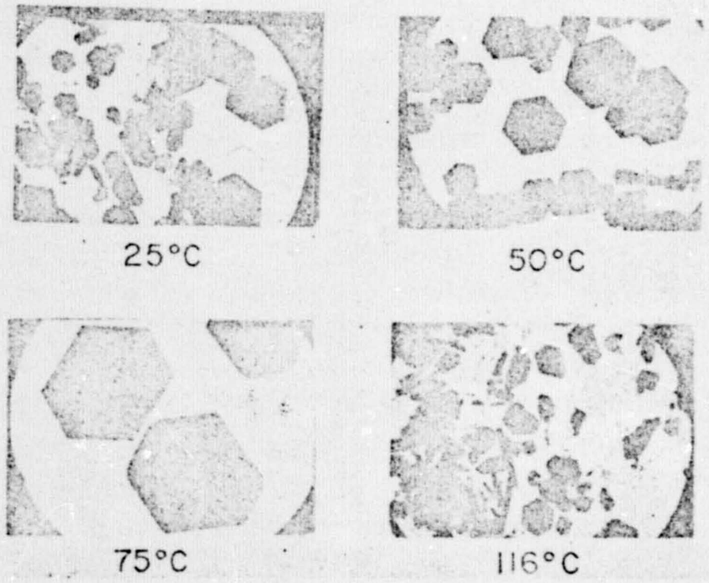
(Slide.)

I have shown a similar plot of theoretical electrode

TRANSMISSION ELECTRON PHOTOMICROGRAPHS

$Cd(OH)_2$ CRYSTALS

10,000 X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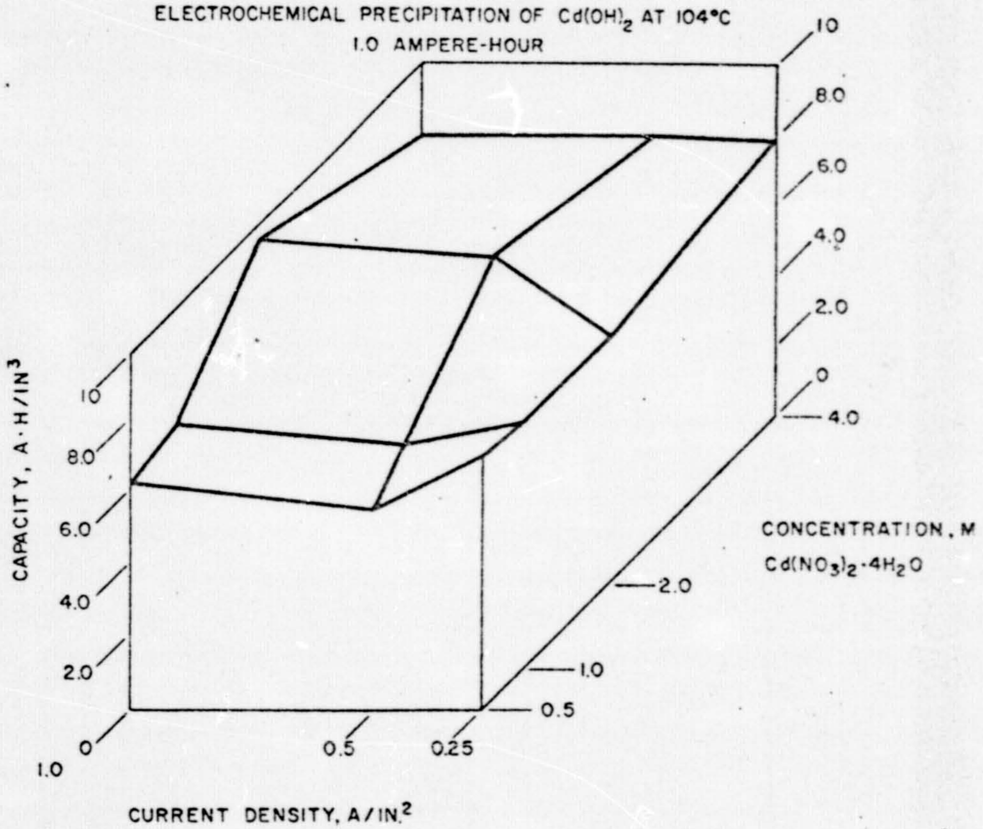

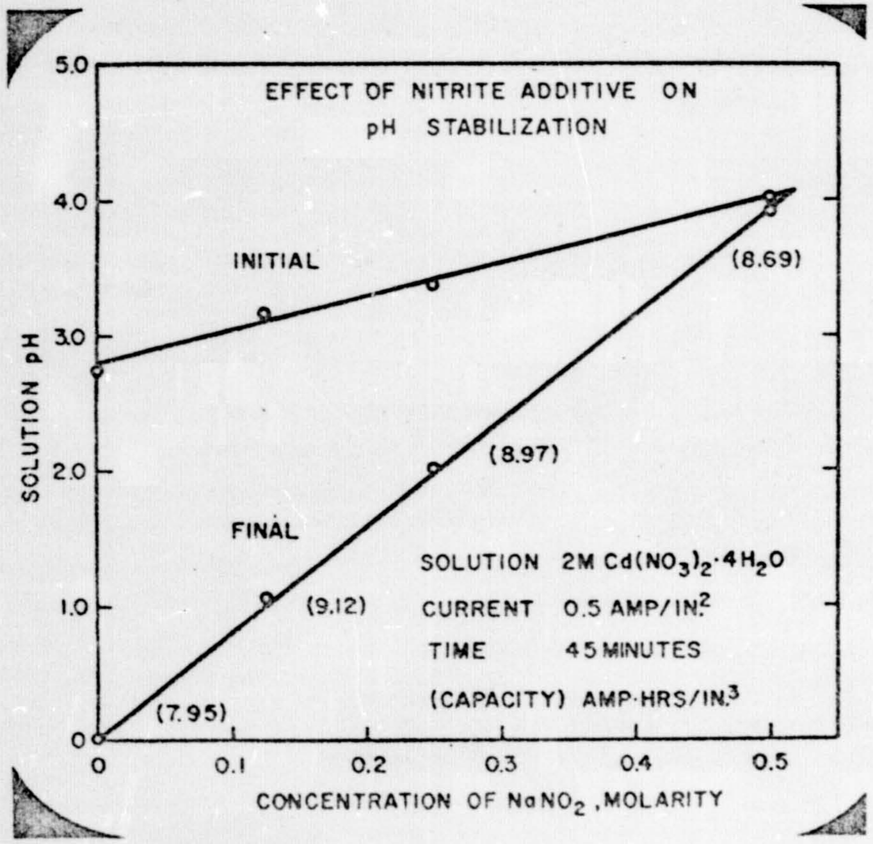

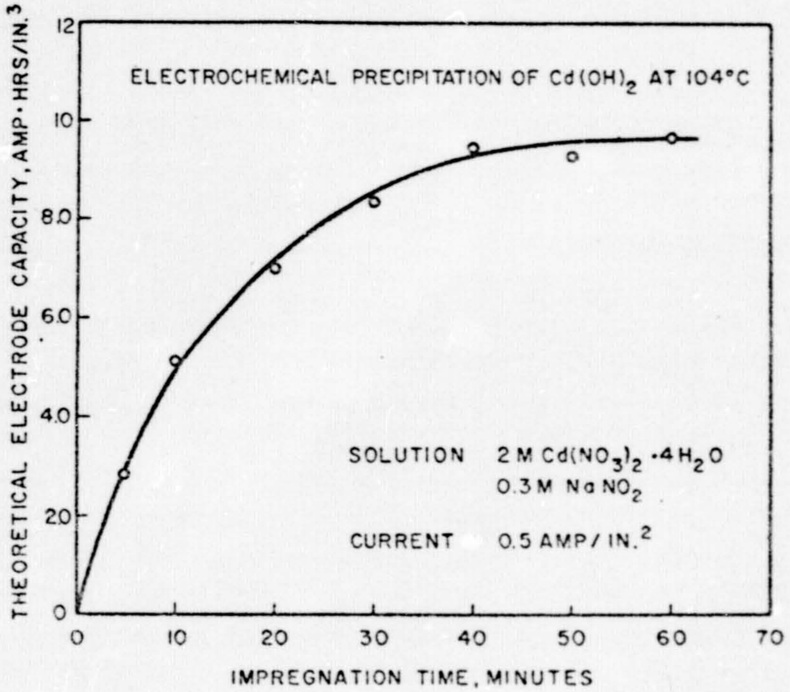

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capacity versus impregnation time. Here again using a two-molar solution of nickel nitrate at a current of a half an amp per square inch.

The maximum loading I've shown here. After 75 minutes you obtain a loading of 2.1 grams of positive active material per cc of void volume which is equivalent to a loading density of approximately 8.5 ampere hours per cubic inch.

I might add that if the plates are washed and dried they can be given an initial or a subsequent impregnation cycle. And on the few plaques that we have done this to we have achieved a loading as high as 11 to 12 ampere hours per cubic inch.

However, the initial objective was to obtain a respectable loading with just one impregnation cycle.

I would like to show now a series of scanning electron photomicrographs in an attempt to demonstrate the salient characteristics of the active material. Normally two pictues will be shown on each slide, one of a commercial electrode prepared by an immersion technique and the other prepared by cathodic deposition, all except on the next slide which just shows you the porous nickel substrate which was used for this study.

(Slide.)

On the left at a magnification of 500 "X" we show you the open structure of the sintered nickel plaque.

And this point here is at larger magnifications up to 2000 "X" magnification. The area was selected here. And it shows you the bonding between the particles in the open structure of the substrate which you would like to retain after loading.

(Slide.)

Now the next slide was taken at 500"X" magnification of two cadmium hydroxide electrodes. The commercial electrode is on the left and it does not show the open structure of the sintered nickel plaque whereas the electrode prepared by high temperature impregnation retains the openness in the pore size of the substrate.

In this case this is not one big crystal of cadmium hydroxide, but it is made up of many, many minute crystals and is deposited uniformly over the exposed nickel surface.

In order to show a little more detail in this we had to go to a higher magnification as shown on the next slide.

(Slide.)

In this case we went up to 2000 "X" showing the contrast. And I might add that the loading of these two plaques is similar, but the contrast is is in with the difference in size of the cadmium hydroxide crystals. In this case you can see the many small crystals deposited uniformly throughout the plaque. And we have still been able to maintain the open structure of the substrate.

This electrode gives us maximum utilization of the negative active material and also rapid oxygen recombination.

(Slide.)

On the next slide we show two positive electrodes. Here again the electrode on the left was prepared by immersion techniques, and the one on the right by high-temperature impregnation methods.

And the thing to watch for again is the open structure of the substrate which we've been able to maintain and still achieve a high loading. The active material is deposited uniformly on the exposed nickel surfaces where in this case most of the void of the plaque has been sealed by the active material.

Now in order to get more detail in the structure we had to go up to 10,000 "X" magnification. And as shown on the next slide, you can see the difference between the two electrodes.

(Slide.)

Here the positive active material gives you a flat low surface area of material in contrast to the -- it is very had to describe, but I must say that it has a high surface area. And this seems to enhance the cycling efficiency of the active material. And the electrodes prepared by the latter technique do give a very high percentage of utilization and very high energy densities can be achieved. These electrodes that I've shown here have been cycles in 30 percent KOH until their capacity was stabilized.

Electrodes produced in this manner perform as well if not better than electrodes prepared by other techniques. And repetitive cycling at high rates in 30 percent KOH does not appear to be detrimental to the structural stability of the active material.

In addition, the electrodes exhibit a high percent utilization of active material cycled in both the flooded and the sealed state.

Now I would like to show you some electrical performance data on cells made with these electrodes and show by way of comparison the results of other electrodes prepared by the immersion technique.

(Slide.)

Here we show the electrode capacity milliampere hours versus cycle number for two negative electrodes. The theoretical capacity of our electrode was 528 milliampere hours. And after forty cycles the percent utilization achieved was 76 percent. The commercial electrode had an initial theoretical capacity of 518 milliampere hours and when cycled showed a gradual deterioration in the measured capacity until after 40 cycles we reached 46 percent utilization.

These electrodes were charged at the C/2 rate for four hours and discharged at the same rate to below one volt. For those of you who are concerned about the money, I suppose one advantage is that you can use 35 percent less cadmium to achieve the same balance of negative to positive ratio in a nickel cadmium cell, if you maintain the high percent utilization of the negative active material.

(Slide.)

Shown in the next slide are results taken from positive electrodes. Here again we've plotted the electrode capacity milliampere hours per square inch versus the charge current. The charge level in all cases was 200 percent. The electrodes were discharged at the C/5 rate. The electrode prepared by high temperature impregnation shows a very good capacity and based on the measurement of theoretical electrode capacity you can achieve 100 percent at the C/5 rate and 120 to 130 percent at higher rates.

The commercial electrode in this case always produces less than its theoretical capacity over the range from C/20 to the C rate.

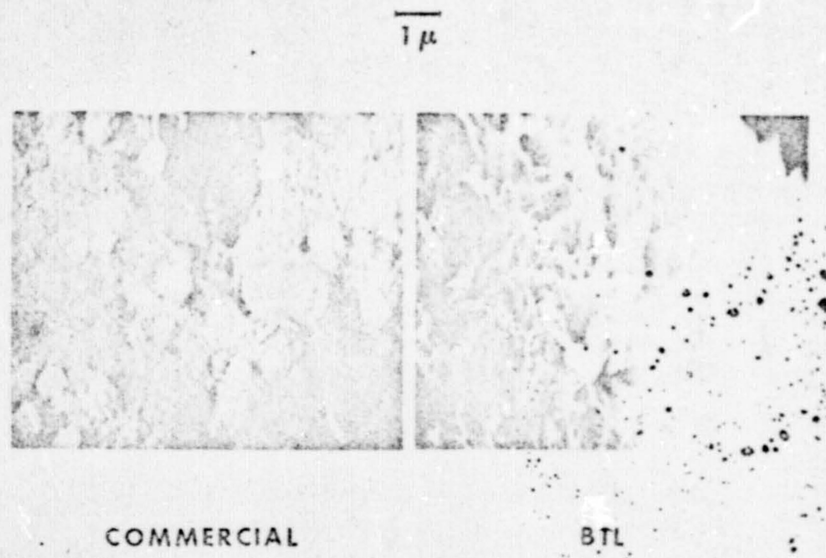
These factors contribute to the design of cells with high energy density and rapid charge capability. For example, the data can be interpreted to show that for the same amount of active material 20 to 30 percent more capacity can be obtained from a cell of equal size and weight.

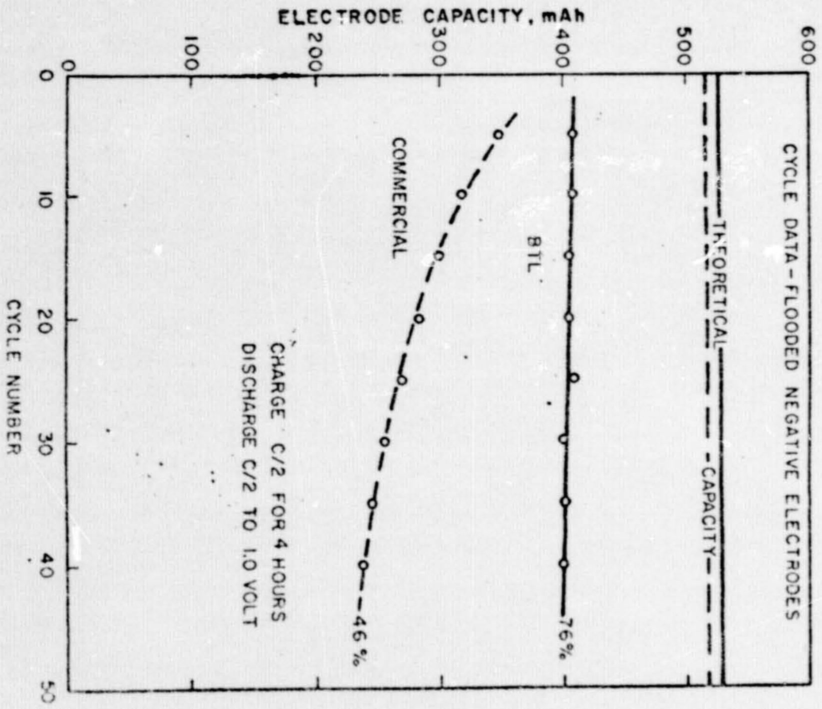
SCANNING ELECTRON PHOTOMICROGRAPHS

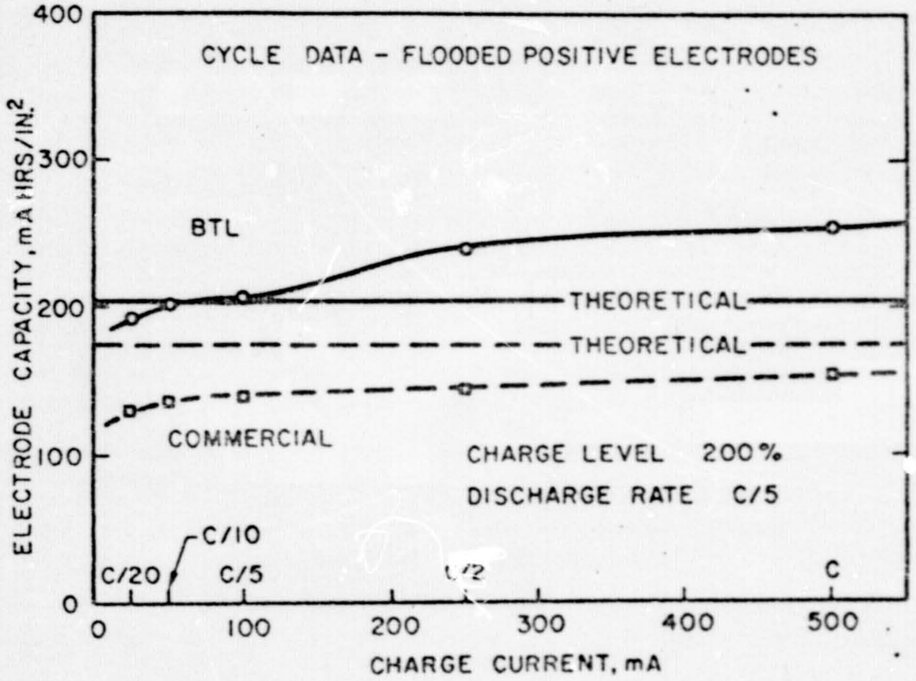
$Ni(OH)_2$ ELECTRODES

SCANNING ELECTRON PHOTOMICROGRAPHS

$Ni(OH)_2$ ELECTRODES







(Slide.)

On the next slide we have taken one of our electrodes and cycled it continually. And we show a plot of capacity milliampere hours versus cycle number. We've charged the electrode at the 2C rate for one hour and discharged it at the C rate to one volt and a temperature of 110°F. We show that the capacity gradually increases with cycling and then levels off.

This electrode has now gone over -- I think we are up to 400 or 500 deep discharges with no degradation in capacity. The fact that the electrodes give better than 100 percent of their theoretical capacity based on a one-electron transfer is not easily explained.

However, the results from subsequent tests do show that a loss in plaque weight of less than 2 percent is observed after the active material is removed. So we have very little effect of corrosion.

However, data exists which suggests that the formation of high-valent nickel oxides may occur when the electrodes are charged at high rates. This would account for a multiple rather than a single electron transfer. And it would thus make our calculations of theoretical capacity incorrect.

Sealed cells made with our own electrodes have performed well under a variety of use modes. And I would like show you some results obtained from a miniature hermetically sealed nickel cadmium cell designed for Bell System application.

(Slide.)

The cell has a theoretical energy density of one watt hour per cubic inch and is capable of being rapid charged.

Here we have a plot of the measured capacity to one volt versus the charge current in milliamps. Here we've used a charge level of 120 percent and a discharge rate of C/5. The capacity of the cell is shown by the solid line here. The theoretical capacity by the dashed line. And here we show the effect of pressure at the end of charge under cycles varying from C/20 up to the 2C rate. This cell can be continually charged at the C/5 rate without exceeding atmospheric pressure.

However, if the cell is made with other objectives in mind,-- we have made similar cells using a different separator and maybe a little less electrolyte. And a cell of this sort can and has been cycled at the 2C rate for four or five hours without exceeding atmospheric pressure and will yield 100 percent of its theoretical capacity.

(Slide.)

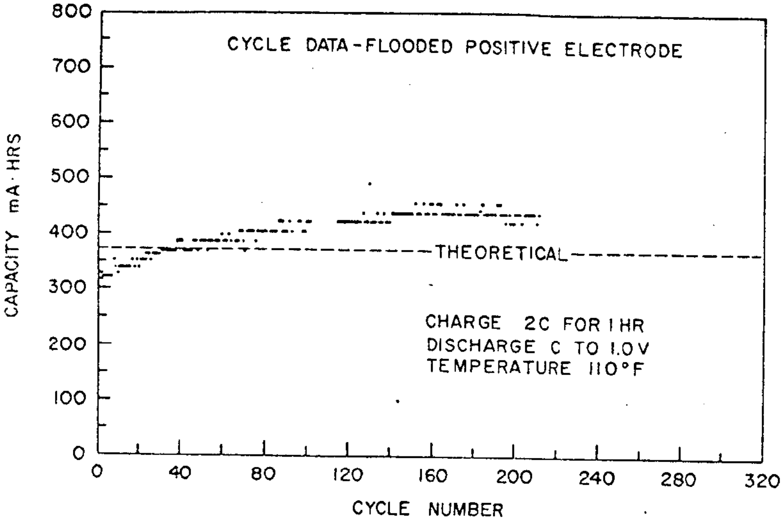
A cell of similar design was put on continuous cycling. And we've shown the capacity, milliampere hours versus cycle number. In this case we've charged at the C/10 rate for 14 hours and discharged at the C/4 rate at 75°.

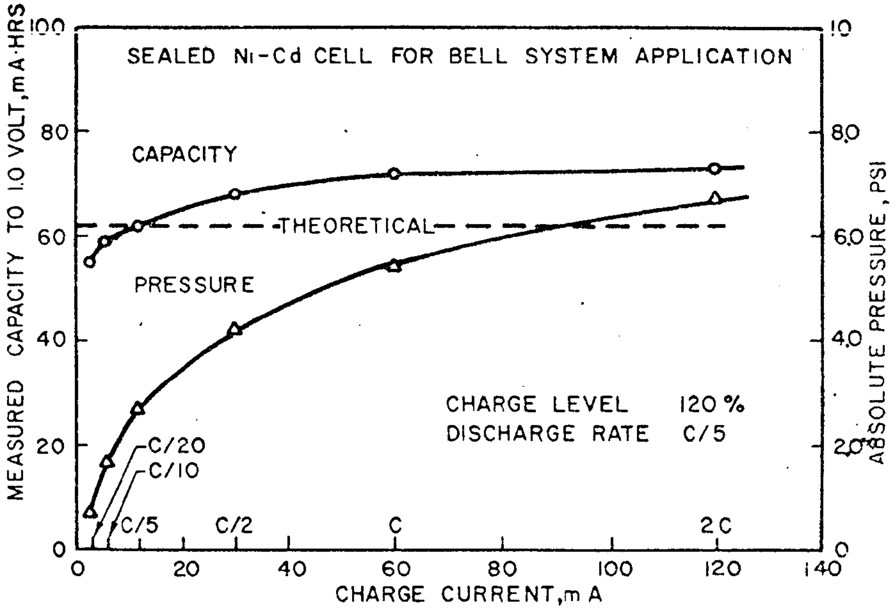
This cell has undergone 250 cycles showing no loss in capacity. I don't want to suggest that the use of electrodes prepared by this technique is solely responsible for the cell performance characteristics shown in the last two slides. On the contrary, I think the behavior exhibited by these cells must be attributed to the careful control of numerous design parameters only one of which is based on the electrode structure. And since this is the topic of a future publication, I will not go into any detail here.

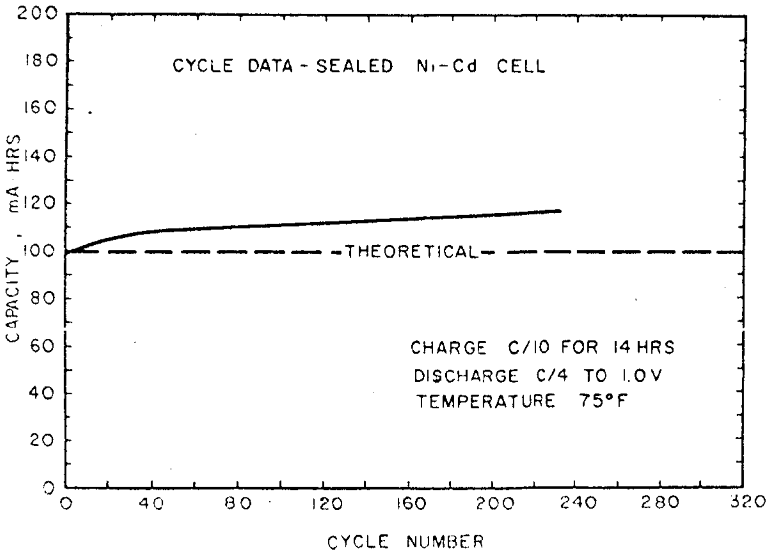
(Slide.)

And then the last slide just shows in the way of summary some of the advantages of the high temperature impregnation process. And number one and very important in terms of economy is an order of magnitude shorter impregnation time and too I think we've shown by the scanning photomicrographs that we have an improved distribution of active species at a very respectable loading.

And, three, we have been able to achieve 30 to 70 percent greater utilization of the active material in the sealed state. And, four, the process we feel is amenable to continuous automatic processing. Essentially, it is an electro-plating process in which you can control very accurately







ADVANTAGES OF BTL IMPREGNATION PROCESSES

1. ORDER OF MAGNITUDE SHORTER IMPREGNATION TIME
2. IMPROVED DISTRIBUTION OF ACTIVE SPECIES
3. 30-70% GREATER UTILIZATION OF ACTIVE MATERIAL IN SEALED STATE
4. AMENABLE TO CONTINUOUS AUTOMATIC PROCESSING

the current and the time of impregnation. And I believe the method could be automated to give you the uniformity, the reproducibility that you might be looking for.

Thank you.

(Applause.)

HALPERT: Dick says he will be very happy to answer any questions you have with regard to this particular presentation.

Dr. Fleischer.

FLEISCHER: One of our early experiences with vacuum impregnation was that different batches of nickel powder gave different results. Have you checked the uniformity of the various batches of powder that you might be getting from time to time?

BEAUCHAMP: As far as it would affect the loading of a plaque?

FLEISCHER: Exactly.

BEAUCHAMP Yes, we've been maybe somewhat more limited. We've worked with Inco powders 287 and 255. We have also for purposes of comparison taken commercial electrodes, dissolved out the active material, reimpregnated them by this method and have been able to achieve the loadings that I've shown you here. However, I must agree with you that I think the uniformity of a plaque is probably dependent more upon the center characteristics than it is on the impregnation method per se. You have to start with a uniform product or a uniform substrate if you expect to achieve a uniform loading independent of the method of impregnation.

HALPERT: Yes.

KANTNER: Ed Kantner of Gulton Industries.

I might make one comment in answer to Dr. Fleischer's question. We have looked into this problem of nickel powder, that is, batched nickel powder to see how it affects some of the characteristics that we normally talk about.

And our results indicated that the variations with batch number or lot number is completely random. So there is no trend there.

FORD: Ford, NASA-Goddard.

You showed photomicrographs of the critical structure. I assume it was on new plates, uncycled plates or right after impregnation?

Have you looked at the change in structure over a period of 240 or so cycles?

BEAUCHAMP: I am sorry if I didn't mention this.

The scanning photomicrographs were taken on electrodes that were cycled to a constant capacity.

Now we have taken pictures of electrodes prepared after impregnation with no cycling and also the ones I've shown you on electrodes that were cycled to a constant capacity. And they looked so similar that it was an equal choice as to which ones to show.

COHN: Cohn, NASA.

I have two questions. Could you give us the energy density in watt hours per pound? And could you tell us whether you found any difference in cadmium fading for your electrodes versus the commercial ones, so-called negative fading.

BEAUCHAMP: The second question first. The only material I have with me now is a slide that shows the difference in fading after only 40 cycles between our electrode and a commercial negative electrode.

Watt hours per pound. This is always a problem with units to talk about. I can't really draw those off the top of my head here.

Dean, do you have any ideas?

VOICE: We could calculate it for you.and call you.

(Laughter.)

BEAUCHAMP If I try to do it up here, I'll make a mistake. But I think the loadings that we've been able to achieve are comparable to those that you would find in a normal commercial product. Be it good or bad, I'm not saying. I just would want it to show that you can stop at any loading that you desire with this process.

GROSS: Gross, Boeing.

The resistance due to diffusion that you lower by having an open structure would certainly appear to be very important. And this is one parameter of plates which is seldom reported and which I would like to see reported and probably would turn out to be an important factor in allowing the high performance. Have you made any measurements of this?

BEAUCHAMP: Probably indirectly through measurements of the porosity of the plaque both before and after cycling and both the flooded and the sealed state. I guess we have fairly definite ideas on this that we probably will get into later in this meeting. But we feel it is important to maintain the open structure of both plates on the positive for better utilization and on the negative for better recombination.

I think it is important to talk about grams per cc of void as well as ampere hours per cubic inch. I think they can both tell you a different story. And I think you have to specify both.

KUGLER: Kugler, ESB.

I was wondering if you have noticed any difference in the swelling of your plates versus commercial plates on a highly loaded positive?

BEAUCHAMP: On the positive electrode we do notice, as we do with plaques prepared by both techniques, a slight increase in thickness after formation.

The plaques that are loaded to very high levels of energy density I believe have to be made somewhat stronger than plaques that are more lightly loaded. But if the substrate is of sufficient strength -- and I'm talking about a plaque which is still 75 percent porous -- it can be cycled repetitively at high rates, C/2, continually without showing any deterioration in capacity or in the plaque structure per se.

But it is something that you have to watch. The strength of the plaque will, under these conditions, reflect the capacity deterioration.

SULKES: **Sulkes,** U.S. Army Electronics Command.

Do you foresee any problem with scaling with this type of process, maintaining a uniform temperature and concentration in the solution, effects on the plates, uniform current density distribution and so on?

BEAUCHAMP: Well, I can take the easy way out of that one I suppose and say that so far that has not been our problem. Everything I've shown here has been done on a laboratory bench.

I would hope that the process could be scaled up. And I can't help but envision it as being similar to scaling up any electroplating process with some difficult, such as temperature. I would think the solution concentration, any additive such as a nitrite in the pH of the solution should be monitored on some sort of a circulating bath, which is something that is already done in the plating field.

So I may be a little optimistic at this point, but I think it can be done and I think it can result in very uniform plaques.

STEINHAUER: Steinhauer, Hughes.

The question of uniform nickel powder has been raised, but what effect do you feel the thermal exposure during the sintering process has on the uniformity of plaque and the ability of the process to work?

BEAUCHAMP: Are you referring to the operation I used just prior to impregnation? The cleaning of the --

STEINHAUER: No, primarily during the metallurgical sintering, whether you use a dry process or a slurry process.

In other words, you can have uniform nickel powder, but when you sinter in a furnace you can either do this in steps of different temperatures and times or you can do it in one shot. What effect do you feel that has on maintaining an open pore structure and uniform structure?

BEAUCHAMP That's a loaded question.

I think it is important -- I haven't looked into

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this too much myself. A lot of this work had been done before I came to the labs. We have more or less settled on one set of conditions for the preparation of plaques.

However, I think that the uniformity of the nickel powder and the subsequent sintering operations are important. At this point I would say they are probably important as to the maintenance of ample strength of the substrate, especially on plaques which are more heavily loaded.

We use no classification of our nickel powders. But we do use clean room facilities which we can do on a very small scale. Our plaques are so big by so big, so I'm not talking about a commercial process.

We do catalog the screen plaque weight on every plaque we make, so we do have a history to go back to. But here again, it is only on a small scale operation. And maybe we haven't been able to see the effect of variation in sintering conditions that other people could.

However, as far as the impregnation process is concerned, like I said, I've been able to impregnate commercial plaque material, in fact even material in which we've dissolved off the active material and reimpregnate it as either nickel or cadmium.

Now this is not the most desirable substrate, but it just demonstrates that the process can be done somewhat independent of the substrate.

SCOTT: Scott, TRW.

Have you explored the upper limits of loading with respect to the stability of capacity, you know, as a function of cycle life? How high can you go and still get the type of stability that you showed on your slides?

BEAUCHAMP: I guess I have definite ideas on that. They may not agree with anybody else's. And I am not sure I am free to comment on that. Deane may get into this later.

But we do like to see our negative electrodes loaded to a specific value. And we feel this is very important. And the positive electrode is also sensitive to loading.

However, if I say something definite, I'm sure I'll turn around tomorrow and somebody will show just the opposite. In the nickel cadmium field it seems as though you can run the same experiment to show many different things.

And I always have felt, however, that loading is important. It is important to specify both the loading and the energy density. And I always contend this is true.

PARRY: Parry, Tyco Labs.

We have taken a brief look at the high temperature electrochemical process and we have succeeded in reproducing a lot of the results that Dick has talked about this morning. But I thought a few qualitative comments on our experience might be of use to other people.

First of all, it is a process that is very much more sensitive to the exact conditions of precipitation. We found that we got some very unattractive appearances on some occasions. We had electrons with dark spots in the middle or halos around them. We've had very heavy deposits around the edges and almost nothing in the middle. And the process is very dependent on the exact conditions that you use.

Also some of the colors that you see are quite different from the normal inpregnation process. The negative electrode where we reproduce the high loading and high utilization are uniformly black in color as opposed to the normal grayish color of the negative.

With the positive, even when the electrode is unifommly spaced between two counter electrodes, we have seen a plate that is green on one side and black on the other. So it can be quite an interesting thing to look at.

One other interesting point that we found with the negative electrode, despite the fact that you have relatively large cathodic currents, we've seen very little metallic cadmium in the plates after the impregnation process. It is 99 percent cadmium hydroxide and one percent cadmium, which is somewhat surprising.

HALPERT: Thank you, Dick, for an enlightening talk.

I think at this point we will break for coffee.

We will reconvene in about ten minutes.

(Recess.)

HALPERT: To start off this session Dean Maurer from Bell Labs wanted to make some comments with regard to scaling up of the process that Dick Beauchamp talked about.

MAURER: I just wanted to comment that we are working with a number of the West ern Electric licensees. As you know, Bell Laboratories is part of the Bell System. And we are working with the Western licensees on batteries to develop some scale-ups for this process.

And, of course, we are amenable to working with NASA or other government agencies to do the same thing. So the scale-up process is in process.

HALPERT: Okay, thank you.

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At this point we will go to our next speaker for this morning, Dr. John Parry of Tyco Laboratories has been doing quite a bit of work with regard to the processing of nickel plaques and nickel and cadmium plates for aerospace cells and looking at the processes and the factors affecting the production of these plaques and plates.

I present to you Dr. Parry.

PARRY: In giving Jerry a title for this talk I included the words "quality control" in the title so that I could sort of slip in under the wires to talk about the work we have been doing for NASA-Goddard at Tyco.

In actual fact, I don't think I'm rigorously talking about quality control but rather the characterization tests that we've been using at Tyco to identify the degree of uniformity in the plaque and pate materials that we have been preparing.

I think that the characterization tests I'm going to talk about are relevant to quality control and almost certainly to post mortem analyses of failed cells.

We have looked at the whole nickel cadmium battery plate manufacturing process from the powder to the finished plates. We have looked at tests for identifying uniformity of powders, looking at the physical properties of the plaque and also the characteristics of plates.

Now when I set out to write this talk I thought that I would just skip over the work we did with powders and plaques, because this work has appeared in print in reports. This paper deal mainly with the work that we've done on plates more recently that hasn't yet been disseminated. But it is obvious from the discussion earlier this morning that there is still quite a lot of interest in the influence of plaque properties on the final plate.

So maybe in discussion we can get into some of these aspects. I was just going to skip through what we did with powders and plaques.

First of all, with powders we measured bulk density, surface area, particle size distribution by sedimentation and grain size by X-ray diffraction. We thought these were the factors that were most likely to be influential in the sintering process.

Now you get some interesting correlations between these physical properties, but I think as far as quality control is concerned or identification of the qualities of powder, you can do this all with bulk density. You can get all the answers you want by measurement of bulk density.

With plaque we measured porosity, resistivity, surface area and mechanical strength.

(Slide.)

These are measurements that we made with loose sintered powders without a support screen. So we don't have any of the complicated features of having something running through the middle of the porous mass.

I just want to run through these quickly. You get a reasonable correlation between resistivity measured by a full point method to avoid contact resistance and porosity.

(Slide.)

Again, the reason for correlation between mechanical strength of the plaque and the surface area.

(Slide.)

And between mechanical strength and resistivity.

So amongst the measurements that we made they all seemed to be looking at the same thing, with the exception of the surface area. This is not too surprising. And I think it is understandable even in the case of the surface area.

What you're looking at is the neck growth between the particles of nickel powder. The more neck growth you get the greater the mechanical strength of the plaque, the lower the resistivity and also the lower the surface area.

Porosity is I think a little more of a casual relationship. It is not as direct as the other three. But it comes down to the fact that if you want to assess the quality of a plaque or its uniformity, you can do it with any one of these measurements that I've listed. So I think the approach that should be taken is to use the one that is most convenient.

Porosity I say is -- first of all, it is not very sensitive. When you're talking about half percent changes in something that is 80 percent porous, you are really talking about quite a significant change in terms of the amount of solid material that you've got.

So I don't particularly like porosity as a measurement. Resistivity is fine when you're dealing with the loose sintered plaques without the support structure that we are looking at here. But as soon as you put a support screen in the structure, the sensitivity goes down quite a bit.

Surface area is fine, but it is a tedious measurement to do and there is a fair amount of calculating afterwards. So really it is not a convenient approach. I want to come to the one I want to plug, which is mechanical strength. And we have developed a four-point bend test which is very easy to carry out and I think gives sensible information in terms of defining the quality of a plaque.

(Slide.)

This is the set-up you use. This is set-up in an Instron testing machine or an equivalent. You can do it with a very much cheaper set-up than the equipment in which we did the measurements.

Essentially you have four pole pieces. The sample goes between them and the pole pieces as you see there the inner ones are at the quarter points of the distance of the lower two.

And as the top is driven downwards, the plaque begins to bend and eventually you get failure -- this goes into near pure bending in this four-point method as opposed to a three-point test which tends to end up as a triangle.

This goes into pure bending, and you actually see failure in the center at this point.

Now the advantage of the mechanical strength measurement is that it is independent of having a support structure in the middle of the plaque. Most of the strain is taken in the surface layers of the center, so the measurement you get is essentially a measure of the coherence between the nickel particles that you've sintered to form the plaque.

So it is a sensible measurements for a typical nickel cadmium battery plaque that is made with a support

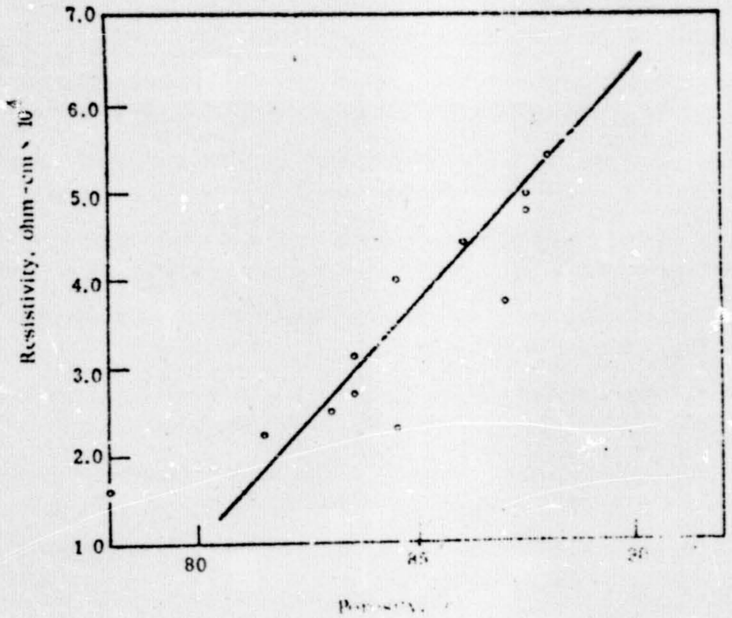
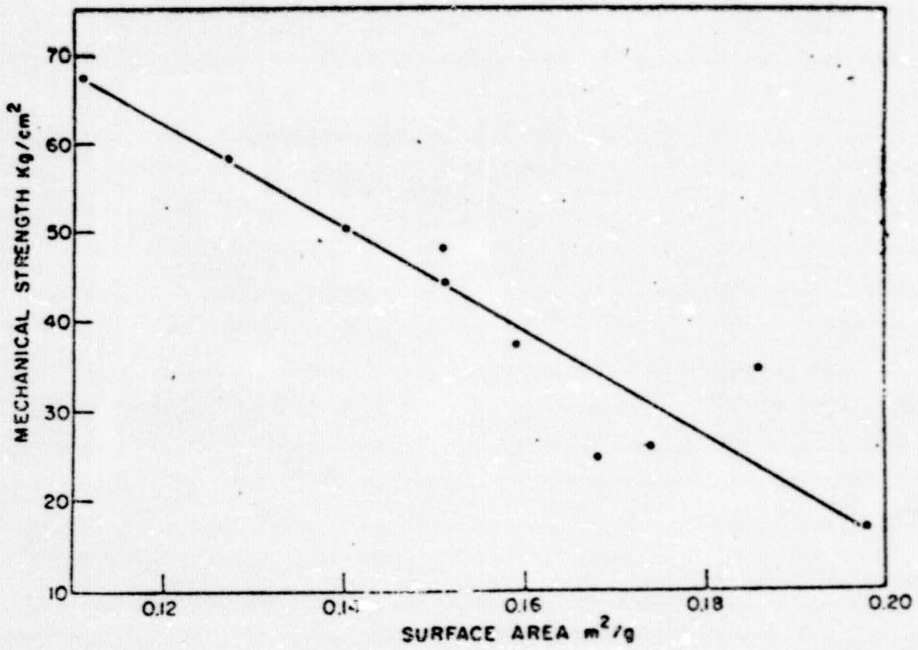
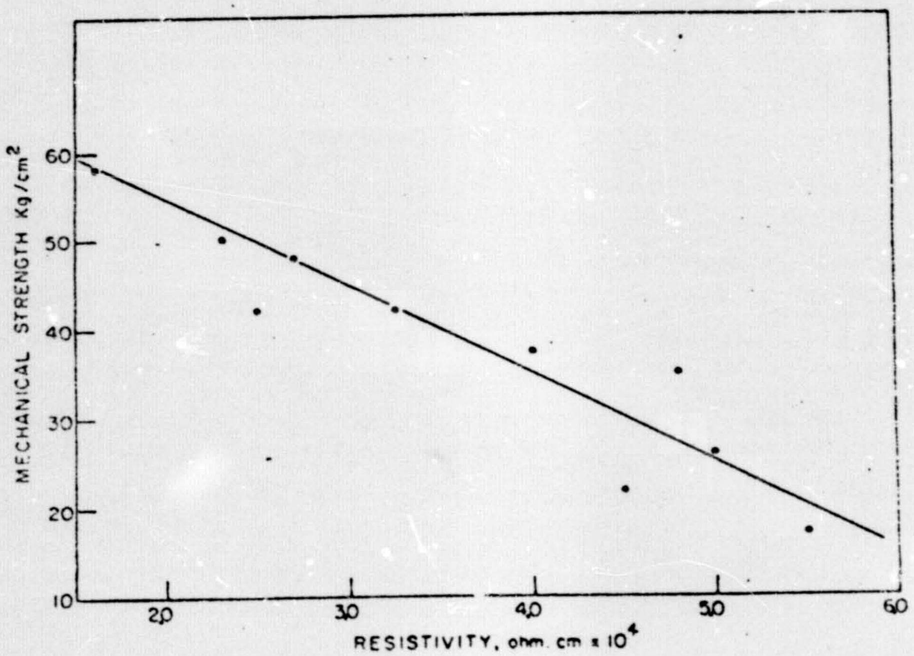
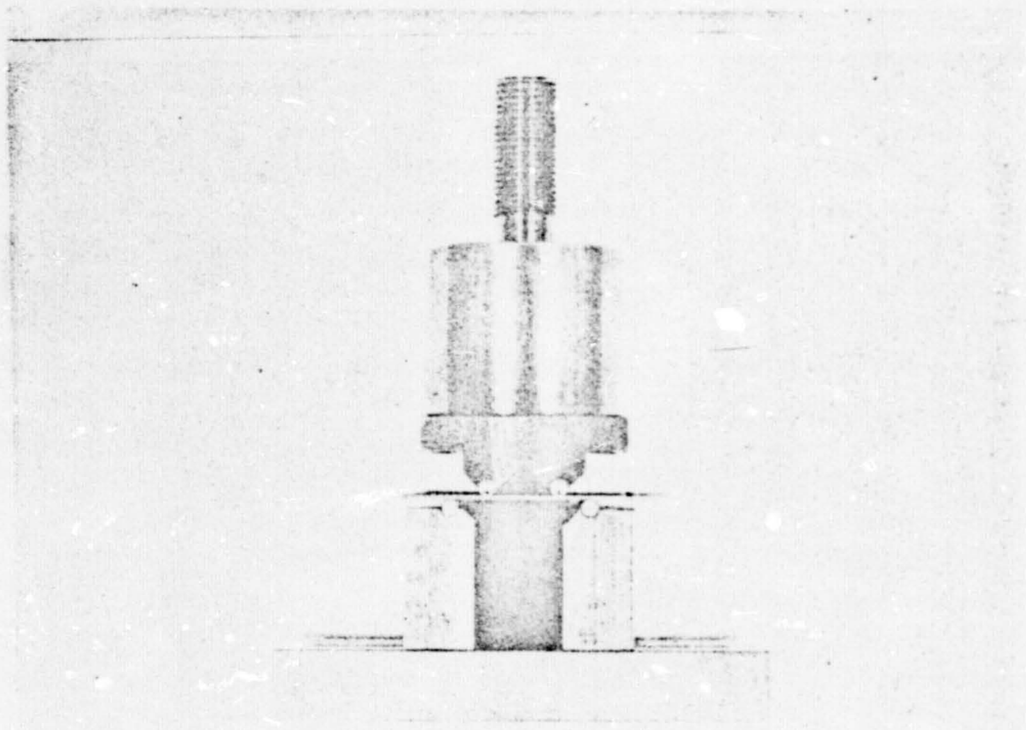


Fig. 7. Resistivity versus porosity







structure and is one that can be carried out very rapidly and routinely.

I think it has been used by other people reasonably successfully. Perhaps there can be some comment on that afterwards.

Just one other word in passing, I am very unhappy about any attempt to measure pore size distribution by measuring pore symmetry. I am not going to go into detail. Again this is in print. But if anybody wants to question me afterwards, I can give the details.

The main thing I wanted to talk about was the work we've done on characterization of plates, in other words, chemical analysis of the active materials of nickel cadmium battery plates.

The techniques we've been using are probably pretty elaborate for quality assurance purposes, but we have set out to make comparisons between different methods of impregnation and also varying conditions in these methods of impregnation.

So we are looking for relatively small changes in morphology, distribution and so on. So we have gone I think into somewhat more detail than might be necessary in the routine process where the conditions are not changing very much from day to day.

There I think it is possible if all of the s 39

conditions are maintained, it is possible to get a reasonable idea of the quality of a plate just by weight pick-up. But for what we wanted to do we wanted more information.

Essentially what we wanted to do was to define utilization of the active materials. We wanted to see how utilization changed with impregnation methods and how it changed as a function of the duty cycle of the plates in operation.

So what we were setting out to do was to measure utilization. I don't think I need go into the background of the importance of, as far as hermetically sealed cells are concerned, of maintaining positive to negative ratios or accurately defining the balance of charge in the negative plate at the time of starting.

But chemical methods of analysis I think are needed to be able to define these things precisely. This also depends on the method you use for impregnation, particularly with the negative. If you are going to end up, as you can with say the Fleischer process of impregnation, with a mixture of cadmium hydroxide, there is no way in which you can translate the weight gain into a simple indication of how much active material you have there.

If you have a mixture of cadmium and cadmium hydroxide, there's no figure you can use to convert this to a theoretical capacity. So there is a very definite need I things for methods of chemical analysis.

Now with the negative plate this is not I don't think a particularly difficult problem. The components that you have in the negative plate, cadmium metal, cadmium hydroxide and nickel. The problems are -- well, first of all, you don't know the relative amounts of cadmium to cadmium hydroxide in some of the impregnation methods in the green plate. And particularly on cycling you don't know how much of the material is actually being charged and discharged.

So what we need to do is to define for the particular plate how much of each component we've got there. We are also interested to some extent in how much corrosion of the nickel plaque occurs during both the impregnation process and the cycling. Although this applies more to the positive than to the negative.

As far as negative plate analysis is concerned, you can selectively extract cadmium hydroxide in the presence of cadmium metal by complexation ammoniacal ammonium chloride. This is commonly called the muspratt solution.

Two hours would normally extract the cadmium hydroxide to no further weight loss in our experience for a typical plate. One can then take the solution containing the cadmium in the complex form and analyze for the total cadmium by compleximetric titration with EDTA using eriochrome black T as the indicator.

Then with the remaining plates which now contain metallic cadmium and nickel you can dissolve up the whole thing in nitric acid, evaporate to get rid of the excess acid after dissolution, adjust the pH-10, and analyze again for cadmium. hydroxide.

It is possible to do cadmium in the presence of nickel again by compleximetric titration. First form the cyanides and then break the cadmium complexes with formaldehyde and titrate as before with EDTA. You can then carry out a second determination for the amount of nickel.

(Slide.)

These are some of the results, just typical results to indicate what can be obtained in analysis of negative plates. Essentially what I've done here is to check on the method. And these plates were prepared by impregnation by the Fleischer process without nitric acid in the cadmium nitrate. So there is little or no corrosion of the substrate during the impregnation process.

Essentially what we've done here is to take the plate weight initially, determine the amount of cadmium hydroxide, then determine the cadmium content, add these two together and subtract it from the first one to get a figure for the plaque weight. We have then compared this with the weight of the plaque per unit area prior to the impregnation process.

And I think the agreement is quite reasonable. These figures seem to be just a little bit higher in every case all except this one, which is just a little lower. But there is pretty good agreement between the plaque weight determined by subtracting out the weight of the active materials from the plate weight per unit area with the weight per unit area of the plaque as we started.

I did some further calculations on this just to give us some idea of what you can get out of a chemical analysis that you can't get from just weight increase. If you will look, these are essentially in pairs. They represent attempts to put different amounts of material into the plaque.

The weight gain here is not too uniform. There is quite an improvement when you look at the total weight of active material. I don't know if we can mix these. Could I have the piece of paper that I have some figures scratched on?

(Slide.)

This is column four from the previous slide. As I said, the weight pick-up wasn't particularly uniform. But if you look at this in terms of the weight of active material, there is reasonable agreement. But if you look at it in terms of the total cadmium, in other words, you convert the amount of cadmium hydroxide to cadmium and add the two together, you see that there is an even further improvement. It is closer than one percent. So weight gain can be misleading in terms of distribution and uniformity of active material.

If you do carry out the chemical analysis you can see that you get a much clearer picture of whether you've got a uniform distribution or not. I think in this case it turns out that the weight gain is misleading in that the two weight gain figures actually agree. But if you compare the amount of cadmium that you have distributed in the plate, the agreement is not all that good.

So I think as far as the negative electrode is concerned, the process is reasonably straightforward. And I don't think I need spend any more time on it.

With the positive plates we have a very much lmore difficult problem. Essentially now you have nickel in three different valence states. You've got the plaque. You have the discharge material. And you have the charge material. You have the added complication that both the discharged and the charged states after cycling exhibit nonintegral stoichiometry.

I think what I want to do is put my presentation in the direction I want to do at this stage. And I think the real problem that we are faced with here as far as any chemical analysis is concerned in identifying these three separate components is one of the value of the rest potential of the positive electrode.

With the negative electrode which is sitting pretty close to the hydrogen potential you never have any risk of -- or you have very little risk of corrosion of the nickel substrate.

But with the positive electrode sitting at more than a volt positive to hydrogen potential, the only thing that's preventing severe corrosion of the nickel substrate is the fact that it has a passive film. Now the passive film happens to be bivalent nickel and quite similar to the discharged state of the positive-active material. It differs only in its degree of hydration in effect.

So that any attempt you make to dissolve up the active material in the positive plate is simultaneously going to dissolve the passive film on the nickel. And as soon as the nickel metal is exposed you are going to get corrosion.

This is going to need an associated cathodic process. And this aspect is going to come up in some of the discussions that I'm going to present to you. But in most cases you have dissolved oxygen in the solutions you're dealing with. And this is all too readily reduced. And you get significant corrosion rates or significant amounts of corrosion of the nickel substrate.

To give an idea of what can happen, the next slide, please.

(Slide.)

These are some tests we did on physical mixtures of nickel hydroxide and carbonyl nickel powders. Now these are not plates. This is just a physical mixture of nickel hydroxide and carbonyl nickel powder.

The nickel hydroxide was prepared by precipitation from the nitrate and was dried at quite a high temperature to make sure it had no water in it. We did X-ray diffraction measurements on it to determine the fact that there is no water content in the nickel hydroxide.

So starting with 50 percent mixtures of the nickel hydroxide and nickel powder exposed to the Muspratt solution, also in contact with air, you find that you get on calculation from the weight loss an apparent nickel hydroxide content - 10 percent higher than the mixture you started with. And this is fairly consistent through the measurements that we carried out.

We also looked at the straight nickel powders. We looked at the 287 and the 255 under the same conditions. We saw 14 percent weight loss for the 287 powder, and an 18.4 percent weight loss for the 255.

The bigger figure there probably reflects the difference in surface area between these two materials. And the fact that we see a 14 percent weight loss there for a difference say of 10 percent in the other ones probably means that there's some protection of the surface to some extent by the finely divided nickel hydroxide.

This, of course, would correspond to the conditions that you get in a positive plate where the nickel substrate is to a large extent protected by the deposit of active material. But I don't think in any analytical method you can rely on this to protect the nickel substrate, particularly towards the end of an extraction process when you've removed most of the active material, you're going to have a lot of the nickel substrate exposed.

If you compare this with the amount of nickel oxide you normally have on the carbonyl nickel powders, we did reduce one of these in hydrogen at 600 Centigrade. And we got what I think was a relatively high weight loss of 1.3 percent.

So you've got a potential problem -- that's a good choice of words -- potential problem related to the rest potential of the positive electrode. You've got a problem in trying to carry out an analysis of positive plates, because of the tendency of the substrate to corrode and confuse the figures that come out.

I might add that we did try quickly under these conditions adding hydrazine to the solution and seeing the effect of having a reducing agent present in the extraction solution. And we saw no difference under these circumstances. I think it is possible that Dr. Kruger's method which was described at the Power Sources Conference where the extraction is carried out in acetic acid with air rigorously excluded from the system that it would be possible to carry out an analysis without corrosion of the substrate.

We had gone in another direction prior to learning about that method. I would like to describe this approach. It is a typical electrochemist's approach in that if the rest potential is not what you want it to be you can tint you study to a point where it will behave. So we took these positive plates and set them up in the extraction solution at a low positive potential. It was just 25 millivolts positive to the hydrogen electrode.

Prior to doing this we wanted to test what potential range we could work in where there wouldn't be nickel dissolution under the conditions that we were working, so we took some of the Muspratt solution, set up a nickel plaque and did current voltage curves to find out what regions of potentialwe could work in without getting dissolution of the nickel. And we found quite a reasonable potential range between zero on the hydrogen scale and say plus 200 where we could work quite easily.

We also checked that at these potentials you're not going to plate out nickel. Having extracted the positive active material and gotten quite a high concentration of nickel in the solution, are you at these potentials going to plate out nickel? So we checked with the same extraction solution with nickel added to make sure we wouldn't deposit metallic nickel on the plaque.

Also I think it is pretty well documented in the literature that at this potential you can't reduce nickel hydroxide to metallic nickel. So what you observe, you immerse the nickel plaque, strap the potential down to plus 25 millivolts. The currents we observe are usually less than a half a milliamp per square centimeter. I think this is due to residual oxygen maybe adsorbed on the active material or the fact that we can't get it completely out of solution without taking more precautions that we have been.

We then have circumstances where we can let plates sit in the extraction solution for as long as we want to insure complete extraction of the active material. And this is I think one important aspect of the whole process that you can let the plates sit in the extraction solution as long as you need to make sure that you've got complete extraction.

And as I stress, towards the end of the extraction process you are exposing more and more of the nickel substrate

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and corrosion of the plaque is a lot more likely.

The other thing that we do in carrying out the analysis is that we don't rely just on weight loss of the nickel plate in extraction. We've actually been determining the nickel in solution with dimethyl glyoxime.

(Slide.)

These are some of the typical results -- well, no, they're not typical. These are selected results to demonstrate one or two points. First of all, let's start with the righthand column as to what these plates are.

Green plates are immediately after the impregnation process without formation, without cycling. And if we make a comparison between analysis of a green plate with potential control and without, in fact we see that there is not too much of a difference between these two analyses.

For the green plate it appears that there is enough protection of the substrate with the active material to prevent too much corrosion. This is the weight before extraction. This is the weight of the plaque after extraction. And we can compare this with the weight of the plaque per unit area prior to impregnation.

For these particular plates they were carried out in the presence of nitric acid. There was some corrosion of the substrate during the impregnation process. So the difference in weight that you see between these two represents

Table I. Check on Analytical Methods for Negative Plates

(1) Plate Weight, g cm^2	(2) Cd(OH)$_2$, g cm^2	(3) Cd Content, g cm^2	(4) Total Weight of Active Material (2 + 3)	(5) Plaque Weight, g cm^2 (1 − 4)	(6) Plaque Weight Prior to Impregnation, g cm^2
0.2332	0.0384	0.0171	0.0555	0.177	0.170
0.2262	0.0264	0.0269	0.0533	0.163	0.165
0.2978	0.0786	0.0483	0.1269	0.171	0.167
0.2985	0.0579	0.0697	0.1276	0.171	0.167
0.3429	0.1221	0.0447	0.1668	0.176	0.166
0.3325	0.1379	0.0259	0.1638	0.169	0.165
0.3575	0.1080	0.0811	0.1891	0.168	0.165
0.3604	0.1142	0.0772	0.1914	0.169	0.165
			Mean values:	0.170	0.166

Table II. Analysis of Physical Mixtures of $Ni(OH)_2$ and Carbonyl Nickel Powders

Sample	Method	Apparent Wt % Ni(OH)
50% $Ni(OH)_2$, 50% Ni (287)	Muspratt	60.1
50% $Ni(OH)_2$, 50% Ni (287)	Muspratt	60.1
50% $Ni(OH)_2$, 50% Ni (287)	Muspratt	60.1
40% $Ni(OH)_2$, 60% Ni (287)	Muspratt	50.0
		Weight Loss
100% Ni (287)	Muspratt	14.0
100% Ni (255)	Muspratt	18.4
100% Ni (255)	Reduction in H_2 at 600 °C	1.3

ACTIVE MATERIAL IN NEGATIVE PLATES g/cm^2

As $Cd(OH)_2$ + Cd	As Cd
0.0555	0.0466
0.0533	0.0472
0.1269	0.1188
0.1276	0.1142
0.1668	0.1383
0.1638	0.1319
0.1891	0.1642
0.1914	0.1648

Table IV. Analyses of Positive Plates

Sample	Potential Control During Extraction*	Plate Wt Before Extraction, g cm^2	Plaque Wt, g cm^2 After Extraction	Plaque Wt, g cm^2 Before Impregnation	% Wt Loss on Extraction	% $Ni(OH)_2$ by Analysis	% H_2O in Active Material	Comments
1a	No	0.2309	0.1931	0.2036	16.4	15.0	9	Green plate
1b	Yes	0.2300	0.1907	0.2036	17.0	15.0	13	Green plate
2a	No	0.2067	0.1670	0.1750	19.2	19.2	—	Cycled plate in discharged state
2b	Yes	0.2133	0.1769	0.1750	16.8	17.2	—	Green plate
3a	Yes	0.2530	0.2046	0.2036	19.1	19.3	—	Green plate†
3b	Yes	0.2503	0.2004	0.2036	19.9	19.3	(3)	Cycled plate in discharged state†
4a	Yes	0.2448	0.1922	0.2027	21.7	21.6	—	Green plate
4b	Yes	0.2464	0.1915	0.2027	22.3	18.7	15	Cycled plate in discharged state

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* Extraction in Muspratt solution at 70 °C, potential control at 25 mV versus RHE.

† Plates impregnated by Fleischer method without nitric acid in impregnation solution.

corrosion of the substrate that has occurred during impregnation.

If you look at the weight loss on extraction and the nickel hydroxide by analysis, this comes out very nicely, very good agreement. The difference in the weight loss can be accounted for in terms of the different amount of water in the active material. I don't think we were at this time taking special precautions to make sure that all these plates were dried in identical conditions.

This stresses the importance of actually measuring the nickel in solution rather than taking the weight loss as a guide to the percentage of nickel in the active material.

In the case of 2A and 2B we are comparing a cycled plate in the discharged state. I have to mention here, of course, if you're going to use potential control, you can't do it for a plate in the charged state. Pulling the potential down to plus 25 millivolts.discharges the plate automatically.

We do this prior to the analysis in fact, so this is a cycled plate in the discharge state and a comparison with the green plate. Now in this case the plates are prepared without nitric acid in the impregnation solution.

And under these conditions one sees very little corrosion of the substrate. So there was no corrosion during impregnation. So the difference we see between this figure and this figure represents the amount of corrosion of the substrate during the analysis.

In the case of 2A there was no potential control during extraction. In the case of 2B we expercised potential control. We see the quite significant difference, something like 6 or 7 percent between the weight per unit area of the plaque when the analysis is carried out under potential control for these two plates.

This is reflected in the difference in the amount of nickel that you see too. The corrosion of the plate is contributed to the amount of nickel in the solution. In this case you see a larger figure for nickel, as determined with the dimethyl glyoxime.

In the case of 3A and 3B this is an example of what can be achieved if you use potential control for the cycle plate in the discharged state. I should go back and explain why the cycledplate is much more difficult to handle than the green plate.

This is because on discharge you never get the nickel valence back to two, so you always end up with some material in an oxidized state in the active material. And it is the electro-reduction of this material that couples with the nickel dissolution process that is the corrosion of the plaque.

Now the active material that you can't discharge is probably protected by a film of nickel hydroxide which is not a good conductor. So you end up with positive active material in the charged state that is completely encapsulated as it were with discharged material.

But then in the analysis of this plate you begin to dissolve out the nickel hydroxide and you make available that material in the charged state. This is the material that is reduced to compliment the anodic dissolution of nickel from the plaque. So that in comparing 3A and 3B we are comparing the cycle plate in the discharged state now under potential control.

And again these plates were prepared without nitric acid in the impregnation solution. So now we see much better agreement between the plaque weights after extraction as less than probably one or two percent error in the plaque weights per unit area after extraction in this case compared to something over six percent in the previous example.

Again, there is good agreement between the figures obtained for the quantity of nickel in the active material.

And all I wanted to bring out in the case of 4A and 4B is that weight gain is not necessarily a good guide to the amount of active material that you've deposited in the plate. These were weights in the greenstate, I might add, where there is apparently good agreement between the weight pick-up.

But if you compare amount of nickel in there, there is quite a significant difference because of the greater water content in the case of sample 4B.

I don't put too much emphasis on the actual values for the water content here because particuarly for the cycled plates you also have some potassium in the active material. And unless you determine how much potassium is there you can't determine quantitatively how much water you have in the active material.

So essentially what we got out of this method is by potential study control you can analyze the plate in the discharged state to tell you exactly how much active material you've got there and how it is distributed in a plate, if you carry out an analysis on several parts.

As far as utilization is concerned, we need some more information. We now know the amount of active material there, but we don't know how much of it is cycling. Possibly this isn't as big a problem with the positive as the negative, but it would be interesting to try and define what it is.

In order to do this we really need to determine the stoichiometry of both the charged and the discharged state. And I'm of the opinion at this time that we still can't answer this question completely.

But let me give some indication of how far I think we can go. Thus far we have restricted our examination to determination of the state of charge as the equivalent active oxygen content using potassium iodide, liberating iodine and titrating iodine with thiosulfate.

There are other methods of doing this. And there are some very elegant methods described in the literature. But most of them, as far as I can see, demand washing and drying of the plates before you carry out the analysis.

And in the case of plates that are charged, fully charged or overcharged, this immediately gives you an error. As soon as you wash and dry the plate the self-discharge process is rapid enough to give you a significant loss of equivalent active oxygen content.

So I dismiss immediately any method that requires washing and drying. I think it is possible that you can use some of these methods at a low state of charge, say up to 50 percent state of charge for the positive electrode. But as soon as you try to measure something realistic, because we usually want to use all of the capacity that's available in the electrodes, you run into trouble.

When we started out we were getting very low values for the active oxygen content -- and this I think was because we were washing and drying the plates. We went from a method where we were washing and drying to one of direct transfer into the iodide solution.

(Slide.)

This indicates the difference that you see for two samples that are washed and dried and direct transferred. The active oxygen content turns out here. We calculated the apparent nickel valence from the active oxygen. And you can see that by direct transfer you do make a significant difference in the figure you get for the active oxygen and for the apparent valence of the charged state.

These figures are still quite low I think. So the first improvement is one of not washing and drying the plates prior to analysis. Now we still have a corrosion problem in this analysis too.

The interaction of the active material to generate iodine in solution,or I_3- ions, what it means is that we now have an electro-reducible species in solution, one that can complement this anodic corrosion of the nickel plaque quite easily.

The plate is sitting at a high positive potential. The potassium iodide is capable of complexing nickel 2 to some extent, sufficient I think to dissolve any passive film. So immediately you have a nice coupling between the iodine and solution, the I_3- ions, and the nickel plaque. And you get significant corrosion of the nickel plaque.

We found that if we examined the apparent active oxygen content as a function of extraction time, it first show a slight increase, of course, for the first two hours. And then over the next 24 hours it fell off quite rapidly until you ended up with almost nothing.

And you do need quite long contact times to do a reasonably accurate analysis. Contact time needs to be about six or seven hours. Well, there's a very nice way of getting around this particular problem which appears in a paper by Harival, but in French, so maybe some people are not familiar with it. It is very simple. Instead of accumulating the I_3^- in solution you add thiosulfate at regular intervals during the contact time. In our case this was about every 15 minutes. You wait until you see a pale straw color of the iodine appear and then you promptly put in another measured amount of thiosulfate, another five and follow the process right through to the end until the times get longer and longer and until there is very little risk towards the end and you can add your starch and get the exact end point for a proper titration.

So using Harival's technique of simultaneous addition of thiosulfate, I think you can get rid of the corrosion problem as it relates to coupling with I_3^- in the solution.

(Slide.)

Using this method, now using direct transfer and using Harival's method for the analysis you can push the

Table VI. Effect of Washing and Drying of Sample on Active [O] Determination

Sample	Weight per unit Area, g/cm^2	Wt % $Ni(OH)_2$	Wt % [O] in Active Material* Washed and Dried	Wt % [O] in Active Material* Direct Transfer
1	0.2503	19.1	4.35 (2.50)	6.97 (2.80)
2	0.2008	13.1	4.36 (2.50)	8.27 (2.95)

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* Figures in parenthesis are corresponding apparent nickel valencies.

Table VII. Apparent Ni Valence as Function of Charge, Overcharge, and Overdischarge

Charged State

Sample	% Charge at C/2 Rate	Wt % [O] in Active Material	Apparent Ni Valence
1	50	6.0	2.69
2	100	7.5	2.87
3	150	7.5	2.87
4	200*	8.25	2.96
5	200	8.95	3.04
6	200	9.25	3.07
7	200	9.35	3.08
8	1000	9.75	3.13

Discharged State

Sample	Time of Over-discharge, Min	Wt % [O] in Active Material	Apparent Ni Valence
9	0	3.2	2.37
10	5	2.7	2.31
11	15	1.8	2.21

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*20 min stand at open circuit prior to analysis.

apparent nickel valence up as high as 3.1, depending on the degree of overcharge. Up to 100 percent overcharge I think you have just about approached a nickel valence of 3. Thereafter, the overcharge doesn't make all that much difference.

Now this figure is still somewhat unsatisfactory. And although it is bigger than any other figure I've found for actual analysis of nickel plates in the literature, there are figures for the simple oxides analyzed by themselves, but as far as plates are concerned, I haven't seen any figures bigger than 3.13.

If you then compare this with the capacities as measured for these plates and also take into account that we carried out analyses in the discharged stated, I have a lot more confidence in these results because now you don't have any active material in the charged state to couple with the nickel plaque to give you corrosion.

If you use Harival's method, you can get a good value for the apparent nickel valence in the discharged state. And as you can see, it depends on some degree of overdischarge to get now to the normally recorded figures of 2.2.

This might be related in some way to hysteresis. We were discharging relatively rapidly,and maybe if the plates were allowed to sit for a while we would see this 2.2 figure spontaneously.

But if you calculate the apparent valence of the charged state from taking 2.2 and one-electron transfer for the total process, you come up with the conclusion that this figure of 3.13 is still 23 percent too low.

In other words, there are still losses of active oxygen associated with this method of analysis that we haven't accounted for. So a determination of the state of charge, defining the state of charge in an overcharged plate, is still something that you can't really attain.

I think the best we can define for the positive plate at the moment is a reasonably accurate analysis of the state of charge in the discharge state. And we can say very definitely that the charged material that isn't discharged is not cycling.

What we can't define is how much nickel in the divalence state doesn't accept charge. So I think that's as far as one can go in terms of defining utilization of the positive plate.

I did skip rather quickly through why this figure is still low. I think it is still this corrosion of the substrate that what one can see is spontaneous self-discharge of the active material coupled with the anodic process of corrosion of the nickel.

In other words, some of the active material that you are looking for in the positive plate is discharging and coupling with a nickel metal to nickel 2 plus, occuring in solution at the same time.

So the figure you see for active oxygen almost inevitably must turn out too low. If anyone has any methods of determining state of charge for fully charged or overcharged plates, I would very much like to hear about them.

Thank you.

(Applause.)

HALPERT: Are there any questions or comments.

MAURER: The first comment is that one way to determine the state of charge of a plate is, of course, to put it in KOH and connect it across the resistor. It works efficiently in practice.

But McArthur showed a few years ago in a paper he presented that the discharge reaction is proton limited. There is proton diffusion in the active material which is a rate limiting step.

This occurs when a potential of the electrode falls below its plateau voltage. If you go through the standard diffusion equations you find the voltage of the electrode then should follow a diffusion-limited curve.

A plot of this voltage, log of the voltage versus time, will give you a series of straight line segments that fall in the proper ratio of 1 to 9 to 27.

The point is that the electrode must be discharged for a very long time in the shorted state to completely discharge it. The protons are diffusing at a very low rate now because they occupy lattice sites that are nearly completely filled.

So diffusion rates are very low, and times of the order of weeks are required to get these diffusion currents down below let's say the microamp region in an electrode that is of the order of a half ampere hour in size. So this can account for the apparent valence being 2.2 instead of 2.0.

PARRY: I should have chosen my words more carefully. I meant something other than discharging to determine the state of charge.

I think one needs the alternative process in order to be able to define how much of the active material is cycled.

FLEISCHER: No matter how low a rate you go to in discharging a sintered plate, I doubt if you would have the patience to discharge it and get a green nickel hydroxide. You will always have a black plate left at any rate which would be considered as practical to do the experiment.

I once took a plate that had been discharged and allowed it to stand in alkali, and it took just about one year for the black nickel to discharge completely and to get a green plate.

So I think one of the problems here is that we have isolated nickelic hydroxide or cobaltic hydroxide, which is far more stable than nickelic hydroxide.

The other point that I wanted to bring up was just to mention about Muspratt solution. When I was looking for a method of determining cadmium, I recall that cadmium hydroxide might be soluble like zinc hydroxide or zinc oxide. And I recall reading a paper years before that in the Journalof the Ceramic Society which said that zinc oxide could be determined in zinc dust by extracting with Muspratt solution which consisted of ammonium chloride and ammonium hydroxide.

But I was never able to locate the exact reference, having gone through all of Muspratt's encyclopedia and anything that referred to Muspratt. So the name of Muspratt was just given because I remembered that that was what it had been named.

PARRY: I must confess that my indoctrination in this came from Dr. Fleischer.

(Laughter.)

GROSS: John, one minor point on your mechanical test. This test has been developed by materials engineers for measuring the stress of brittle materials like glasses. And the reason that it was developed was because they wanted to actually be able to calculate the stress at the surface

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when the material broke.

Now when you're using this test as a process control to determine the processes, you don't really need to know what the stress is. But if you want to compare plaques from different manufacturers which might be of different thicknesses and different structure, then I think it would be wise to carry the calculation out to the end and actually calculate the surface stress. So we can then get a comparison of different plaques.

PARRY: Well, this we have done. It has been done. It has been completely analyzed. This work was done by one of our materials people at Tyco. And we have gone through the complete analysis to get a final figure, you know, in kilograms per centimenter squared. It's not a qualitative test.

One point I forgot to put in earlier, if anyone is interested in that device, I do have a few drawings with me of the pieces.

HALPERT: Thank you, John.

I might mention that we've done some work using the a mechanical strength test as well and have found it works quite well even looking at plaques and plates of the same manufacturer, because they still differ. In looking for quality control this is an aspect that should be considered although it is a destructive test.

I might also mention the fact that this is sensitive to the substrate being relatively placed in the center. If it is closer to one side, then you'll always have to measure it with the same side down, when youre trying to do the cracking and stressing.

N71-28662

We thank you, Dr. Fleischer, for putting the historical record on the Musspratt solution in notes, so now we all know where it came from.

Our next speaker this morning is from Comsat Labs where they've been doing quite a bit of work on extraction of the negative plate

Jim Dunlop has done quite a bit of work in that area. And I would like to present him now.

XXX **DUNLOP:** I thank Dr. Parry for his presentation this morning since it covered about 50 percent of what we were going to say.

For the record, we have in the past two years been involved in the Intelsat IV program and through this program have been looking at methods for analyzing nickel cadmium cells that we have received for use in this program.

Now we've done a considerable amount of electrical performance testing. Hughes Aircraft and GE has also done a considerable amount of electrical testing.

These include areas such as acceptance testing, accelerated testing, eclipse operation, storage and reconditioning. One of the things that we have faced in the course of looking at the electrical performance data is that we don't really have a complete story. I think many of you who have been involved in a program, an aerospace program, know what I'm talking about here, where you'll see a spread of data when you're making electrical performance measurements. And you're not sure just what it means. You don't know whether it is something you did or whether it is something the battery manufacturer did or just what is causing the spread that you're seeing in your measurements.

So what you would like to do is have a procedure where you could somehow or other get a complete picture of what is taking place inside this cell. And this is what we have tried to do. And I am going to describe briefly this morning the program that we have evolved from our Intelsat IV test program.

The program that we have evolved is a method of obtaining both the electrical performance and also the chemical analysis and trying to correlate these results to get a complete picture of what is actually going on in that cell.

It is interesting to do this at different steps in your program so as you run say a storage or reconditioning and accelerated test you can compare your results as you go along to try and find out what is taking place with time in the cell we're cycling for storage or reconditioning, et cetera.

We are actually going to make a more complete presentation of the results of our program probably sometime next year in conjunction with the people at Hughes Aircraft and maybe GE.

In doing the chemical analysis for these cells we have been assisted by a number of people including Dr. Fleischer, some people at Wright-Patterson Air Force Base and Battelle, people here at NASA-Goddard, people at GE. And we have used Tyco's work as well.

I am going to have Kurt Van Ommering who is working in our labs actually go through the procedures that we've used for the chemical analysis.

Before I do this I would like briefly to use some data that we have from this program to show the kind of variation in electrical performance measurements that you will normally see in a test program.

First graph, please, Marty?

(Slide.)

I might apologize a bit for this graph if you have difficulty seeing it, we purposely intended it that way since GE is in the audience.

(Laughter.)

What I am showing here is a number of cells on the vertical axis. And then the horizontal here is the time to discharge at a C/2 rate going from 120 minutes out to 180 minutes. First I would like to point out that all these cells exceed 120 minutes which is at the C/2 rate the rated capacity for the cell. But you will notice that there is a large spread in the data.

The numbers here correspond to different lot numbers. You will see lot one cells in this range, lot two cells, three cells, four cells and so forth.

The spread is from somewhere here at 120 minutes out to beyond 180 minutes, which is a considerable spread in the capacity for the individual cells.

(Slide.)

Just a similar type of curve where we are presenting in the top graph here variation in cell capacity for a discharge, final discharge before the cell was sealed off. And again you will notice a considerable spread in the data. The numbers here again correspond to cells from different lot numbers.

Down here is the data taken on the first reconditioning cycle for the cells received at Comsat. And here they are better grouped with a few cells breaking out.

(Slide.)

This is the same kind of data again, except here in the bottom slide we're showing the capacity measurements after 30 cycles at room temperature or 25°C. I want to point out here that the cells for lot six are very well grouped

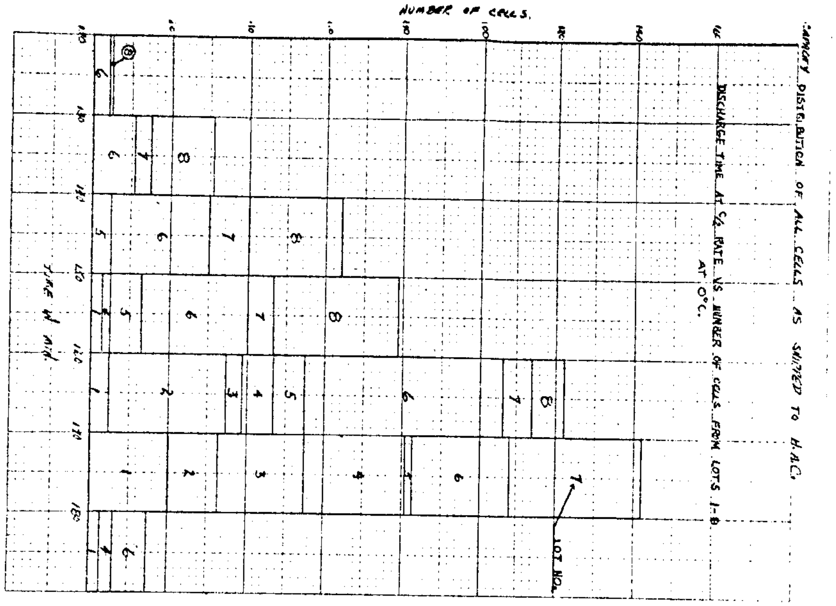

FIG. 1

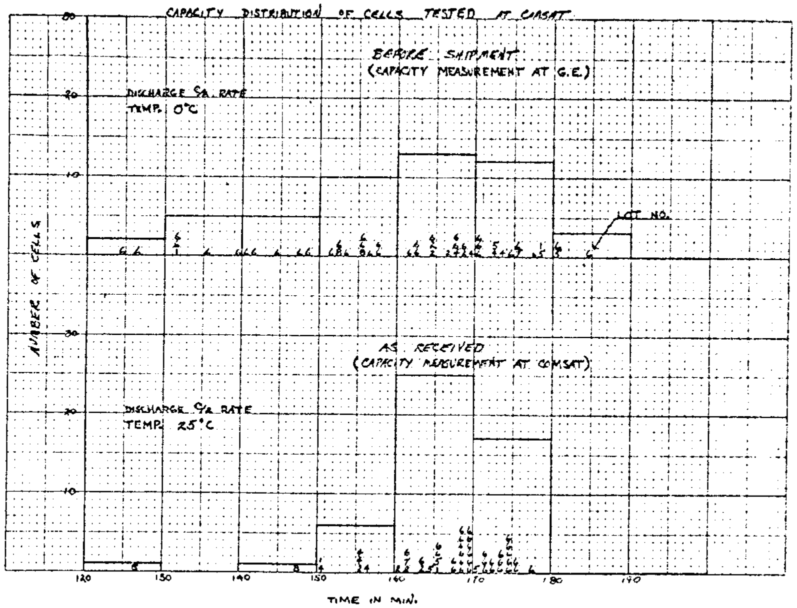

FIG. 2

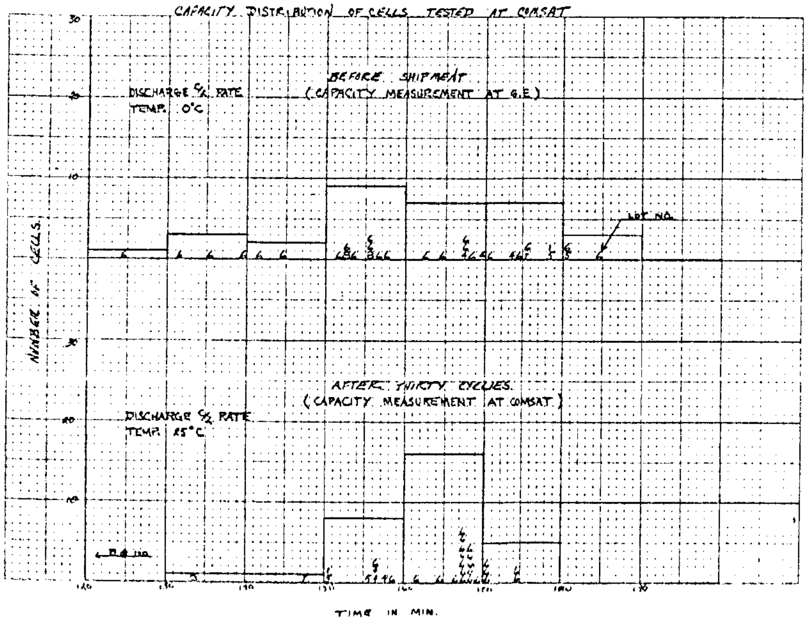

FIG. 3

around 165 to 170 minutes.

The lot four cells are grouped a little bit lower. And there is a smattering of other cells here.

One point to bring out in this graph is that if you are making a battery it might be worthwhile to use cells from this same lot to make up the battery since you seem to get a little better grouping with cycling for cells coming from the same lot.

If I could have the lights now, please.

I do not want to dwell on the data here. I merely picked some data to make a point here that if you just take electrical data you can get a -- and you look at it at different periods in time -- that you can get quite a spread in your capacity measurements. It may be a problem with your charging. It may be a problem with your manufacture.

If you want to find out, then you really need to carry your work a little farther and go through some kind of complete analysis on your cell. And this is what we've done. And the analysis that we use attempts to determine the total amount of active materials that we have in the cells, the amount of active material that we're utilizing, the amount of precharge that we have in the cells. And we also look at the electrolyte to determine the carbonate build-up with time.

I want to describe very briefly to you the electrical performance measurements that we make when we're preparing to do this analysis. And then I'm going to let Mr. Van Ommering describe the chemical analysis that we use.

What we'll really do is that we'll take a cell out at some stage in the program when we decide that we want to evaluate this cell and find out as much as we can about it.

We then charge this cell at a controlled temperature around 20°C for 16 hours at a C/10 rate, so that we charge it up fully. We then discharge it at a C/2 rate again at 70°F until the cell goes to zero volts.

We then change our discharge rate to a C/10 and we continue the discharge. At the time that the cell goes into reversal, we puncture it with the puncturing device made here at Goddard.

We take gas samples as the cell goes into reversal and continue to run the cell in reversal until we get down to minus a half a volt. At that time we open the cell up and we put it in a nickel soxhlet similar to the procedure that was done at Battelle.

I'm going to now have Mr. Van Ommering come up here and describe what we do once we've got the cell into this soxhlet I want to make a point before he does this that what we've done now is completely discharged both electrodes in this cell electrically. And we've taken gas samples during the time we're in reversal so that we know which electrode is limiting us on discharge once we do go into reversal. And we've also determined how much, hopefully, precharged material we have in cadmium here in the reverse process that's usable.

N71-28663

XXXXXX VAN OMMERING: Well, I don't really have to say too much because as far as the cadmium plate analysis is concerned we use the same method as Dr. Parry does at Tyco. But on the electrolyte analysis when we have had the cell in the nickel soxhlet for 48 hours we get the cell out, take the solution from the soxhlet and dilute it to a certain known volume.

And then we analyze it by taking a sample and titrating with hydrochloric acid, first to an end point of phenolphthalein in which we determine first the KOH compound and then half of the carbonate content and then to a second end point with methyl violet indicators so that we can determine the whole carbonate content from the weight loss of the plate stack of the cell.

After we have dried it we can determine the total weight of the electrolyte as well as a concentration of the KOH. The cadmium plate, as I said, we use the same procedure as Tyco, so it wouldn't be too interesting to repeat the whole thing.

For the nickel plates we have tried several methods

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at Comsat. First a simple Muspratt extraction. But that give us unreproducible results exactly as Dr. Parry pointed out.

We tried to use the Tyco procedure. It gave us some technical trouble, so we then went to the GE procedure, which you would expect to be best for GE cells.

(Laughter.)

We did it the way Dr. Kroger described it. First we break the extra material and the nickel sinter from the plates and then grind it to a fine powder. Next we take a sample from it and put it in acetic acid with added a certain amount of ferrous ammonium sulphate. The ferrous ammoniumsulphate is partly oxidized by the charged nickel. We determine then after an hour of reaction in a closed vessel the amount of ferrous ions by simple titration with potassium permanganate.

From the amount of ferrous ions we calculate the amount of ferric ions and show the total amount of charged nickel. The total active material in nickel plates is also determined by an extraction in acetic acid. We add hydrazine sulphates that should prevent all the metallic nickel from going into the solution.

We didn't really have too much time to check it all out, if really no metallic nickel is going to the solution, but the results we get so far are fairly reproducible.

I can give you some numbers which are perhaps not to be trusted too well, but we found for a plate from a discharged cell about .3 ampere hours of charged nickel still in the plate. Charged nickel is not usable in electro-chemical operation of the cell.

The total number of ampere hours in the plates was about 2-1/2 ampere hours. And if all the numbers are right, it should mean that we can completely charge the whole plate and not completely discharge it. Well, I think that is about what Jim wanted me to say.

DUNLOP: I think what I can do now,if we take the next slide, is summarize how this looks then.

Thank you. Why don't you stay right here in case we have some questions.

(Slide.)

What we have here presented in bar graph form shows the results of the analysis on three different cells. This particular cell here the measurements were made after a 30-cycle burn in. This particular cell here and here is after one eclipse season and a 135-day storage at C/45 triple charge rate.

The total cadmium is very uniform, fairly uniform, in these cells. We're finding it within plus or minus one ampere hours, the same amount of total cadmium, about 46 ampere hours equivalent.

The amount of cadmium that we can actually use is shown at this point here. After the 30 cycles we are able to utilize -- this is the part that we can't utilize. After storage and reconditioning, this is the part that we can't utilize. So that you see with time the amount of cadmium that we're not able to utilize is increasing. As I remember it, our utilization after about 30 cycles is on the order of 70 to 75 percent.

And after the storage and reconditioning, it is about 70 percent. At the very beginning it is around 80 percent. This is a kind of loss of utilization that we're experiencing with time. This is the amount of precharge at this level here.

The amount of precharge that we can use varies and actually seems to increase slightly with time, or at least that's the effect that we have on these three cells.

The total amount of precharge is the same, but this marked in area is the amount that we're actually able to utilize. The amount down here is a part of the precharge cadmium or charged cadmium that we actually cannot discharge, electrically, at a useful rate.

And between here and here, this is a measurement of the positive capacity in that cell.

I think the interesting thing about the bar graph is that it is a good graphic representation of what we're able to conclude from the combination of the electrical performance measurements that we make and the chemical analysis that we do.

(Slide.)

This gives a brief description of some of the cells that we've used in the chemical analysis. I don't think I'll talk too much about it.

(Slide.)

Briefly, they are divided into three categories, before burn-in, after burn-in and after cycling. There is a lot of information here. I think I'll only point out a couple of things. The total cadmium in ampere hours chemically determined, as you can see, is fairly uniform for all the cells.

The total cadmium utilization -- there is a variable here at the beginning of life. After the 30 cycles it is quite constant. This is an argument here for making your performance measurements after 30 cycles. It seems that you get more consistent results after you've cycled the cells a few times.

This is the utilization after the 30 cycles and after the eclipses and after the storage. You will notice that the utilization has dropped from about 72 or 73 percent down to about 70 percent.

The average weight of the negative plates is shown

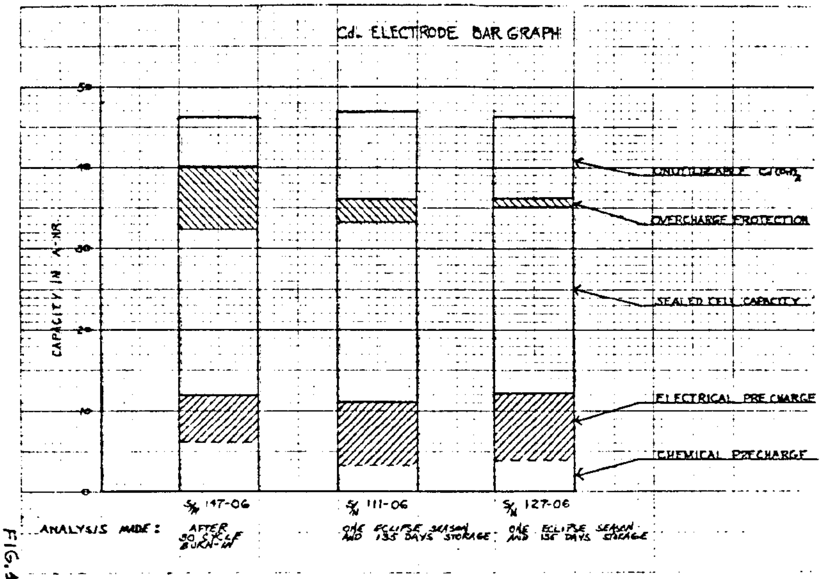

FIG.4

TABLE I

General Electric S/N	Time of Analysis
01022402-048-02	As received from G.E.
01020102-004-01	After acceptance test (negative limited engineering cell)
03070308-099-06	After acceptance test (negative limited)
03070308-138-06	After 30 cycle burn-in test (negative limited before 30 cycle test)
03070308-142-06	After 30 cycle burn-in test
03070308-147-06	After 30 cycle burn-in test
03070308-111-06	After one eclipse season and 135 days of trickle charge storage.
03070308-127-06	After one eclipse season and 135 days of trickle charge storage.

	BEFORE BURN-IN			AFTER BURN-IN			AFTER ECLIPSE AND STORAGE	
	048-02	004-01	099-06	138-06	142-06	147-06	111-06	127-06
Cell Neg Elec. Capacity in A-Hr	34.3	14.2	17.0	27.3	27.4	26.8	29.9	31.3
Cell Pos Elec. Capacity in A-Hr	20.0	22.8	22.7	20.1	22.1	21.1	22.0	22.8
Cell Neg Elec. Precharge in A-Hr	14.3	0	0	7.2	5.3	5.7	7.9	8.5
Flooded Neg Elec. Capacity in A-Hr.	37.8	27.1	26.0	33.7	32.7	34.2	32.8	32.5
Wt. of Electrolyte	67.8g	59.4g	59.5g	----	59.1g	59.3g	56.9g	60.0g
Wt. of KOH	17.3g	15.7g	18.5g	----	14.8g	14.6g	14.1g	14.8g
W/O of KOH	25.4%	29.4%	31.0%	----	25.0%	24.7%	24.8%	24.6%
Wt. of K_2CO_3	3.9g	5.0g	0	----	5.8g	5.5g	7.0g	6.2g
W/O of K_2CO_3	5.7%	8.4%	0%	----	9.8%	9.4%	12.3%	10.4%
Discharged Cd. in A-Hr(Chemical)	45.8	38.3	36.5	40.5	39.2	39.9	43.5	42.4
Charged Cd. in A-Hr(Chemical)	0	5.9	9.3	6.3	5.3	6.3	3.4	3.8
Total Cd. in A-Hr(Chemical)	45.8	43.9	45.8	46.8	44.5	46.2	46.9	46.2
Total Precharge in A-Hr(Chemical)	14.3	----	----	13.5	10.6	11.9	11.3	12.3
Total Cd. Utilization	82.5%	60.4%	57.0%	72.0%	73.5%	74.0%	70.0%	70.5%
Precharged Cd. Utilization	100.%	0	0	53.0%	50.0%	48.0%	70.0%	69.0%
Elec. Overcharge Protection in A-Hr	3.5	----	----	6.4	5.3	7.4	2.9	1.2
Wt. of Neg plates	254.3g	252.7g	247.8g	254.0g	244.8g	251.1g	251.6g	245.7g
Avg. Wt. of Neg. Plates	21.2g	21.1g	20.6g	21.2	20.5g	20.9g	21.0g	20.5g
ΔWt of Neg Plates	2.4g	----	1.9g	1.8g	3.1g	1.7g	2.1g	2.2g

here. And the delta of the negative plates, which is the variation between the weight of the heaviest plate and the lightest plate, is shown.

There is a variation in weight between plates here. It is around two or three grams.

I think in conclusion here we would say that to date we have been able to find that with the analysis procedure that we're using we do seem to be able to get a much better understanding for the cell behavior with time.

One point that we will report in our paper next year is that with the various storage and reconditioning procedures that we're now running, we're into about a year and a half of testing on this and we're taking cells out about every six months from this program to go through an analysis.

And we are finding that there is a carbonate build up with time. What we're looking for in this time increment thing is what is changing in the cell that's going to eventually lead to some kind of failure.

And I think this type of a program is very useful in that type of analysis.

I will also point out that this is a destruct test, so that when you do it you are destroying the cells. And it does take time. And it does take some equipment. So I don't exactly know how to recommend that you use a program like this. I want to point out that if you do decide to use a program like this either in your own facilities or in conjunction with somebody else that it does take some time some effort and some money to do this. But I do think that what you can get out of a program like this can be most rewarding.

And that's it.

(Applause.)

HALPERT: Thank you very much.

I am sure Jim and his associate would be very happy to field some questions.

REED: Reed from Battelle.

First, a comment about the Muspratt analysis. My indoctrination is that Dr. Parry's came from Dr. Fleischer, but I don't think it has been pointed out this morning that it is important that these extractions be done in an oxygen-free environment.

It is my understanding that even the extraction of the cadmium hydroxide into the ammonium hydroxide, ammonium chloride solution should be done, say, with nitrogen being bubbled through the extraction solution so that you do not oxidize a metallic cadmium remaining in the plate. And, furthermore, I believe that this procedure of bubbling nitrogen through the solution will prevent much of the plaque oxidation which Dr. Parry refers to.

VAN OMMERING: We usually bubble nitrogen through the solution when we analyze the cadmium plates.

REED: I thought you probably did, but this has not been pointed out so far this morning. And I didn't want people to be misled.

Now a question about your results. It appears to me that you should be able to determine from these analyses at various times showing the decrease in the utilizable cadmium whether the nonutilizable form of cadmium is indeed metallic cadmium or cadmium hydroxide.

DUNLOP: We do.

REED: What do you find?

DUNLOP: Well, we showed it on that slide.

REED: I wasn't able to determine it from the slide.

DUNLOP: Do you want a copy?

REED: Yes.

DUNLOP: We have a couple of copies of that bar graph that we would be glad to pass out which I think will suffice here.

But I think it is a combination of both, as a matter of fact. And it does vary with time. In this particular case, interestingly enough, at the beginning of the program we had variation -- we did a complete electrical discharge before the analysis. But we found that there was a significant amount of metallic cadmium remaining in those plates.

It turns out that with cycling we are able to discharge those plates further with time. And our loss in utilization is really showing up as discharged cadmium. And the amount of metallic cadmium is actuallydecreasing.

JACOBS: Jacobs, Union-Carbide.

You mentioned that there was a carbonate buildup with time. I wasn't sure I understood. Is this just storage time on shelf or is this with cycling.

DUNLOP: Well, the program that I was referring to we have four different real time tests in progress. The difference between the four programs is that there are four different storage and reconditioning modes. What we're doing is simulating real time testing in this program where we run an eclipse cycle using the variation and depth of discharge each day like we expect to experience in the program with also a temperature variation each day. And then we go into an eclipse storage mode where we use different combintions of either storage in a discharge mode or storage in a triple charge mode with and without reconditioning.

JACOBS: Thank you.

BILLERBECK: Billerbeck from Comsat.

I just wanted to add one comment there. All this work is on synchronous orbits, by the way. And we are looking at these various modes to try and find an optimum mode for storage in the time we are not utilizing the battery on synchronous orbit.

RYDER: Ryder, Gulton.

You show about 46 ampere hours for the capacity. That is a measured capacity I assume.

DUNLOP: From the chemical analysis.

RYDER: Okay, that's not an actual electrical capacity?

DUNLOP: No. The actual electrical capacity at the beginning may be as high as 34 to 38 ampere hours.

RYDER: Okay. That was really the question. Your nominal cell capacity then I take it is what -- about 20 ampere hours.

DUNLOP: Fifteen. It is rather interesting.

RYDER: You showed some data based on a certain period of time where the cadmium is declining. Do you have any additional data since then to indicate whether this is continuing with additional cycling and/or storage?

DUNLOP: We're continuing the test. That's the latest data we have. And that is taken after about one year of operation.

RYDER: That is the latest data?

DUNLOP: That is the latest data. We actually will publish this report, hopefully next year which will include probably two years of testing.

RYDER: So then you would have about 34 ampere hours degrading to about 70 percent of that on a nominal 15 ampere hour cell?

DUNLOP: Yes, that's correct.

RYDER: Thank you.

HALPERT: Any further questions?

FORD: Ford of NASA-Goddard.

Jim, I have three questions.

You mention a 30-cycles. Could you describe the type of cycle? Is that a synchronous orbit cycle?

DUNLOP: No. There is nothing really magic about that 30 cycles except that we run it at controlled temperatures below 75°F. And we discharge it to approximately 80 percent of the depth of discharge at a C/2 rate. It is basically an ampere hour turnover exercise.

FORD: What you're really suggesting in this is something like a burn-in.

DUNLOP: That's what we called it really, a burn-in test.

FORD: Okay.

The second question. In measuring your precharge and during your test have you made an attempt to correlate this with the level of precharge that you would expect to have based on manufacturing data?

DUNLOP: Yes. Let me answer that question this way: I think this is the answer you're after. We have talked with the people from GE about it, and based on what they think they're doing, there is very close agreement here between what we measure and what they think they are putting into that cell.

FORD: Okay, which leads me to the next question, your reversal.--

DUNLOP: I hope that's right.

FORD: -- is at C/2 I believe.

DUNLOP: Right.

FORD: Do you get repeatability in that test, because as we will get into this afternoon some of the data we're getting says that that test can give you anywhere from zero percent to 130 percent of the actual precharge that was put into the cell.

DUNLOP: One of the points that you see in this program and you will see it on that graph is that when you do run it into discharge, all you're doing is discharging the amount that you can discharge at that rate. There may be a lot of metallic cadmium remaining in those plates that you later determine you didn't discharge electrically. So one of your problems -- the thing that was interesting about the data that we got from this program so far was that at the very beginning when we first received the cells there was a wide variation in the amount of precharged cadmium that we measured electrically. But the amount, once we did the complete analysis, of precharge that we determined to be there was the same. But it was not discharged electrically. You could recombine it with oxygen, by the way, at a slow rate, or you could discharge it at a very slow rate. But you couldn't discharge it at a useful rate. After the 30 cycles the situation gets better. It seems to be fairly uniform.

FORD: You do the reversal with the plate stack in the case?

DUNLOP: That's correct.

FORD: Have you run into the situation where the cell could not be reversed in the can?

DUNLOP: We can always reverse them. The question is which electrode is limiting.

FORD: I mean in a situation we've seen also on several occasions -- and this is particularly characteristic of cells that have been on cycle for some time -- and I'm talking about three-quarters to a year, sometimes it shows up earlier than this, and we see a situation where as you go into reversal you will hit a negative potential of about 150 to 180 millivolts. It will hang there for about five minutes and then in fact the potential starts going back towards zero. And no matter how long you reverse it at C/2 nothing ever happens. I think we might discuss that later on this afternoon.

DUNLOP: We haven't seen that, Floyd.

REED: Reed from Battelle.

What separator is in the cells you are using?

DUNLOP: Pellon.

REED: I was wondering when you talked about the increase in carbonate concentration with time whether you had seen a similar phenomena with say polypropylene separators?

DUNLOP: We don't have any data to compare with.

REED: That's what I thought.

DUNLOP: We may some day.

HALPERT: Thank you very much.

We have about 10 minutes before we have to hustle over to the cafeteria. And I have done some work in our labs in the Materials Branch. I thought I could present some of the data on plate weights which may be of interest.

This is kind of stepping back a step before Jim's talk in relation to taking a look at the plate weights before they are actually put into cells and formed.

The purpose in doing this was to try and get some other means of quality control in which we could look at the plates before they were actually being put into cells. One of the purposes was, of course, to see if we could predict ahead of time what kind of failures there would be and how the plates would operate and what capacity you would have and do this nondestructively before the cells were assembled.

One of the first things we did find in looking at a lot of the data was that there was a pretty high weight-capacity correlation. I think this may have been known in the past but hasn't been used to a great extent in actually building the cells. We apply this to a number of the plate groups which we have received from the various manufacturers and compare this with the materials from OAO battery 32 and 33.

I would like to run through a few slides showing you what we did.

(Slide.)

We did a plaque and plate evaluation by running a number of different types of tests measuring all the variables including surface area and pore size and the like on plates in particular. We did work on plaque and plate weight. We related the capacity to the plate weight and showed we can actually predict capacity.

I will show later that we use this in the latest OAO cell fabrication with success.

(Slide.)

I will just run through these very briefly. This is just our particular evaluation procedure in which we inspect packaging and verify traceability, get a visual impression of what some of the plates look like. And I will show a few samples here in a few minutes that can cause problems. We determine the weight average and distribution of every plate within the batch. Our batches generally run from 50 to 100 samples of plate and plaque if we can get them. We then select some samples for test and seal and store the remainder.

(Slide.)

We go through now a specific investigation of sixteen plates. Again we look more carefully and make a dimensional measurement. We weigh each plate and measure thickness distribution at four places on the plate. We measure mechanical strength and surface area and run some of these other physical chemical tests which I won't describe today.

We then take 10 of the plates and run a flooded plate capacity in which we run single plates versus two opposing electrodes. And then we measure afterwards some of the other properties. Today we're only going to talk about this plate weight and capacity correlation.

(Slide.)

On the next slide I show some of the samples of plates which caused us some problems. You can see the cuts in the upper left, cuts in the particular plates going in both

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directions. In the one on the upper right we see that the plate has been unevenly compacted. And you can see the areas in which some of the pores from the substrate don't even show through.

On the bottom -- it is difficult to see, but there is a degree of warping in the plate before we even get it. And then over here on this bottom lefthand side we see lots of holes in the plate, unevenly distributed.

In another batch in the next slide here we see nonuniformity in distribution of the substrate screen.

(Slide.)

In this particular case we were using screen throughout the plaque. Again there are scratches and some breakage. And then here on the bottom is a nonuniform distribution of the active material. All these we believe are sources of nonuniformity and lack of the kind of quality control that we need for the high-reliability cells that we're using.

(Slide.)

In the next slide we show some of the weights of plaque. These are samples of plaque which we have taken and measured, variation of plaque throughout the entire batch. The averages are given just under the bars. 13.2 for this group, and 14.5. These plaque distributions are not bad; that is, they held fairly uniform.

Another group over here was held quite uniform, but you can see that these vary all over the lot. And you can imagine what's going to happen if you try and do any kind of plate measurements based on the plaques that have not been uniformly controlled.

(SLIDE.)

We then went ahead and measured some plate weights from batches. And we can look at the next slide. We will give you negative plate weight distribution. And again here in this particular graph, which is slightly different from the last, the average, plus or minus .5 grams, is given in the top line for this particular LR group of which there are 53. This is 0.5 to 1.0 gram variation and 1.0 to 1.5 for this particular group.

And you can see here we go down. There is a fairly wide distribution here and here. And this particular group used in the OAO batch just happened to come through with a big blank right here in the center.

But quite a few plates, as you can see, in the batch that we got were in this particular area right here.

In this particular TA group we see a very closely controlled plate weight. And you will see that again a little later. And then later on again we see quite a wide variation in the weight of plate. It is also true for the positive.

(Slide.)

FIGURE 1

GSFC PLAQUE AND PLATE EVALUATION PROCEDURE

A. BATCH OR LOT INSPECTION

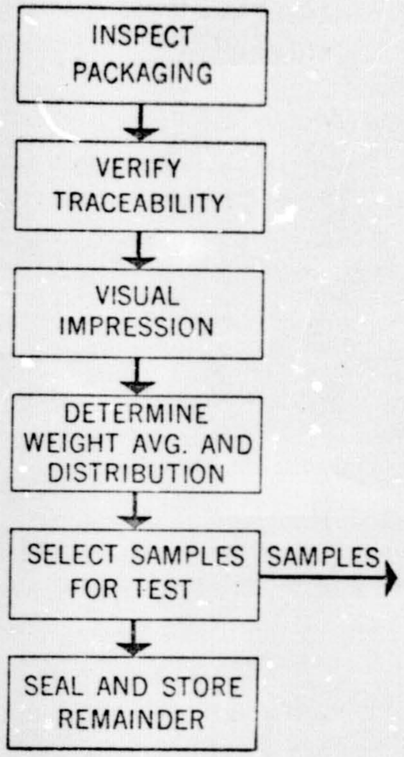
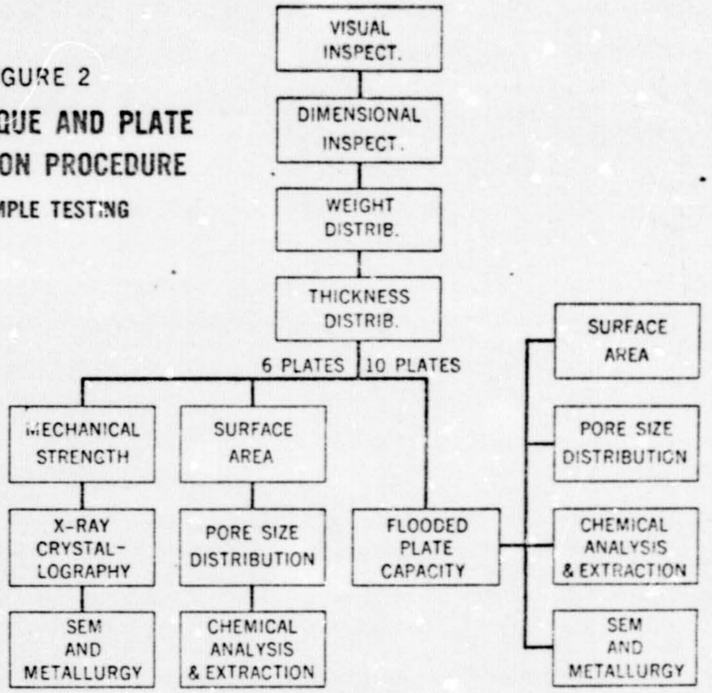


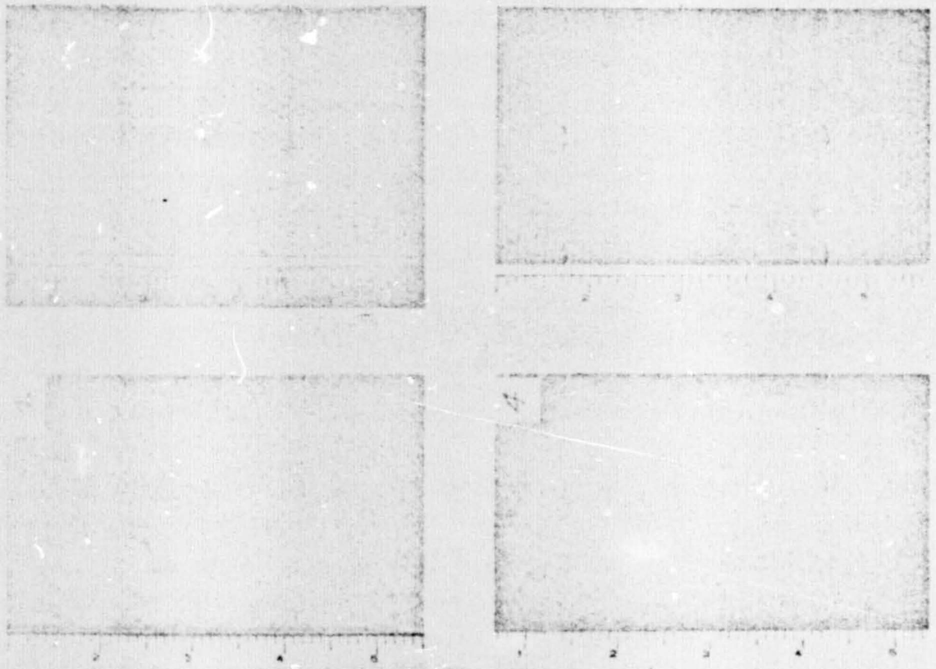
FIGURE 2

GSFC PLAQUE AND PLATE EVALUATION PROCEDURE

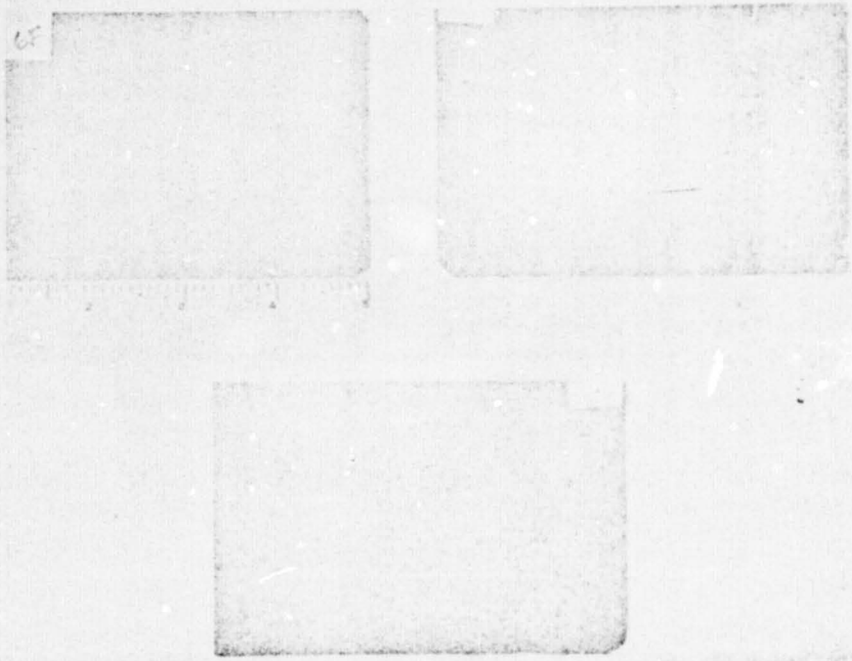
B. SAMPLE TESTING



VISUAL DEFECTS



VISUAL DEFECTS



In the next slide we show some of the positive weights. And again the fairly wide variation. In some cases it is more closely controlled than in others in comparing that with the OAO battery 32 and 33 group which is shown in this particular grouping.

We then, knowing these particular values, take the ten plates carefully looked at, and we would make capacity measurements, flooded plate capacity measurements.

(Slide.)

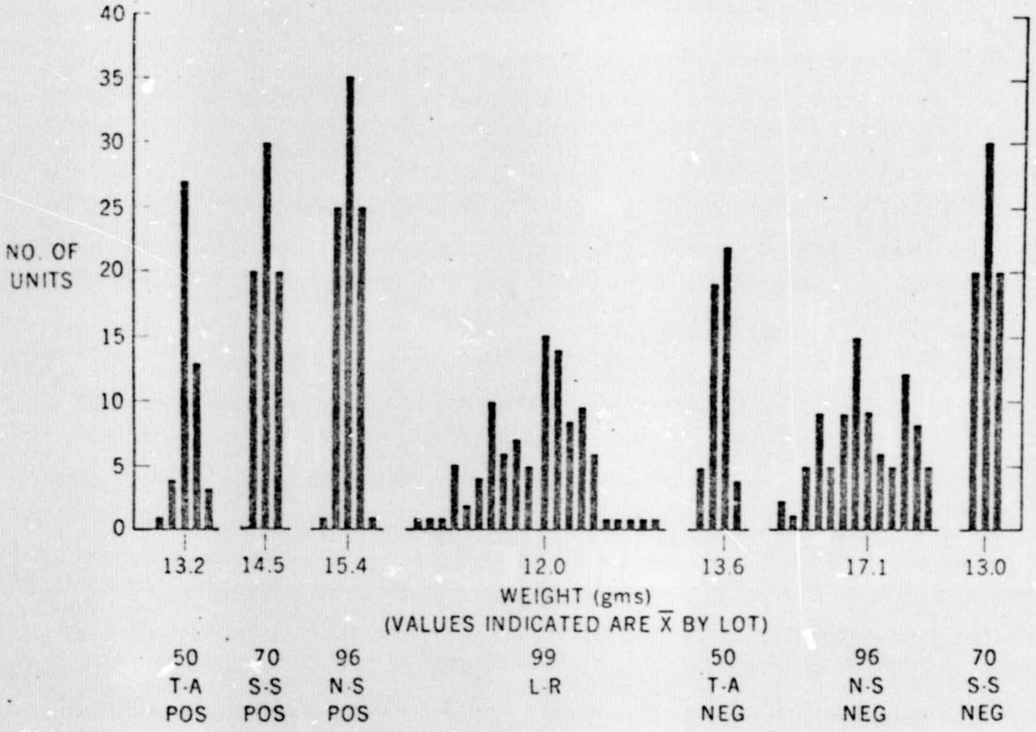
In the next slide we show the distribution of one particular group. This happens to be the negative plates for the group that goes into the OAO battery 32 and 33. This happened to be one of the ones we picked at random. These were all picked at random.

You see a fairly good straight line, if you want to include that in the batch. Even if you don't include it, you can see that there's a relatively good straight line even here.

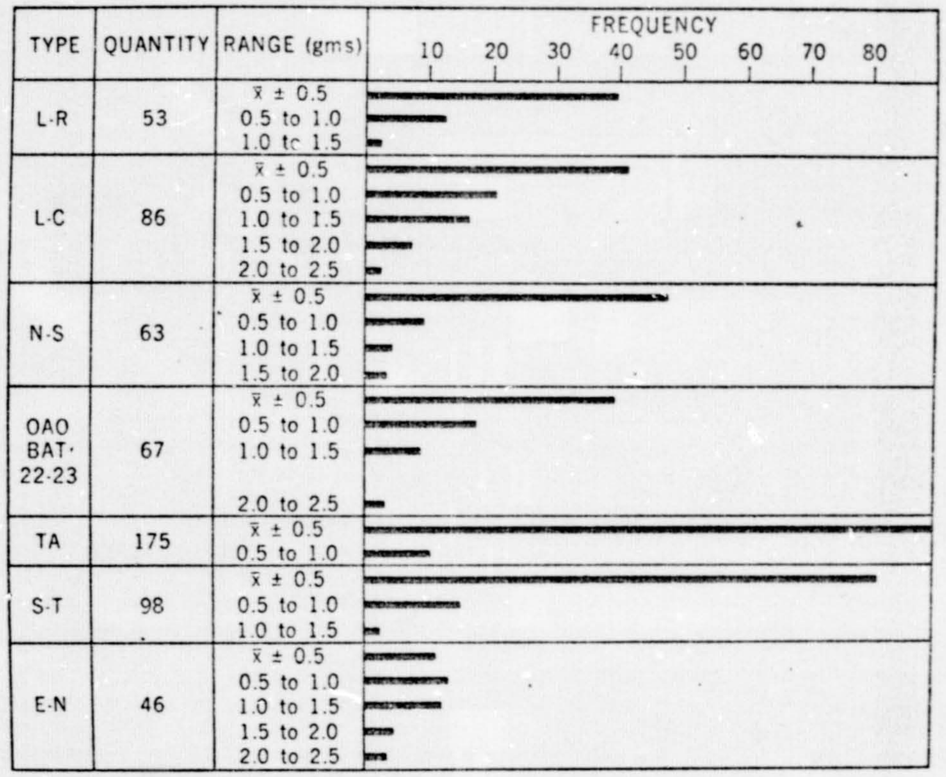
If you consider the weight and the standard deviation of the ten plates and the capacity and the standard deviation of the capacity of the ten plates, we have these numbers here.

And if we just take out this one particular bad one, we come way down to .42 and have a standard deviation in capacity of .06. The number we decided to use for the OAO

PLAQUE WEIGHT DISTRIBUTION

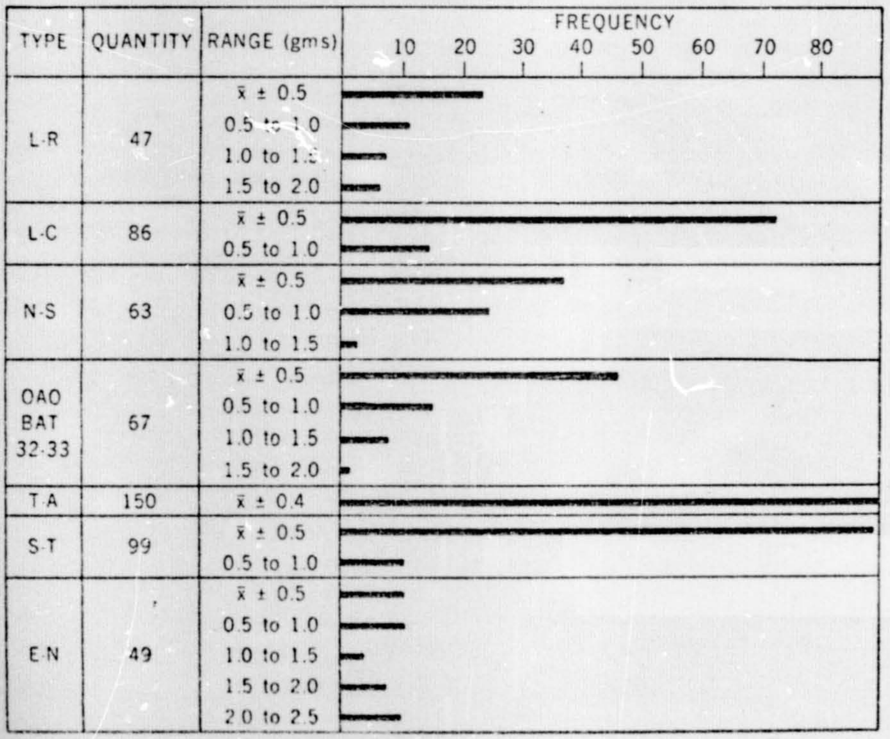


NEGATIVE PLATE WEIGHT DISTRIBUTION

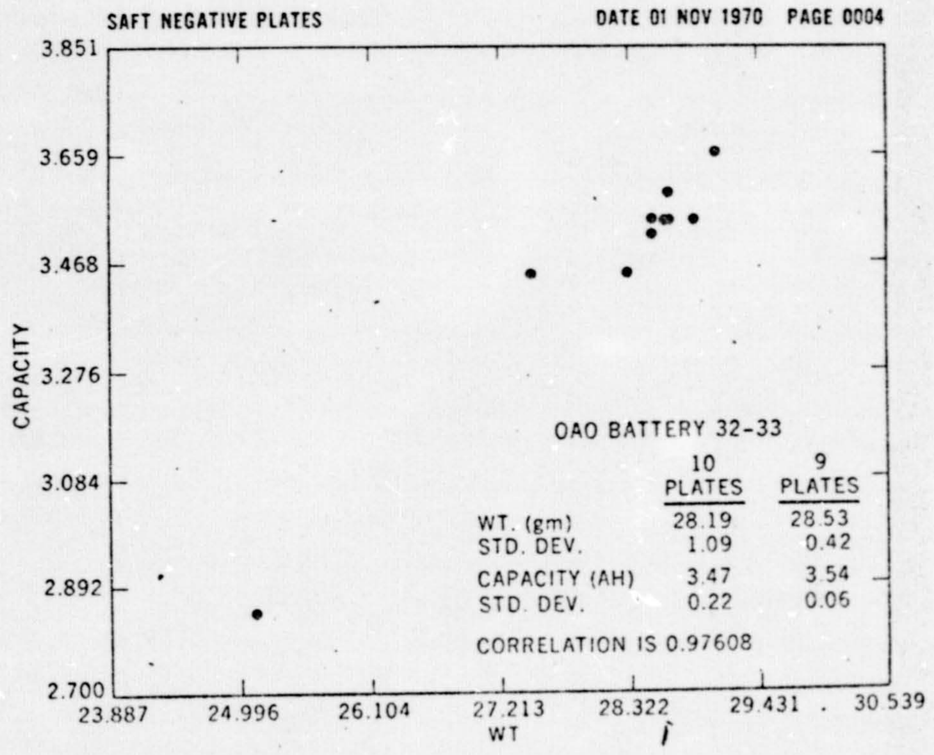


TYPE	QUANTITY	RANGE (gms)
L-R	53	$\bar{x} \pm 0.5$
		0.5 to 1.0
		1.0 to 1.5
L-C	86	$\bar{x} \pm 0.5$
		0.5 to 1.0
		1.0 to 1.5
		1.5 to 2.0
		2.0 to 2.5
N-S	63	$\bar{x} \pm 0.5$
		0.5 to 1.0
		1.0 to 1.5
		1.5 to 2.0
OAO BAT-22-23	67	$\bar{x} \pm 0.5$
		0.5 to 1.0
		1.0 to 1.5
		2.0 to 2.5
TA	175	$\bar{x} \pm 0.5$
		0.5 to 1.0
S-T	98	$\bar{x} \pm 0.5$
		0.5 to 1.0
		1.0 to 1.5
E-N	46	$\bar{x} \pm 0.5$
		0.5 to 1.0
		1.0 to 1.5
		1.5 to 2.0
		2.0 to 2.5

POSITIVE PLATE WEIGHT DISTRIBUTION



TYPE	QUANTITY	RANGE (gms)
L-R	47	$\bar{x} \pm 0.5$
		0.5 to 1.0
		1.0 to 1.5
		1.5 to 2.0
L-C	86	$\bar{x} \pm 0.5$
		0.5 to 1.0
N-S	63	$\bar{x} \pm 0.5$
		0.5 to 1.0
		1.0 to 1.5
OAO BAT 32-33	67	$\bar{x} \pm 0.5$
		0.5 to 1.0
		1.0 to 1.5
		1.5 to 2.0
T-A	150	$\bar{x} \pm 0.4$
S-T	99	$\bar{x} \pm 0.5$
		0.5 to 1.0
E-N	49	$\bar{x} \pm 0.5$
		0.5 to 1.0
		1.0 to 1.5
		1.5 to 2.0
		2.0 to 2.5



OAO BATTERY 32-33

	10 PLATES	9 PLATES
WT. (gm)	28.19	28.53
STD. DEV.	1.09	0.42
CAPACITY (AH)	3.47	3.54
STD. DEV.	0.22	0.06

CORRELATION IS 0.97608

34 and 35 builds was plus or minus 3-1/2 percent. Anything outside plus or minus 3-1/2 percent would be thrown out. And so that would have eliminated this particular one too, so you can see we would have had a pretty nice narrow grouping for this particular batch.

(Slide.)

The next slide just takes a bunch of these, the data, and actually just remove the plates one at a time to look for the standard deviation.

And we can see over on the far end that the correlation coefficient holds pretty well. This actually comes out higher. The wrong piece of data was removed. It should have been higher.

But nevertheless all of them are above the .8 correlation and, of course, the .98 because of the plate that was exceptionally low. What this allows you -- it can be calculated by a computer very easily -- it allows you to calculate a regression equation which relates capacity to the weight, a simple equation to calculate.

And if we plug in the average weight of 28.86, we should get a capacity of 3.56. And this is true I would say in almost all the batches. There are a couple of cases of batches that this correlation coefficient was very low. And it is something we would have to look into a bit further.

But out of the six groups of materials we looked at positives and negatives, and that means 12 groups, the relationship held in 9 of the 12 cases, so I think it could be considered applicable.

Now what you can do with this is to actually take 10 plates out of the batch before you run the batch. Before you actually use it in a cell pack, take the 10 plates, run them. You can determine then what you can expect in the way of capacity from that group.

And by throwing out the high and low, which is not a complex matter, we would then improve the uniformity of all the cells. As I say, we di dthis with batch 34 and 35 cells. I think it should be in the next slide.

(Slide.)

This is just another way of showing what happens when you take them out. This particular batch happened to be of a very low sigma. And we show that we don't remove any plates here. This should be .03 for a sigma for this particular capacity group. These were the negatives. And this particularly is positives.

(Slide.)

In the next one we show what happens. This happens to be the same group of negatives in which we just removed the one low plate and we reduce our capacity uniform sigma down quite a way.

And the positives again, this was plus or minus 3 percent. And our values we were looking at were plus or minus 3-1/2. There was 3 percent here. We didn't have to remove any plates. And this is the standard deviation capacity for the positives.

And so in this particular group -- and in the positives we didn't have to take out any.

(Slide.)

Now on the next slide I think we show what happened in the OAO cell selection. In OAO-B, batteries 32 and 33, there was no selection used. And we see that if we take all the cells now -- these are cells after cycling -- and look at the capacity, we see the range here from about 149 minutes I guess up to about 166. That should come out to be 17 minutes. I don't know if I gave you the right numbers. And there is a total of 2.8 ampere hour spread.

And in battery assembly 34 and 35, which is the latest one that was built and which we did use, the plate selection, we see here we've cut down the deviation to 90 minutes or 1.5 ampere hours. And you can see a much narrower spread.

So in conclusion I would say that although the weight measurement and capacity measurement of flooded plates is not a highly scientific type test, it does give you an indication of the capacity that might be expected from a group of plates and could be used as a criteria for plate

WEIGHT–CAPACITY STATISTICS–NEGATIVE PLATES

	AVG. WT. LOT	PLATES REMOVED	WEIGHT TOLERANCE	NO. OF PLATES REMAINING	AVG. WT. (gms)	STD. DEV.	AVG. CAP. (AH)	STD. DEV.	CORR. COEF.
SAFT COM. OAO BAT 32–33 NEG	28.86	-	11%	10	28.19	1.09	3.47	.22	.98
		B	3.5%	9	28.53	.42	3.54	.06	.81
		BH	3%	8	28.46	.40	3.52	.05	.77
		BFHI	2%	6	28.56	.12	3.53	.04	.88

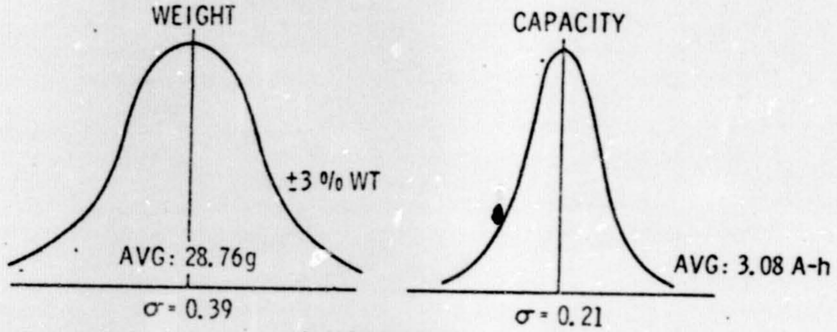
REGRESSION EQUATION

CAPACITY = .092 (WEIGHT) + 0.90

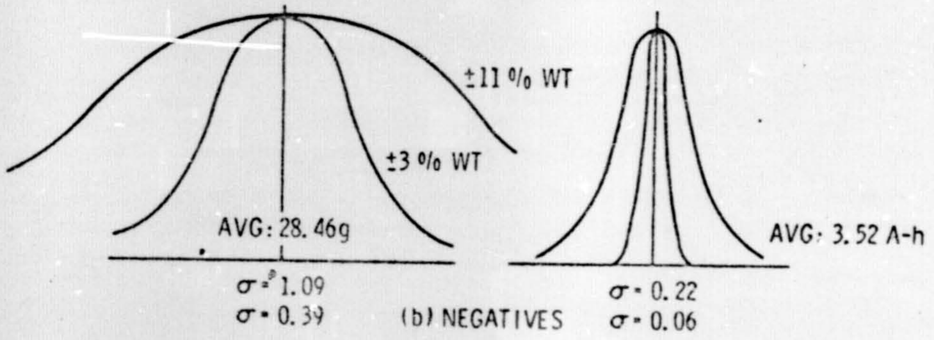
AVERAGE WEIGHT IS 28.86

THEREFORE

CAPACITY = 3.56 STD. ERROR = .03

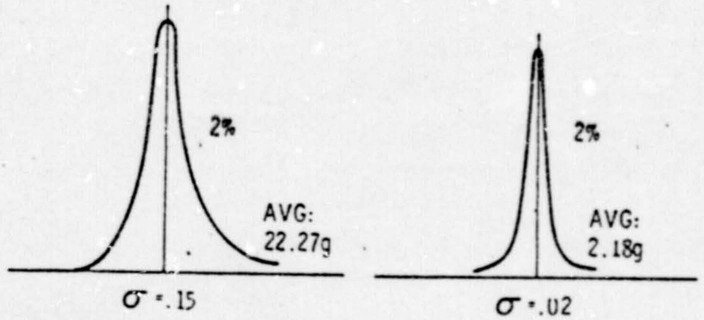


(a) POSITIVES

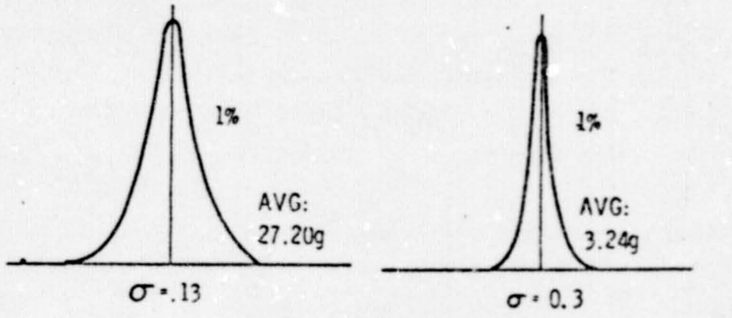


(b) NEGATIVES

Figure 1. BAT. 32–33



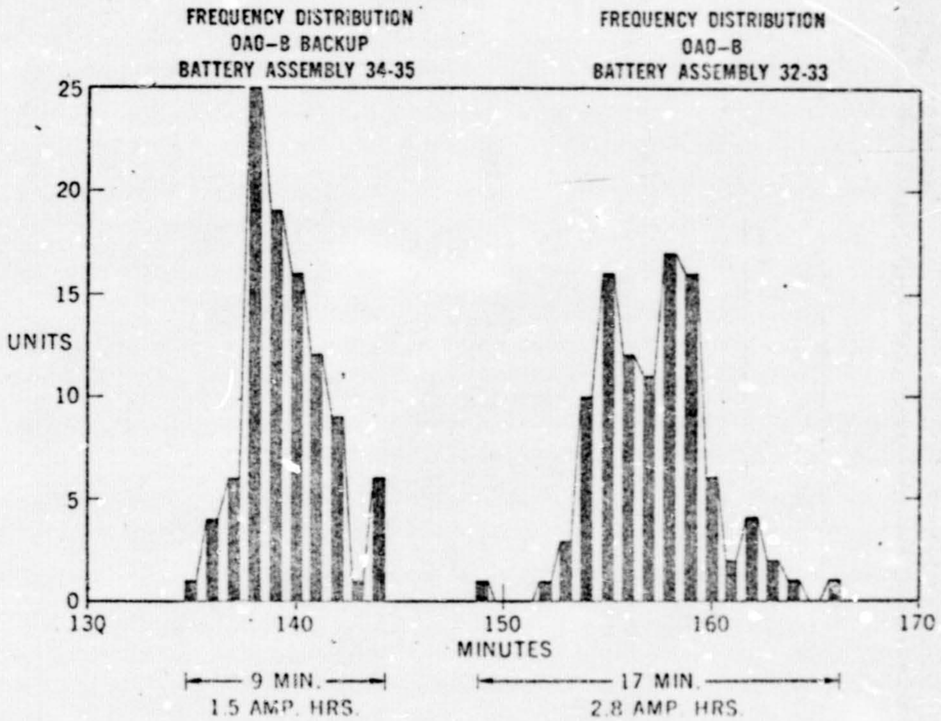
(a) POSITIVES



(b) NEGATIVES

Figure 4. T–A

OAO CELL SELECTION CYCLE – DISCHARGE
RATE C/2 = 10 AMPS



selection prior to cell assembly.

Thank you.

(Applause.)

(Whereupon, at 12:30 p.m., the meeting was recessed for lunch to reconvene at 1:30 p.m. this same day.)

SESSION 2

AFTERNOON SESSION

(1:30 P.M.)

HALPERT: I would like to welcome you all back from your lunch break.

I do have a couple of announcements to make. One is that we have a list out in the lobby there, some pages with your names, a place for name and affiliation. We would like to have that for our records. Please make sure you sign that before you leave, or sometime this afternoon preferably, so that we can submit some of those with our records.

For those of you who did not send me back a brown card with your name and address and all that, so that we can have your record and your permanent mailing address, I would appreciate if you would see me later, during the next coffee break, and I would be glad to pass them out.

Thirdly, there is a publication up here, for those who might be interested: Secondary Aerospace Batteries and Battery Materials, A Bibliography. Some of you have a copy. We have some extra copies, and if anybody is interested, come by and pick them up. We have some more copies we can make available if these go.

This afternoon we are starting our Session 2. Mr. Floyd Ford is our Chairman. Floyd has done quite a bit of work on trying to straighten away the problems for the OAO battery and now doing some work with a space station module, and a very capable gentleman, and I present him to you now, Floyd Ford.

FORD: Thank you, Jerry.

Welcome to the afternoon session. The topic of this is Precharge, precharge effects, cell testing and life testing.

So, as you see, it is a pretty broad topic. It is going to be somewhat controversial, I think.

I would like to remind the speakers that this will only be as formal as you want to make it as you are up here. I had a comment this morning that the gentleman said, gee, I didn't come prepared for this type of presentation. Well, really I would like to suggest that this is the opportunity, to borrow an expression from the Hippies, to do your own thing.

So, as you come up, feel free to give your presentation in any manner you choose. If you have slides, if you have a viewgraph, or just have the regular chart paper, they can be shown.

This morning we talked about the process methods, the test on the basic materials for the process, and analysis of the basic materials.

We are going to address ourselves this afternoon to the cell processing, actual working up to a piece of hardware, which ultimately is the reason we are here, every one of us, is that our final goal is to develop a piece of hardware for flight use.

The gentlemen you will be hearing from this afternoon and -- we just worked this up during the lunch hour -- are Dean Maurer from Bell Labs; myself, Floyd Ford from NASA Goddard; Steve Gaston from Grumman Aircraft, Dr. Harvey Seiger, Division of Textron; Sam Bogner from JPL; Don Mains from Naval Ammunition Depot, Crane; Earl Carr, Eagle Picher.

Ed Colston of NASA Goddard; and then Sidney Gross of Boeing. Without further to say, I would like to introduce Dean Maurer from Bell Labs.

MAURER: There have been several reports recently concerning the matter of precharge on the negative electrode, and the general conclusion has been that because the negative electrode fades in capacity with long-term cycling, leading to capacity fading of the cell, due to negative limitation, the way around this problem is to add precharge to the negative as the cell is assembled to account for the loss in capacity due to fading of the negative.

What I want to show here this afternoon is that in addition to that precharge or the charged cadmium, we also need to worry about the cadmium hydroxide on the electrode.

The Bell Laboratories has been working recently with several of the Western licensees to develop a 23 ampere hour cell for terrestrial applications. The environment in the terrestrial application is somewhat more severe than the satellite environment. The use mode is continuous overcharge. It is a reserve battery. And the temperature ranges from a high averaging 120 Fahrenheit, with excursions to 140 Fahrenheit, and a low temperature of 32 degrees Fahrenheit and battery heaters to keep the cell at that temperature when the outside ambient gets lower.

However, the cell should be capable of operating below this ambient, in case the battery heaters fail. And we can expect temperatures approaching minus 40, but more likely minus 20 degrees Fahrenheit.

We obtained some of these cells that were built to laboratory specifications and we looked -- we also obtained plates, samples that went into the cells -- and these plate samples indicated that for the 23 ampere hour cell, there should be the order of 8 ampere hours negative precharge.

We proceeded to do some experiments on the cells to look at pressure versus charge rate, and temperature, and to start out we decided to put the cell down to zero state of charge by reversing it.

We reversed the cell and -- by the way there were reference electrodes in these cells, so that we could monitor which electrode was reversing -- we reversed them and found that there were not 8 ampere hours of negative capacity, but more like 12 to 13 ampere hours.

We returned the cell to charge at C over 10 for a period of roughly 20 days, and repeated the reversing procedure and found that we had an additional 8 ampere hours of negative capacity.

Now, first of all, we rule out leakage of oxygen from the cell. These cells used Zeigler seals, which you will hear tomorrow from Ed McHenry, are absolutely leak free. But furthermore, we had helium-leak checked the cells and also pressure tested them for the absence of leaks.

We looked into the electrode mechanisms for a possible explanation of this phenemonon. And looking at the efficiency of the negative electrode, it turns out that roughly 60 percent of its theoretical capacity is used on cycling initially. This fades to roughly 45 percent in 50 cycles.

The 40 percent of the electrode that is not used electrochemically is present, I am sure, as charged cadmium. The work of Dunlop this morning supports this contention.

The mechanism then for the phenomenon I described, is that the oxygen from the positive on overcharge oxydizes the inactive, the electrochemically inactive cadmium of the electrode, converting it to cadmium hydroxide, but to keep the charge balance in the cells since nothing is gained or lost, some of the cadmium hydroxide of the electrode is charged to cadmium metal. But this particular material is electrochemically active.

So, in effect, by overcharging, you increase the quantity of electrochemically active cadmium.

To demonstrate this on electrodes, we put several as-received electrodes, and also some of the ones that had beer cycled for 50 times, in an oxygen bomb, wet with KOH -- the KOH was wicked into the electrode from the bottom of the bomb. -- at 90 degrees Centigrade for two days at 100 pounds of oxygen.

These electrodes then were removed, washed and dried and then put into 30 percent KOH flooded cells with larg counter electrodes, and we measured the amount of capacity that would go into the electrode before hydrogen evolution, before you see the hydrogen step. And this is shown on this viewgraph, along with data from electrodes as received.

(Slide.)

And we see that on the first cycle, we get 72 and 63 percent of the theoretical capacity in before hydrogen evolution, versus 90 on the oxygen-treated electrode after 50 cycles, and 95 as received with oxygen treatment.

On the second cycle, these figures all decrease. The as-received electrodes essentially give a constant performance, but the oxygen-treated electrodes decline towards the values of the as-received electrodes.

So that the oxygen treatment leads to electrochemically active cadmium hydroxide, the electrochemically inactive cadmium can be oxidized to electrochemically active cadmium hydroxide. But this fades after cycling.

Now, to explain this a bit more, we can look at these typical bar graphs.

(Slide.)

We have a bar showing the positive electrode and the negative electrode with an amount here shown in red as electrochemically inactive. The active portion being the cadmium, the cadmium/cadmium hydroxide that corresponds to the working capacity, and the excess negative capacity.

Now in the cell on overcharge, then, we have the oxygen reacting with some of this cadmium converting it to cadmium hydroxide, and at the same time some of this cadmium hydroxide being reduced to metallic cadmium which is now active, and this gives rise to the extra reversal capacity that I mentioned initially.

Now, at time zero, this cadmium hydroxide was active, as I showed from the bomb experiments. In a working cell, as it ages, I am sure that a portion of this cadmium hydroxide is not active, and in fact the morethe cell ages, the more of this material remains electrochemically inactive. And this can be seen in the performance of one of these cells on overcharge.

(Slide.)

This regime was C over 20, continuous charge. One week at 20 degrees Fahrenheit gave an end of charge pressure of 4 [illegible] pounds, capacity of 31 1/2 ampere hours. This was followed by a week at 110, capacity of 26 ampere hours, 4 pounds pressure. One month at 110. That was a month after this week, 4 pounds and 30 ampere hours capacity.

Then the cell was put at 20 degrees Fahrenheit for a month, and we find an increase in pressure capacity of roughly 34 ampere hours.

This pressure increase was not -- was gradual initially for the first ten days or so. The performance was similar to the performance the first week at 20 degrees. But eventually the pressure started to increase and build up to

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the higher values.

Now I should give you one other piece of data and that is that this cell contained about 46 ampere hours electrochemically active material, on the negative. The positive electrode was roughly 34 and with 8 ampere hours put in as precharge cadmium, you see we are close to the total electrochemically active cadmium capacity of 44. So that only a small change in these states of charge, only a small shift of this material into an inactive state, would get you into a dangerous region of running out of cadmium hydroxide.

(Slide.)

And this is in fact then what happened to give rise to this pressure buildup.

So what I am saying is, that in addition to the X ampere hours of precharged cadmium that you put into the electrode to account for cadmium fading with cycling, you need also to be sure to have a large excess of cadmium hydroxide probably at least equal to the total precharge plus electrochemically inactive cadmium that the cell has in order to assure a reliable performance over an extended period of time.

(Slide.)

One more piece of data I will show is the cell with the 8 ampere hours of precharge was charged at various rates and temperatures, giving these type of data. This is roughly C over 20 and C over 5 for this cell, and these are pressures in pounds per square inch absolute. The cells are evacuated before they are cycled. 85 Fahrenheit down to minus 20.

So we have at least zero degree performance. This only 18 pounds absolute pressure at the C over 5 rate, so that if we maintain these design principles and add the improper amount of excess cadmium hydroxide to the cell, this cell should reliably operate for long periods at elevated temperature.

I want to add at this point, a plug for the electrochemical impregnation process on the negative.

As you heard this morning, these electrodes have not faded with cycling compared with commercial electrodes which did, allowing you to design a cell with principles that I have just described, having a two to one total cadmium to positive ratio -- I am sorry -- flooded ratio of two to one, and 80 percent of the cadmium hydroxide will be utilized, compared to something which fades down to 45 or 50 percent on cycling. This scales up into a cell which has a thickness of 1.6 inches for the electrochemical negatives, and 2.7 inches for commercial negatives, so that the cell with high reliability for long-term overcharge, and I imagine also for cycling with the electrochemical negative, would have a higher energy density.

(Applause.)

FORD: Thank you Dean.

At this time we will entertain questions.

SULKES: In your, roughly, 5 weeks of 110 degree overcharge, especially with the internal temperature of the cell building up, it would appear that a large amount of your separator has been attacked, which would result, of course, in the building up of your cadmium capacity.

Have you back-calculated how much of that has actually taken place?

MAURER: I haven't made the calculation, but based on some experience with separator degradation, it would not be appreciable in that period of time.

I agree that it would be in a longer time, 6 months, perhaps. But these cells also have polypropylene separator.

DUNLOP: Dr. Maurer, you talked about the amount of adjustment of your precharge with respect to your discharge of cadmium for overtime protection, and you said that you should have an equivalent amount of cadmium -- discharged cadmium above the positive capacity to match the -- I think what you said -- the precharge plus the electrochemically inactive cadmium. Is that correct?

MAURER: That is right.

DUNLOP: It would be about an equal ratio between the two?

MAURER: Just as a rule of thumb.

DUNLOP: Another -- were you talking about a cell for what application?

MAURER: I am talking about a cell for a long-term overcharge applications, but I would think the same principle would apply for cyclic applications as well, because essentially the same sorts of things eventually happen. The negative becomes inactive.

If the cell didn't see very much overcharge at all, then these processes would be slowed down appreciably, of course.

DUNLOP: Have you had any experiences with discharging, or depth of discharge as to how it affects the utilization of the cadmium?

MAURER: Essentially, no. Most of our work has been with 100 percent depth discharge on cell cycling. That is down to eight-tenths of a volt.

DUNLOP: Does this influence the utilization of the cadmium?

MAURER: I think it would.

I think the deeper you discharge, the more likely you are to isolate cadmium.

DUNLOP: Okay.

And another thing I would like to mention here is that we do pretty much -- initially we support your initial statements that you may find a large amount of active cadmium in your plates, which cannot be discharged electrically.

But if you do discharge it electrically, either by an oxygen recombination process, or by a slow discharge process, then that you may be able to utilize this for a short period of time, but it may go right back eventually to the state where you can't utilize this.

MAURER: I think a lot of us have taken cells apart and found that part of the negative was out -- in the separator, for example. And I can't imagine that that will ever become very electrochemically active in an ancient cell, let's say.

LEUTHARD: Leuthard, Martin Marietta.

Have you done any testing, or would you like to comment on the effects of high-temperature exposure for long periods of time on the negative, process to the precharged and the uncharged negative?

I am thinking specifically of something like 135 degrees C for maybe 100 or 200 hours.

MAURER: We have not looked into that temperature range with any of the sterilization problems.

Most of our high temperature is in the neighborhood of 140 Fahrenheit, which is 55 degrees C.

So, no, I don't have any experience in that, of the type that you are describing.

High temperature of the type I described I think gives rise to material out into the separator, problems of this sort. Carbonation of the cadmium, if we had nylon separator.

LEUTHARD: Thank you, Doctor.

FLEISCHER: Have you looked into the uniformity of distribution of the charged cadmium on various plates, after you have had them on charge and overcharge for a while?

MAURER: No.

FLEISCHER: Because obviously if your electrolyte distribution changes at all, you will change the current density on different plates, so that you actually do not have a defined condition in these tests, until you have established that there is a uniform current, and that we may be deducing figures that take place on a smaller amount of the plates at higher current densities that correspond to what your overcharge current is.

MAURER: Well, except that the cells gave the capacities you would expect to see. And if much of the plate became inactive due to electrolyte redistribution, then you wouldn't expect to see the capacity as high as it was.

The one month at 20 degrees, followed by all of those other months, was giving 34 ampere hours.

FLEISCHER: But you started with 8 ampere hours excess cadmium, which doesn't change.

MAURER: Right. But if we had much redistribution of electrolyte, you would expect some of the positive electrodes to become inactive.

FLEISCHER: But it may not take very much distribution. YOu also have to assume that your reaction is always taking place over the same area, so you are consuming water and not changing the concentration of electrolyte in certain places.

There are a number of things that can happen if you analyze the whole problem completely, so that your tests should be followed up by analysis of the negative plates.

MAURER: Yes.

FORD: I believe we have a question in the rear.

CATHERINO: Catherino from General Electric.

The statement was made, actually that you repeated the second time, concerning the extent of fading of a commercial cadmium plate.

Now I am sure most of the people here understand it, but for those who are not aware of it, the statement should be taken with a grain of salt.

MAURER: IN what sense with a grain of salt?

CATHERINO: This business on utilization.

A commercial plate, after being cycled for a period of time, and the quoted figure was -- the implication was -- that all commercial plates fade to 30 percent, to 40 percent. Well, this isn't true.

MAURER: That is right. I agree with you.

The specific commercial plate that I am talking about faded 45 percent. I know other commercial plates fade different amounts.

FORD: Yes?

RAMPELL: Rampell, General Electric.

You mentioned the cadmium hydrate in the separator being electrochemically unavailable.

I agree with you, but there is one time that it becomes available, and that is during reversal. You will reduce a certain amount of it, which will give you a short after you go below zero volts in many cases, and that adds to your so-called total negative supply.

And that should be taken into account when people reverse cells to get the total negative. We found it preferable to remove the separator and open up the distances between electrodes in order to get an accurate negative capacity.

MAURER: These cells that this work was done on, were quite new, so that the amount of cadmium in the separator was not appreciable at this stage.

Also, the oxygen pressure buildup was following a linear relationship, which indicated that the current was not flowing through shorts.

RAMPELL: Now, one other item.

After you cycled the cells, or else maintained it on overcharge at 110 degrees for about a month, you developed a substantial amount of inactive cadmium, and thereafter you, I assume, more or less immediately went back on to 20 degrees Farenheit, and of course, produced higher charge voltages and higher pressures.

However, perhaps if you had gone from the 110 degree Farenheit regime to a room temperature regime, you would have had a mechanism of oxygen entering into producing again a more active cadmium electrochemical reactive cadmium, and then if you put it on 20 degrees Farenheit, you might not have gotten the same results.

MAURER: That is possible.

Right. If we had --

RAMPELL: The reason I am bringing it up to you is, in satellite applications, where you have a cycling of temperature and pressure, they may not have the same outcome as was inferred.

MAURER: Right. Yes.

These tests have no conditioning between one set of temperatures, and the other, and the reason, of course, is obvious, that on the telephone pole you can't do any conditioning.

SULKES: Just one question.

When you reverse, you are using this technique of puncturing the cell, is that how you are doing that?

MAURER: We have a valve and pressure transducer on the cell.

And the way it is done, the cell is attached to an extra volume initially evacuated, and the gas flows into this extra volume, so that we are not pumping on the cell all the time.

FORD: Any other questions?

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On inactive cadmium, loss of precharge, high temperature sterilization?

Thank you, Dr. Maurer.

VOICE: Since the first subject was related to precharge, and my talk is also related to precharge, I thought it appropriate that I present the two slides that I have at this time for discussion.

This data that I am going to present, resulted from a recent build of an OAO battery,where we actually, for the first time, quantitatively measured the precharge that the cells received. But I think I need to back up a little bit to get you into the right frame of mind, of what the state of charge of the negative electrode was prior to the precharge adjustment, so we will go back to the formation or the electrochemical cleaning, whichever you prefer to call it, where the plates are charged and discharged in a flooded bath. The cells were discharged to .75 volts to measure the positive plate capacity.

They then had a resistor placed across the cell to bring it down to less than one-tenth of a volt. When all cells in a series string were below this one-tenth of a volt, they were reversed at C over 10 and the reversal was to carry each cell to a minus two-tenths of a volt.

Now, with a little background on this, we had seen some data previously where we had reversed cells to a minus a half a volt, and we felt like from the data we had at that point, that the minus half a volt reversal did indeed have some effect on cell performance. We are not so sure of that today, since there are other complications.

Now in this case, the negatives were discharged against the positives in a flooded bath to minus two-tenths of a volt on each cell.

It is interesting to note, before we did this, we looked at the amount of excess negative versus voltage, and this minus two-tenths of a volt represents about 80 percent of the excess negative being in the discharge state. This is 80 percent plus or minus approximately 5 percent, which means that we left 20 percent of the excess. Remember, I am saying excess negative, not total negative. We left about 20 percent of the excess in the charged state at the end of the formation discharge.

Following this, we pulled two samples from each lot of 50 cells, and we did a -- we measured the residual precharge left prior to washing and drying.

Out of 10 samples we measured precharge in the ampere hours of 1.1 to 2.3.

The reason I point this out is immediately followin washing and drying, we pulled 10 more samples out of the lot, and the precharge as measured, which we -- I am sure most of you have seen the term (Tml) the precharge was measured to be zero, so the question arises, what happens to the precharge that remains in the negative at the end of the formation discharge? Why can't you measure that after washing and drying?

I don't have the answer to the question, and perhaps we can discuss it a little later.

The reversal I am talking about for measuring the precharge is that in a flooded condition in a C over 2 rate.

The next step, after reassembling the plate for the flight hardware into cells, KOH was added, and then the cells were subjected to a precharge adjustment cycle. One point on the addition of KOH.

From the recent build we now have data that says if you initiate the precharge adjustment in a very short time period after the addition of KOH, and using the precharge step that I will define in a minute, you will get higher levels of precharge than you would if the cell had soaked for at least two or three hours.

The precharge cycle consists of a vented charge for a given ampere hour input. The reason this method was used -- it has been used on all OAO batteries that I have been associated with.

And I termed this initial precharge cycle as a virgin cycle. The virgin cycle being defined as the first cycle after the addition of KOH.

We have further data now that says that you get different results if you do the precharge on the virgin cycle or do it one cycle later, which we can get into that later.

I want to point these things out as we go along, because they are all subject, they are all subject to controversy and I am sure other people here will have had experience that may contradict this.

At this time, though, I would like to show you the effects on overcharge as a function of precharge.

Now what we did, rather than change the process as most of you people that work with flight hardware programs know, you will do anything to prevent from changing a process that has been qualified. So, in order to prevent this, we took the next best step and we set up apparatus with the conjunction of Gulton Industries and Grumman Aircraft, the prime, to collect the gas during this many charge period.

Could I have the first slide, please?

(Slide.)

I think we should dwell on this slide for several minutes, because I have tried to portray several things here.

On this axis you have the ampere hours of precharge as determined by measuring the oxygen involved during the precharge adjustment. This is ampere hours equivalent calculated by knowing the free volume of the cell and how much oxygen was involved.

On this axis you have the cell pressure at a function of precharge, and this test, the pressure that is shown here, is the result of a 2.3 amp 4-hour overcharge at 32 degrees C.

As part of the standard cell selection test in selecting cells or matching cells to go into flight battery we have three overcharge tests, one at room temperature, one at 40 degrees F and one at 92 degrees F, I believe.

The worst case pressures observed were at 92 F or the 32 C as shown here. And this is the reason I chose these.

But, before we discuss the effects of the pressure, you have here, if you will note, this represents a cell, that represents a second cell and the top line represents a third cell. So if you look initially, without regards to this axis, you will see what the distribution of precharge was on these number of cells for a fixed ampere hour input. It says our precharge ranged from one to approximately five ampere hours.

Incidentally, I plotted these to be -- represent -- each block to represent half an ampere hour. That is the reason I did this to simplify the graph.

So as you see, the results was quite a range of precharge and its effect is that as a precharge was less, the pressures on the overcharge were higher. In this case we had two cells greater than 90 and each one of these blocks we had one cell greater than 90 PSIG.

As the precharge increases, it is quite obvious that the overcharge pressures decrease. And I can point this out by saying if you will simply compare the number of units that is represented in this block, compared with the number of units represented in this block, it is not one of a statistical distribution,the fact is that you do have more units here.

Now fortunately, we only had a couple of units that got up to five ampere hours of precharge. Why do I say fortunately? Simply because of the fact that I believe for low temperature application, high levels of precharge is the most detrimental thing that you can have. The excess negative on this group of cells was in the range of 8 to 12 ampere hours.

If you look at 5 ampere hours, 5 out of 8 is a pretty large percentage of the excess negative being used in the precharge.

In another test that followed this, we used this data and said well, it looks to be that ideally to get pressure uniformity, to get the overcharge characteristics that you would like, and yet to stay in the lower 50 percent of the excess negative to precharge, that you could use about 3 1/2 ampere hours of the negative as precharge.

So, to follow this we carried 10 cells through using a controlled precharge. The idea was, that if we could control the amount of precharge and not change the process, then we could bring ourselves into this group.

However, it has been observed that on this particular precharge technique during the charging period, that the cell voltages were fairly high. I think we typically saw end of charge voltage like 144, 145, and it was also observed that there was some correlation between the ampere hours of precharge and the end of charge voltage. It was not sufficient to use it as a guide -- to select or to predict what the precharge level would be.

So on 10 cells we decided to try an experiment. We carried the 10 cells through and we took out exactly, or approximately 3 1/2 ampere hours of precharge on the 10 cells.

However, we tried a different method, because we wanted to be able to control or limit the amount of pre-charge we obtained. We used the same charge rate, so as a consequence, the time had to change.

The additional change that we made was that we went through a sealed charge on the virgin cycle. One charge C over 10, 24 hours C over 2 discharge in one volt. And then we set the precharge on the second cycle.

We used the two methods. One was what I called oxygen free venting, when we collected the amount ofgas, as we did in these cells. But we limited the time that we stayed on charge, in order to get approximately 3 1/2 ampere hours of precharge. That was the five out of the ten cells.

Five more of the ten cells we used what we have referred to as incremental pressure venting. You charge the cell up, you go into overcharge, and you, as the pressure builds up, you vent the pressure out.

As the results of the tests of these ten cells -- first of all, I think it is safe to say that there was no difference in the overcharge pressures using the two methods. The overcharge pressures, however, on all ten cells, had shifted from a minimum of about 31 up to 68. I have a graph that I think I can put on later on this machine.

The point I want to make is that we did observe that by adjusting the precharge, not on the virgin cycle but on the second cycle, and to our knowledge, this is the only difference because it is the same plate lot that came out of the same formation group et cetera. This is the only difference that caused the pressure to increase.

After we concluded this, we decided that we should take a look and see what the results of measuring the precharge would show.

I think of all the things I have seen in working with batteries, this is the most misunderstood piece of information that I have come across.

(Slide.)②

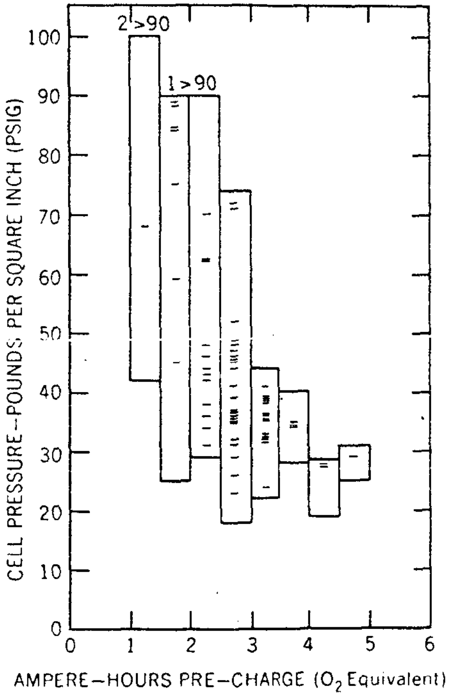
This is a summary of measuring the -- of the precharge measurement as we define TN-1, and let me reiterate what TN-1 is. TN-1 is the ampere hour capacity that we can measure in the cell between zero volts and minus one volt. Supposedly this is the ampere hours of precharge in the cell.

Because of some previous work we had completed at Goddard prior to this production, we had observed that the number was a function of whether the cell was flooded or dry, it was a function of the rate you used.

As a result you see the 2-amp and the 10-amp data, the starved versus the flooded.

It is further characterized to TN-1 measured immediately following precharge adjustment. In other words,

OAO BATTERY ASSEMBLIES
34 & 35 CELL PRESSURE
– END OF OVERCHARGE
2.3 AMPERES FOR FOUR HOURS
@ 32°C TEMPERATURE
TYPE V020HS



SUMMARY OF PRE-CHARGE TEST

OAO BATTERY ASSEMBLIES 34 AND 35

CELL S N	AMPERE-HOURS (O_2 EQUIVALENT)	AMPERE-HOURS (MEASURED-T_{N_1})	PERCENTAGE	RATE (AMPERES)	CONDITION	COMMENTS
501	6.15	4.20	68	2.0	STARVED	T_{N_1} MEASURED IMMEDIATELY FOLLOWING PRE-CHARGE ADJUSTMENT
524	6.69	4.60	68	2.0	STARVED	
1557	3.50	1.01	28	2.0	STARVED	
1477	3.30	1.17	35	10.0	FLOODED	
1505	4.61	2.50	54	10.0	FLOODED	
500	4.95	2.55	51	10.0	FLOODED	
507	2.66	1.11	41	10.0	FLOODED	
513	7.48	4.35	58	10.0	FLOODED	
516	6.10	3.08	50	10.0	FLOODED	
527	2.78	2.05	73	10.0	FLOODED	
496	1.69	1.50	88	10.0	FLOODED	
1500	2.20	0.01	00	10.0	FLOODED	T_{N_1} MEASURED UPON COMPLETION OF CELL SELECTION TEST.
1521	2.49	0.20	08	10.0	FLOODED	
1529	2.66	0.00	00	10.0	FLOODED	
1533	1.15	0.02	00	10.0	FLOODED	
1539	1.12	0.17	15	10.0	FLOODED	
1571	4.94	4.17	84	10.0	FLOODED	
1577	4.42	4.87	110	10.0	FLOODED	

after the precharge: were set in the cell by the action venting and collection, we discharged the cell and proceeded to reverse it.

The second was cells that were pulled upon completion of all electrical test, including cell selections. This is a cell as it would go into a flight battery.

I call your attention again, you see the range of precharge, and you see some numbers here that did not appear in the previous graphs, simply because these numbers were not indicative of the flight hardware.

These two cells were some of the first test cells that went through to look at the technique for measuring or collecting the gas to determine how much precharge there was.

If you look back in the history of the cells, there was a relatively short stand time between the time the cells were activated and the time they were put on charge, for the initial precharge adjustment.

I calculated the percentage of precharge that we actually measured, based on the ampere hour equivalent calculated from the gas that was involved. And as you note, there is some correlation here as low as 28, as high as 88 percent.

But when you get to a finished cell, a cell that has gone through approximately two to three weeks of testing, you find the correlation is even poorer. IN one case you get 110 percent.

Now, what does that mean? I am not sure I understand it today.

What this tells me is that the test is no good. There has got to be a better way of doing this. And I hope people here have some ideas about this.

We do have one glimmer of hope, and that is, I point out all these measurements, that precharge were made with the plates in the case. In other words, the cell was still sealed in the sense that it was vented, but we just opened the -- took the valve off at the Swagelok fitting, flooded it with the electrolyte and ran the test in that condition.

There is some data that now indicates that if you pull the cell out of the case, run it, as I believe the gentleman from General Electric suggested, you run it in an open flooded container, that these numbers will be more indicative of what these say it should be.

The one thing I am concerned with today, is the fact that we are talking about getting the best battery life at zero to 20 degrees C operation. And I have not seen anyone show the necessity of having high levels of precharge in cells for this type operation.

I point out that I am very much aware, being the technical monitor of a contract with General Electric, where they did a study of characterization of control and recombination of electrodes. They tested at 25 and 40 degrees C and they were able to show that the cycle capability at these conditions they were testing at high depths, was related to the amount of precharge.

However, I do not believe at this date that the same thing holds true at low temperature. I feel the most important characteristic that you have to deal with for low temperature applications, is maintaining a very large excess of uncharged negative in the cell.

And with that, I will conclude.

(Applause.)

Now, I will put on the other hat.

Any questions?

Yes, Jim?

DUNLOP: One question, why is it that you don't think you can reverse that cell, and yet [illegible] electrochemically measure the precharge?

FORD: Well, it is not a fact that I don't think I can do it. I know I can't do it in some cases, Jim.

DUNLOP: Do you have any kind of a reason or explanation as to what you think is happening?

FORD: Well, I could give you one, but it wouldn't be mine, and I would prefer to invite the gentleman that explained it to me -- I think he alluded to it a minute ago.

RAMPELL: The separator is loaded with cadmium hydrate.

DUNLOP: Is that a new cell, or is this the cell that has been cycled for a long period?

I got the idea these were new cells.

RAMPELL: If the cell has been cycled a few times, four or five cycles, you are already pretty well loaded with cadmium hydrate. You can prove that to yourself by opening up the cell, taking out the separator, putting it in basic KOH and some sodium sulfide. The separator will turn canary yellow, showing the cadmium sulfide distribution throughout the separator. It is there pretty quick.

Now, as you start the reversal, and actually get below zero volts where you are generating hydrogen from the positive electrode, of course electrons are going over, these electrons will start to reduce the cadmium hydrate adjacent to the plate on a separator, and you will start drawing cadmium dendrites, just like you do in zinc, and you will get partial shorts. Some of them can be quite complete.

Now naturally, the older the cell gets, for example, at the point of cell selection that Floyd had up there, your separator is really loaded and you can get a good short pretty fast.

FORD: Let me clarify a point with the last slide.

Could I have the last slide, please?

(Slide.)

The numbers I showed for TN-1 are the ampere hours measured in this column here, is the ampere hours that we measured to minus one volt.

All these cells were capable of being reversed. It has only been in situations where the cells had received some cycling and in some cases, extensive cycling. We just recently experienced a cell, after about 3500 cycles at 20 degrees C, exhibit this characteristic. The same cell, when pulled out of the case, without removing the separator, I may point out, the same cell, when put in a flooded bath, is capable of being reversed.

I can't help but believe that it is also a function, it is partly due to the cadmium migration in the separator, but it is also a function of the pressure that builds up in the cell over the lifetime of the cell.

We have some numbers that indicate now in that particular cell, using the numbers on plate thickness early -- at least on, call them virgin plates -- compared with the plates that came out of that cell, it says that if you take the expansion of the positive plates over the total number of plates in the cell, at 3500 cycles we have another positive plate in there, the effect on thickness. That is what it amounted to.

Any other questions?

MAURER: Just a question on, when you set the precharge, you say free venting, you mean that you open the cells to the atmosphere and allow the oxygen to escape?

FORD: In this case, the free venting, it was open to atmosphere pressure, we collected the gas in graduated cylinders, by displacing water.

FLEISCHER: I am a little confused about your last statement during your talk about the need for precharge, or the lack of need for precharge.

It might be a good idea to explain why we do put precharge into these cells.

FORD: My understanding on why we do or why we didn't?

(Laughter.)

FLEISCHER: Well, let's have a starting point.

(Laughter.)

FORD: Okay. It is my belief that precharge was put into the cell to offset the effect of negative capacity fading.

FLEISCHER: But there is more than that.

In order to get capacities at high rates, that you are running these cells at, we will say at C over 2 and C rate, you have to have more active negative than you do positive. As your temperature goes down, the ratio of active negative to positive that you need, increases.

Actually at minus 40 in a flooded cell you should be at a ratio of 1.8. So there is a very definite reason for having precharge, and I think this is accepted among all battery manufacturers as far as I know.

The reason for precharge is to allow for the high rate discharge and for low temperature operations.

So you couldn't very well be without it unless you have a very low rate cell for operation.

FORD: Oh, I am not suggesting we do without it completely.

I am suggesting that we minimize the amount that we put in the cell for -- and in particular maybe even take into consideration the application of the cell and how much precharge.

There is no question in my mind that if you got an application from 25 to 40 degrees C, that you had better be blessed with precharge if you want that cell to last.

But on the other hand, if you have got an application from zero to 20, you don't have to have as much precharge. You want to maintain your overcharge capability.

Yes, Dr. Maurer?

MAURER: I wonder if I could drag the portable mike to the board?

FORD: Okay, be my guest.

MAURER: I agree with you that for low-temperature application we need cadmium hydroxide on the negative.

And, let's see, Mel Gottleib at BTL around 1964, or 1965, presented a paper in which he shows the polarization of the negative electrode versus the percent capacity return as a function of rate. And for low rates you get curves that look like this, where this step occurs around 100 percent. And as you got to lower rates, these step back, so that the higher the charging rate, the less capacity you can get into the negative before you go to hydrogen evolution.

These same sort of curve would apply to the same rate, but lower temperatures, and so the lower the temperature you go, the sooner you get into this step. So if you plan to use your cell at minus 20, then you need a greater amount of excess negative than you do if you only plan to operate at room temperature.

The precharge, on the other hand, is there for several reasons, and Dennis Turner reported in'64, I guess, in the Journal of Electrochem Technology, a study of the effect of precharge on flat plate and cylindrical cells, and showed that the oxygen pressure was a strong function of precharge in these cells. And also that the pressure that you get to for a given stated amount of precharge, depends on whether you do or what you do to the cell.

So that, for example, if I plot here -- well, he used the ratio of cadmium to nickel charge capacity, so that one on this scale represents no precharge, and this would be the oxygen pressure. And by varying this ratio in a given cell by either taking out oxygen or adding it, you have got a hysteresis going down. You have got a curve that looked like this, and going up, a curve that looks like this.

And furthermore, if you stop at this point, and cycle the cell for a while you will find that the pressure drops to this point.

So that in adjusting the state of charge of the cell, you need to do cycling before you make measurements on parameters like pressure or cell voltage.

And of course, the other reason for precharge, as I discussed before, and that Dunlap has shown in the GE report, has shown, that the precharge is put in to account for the fading of the negative capacity, which is a different amount, depending on who manufactured the cell.

IN one case we measured 45. I guess GE has something like 60 or something like that, as a minimum capacity.

DUNLOP: Just one comment.

The data that Gottleib has there, that was done with a flooded plate, isn't that correct?

MAURER: Yes.

FORD: Any other questions?

STEINHAUER: Do you feel that we can come up with numbers of precharge applicable to all, or is this going to have to be custom tailored?

MAURER: I will make one answer. I will say it has to be custom tailored.

FORD: I will agree with that.

I think the problem is that -- one of the problems -- they have several -- is that there are so many other variations in the cell parameters that affect characteristics. As the first graph clearly shows, there is really no explanation at this point, at least I don't have one, why with 1 1/2 ampere hours of precharge, you get the spread in pressure from say 20 to over 100 PSIG.

I think at that point the effect of precharge is secondary, and these other first order effects.

So yes, I don't think we can say for a 12 ampere hour cell -- I think we should even tailor it for the application, too. For synchronous orbit I think you have a different need for precharge than you do on a near earth orbit.

I think we are getting into the era of tailor making cells to fill an application. Unfortunately, we don't have the technology to do that at this state.

UNGER: Unger, Goddard, Space Flight Center.

I did a lot of this work that Floyd is talking about as far as the mechanics of measuring things. But what I want to say is, right now to reemphasize what Floyd just

mm37

said about tailor making cells.

I think in general, particularly in the history of spacecraft cells, we have been operating with cells that were fat, cells that had two to one negative to positive available material of ratios. Also cells where we only used the top five, ten, fifteen percent of the capacity in cycling and under those conditions, I think that we got away with a lot of -- well, I don't want to call them hit or miss, just call them empirical operations, where we didn't know just how much of the actual material in the plates was available for various types of things, either electrical cycling, or oxygen recombination, or what have you.

We didn't know precisely what the relative states of charge the electrodes were. We didn't know how much of the excess cadmium, that is to say, was discharged, as cadmium hydroxide, and therefore constituted overcharge protection, and how much of it was cadmium metal, which constituted precharge and how much of all of that was available under certain conditions.

We didn't have to answer these questions. But it just happened that we were using the cells that had enough capacity so that we didn't get into trouble from fading, whether we were a little close to the bottom or the top of a relative state of chart plot, and we were just not operating the cells as severely. We weren't trying to cut the actual amount of material in the cells as close as possible to the predicted usage.

And I think that we are running into problems now, because we are trying to get as much utilization as possible out of the cells, and now no longer can we say empirically that if you do it this way, the cell works right, because now the cell is not being worked in the same manner and it is not working right.

I realize that is a very vague statement, but I think that it lies at the bottom of the problems that we have been having, the problems that we are anticipating.

I don't see how we can force the cells to give us more reliable, more predictable behavior unless we, in turn, control the way they are manufactured, so that we, in fact, are giving them the reliable and predictable characteristics ourselves.

STEMMLE: Stemmle of Goddard.

In Turner's paper of 1964, he recommended a way of setting precharges, which I thought I would mention here, and that is that you keep venting the charge through some sort of a valve arrangement at the pressure you would like to start to maintain at that rate of overcharge, and eventually it will stop gassing, and maintain that pressure.

What he did was when the precharge level was low, like zero, say during the precharge step you are charging it up and you have reached full charge on both electrodes, at that point, the recombination ability in the negative electrode is quite low and it has to be more charged up.

So pressure would build up and more gassing could occur.

But as the negative electrode got more and more charged, its ability to recombine oxygen increased, and so the steady state pressure was lower.

So perhaps it would be a good way to look at, or just might be a method of tailor making itself, if you are going to use it for low temperature regimes, perhaps you should set your precharge at low temperature, and specify the overcharge pressure you would like to see the cell have at your chosen overcharge rate.

FORD: One other quick one. I think we have coffee ready outside.

REED: Reed, Battelle.

I am not sure whether I understood what you are saying right or not about not being able to recover your precharge after washing and drying, but being able to do it if you did it immediately after, is that correct?

FORD: Yes.

REED: Well, could I ask you first how you did your washing and drying?

Was this done under oxygen free conditions?

FORD: No.

REED: Okay, well, that is what I suspected, because we have done similar kinds of things where we have discharged the cell down to the one or zero volt limit in a sealed condition. Then we have opened it and washed it in our nickel soxhlet extractor, under a nitrogen atmosphere, dried it in vacuum, then charged it in the flooded condition to exactly the capacity which is removed in the sealed condition, and then further discharged it to show which electrode was limiting. And in the cases we have found the cells were indeed positive limiting. And we could get further discharge from the negative even after washing and drying under these oxygen free conditions.

FORD: THank you.

An attempt is made to minimize the contact that the plates have with the atmosphere. They are kept submerged under water throughout the washing, but they are dried in the air.

Any other questions?

RAMPELL: A possible explanation for the drop in pressure to the amount of precharge. But in any event, in going up in precharge quantity, you are also venting out -- well, for 3 ampere hours, roughly another CC of electrolyte, say, and also you are increasing the void volume by going from cadmium hydroxide to cadmium.

FORD: Thank you.

Any other points?

If not, we will take a ten minute break for coffee.

(Recess.)

N71-28667

FORD: May I have your attention, please?

Gentlemen, our next presentation is by Steve Gaston, of Grumman Aerospace Corporation, and his topic is Low Temperature Overcharge on the OAO Battery and Cells. Steve Gaston.

GASTON: In working with the OAO batteries, we have observed certain trends, and specifically one of the trends which we have observed is a low temperature overcharge voltage increase as a function of age.

This study entails a review of four OAO battery and cell lots with respect to the overcharge voltage characteristics, and the plus 30, plus 40 degrees F temperature range.

These low temperature overcharges were conducted at specific intervals and after cell reconditioning.

(Slide.)

The first slide shows the overcharge voltage profiles for cells in sealed -- Battery number 30 and 31.

Cell serial number 698 had exhibited a high overcharge voltage profile. As a matter of fact it had exhibited the highest for the 66 cells in the battery.

Cell serial number 733 had shown the lowest overcharge voltage profile for the same cell group.

The upper most set of curves show the data for the first overcharge conducted in battery cells, which occurs prior to the battery assembly, and since the data was taken at specific intervals, only the readings for the first half hour intervals are not available. So you see a blank area.

The three sets of curves below show profiles for the identical cells after 185 days, 500 days and 750 days after activation, respectively.

It is of specific interest to note here that the maximum permissible overcharge current had to be reduced to lower values, since at least one cell in the battery had reached its hydrogen evolution voltage limit.

Specifically I should point out here, the uppermost curve, you continue the overcharge at one ampere all the way through. After 185 days, we continue the same curve, which happened to be 0.9 amps.

At 500 days, at the first voltage drop, we had to reduce it from .9 amps to .5 amps. And then we had to go to .25 amps, so you see the two breaks.

(Slide.)

Graph number 2 shows a trend in cell voltage rise

n43

as a function of age for 4 OAO battery cell lots.

The overcharge at the 0.9 to 1 ampere rate had to be reduced to lower values, starting from the 460th day test, because at least one cell in the batter group had reached its hydrogen evolution voltage range.

It is of extreme interest to note here that the test cells for an identical lot, but stored in a shorted condition, specifically I am pointing to this one here, shortly after filling an initial electrical cycling, performed like new cells during the overcharge.

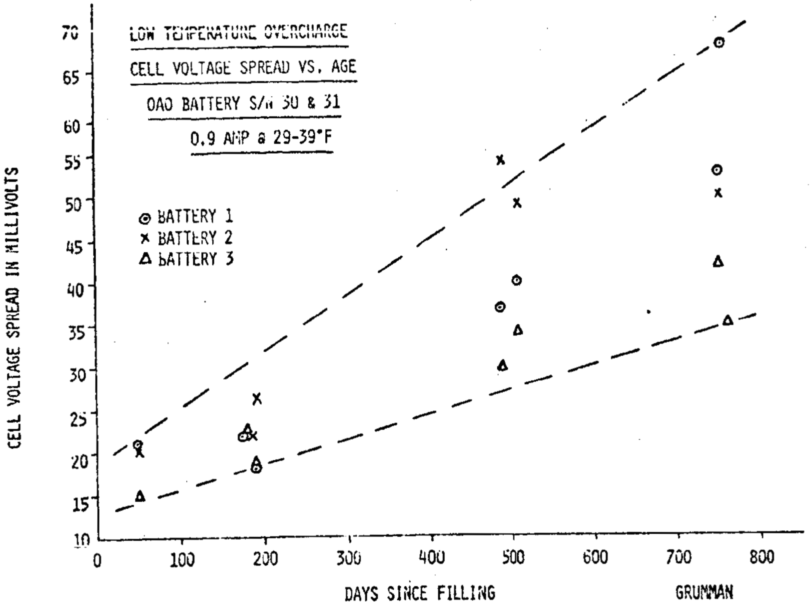
Also a cell component analysis had shown no material degradation in these stored cells. These cells were stored in plastic bags in a clean room at approximately 68 degrees F and low humidity conditions.

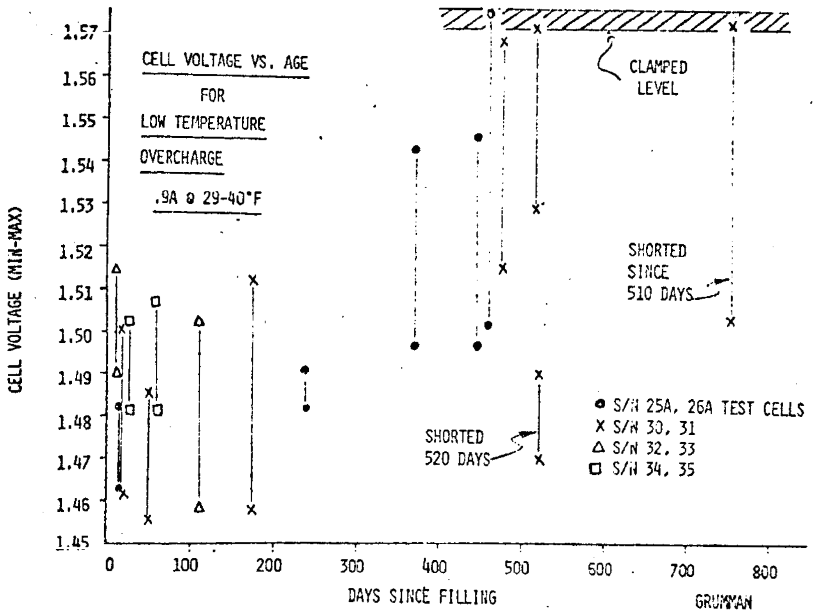
The effect of the storage period between 520 days, which is between this and the 750 day level, the effects of the storage period between 520-750 days are less pronounced and can be noted in both tests the current had to be reduced to a lower than maximum value, because at least one cell in each battery string had reached its hydrogen evolution voltage range.

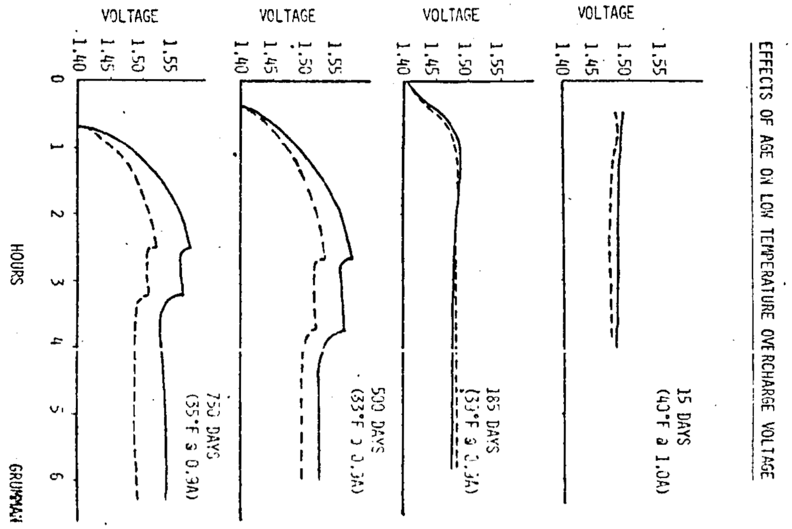
The lowest voltage cell, however, exhibited the lower voltage after 750 days as compared to tests at 520 days.

(Slide.)

In graph number 3, it shows the total voltage


LOW TEMPERATURE OVERCHARGE
CELL VOLTAGE SPREAD VS. AGE
OAO BATTERY S/N 30 & 31
0.9 AMP @ 29-39°F
⊙ BATTERY 1
× BATTERY 2
△ BATTERY 3
CELL VOLTAGE SPREAD IN MILLIVOLTS
70
65
60
55
50
45
40
35
30
25
20
15
10
0
100
200
300
400
500
600
700
800
DAYS SINCE FILLING
GRUMMAN


CELL VOLTAGE VS. AGE
FOR
LOW TEMPERATURE
OVERCHARGE
.9A @ 29-40°F
CLAMPED LEVEL
SHORTED SINCE 510 DAYS
SHORTED 520 DAYS
● S/N 25A, 26A TEST CELLS
X S/N 30, 31
△ S/N 32, 33
□ S/N 34, 35
CELL VOLTAGE (MIN-MAX)
1.57
1.56
1.55
1.54
1.53
1.52
1.51
1.50
1.49
1.48
1.47
1.46
1.45
0
100
200
300
400
500
600
700
800
DAYS SINCE FILLING
GRUMMAN


EFFECTS OF AGE ON LOW TEMPERATURE OVERCHARGE VOLTAGE
VOLTAGE
1.40
1.45
1.50
1.55
HOURS
0
1
2
3
4
5
6
750 DAYS (35°F @ 0.3A)
500 DAYS (33°F @ 0.3A)
165 DAYS (39°F @ 0.3A)
15 DAYS (40°F @ 1.0A)
GRUMMAN

spread between the cells of each battery string during the low temperature overcharge as a function of age. A general increase in cell voltage diversions between the cell in each string can be noted with increase in age.

As a conclusion, a definite trend in the rise of low temperature overcharge cell voltage with increase in age has been established.

This voltage rise is apparently caused by the negative available capacity loss resulting in hydrogen evolution if the overcharged would have been continued.

This hydrogen gas evolution will lead to battery failure when sufficient pressures are reached.

Cells stored in a shorted condition, earlier in their age,, performed like new cells and showed no internal component degredations.

And the recommendation, based on the above information, strongly recommended that the nickel cadmium flight battery cells be kept in a shorted state below room temperature and at low humidity conditions for the maximum possible periods to extend the orbital life.

IN addition, an increase in the cells negative electrode capacity over the positive electrode capacity, which is generally known as the capacity ratio, should yield a longer time duration until the cell's hydrogen evolution voltage is reached.

FORD: Thank you, Steve.

Are there any questions?

Yes, Dr. Scott?

SCOTT: I may have missed how the batteries were stored, in what condition of state of charge and/or cycling were they stored up to the 500 plus state period?

GASTON: BEtween the 500 plus to 700 plus period, the batteries were stored in a discharged, drained condition. However, after 500 plus days, the worst cell had reached the hydrogen voltage limit, and of course the charge had to be terminated because it had reached its limit.

So there is no improvement between 500 plus days and 700 plus days.

SCOTT: I'm sorry.

Prior to 500 plus days, zero to 500 days, how were the batteries stored?

GASTON: Okay, the batteries were -- most of the time they were in the spacecraft they were in a systems test. They have received very little cycling except the initial acceptance testing.

The cycling life was small -- age -- yes. They were active most of the time in the spacecraft under a small trickle charge.

SCOTT: Oh, they were being trickle charged?

GASTON: Yes.

SCOTT: You mentioned,you use the term hydrogen evolution potential range.

What do you consider that voltage range?

GASTON: Of course that is a function of temperature, and I think I defined it best in the specification. It is -- for 35 degrees F, I don't recall the number off hand. But it is the recommended range which hydrogen does -- it is possible that hydrogen can occur at this range. I can't give you the exact number. I believe it is around --

FORD: I believe it is 1.556 -- 1.555 -- 1.556 at 35 degrees F.

SCOTT: Was hydrogen actually measured or observed from any of these cells under those conditions?

GASTON: No, no. We couldn't measure it. These cells were in a battery. If you attach a gauge to the cells and battery, you destroy the battery. It was not measured.

SCOTT: Was there any way of measuring pressure under these conditions that you knew of? Any indication of pressure?

GASTON: We terminated the charge to avoid any pressure buildup. You don't want to destroy a flight battery by going to the pressure point. You terminate it at the point where it is likely to build up pressure.

SCOTT: One final comment. The reason

I am hounding on this is that we have recently conducted some testing at around 40 degrees F and we observed some cells going to this voltage range under approximately the same conditions.

We had gauges on the cells and we measured -- we looked for hydrogen. We saw neither any abnormal pressure behavior, nor did we see any abnormal amount of hydrogen at voltages 155 to 158 at around 40 degres F, so that is what I was asking about.

GASTON: The reason I said range, is because I am not 100 percent sure exactly what this point is.

But there was a definite rise towards this hydrogen voltage range, and we had to take a certain, a safe point at which we terminate the charge.

BOGNER: Did you attempt to recondition these cells, Steve?

GASTON: Yes.

Prior to each overcharge, we reconditioned.

BOGNER: It did not lower the voltage?

GASTON: It did not lower it at all. No change.

RYDER: Bill Ryder. Gulton.

I understand that you were representing batteries, that were taken out of storage after specified periods of time. But in answer to Dr. Scott's question, do I understand you to say that these batteries actually were on a spacecraft, and being subjected to tests of various kinds?

GASTON: Well, maybe I should simplify, or maybe I should elaborate.

The battery which showed the aging, was in the spacecraft for various tests. The cells which were taken from the same lot were stored in a discharge drained condition. So we are talking about a battery, and we are talking a number of specific cells which were taken from the same lot and stored.

RYDER: Oh, okay.

In other words, the data that you are showing, where you are showing storage for certain periods of time, is on cells that were indeed stored for that period of time, is that correct?

GASTON: Let me go back and maybe I can explain it a little bit better.

(Slide.)

We have in this group a total of -- we have the first group of cells which are the points, they are test cells from battery 25-A and 26-A. These cells were tested continuously at NASA Goddard, not batteries, because these were the A-2 flight, A-2 flight batteries in space right now.

FORD: And that is cycling test.

GASTON: This is cycling tests.

These were continuously cycled.

30 and 31, this data with an X, is a battery which was in the spacecraft,and these are battery cells, except those cells down here which were shorted for 520 days. These were cells from the identical lot.

Because 32 and 33, that is a later battery, and 34 and 35, that is the present battery. These are batteries of cells, actually batteries.

RYDER: Okay, so you really have one batch of cells and that was shorted for 520 days?

GASTON: That's right.

RYDER: Then you show the data on those, which as you indicate is performed well?

GASTON: Right.

RYDER: The only point I am making, Steve, and I wasn't sure myself, is the batteries, the data for which you are showing, have undergone some indeterminate system testing, or variable testing. You mentioned trickle charging. Isn't it possible there may have been even some reversal in some instances? What was the trickle charge rate?

GASTON: No, I wouldn't say indeterminate testing.

The testing are known. The trickle charge rates were very low, quarter amp per battery.

RYDER: Is that continuous for that period?

GASTON: Continuous.

Only when the batteries were active on the

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spacecraft. I wouldn't say indeterminate. Yes, we can determine. The data is available.

RYDER: Thank you.

FORD: Other questions?

REED: I would like to make a comment along the lines that Dr. Scott was talking, as far as hydrogen evolution potential.

I think the term may be misused when we are talking about a cell without regard to which electrode, because we know hydrogen can only be evolved at the negative overcharge, and unless you are using some type of reference electrode, for instance the case, if you have both terminals isolated from the electrodes, you don't know whether you are talking about really developing hydrogen or not. There are a number of things that can cause the positive electrode potential to increase, so that your cell voltage would go above this 1.555 figure.

An example, carbonate in the electrolyte has been shown to increase the charge potential of the positive. I believe it was a paper presented by some people from General Electric, Cahotti recently at the Brighton Conference, showed this very well, and some of our more limited data shows this also, that the positive electrode potential will increase under such conditions.

And of course then, you are not generating hydrogen

GASTON: Do you really believe it can increase that much from about 1.50 to about 1.58 with age?

(Slide.)

Because particularly 500 days and 750 days, there is a definite rise and it didn't even stop at that point. We had to terminate it,because like I say, we have a whole battery and we cannot afford to build up pressure in the cells. In the whole battery. Therefore, we had to decide at some point, where to stop the overcharge, and we decided about 1.58 is the point, and that is the recommended overcharge voltage by the battery manufacturer.

FORD: I am sure all of you are familiar with the term overtest. That is what he is referring to. To go beyond the limit is an overtest.

I think we had a question in the back, Bill?

HARSCH: Bill Harsch, Eagle Picher.

Steve, could you put that other slide back on?

GASTON: Okay.

(Slide.)

HARSCH: The cells that are marked shorted since 510 days, the overcharge test run on those cells,is that immediately after a shorted condition?

Or, have the cells --

GASTON: No, they were conditioned like all the others.

HARSCH: After they came up shorted?

GASTON: Well, you remove the short and you give them a low current cycle and they discharge, and then you give it a taper charge, and then you overcharge it. Keep the conditions identical from the day one, so that you/ are consistent in data.

FLEISCHER: Were the individual cells shorted?

GASTON: Individual cells were shorted, yes.

UCHIYAMA: Uchiyama, JPL.

I am still confused now. YOu indicated that on the OAO, the batteries that you had on the OAO had no -- you had no way of measuring the individual cells, is that correct?

GASTON: Yes, we did measure individual cell voltages, oh, yes. We just could not measure the hydrogen gas.

UCHIYAMA: Now, the previous slide that you had up there, where you had the cell voltages, is this the values you have on there, battery terminal voltage divided by the number of cells, or is that indeed individual cell measurement?

GASTON: No, this is a specific cell voltage. And it is a specific cell number, which is the same cell number from the day one.

You see, the broken line represents one cell number which initially was the lower one with respect to the solid line. After 185 days they are approximately the same.

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The lower cell seems to be slightly higher, and of course 500 and 750 days, the lowest cell again had the lowest voltage.

So each specific cell was measured but; in a battery you cannot terminate a cell. I have a string of cells. So in order to terminate the charge in the whole battery -- in order to terminate the charge in a specific cell, I had to terminate the whole string.

FORD: Steve, each one of these cell curves represents 22 cells, a maximum end type?

GASTON: That is right.

GROSS: Steve, can we discount the possibility that the trickle charge created enough temperature differences in your battery that you are measuring temperature differences from a cold, outside cells to the warm inside cells?

GASTON: Yes, we can discount it, because the differences in the cell which show up initially, would show up later on. It is constant. The battery configuration does not change. The temperatures were measured, and it is true, we have a gradient between the outside and the inside -- the external cell and the center cell of about eight degrees F. But the same relationship which held true before, held true now.

The overcharges were conducted under identical conditions. They haven't changed. And the temperatures were measured. They haven't changed either.

SCOTT: One additional point along the lines that Mr. Reed mentioned.

In the tests that I referred to a minute ago, I believe at least one of the cells that showed a high voltage, had a built-in reference electrode, and as I recall, essentially all of the abnormal voltage was measured on the positive, and essentially none on the negative, which indicates to me, at least, the possibility that this kind of behavior can be a problem with the positive, and not the negative, and therefore, may not be a hydrogen problem. It could be some kind of other problem.

GASTON: Okay, it is possible, but we still have that battery, and we still can investigate that further. That is why I don't say it is absolute information. That is why I call them trends.

I see a definite trend in increase in voltage, and I suspect that it is hydrogen.

KANTNER: Ed Kantner, Gulton Industries.

I would like to address this question to Dr. Scott, actually.

I was wondering whether he had made an attempt to determine what the cause of this abnormal behavior of the positive is, or whether he has any ideas of what it might be due to?

SCOTT: Not yet, but soon.

RYDER: Leave that slide on, will you please, Steve, because I am still confused.

GASTON: Sorry about that.

RYDER: Now, what you are showing here, if I understand what you are saying,is readings taken at different times, 15 days, 185, and so on, after filling of the cells. I believe that is the word you used.

GASTON: That's right.

RYDER: And after some indeterminate activity that occurred in the battery in the time between those periods, is that correct now, because I am really confused?

GASTON: I don't know how you define indeterminate activity.

RYDER: You haven't defined it that I have heard.

GASTON: I have a record of what the history of those batteries, and I just summarized it. The batteries were acceptance tested, then they were placed in the spacecraft, and whenever the batteries were electrically active, they were put in a small trickle charge. That data is available. The currents are known, the cell voltages are known, so it is not an indeterminate activity.

Yes, they had seen electrical activity, yes.

RYDER: Okay.

So they were put on a trickle charge, and I guess that is the only thing that was done with them?

And then after that period of time, then you proceeded to put them on overcharge at these rates. Only first you went through a reconditioning cycle?

GASTON: That's right.

RYDER: Now you put them on overcharge at these rates, and when you say on overcharge, what do you mean? 48 hours, 120 hours?

GASTON: The overcharge in this case, you will see, was terminated earlier. In most cases, at most it lasted eight hours. Many cases it only lasted four hours. IN this case it lasted seven hours.

RYDER: So that represented the actual duration of charge, the hours you show on the chart?

GASTON: This is duration of the overcharge.

RYDER: You took them off trickle charge, and that is the actual amount of charge there, after conditioning?

GASTON: No, after conditioning they received what is known as a taper charge until they were fully charged and then they were temperature stabilized and received an overcharge.

And this is the actual duration of the overcharge.

FORD: Are there any other questions?

Mr. Leuthard?

LEUTHARD: Now the trickle charge was at what rate, Steve?

GASTON: It ranged from 0.9 to 1.0 amps.

LEUTHARD: Okay, and then the .9 amps --

GASTON: If you went to the lower temperatures -- in most cases we went to lower temperature, like 33 to 35 we went to 0.9 amps because that represents the maximum permissible overcharge rate, for the 20 amp hour cell.

LEUTHARD: And the .9 amps is the overcharge rate?

GASTON: That is the overcharge rate, yes.

LEUTHARD: Okay, thank you.

FORD: Steve? Stemmle, over here.

STEMMLE: Is it possible to add oxygen to those cells?

GASTON: Not unless we take the batteries apart. The decision has not been made what to do with those batteries. As soon as I take the batteries apart, I destroy the integrity of the battery, and if you ever want to rebuild them, even if we find the cells are good, we would have to reacceptance test it, which is an expensive procedure.

So, until I am thoroughly convinced there is nothing wrong with those batteries, I am not going to take them apart. Because once I take them apart, I destroy some cells and I would have to take new cells, replace them with old cells, so the integrity of the battery is gone.

STEMMLE: But you have no access to the individual cells?

GASTON: Electrically, yes.

Physically -- or as you say taking pressure and so on, no.

STEMMLE: The reason I ask this is because adding oxygen may be a good way to determine whether or not you are getting the high voltage difficulty from the negative orthe positive electrode.

GASTON: It is possible, yes.

(Slide.)

We will just go back to one point, I think, to clarify for Bill Ryder's remark. In this graph I show the test cells for 25-A and 26-A, and if you follow just the dotted line you see the same rise in voltage and these were actually, these cells were tested in orbital simulated conditions. So that certainly, the history is right there.

FORD: The test cells that Steve is referring to were tested at 15 percent depth of discharge on a 90-minute orbit. 30-minute discharge, 60-minute charge. They were charged at 8 amps, discharged at 5 amps and they went through over 6000 cycles throughout the life of them.

What we did observe -- in fact the test temperature, the average test temperature, about 90 percent of the life of the cells were at 55 degrees F which is where the spacecraft battery runs.

So these cells had not seen any unusual test regime, other than the fact that they were run in a condition simulating a spacecraft.

I might point out that we have sufficient data now from the flight battery, the A-2 battery, which has been up almost two years in December, that shows the same type trend.

GASTON: Floyd, correct me if I am wrong.

Didn't we observe hydrogen in those cells at this voltage, didn't we?

FORD: There was one cell that -- in fact, we did exactly what Stemmle suggested -- there was one cell during that test that became a maverick, as indicated by the highest point. We removed three ampere hours of precharge and put the cell back on test, and we brought it back within the overcharge limits that were set for that condition.

I think you will find this information on the test cells thoroughly reviewed in the Power Sources Conference of this spring, which I assume the publication is coming out shortly.

Any more questions on this?

John?

UNGER: Unger, Goddard.

Just one more point there. A number of people have asked, or questioned whether or not you are dealing with hydrogen, and we have run some analyses on certain cells. I have run the analyses, but I am not sure what cells and what batteries, and I was wondering whether or not any of these particular cells, we found hydrogen in?

FORD: 32 and 33. We have the test cells in the lab now, and we have observed at 35 degrees F, hydrogen being accumulated at a very slow rate, I point out. AT 1.51 volts in one particular cells. Other cells that go higher than that, we haven't seen hydrogen.

But we have data that shows that you can get hydrogen in a cell at 1.51 volts, at 35 F.

UNGER: So essentially this means that these maverick voltages may indeed not be the result of behavior of thenegative. On the other hand, they may be. We do have cases of hydrogen generation at slow rates.

BOGNER: Bogner, JPL.

Are any of these cells some that you had a problem with a couple of years ago?

FORD: No.

(Laughter.)

BOGNER: Are the results similar, or not?

FORD: All of these cells have been produced since October, 1968.

It is interesting to note that we are experiencing similar symptoms.

BOGNER: Did it occur earlier on those cells, or show up about the same time.

FORD: It occurred earlier on the problem cells that you refer to.

When it occurred is a function of the depth of discharge, the type testing you do, et cetera. It is a -- we don't really have a good handle on it.

GROSS: Gross, Boeing.

There are a lot of possible reasons that could explain this behavior. One, of course, is the variable degradation of the positive.

I would like to emphasize a point, however, that Al Reed made on the value of including reference electrodes in experimental work. And for the life of me, I can't understand why experimental batteries so seldom have adequate instrumentation, including reference electrodes and pressure gauges.

Now this was a flight battery, I realize, and probably we couldn't do that. But there is no reason any more to have to speculate. We should make sure that all our laboratory batteries are adequately instrumented, so that we know what is going on.

FORD: Dr. Fleischer?

FLEISCHER: I would like to make a suggestion. If you are going to open any of these cells, and analyze them, that you analyze the electrolyte from the positive and negative plates separately. I would suspect that after that long period of time, the concentration of the electrolyte in hydroxylines at the positive plate, probably be less than that at the negatives, because you are transferring oxygen to the negative plates.

I found this in small button cells, and I wouldn't be surprised if you found it here to an exaggerated extent.

GASTON: In answer to the question, or the comment the gentleman from Boeing, we do have, in each group, we do have an auxiliary electrode cell, so we do have an idea when the oxygen limit is freed, or when the oxygen evolution is made.

Unfortunately, in hydro cells -- not the ones, the high range of the voltages -- so it was not the limiting cell in the string.

Another comment I would like to make is that the positive capacity of the cell had not deteriorated, so when you compare capacities of these cells, they are identical. As a matter of fact, in some cases, they are slightly better than they were initially. So I don't know whether we can -- in my opinion, I am not clear whether we can blame the positive electrode for the voltage rise that you say might possibly do, cause.

FORD: Just one comment, out of the group of cells from serial number 32 and 33, we just recently, we had cells on test at Crane. We ran a ratio test. We found a positive plate capacity of over 29 -- approximately 29 1/2 ampere hours -- there was no such cell in existence on the production lot. We found a negative plate capacity of approximately 34 1/2 ampere hours, and I remember the ratio came out to be 1.18 in that range.

These cells exhibit a ratio, total negative to positive ratio of about 145 during formation in the early electrode capacity tests that were run.

ARe there any other questions on this particular subject?

Yes, Mr. Cohn?

COHN: Cohn, NASA.

I would like to make a comment, rather than ask a question. It seems to me one must draw some lessons from this, and I haven't heard anyone here say anything about what does this all mean? Have we learned something for the next battery for the next spacecraft, or what have you?

And it seems to me there are two things that -- I would like to be corrected if I am wrong on this -- one is that you are setting the voltage cutoff too high now because you actually do get hydrogen evolution, so something is wrong, and the second thing that is obviously wrong is that you are trickle charging. You should not be trickle charging for 500 days or 200 or 300 days, because you are obviously wrecking the battery.

So it seems to me one has to learn these lessons and apply them and express the fact that one has learned some lessons so that other people don't make the same mistakes.

FORD: I would like to clarify that point.

When you say the batteries in the spacecraft, and that is the life of 30 and 31 battery, it wasn't the spacecraft. The battery is on open circuit every night of the week, it is on open circuit during the weekend, unless they have integration and checkout for the spacecraft. The battery is used during the daytime and it is operasted under the same type of voltage control system, or it may be at a reduced voltage to maintain the overcharge in the battery.

And the limitation factor there is the amount of heat that they can dissipate at room temperature. So the trickle charge rates during the daytime are in the range of about C over 35 to C over 40. But the battery is on open circuit and charged, and I feel very strongly that this is also a factor in the degradation characteristic of the cells.

GASTON: Let me make just one comment.

My determination was, is that you use the battery as little as possible in the spacecraft for any systems test.

As a matter of fact, if possible, you don't use it at all, which is, of course, not possible. So, under the ideal condition, keep it in discharge rate condition as long as possible, and then you have a battery which appears like a new battery.

And of course, the other recommendation is increase the negative to positive capacity ratio.

STEMMLE: I would like to contribute a comment from Dr. Gomis of SAFT that he made a couple of weeks ago when he was here talking with us. He said that -- well, he pointed out that during overcharge, whether it is trickle or otherwise, there is uncompensated concentration gradient of hydroxylines on the negative electrode.

One way of considering normal cycling is that there is a concentration gradient of OH that builds up on one, and then it shifts to the other on the other half of the cycle. But during overcharge it is uncompensated.

And he has found in some old cells that he has taken apart, solid KOH, crystals of it on the negative electrodes, so I think it does contribute to the degradation of the cells.

FORD: I think we have time for just about one more question. We want to move on.

Any other questions on this particular subject?

Okay, thank you Steve.

At this time I would like to introduce our next speaker, Dr. Harvey Seiger. He really needs no introduction. He has been around longer than I have. He is with Heliotek Corporation, a Division of Tektron, and at this time he would like to have a discussion on the NASA Supported Contract, which is NAS-511547, which dealt with the characterization of control and recombination electrodes.

I don't know if you are all familiar with that report, but it dealt primarily with the fading mechanism associated in nickel cadmium cells and its effect on cycle life.

Dr. Seiger?

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SEIGER: Sometime in July or August, I received a copy of the final report on the characterization of the recombination and control electrodes under the contract NAS-511547.

And there were three areas in this report that caused concern. Now, if this were a journal article, I would be able to write a letter to the editor, and have some response from the authors in the discussion section.

Well, there are several alternative ways of my asking the questions, but only one way that I really consider ethical. So I wrote to one of the authors and pointed out, "There was always a fear that at some future time someone will try to argue a point based on invalid statements in some report."

Now, my letter was answered. My first question was not responded to. The second question was unsatisfactorily answered, by stating some statistical results that I am unable to generate. And also by stating some things that are not in the report at all, nor referenced in the report, and this, of course, implies that such information was not used in formulating the conclusions.

The third question was also unsatisfactorily answered. In fact, it was not really answered.

Now I mentioned my concern about the report to Chuck MacKenzie, who asked for a copy of the letter. This resulted in an invitation to ask my questons here in a pretty much formal manner, and the authors were asked to present their views here too, so I expect to be followed.

Now, before getting into the technical details, I think that the battery workshop is a good forum for discussion about reports. Perhaps we can have it run in a manner similar to the discussion session in the Electrochemical Society Journal. In this way, comments may be screened and passed on to the authors and the authors have an opportunity to reply prior to presentation here.

It so happens that this is pretty close to the procedure that we are using here now, and I think it might be helpful to the government, to the battery users and to those doing the contract work resulting in the reports.

I will tend to the technical details behind my questions, and start with the first one to which there was an answer.

It is concerned with the data on platinum migration which I have given in page B-1. Now, I haven't got the facilities to show the page B-1. Permit me to turn to it and to read a little.

Cells were made, that contain two recombination electrodes. EAch such recombination electrode contains by design, five milligrams of platinum per square centimeter for a total of 37.5 milligrams, plus or minus 10 percent of platinum on the average.

Now, next, they have some data in a table, and I happen to have worked some statistics with the table, so if I may have my first worksheet please?

(Slide.)

Before I get into that, in the table, there are some data for the analysis of platinum, and they give the terms of the cycle conditions, the temperature and the depth of discharge.

There are two pieces of data corresponding to the last two cells, which are 7 and 8. These are the two recombination electrodes from a cell from task 2, cell number 2.

9 and 10 are from another cell in task 2, cell number 4.

Although these are represented as having a 50 percent depth of discharge as the first three cells, I checked through the report, and last Friday I found that they had really been going through only a 25 percent depth of discharge.

And so, if we look at the numbers, at the data that they have, ranging from number 1 to number 6, we can see that they differ much from the mean value of 37.5 that they designed their electrodes to have.

Well, this about washes out really the question that I had, because here we have three cells who are much different and show no overlap between the data that are presented. However, I did do the statistics, and I would rather use them, and not let them go to waste, and see whether they can be used even as they were originally given, to establish that there was no platinum migration.

The sentence that I object to, let me read it: "It is apparent from the above analysis that the platinum has not moved out of the recombination electrodes."

Well, how do we treat data if we want to show whether a sample has changed or not?

We strike an average of all the data, and we compare it to the expected value, which is 37 1/2 milligrams, plus or minus 10 percent as given in the report, and we will use a student T test in order to see whether these numbers are the same or whether they are different.

And when we do this, we have to set up the null hypothesis. We make the assumption that they are not different, that these numbers are really the same, and we are going to look for a probability that this is so.

The student T function, and I use the one-sided function, because they are looking for migration, which means that it must decrease. The one-sided function is taken from a book by Volk, and it is given up there as T is equal to X Bar, which is the average determination of the experimental determination, and M is the mean value of 37 1/2 milligrams.

We have the square root of N, which are the number of samples, and we have our approximation to the standard deviation.

Since we are dealing with ten samples, ten pieces of data, we are pooling it because this was indicated by the letter from GE, that they have pooled it. The number of degrees of freedom is nine.

The average value is 31.7. It is different, it has decreased from the mean value by about 15 percent. The deviations on the next column, they sum to zero as they should. The deviation squares are on the third column, and the sum of the squares is 202.10. And from that we are able to calculate out and get our approximation to the standard deviation, which is 4.74.

We now have enough numbers to put it into the student T function, which is T is equal to 31.7 minus 37.5, over 4.74. All that multiplied by the square root of 10, which is equal to minus 3.87.

I am saying all this for the purpose of the recorder.

Now, at what level shall we test the significance of this value of T?

The authors responded that on a 95 percent confidence level there has been no migration, so we will use the 95 percent level to test for significance. And I happen to have the values of the distribution of T for a probability of .05 with 9 degrees of freedom from one-sided. That happens to be equal to the same as the probability value of 90 percent for 9 degrees of freedom for a two-sided test, which is minus 1.833.

For interest, I happen to have that for a two-sided test, too.

Since we find that the absolute value of T is greater than the value of P taken from the tables, the null hypothesis is rejected. And hence, the statement that the mean value of 31.7 has not -- that mean value, that statement has not been proved.

And so I have to formulate a question, and with these kind of data, plus my first considerations about differences of cell 2 from test 2 and cell 4, which really shouldn't be pooled, I formulate this question which is:

Since the experimental data do not support the statenent made about platinum migration, how can such a statement be justified?

(Slide.)

NOw the second area I have deals with the shunt voltage regulator hypothesis, and my question deals with the lack of consideration of the electrochemical processes that occur at the recombination electrode when current is passing through it.

If we formulate a hypotheses, we should make it self-consistent by considering all things that are occurring. There are several comments that must be made about this part of the report additionally.

ON page 103, the low-pressure hypothesis is noted. And an example is given for a cell from a previous report, with a recombination electrode. The cell yielded about 7 ampere hours after a C over 10 charge, and 12 ampere hours after a C over 2 charge. A similar result with a similar experiment has been observed in another laboratory by Lerner, and led him to postulate the low-pressure hypothesis.

Now, in this experiment, which is considered an extension of the earlier one, resistors were placed between the recombination electrode and the negatives, so the early experiment was done with merely the contact resistance, and we are now increasing it by a tenth of an ohm in two cells,

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and in two others, increasing it additionally up to two ohms.

Now the data are in table 28. I can't show you that, but I have it here if anyone is interested. 6 ampere hour cells were charged at C over 10 and they did yield 6 ampere hours whether the resistor was a tenth of an ohm or two ohms.

The experimental observation is that on continued cycling, the dischargeable capacity of the negative electrode decreased.

Now, let's see what is done with this information.

On page 128, the last paragraph explains only areas of the negatives with low film resistance would be recharged. So if you have an area with a high film resistance, it would not be recharged.

Now this is worded more strongly on page 132 on the third line, where it was stated that the massed areas of the negative electrode will have a rapidly diminishing charging rate, and these areas are: "These areas are unlikely to be recharged."

Now, let us contrast these questions to the last observation -- pardon me -- these quotations -- to the last observation stated on page 133, where they say the lost cadmium capacity is still present in the cell, but is unavailable at practical discharge rates.

Off the record for a moment.

(Statement off the record.)

SEIGER: BAck on the record.

NOw, is the purpose of this eight-page long ad hoc hypothesis to show how the electrode can't be charged in accordance with the quotations on page 128 and 132?

Or, is the purpose to show how the cadmium is there, but can't be discharged at the rate used in accordance with the quotation on page 133?

Well, upon my first reading, and my past experience with such cells, I reckoned that the hypothesis was promulgated to explain a failure to charge, and the hypothesis does indeed develop this premise.

With the confusion that surrounds this, I must set my sights on only one item in this. There is a circuit on page 130, which shows two parallel circuits, one for the recombination electrode and the other one for the negative electrode.

Now current going through the recombination electrode branch prevents charging, using the quotes on pages 128 and 132. It prevents charging of the negative electrode.

Now, what is the current doing electrochemically when it goes through the recombination electrode?

There are three items that we can postulate off hand.

Number one, we can say that the oxidation state of the of the recombination electrode is changing.

nm75

But, let's reject that one, because the materials are either already reduced, or they are inert.

Second item, we can postulate, is, well, hydrogen is being evolved. That would account for the current going through the recombination branch.

Let's reject that one too, because the pressures are low and hydrogen does not react with the positive electrode under these conditions.

Item three, oxygen is being consumed.

If this is accepted, then the entire shunt voltage regulator hypothesis degrades to Lerner's low pressure ad hoc hypothesis.

Instead of eight pages, we can substitute one or two pages.

Now, there are decrease in capacity of the positive electrodes given in the experimental evidence. Since this behavior is not accounted for in any manner, we cannot endorse any hypothesis, nor move it to a rank of theory.

I should point out that the two hypotheses would direct any efforts towards solution of the problem, to two different electrodes. So that the area does have some technological importance.

I may now formulate a question with two parts, which is directed towards the authors:

A. How can you resolve the aspect of the hypothesis that postulates uncharged areas with the stated observation that the material is present as cadmium charged, but is undischargeable at the rates used?

B. How can you justify not accounting for the current in the recombination circuit in terms of the electrochemical processes in that branch?

My third area of concern deals with the conclusions on hydrogen recombination.

May I have the third chart, please?

(Slide.)

While Tom is getting that up, I should mention that Paul Ritterman observed that hydrogen can be recombined in cells such as these with fuel cell electrode present. The references for this one are the second and third quarterly reports to the United States Air Force under contract AF33-(615)-5357. And credit by reference should have been made in this report, and I do want to thank Chuck ~~McKenzie~~ MacKenzie for locating the references for me.

Now, on page 121, there is an equation expressing the pressure decay for hydrogen in cells having a recombination electrode for their experimental data.

Now this equation is right up here on the third worksheet taken directly out of the report. It is Y equals A plus BX. Well, Y is the pressure, X is time, A and B are constants. Where A is the boundary condition and X equals

SHUNT VOLTAGE REGULATOR HYPOTHESIS

P113 LOW PRESSURE HYPOTHESIS - POOR CHARGE ACCEPTANCE OF POSITIVES WHEN A RECOMBINATION ELECTRODE IS PRESENT.

P114 TABLE 28 c/n CHARGE DATA DIFFERS FROM P103 lines 3-5.

P128 CURRENT SPLITTING

1. CURRENT PROCESS IN Cd BRANCH IS CHARGING

   $Cd(OH)_2 + 2e^- \longrightarrow Cd + 2\,OH^-$

2. CURRENT PROCESS IN RECOMBINATION ELECTRODE BRANCH NOT DISCUSSED.
   AS ABOVE CONSERVATION LAWS OF MATTER AND CHARGE SHOULD BE USED.

   POSSIBILITIES :
   a) OXIDATION STATE OF ELECTRODE MATTER IS REDUCED (RULED OUT BECAUSE MATERIALS ARE IN REDUCED STATE OR INERT).

   b) HYDROGEN IS EVOLVED (RULED OUT BECAUSE PRESSURE IS LOW)

   c) OXYGEN IS CONSUMED - LEADS TO LOW PRESSURE HYPOTHESIS.

$\left\{\begin{array}{l}\text{P132 LOCAL UNCHARGED AREAS} \\ \text{P133 LOST Cd CAPACITY STILL IN CELLS.}\end{array}\right.$

PLATINUM MIGRATION DATA
"t" TEST

p.81

ONE SIDED NULL HYPOTHESIS

$$t = \frac{\bar{x}-m}{S_{(x)}}\cdot\sqrt{n} \quad , \quad m = 37.5,\ n = 10,\ D.F. = 9$$

	x	d	d^2
1	31	-.7	.49
2	25	-6.7	44.89
3	26	-5.7	32.49
4	28	-3.7	13.69
5	33	1.3	1.69
6	28	-3.7	13.69
7	38	6.3	39.69
8	36	4.3	18.49
9	36	4.3	18.49
10	36	4.3	18.49
	$\Sigma x = 317$	$\Sigma d = 0$	$\Sigma d^2 = 202.10$

$\bar{x} = 31.7$

$$S_{(x)} = \sqrt{\frac{\Sigma d^2}{n-1}}.$$

$$S_{(x)} = 4.74$$

$$t = \frac{31.7-37.5}{4.74}\cdot\sqrt{10} = -3.87$$

95% level test for significance

$P_{.05,9(1)} = P_{.10,9(2)} = -1.833$
$[P_{.05,9(2)} = 2.262]$

Since $|t| > |P_{.05}|$, THE NULL HYPOTHESIS IS REJECTED

Hence, the statement that $\bar{x} = m$ has not been proved.

HYDROGEN RECOMBINATION

P 121 $Y = A + BX$,
Y = PRESSURE
X = TIME
A, B are consts.
(A = pressure at X=0)
(B = Slope)

RATE = PRESSURE DECREASE PER UNIT TIME

$$\text{RATE} = \frac{dY}{dX} = B.$$

QUANTITY OF $Cd(OH)_2$ IS NOT IN RATE EQUATION.
THEREFORE, UNDER CONDITIONS OF THIS EXPERIMENT THE RATE IS INDEPENDENT OF QUANTITY $Cd(OH)_2$.

zero. The initial hydrogen pressure.

B is the slope, and as we shall see, it is later identified as the rate of hydrogen consumption.

Now the experiment was run having a resistor between the recombination electrode and the negative electrode. The question of limitation of the rate by the resistor was considered -- not in the report -- I considered it, and I concur with the authors that the reaction can be studied even under these conditions.

Since the conclusion I question is concerned with the rate dependency on quantity of cadmium hydroxide, let's obtain the rate directly from this equation.

Now rate is the pressure decraese per unit time, which we can get very simply by taking that equation and using simple differential calculus obtaining DY by DX is equal to B.

The quantity of cadmium hydroxide is not in the rate equation, and therefore, under the conditions of which the experiment was run, the rate is independent of the quantity of cadmium hydroxide which brings us to the third question.

Since the experimental data do not support the conclusion, how can the conclusion be justified?

Thank you. I have the questions written down here. I would like to put them up, in case anyone needs a reminder.

FORD: Are there any questions at this point?

CATHERINO: First of all, I would like to thank what's his name --

(Laughter.)

-- for taking the time, actually, to go through this thing and to give a critical evaluation of it.

Now, I think a perspective has to be established. A lot of this was read out of context, and perhaps a great many people haven't read the report to understand just what was said in it.

Now, I can only tell you, and if you care to have a copy of this report, you can either send me a note or anyone down at the Battery Products Division in Gainesville, and we would be very happy to send you a copy of this original report.

Now in perspective, these points that were raised amount to ancillary arguments, but do not really get down to the substance of the report, so that in essence, by not even answering the questions, the substantive aspects still remain. However, let's go through some of these.

First of all, I would just point out that the letter he was talking about was sent to Bill CArson, and I would just like to read the first part of the reply.

I have sent on your letter of August 6th to my colleagues at Gainesville, who wrote the bulk of this report. And as Bill Carson continues, -- as usual, I find myself disagreeing with you on all the points you raised.

Then he goes on -- well, the reply was, of course, quick, and it was pointed out in there that he couldn't go through a detailed, point by point rebuttal, but I will try to get to the essence of this if I can, in a short time.

First, let me answer the question on the hydrogen recombination.

Here again is the problem of trying to read too much into a rather trivial statement.

Is there a dependence?

Well, I think the rather detailed analysis showed that a zero order dependence exists on cadmium hydroxide over most of the reaction.

But after speaking with the people involved in this report, they made it rather clear that this was really going a little too far. The intention was -- well, let's look at this this way -- hydrogen is oxidized on the recombination electrode. Something has to be reduced. That substance is cadmium hydroxide. If there were no cadmium hydroxide, there could be no hydrogen oxidation. Therefore, the dependence is obvious.

Point two, the platinum electrode migration -- now I might just say thatpage B-1 that was quoted, does turn out to be in the appendix. And the points are well taken. I have to admit, there was some information that was left out. Actually a few sentences.

IN this work, the recombination electrode is taken, and some of the catalytic material is removed, in order to expose part of the screen. To this screen, then, a tab is welded.

Now, if one compensates for the removal of this catalytic material, the data falls right where it is supposed to be.

So, really, we are at fault there for omitting those few descriptive sentences.

On the last part, the low pressure theory versus the shunt voltage mechanism, essentially these are two formulations of observed hypotheses. ONe involves -- well, the low-pressure theory involves the effects on the positive. The shunt voltage mechanism involves the effects on the negative.

Now, these are really formulations of fundamental phenomena that have been observed.

Now if we care to quibble about the details of how we set up this mechanism, this would make good cocktail lounge patter, but here we are looking for a way to make a better cell.

Now GE does not take any position one way or the other on the low-pressure hypothesis. However, it took this idea of the shunt mechanism, voltage shunt mechanism, and applied it toward making a better cell.

The point is basically this, the negatives were fading. Something had to be done. A precharge was used, and as a result, a better cell resulted.

Now, in effect, there was the first point that was raised that wasn't really too clear to me, but otherwise, I believe that all points have been taken care of.

FORD: THank you, DR. Catherino.

ARe there any other questions on this subject?

Any comments?

I am sorry we don't have extra copies of the report to pass out. If we did, you wouldn't have time to read it anyway.

(Laughter.)

John Unger?

UNGER: Dr. Catherino, I just wanted to clarify the response on the hydrogen recombination. You indicated that if hydrogen was being oxidized at the recombination electrode, that this would require that somewhere, something was being reduced. And you indicated that the only possible species for this reaction was the cadmium hydroxide.

Under what conditions was this?

Would this be during charge, or would this be an open circuit stand, or perhaps during discharge that the hydrogen --

CATHERINO: I am quoting from memory from merely reading the report.

The way this was done, the cell was opened and filled with hydrogen, and the hydrogen pressure was then monitored, and it went to zero.

UNGER: But what was the condition of the cell? Was the cell shorted, the active electrode to the cell?

CATHERINO: I am not sure. I believe this was open circuit.

SEIGER: You had two conditions. YOu had one of open circuit, and in some cases, you actually performed a discharge.

And the equation drawn was written on the open-circuit conditions.

UNGER: All right.

Well then, in that case, obviously the negative electrode is the only thing connected tothe recombination electrode. I just wanted to clarify those conditions, because under certain conditions there are lots of other reactions that could be going on inside the cell.

CATHERINO: In this connection I would like to just raise the point here that although the report was entitled the Characterization of Auxiliary and Recombination Electrodes, it turned out to be more of a study of precharge, which is basically what most of this conference is about this afternoon.

SEIGER: There are several questions that you really did leave unanswered. For instance, when you go back to page B-1 -- incidentally, I tried to be extremely careful, Dr. Catherino, and I do remember your name -- on reading the statement, so that I shouldn't change the meaning of anything by taking it out of context. And I will challenge you to show where meanings have been changed. Let anybody here read the reports. They will see that I haven't changed them. Let me rebuke you on that.

I would like to say, that in the task 3 cells, which were indeed run at 50 percent depth of discharge, you may have scraped off your material, in which case, the question comes up, how come then, in the task 2 cells, run at 25 percent depth of discharge -- and let's record again, that these two cells were run according to this report, at 25 percent, depth -- how come these give numbers that are much closer to the design of 37.5. These numbers are respectively 38, 36, 36, 36.

So, with that kind of evidence, and the other things that I have found in the report, I hold your statement suspect, and I will question you further on that.

Frankly, I would like to resolve these. Let me read very particularly the statement right from the report on page B-1. It is apparent from the above analyses that the platinum has not moved out of the recombination electrodes."

I don't know whether it did or it didn't. The way the experiment was set up and run does not substantiate that conclusion. So one can't say it is apparent.

Now, this particular statement winds up in about three places, two others besides here. And one of them is in the conclusion.

Now, if it is in the conclusion, I think you ought to give a little more weight to it.

CATHERINO: Now may I reply to that?

That particular piece of evidence was intended to support the problem of changes of reactivity of the auxiliary electrode. This was attributed, and there is sufficient evidence in there to substantiate, that this was due to movement of electrolyte.

Now, in order to pursue this, an attempt was made to relate it to the catalytic material on the recombination electrodes, and I have to point out again, that you say there are certain differences involved. The materials taken off by hand, it has tried -- we tried to meet certain specifications in building that recombination electrode. There are times when the tolerances are difficult to achieve.

SEIGER: VEry simply.

Let me repeat the question.

Could you, from the data that you have, the way it is reported here on page B-1 -- and I will read the entire thing if you so wish -- could you so state that it is apparent from the above analysis that the platinum has not moved out of the recombination electrode?

From what you are telling me, you don't have any evidence whatsoever, to make that statement.

CATHERINO: Oh, of course we do.

SEIGER: Where?

CATHERINO: I just said --

SEIGER: It is apparent from the above analysis --

FORD: Gentlemen, I will have to cut it.

I would like to suggest that you get together over cocktails, because I think it will be an interesting evening.

(Laughter)

I would like to take the chance to entertain other comments on this..

Steve, you had your hand up?

Are there others?

GASTON: Gaston, Grumman.

I just have a general question.

The platinum migration apparently is no longer a problem. I have seen earlier reports where it was a problem.

Actually, what has occured in the construction of the recombination electrode, which makes the migration no longer a problem?

CATHERINO: I think in this case, you see, this is a relative measure that you are talking about, when you say platinum doesn't migrate.

Now, if you want to take this down to a microscopic level, for example if you put in a lead electrode, which is extremely sensitive to the presence of platinum, this becomes important. And you can show some migration may take place here.

Now in this particular case, analyses of the membrane materials in there, of the -- searching the inside of the cell, did not show any platinum located in other places. And also the analytical data, when appropriately corrected with this information it wasn't in, also falls in within the appropriate confidence intervals, to show that within the analytical method, no platinum had migrated.

FORD: Okay, let's take one other question, and then we will have to close it, I believe.

WEININGER: My name is Weininger, G.E.

This happens to be no connection with defending this particular report, but I happen to be one of the editors of the journal that Harvey has mentioned, and maybe as a matter of comic relief, he might be interested -- Harvey -- that for two or three years we have been considering to give up and disband with this particular section.

(Laughter.)

Whether or not this is a good analogy, I leave up to you, the audience, to decide. But it raises a different point, which I am serious about, and it is interesting because in the editorial board I am one of the minority who believes that references to contract reports should not be allowed in the Journal.

The reason is that reports, possibly one like this under discussion here, are written in a great deal of a hurry towards meeting a deadline, and most of all, are not reviewed by external referees. And for that reason, I think it is difficult to justify giving equal reliance to these final government reports, as we are to other literature references which are reviewed.

And this is strictly a minority opinion.

FORD: Thank you.

I think that with that we will close it.

I would like to thank Dr. Seiger for his vigorous going over this, and I would also like to thank Dr. Catherino for responding.

CATHERINO: I would just like to add one other thing.

Would you please tell them what the results of the test were for the hardware?

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FORD: Oh, okay.

These were the first recombination electrode cells that I am aware of that have gone over a year. We currently have second generation of these where we are looking at the higher resistor.

I might point out that the results of this work has gone directly in the Apollo telescope mount batteries which General Electric is producing for Huntsville at this point.

N71-28669

Without further ado, I would like to introduce Sam Bogner, of Jet Propulsion Laboratory, and he would like to take a few minutes on the Mariner 71 Batteries.

Sam?

BOGNER: I have a couple of topics to discuss. It is not quite as technical, I guess, as some of the discussions we have seen lately this afternoon, and it is at the far extreme of Jerry's first slide that he put on this morning.

I am going to more or less talk about the hardware, and maybe getting back close to what Steve Gaston was talking about, what do we do with the battery after we have got it? How do we keep in top condition, and make sure it is a good battery when we fly it?

So the particular battery I am talking about is for the Mariner spacecraft, and this is a picture of it.

The battery actually fits in one of the -- what we call the bays. We have eight bays on the spacecraft, with thermal control right on the bay.

So the battery fits right into that bay and it is easily put on and removed from the spacecraft in comparison to some other spacecrafts.

(Slide.)

The design of the battery, the packaging concept, is that it is an integral part of the structure, so the battery helps hold the spacecraft together. It consists of 26 cells laid in two rows. Each cell is insulated with a wrap of fiberglass. The cells are retained in the chassis by compressive forces. We use no potting, and we have good heat conduction through louver control.

The size of the battery is approximately 20 inches by 18 inches by 4.1 inches.

The cells that we use are 20 ampere hour cell.

The battery is mounted both to the inner and outer ring on the spacecraft buss. We have temperature transducers on the center cells and also thermal switches, that shut off the charge, should we get it too warm.

(Slide.)

This is what the battery looks like. Here it is being prepared for thermal vacuum testing.

The temperature transducers measure the temperature of the battery, are located here -- one on each side in the center of the battery, where we expect the temperature to be the warmest. However, during thermal vacuum testing, we found out that we only have about a 3 degree spread from one end of the battery to the other, so we have a fairly uniform temperature.

(Slide.)

This is a start of the assembly of it. Here are the cells being wrapped.

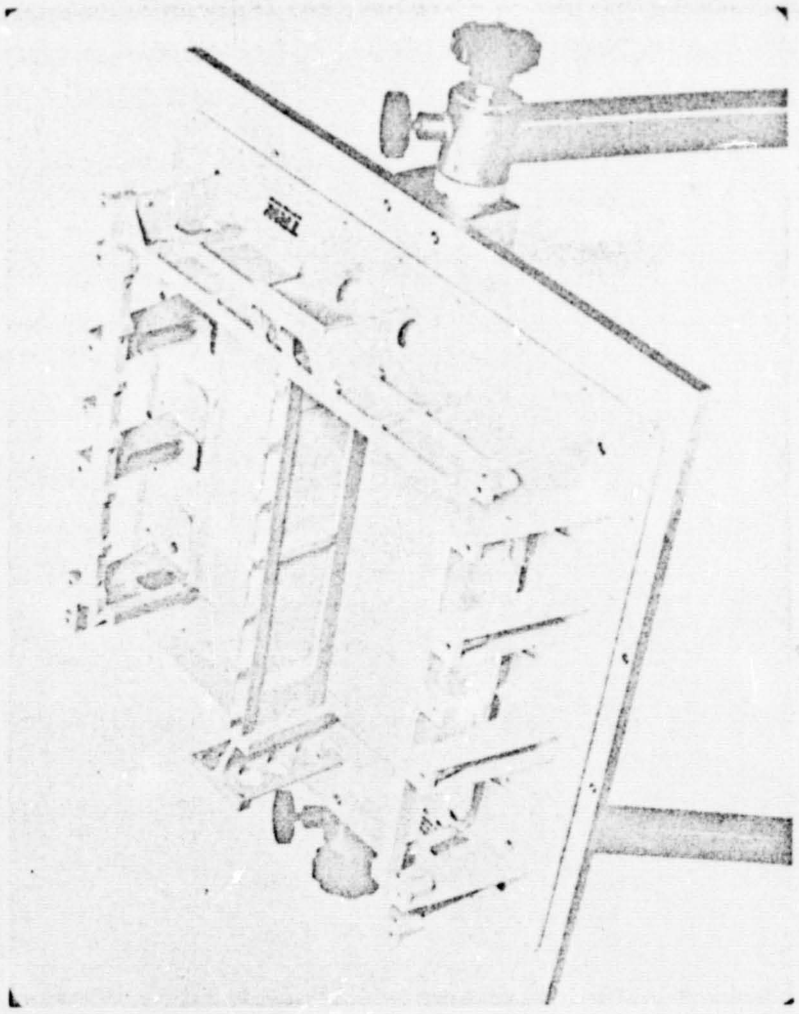
(Slide.)

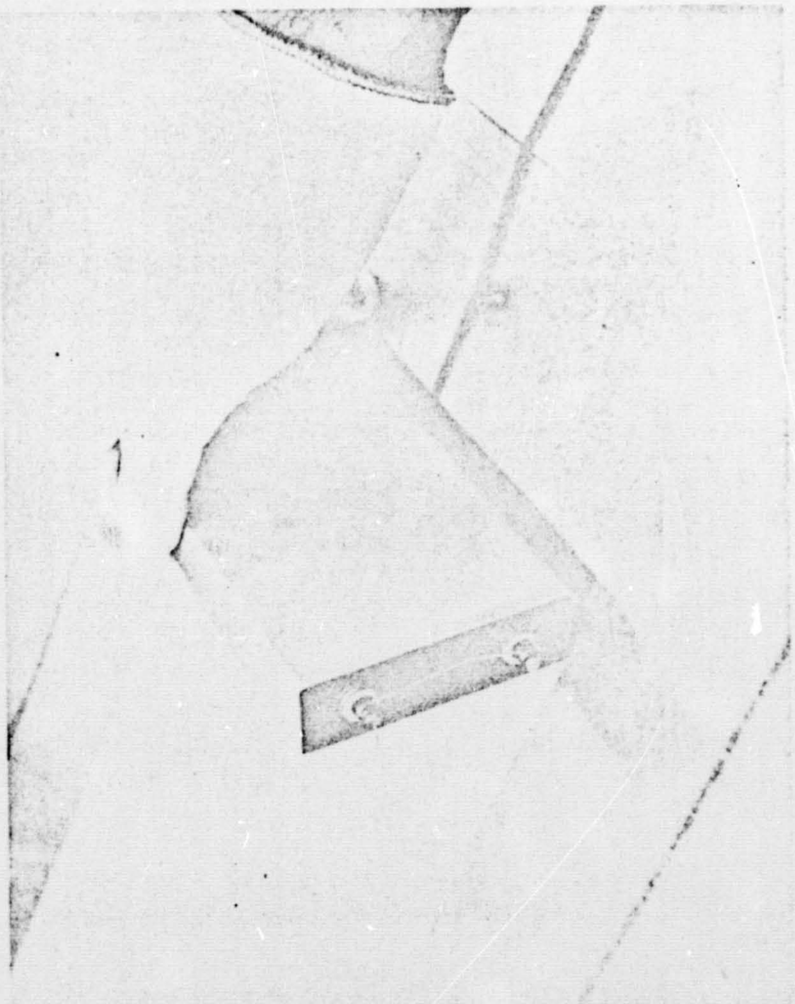
This is the chassis for the battery which is machined out of a solid block of magnesium, so it is quite a job producing that chassis.

This is a cell compression picture, where the cells are prestressed to get the correct lengths, so we have the proper compression when we mount them in the battery.

By the way, this battery was built by TRW. Here it shows the center cell and our thermal plate that the temperature transducers are mounted on and the thermal switches, so that we have kind of an average temperature across the cell.

Another picture of the mounting of the cells in





MM 71 BATTERY DESIGN

- PACKAGING CONCEPT
  INTERGRAL PART OF SPACECRAFT STRUCTURE
- 26 CELLS IN TWO ROWS
- EACH CELL WRAPPED IN GLASS TAPE
- CELLS RETAINED IN CHASSIS BY COMPRESSIVE FORCES
- NO POTTING
- GOOD HEAT CONDUCTION
  LOUVER CONTROLLED
- SIZE
  20" x 18" x 4.1"
- MOUNTED TO INNER & OUTER RINGS OF S/C BUS
- TEMPERATURE TRANSDUCERS ON CENTER CELLS
- THERMAL SWITCHES ON CENTER CELLS

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the chassis. We have a coating or layer of RTV compound so we have good thermal conduction between the baseplate of the battery -- if you tilt that up -- the part that you can't see is the part that is on the outside of the spacecraft and the louvers are mounted on that side of the battery.

This is another step in the assembly where they are putting the keeper bars along the sides of the cells, or the ends.

Here they are compressing the cells back before they tighten down the keeper bars.

(Slide.)

And here was some testing that we did. Our project management, I guess, shortly after the Apollo incident, were kind of interested in what kind of pressures these cells would hold. So we ran some pressure tests. This particular cell was a GE cell, and we tested this one unrestrained. The picture here was taken at about 300 pounds and we looked at it at 500 psi, and it was still the same shape.

After that we didn't look at it any more.

(Laughter.)

(Slide.)

This is the cell after it left go, and it left go at approximately 1100 psi.

We blew these cells using compressed nitrogen and increasing the pressure at about 50 pounds per minute. So perhaps if we had pressurized them a little more slowly, they might have burst at a little lower pressure.

(Slide.)

This is another shot of a Gulton cell that we tested restrained, and --

(Laughter.)

-- here is part of it. This is the kind of testing I like. That was about 1300 psi.

(Slide.)

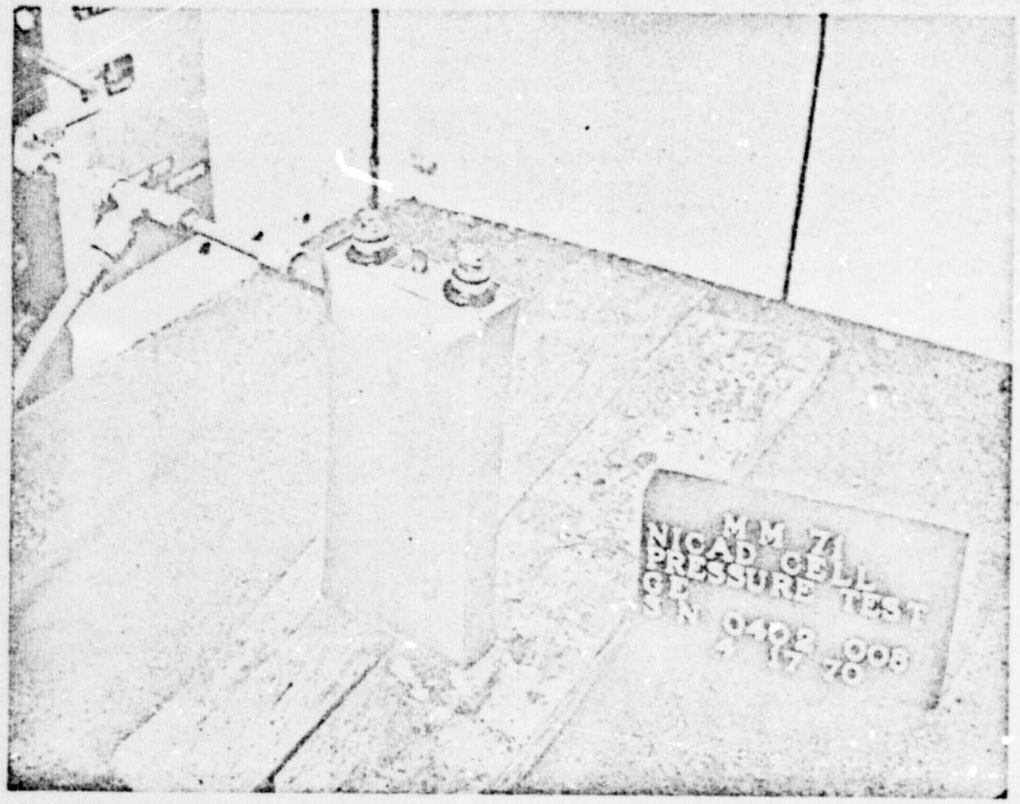
This is a typical charge discharge of the battery. And that we performed in thermal vac.

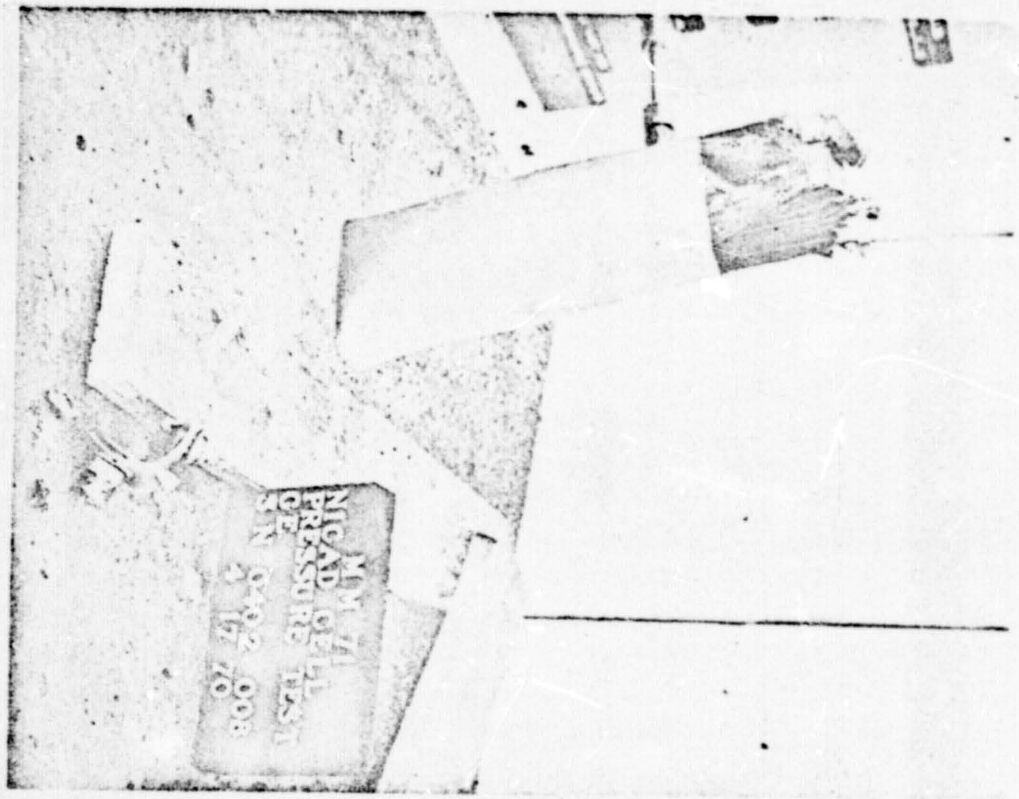
The battery baseplate is actually the temperature control in the thermal vacuum chamber. It wasn't the battery itself, it was the baseplate the battery was sitting on. So we got about 27.6 ampere hours, and we built a total of ten batteries on this program, and most of them are running plus or minus about one ampere hour.

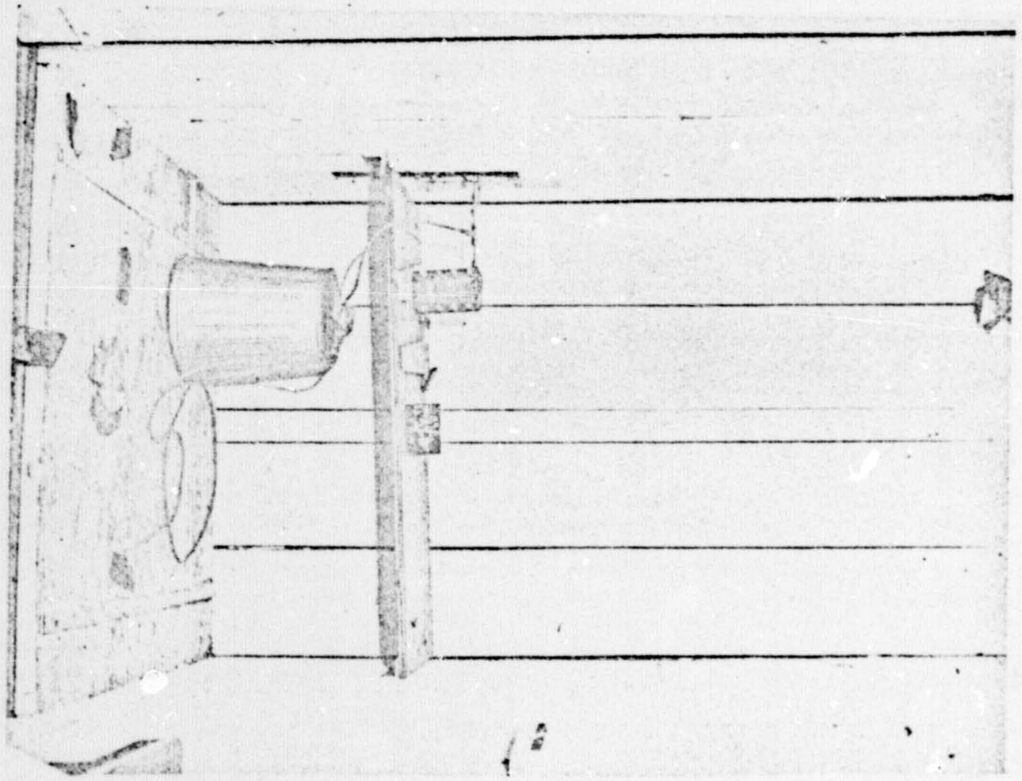
So they are all pretty close right now.

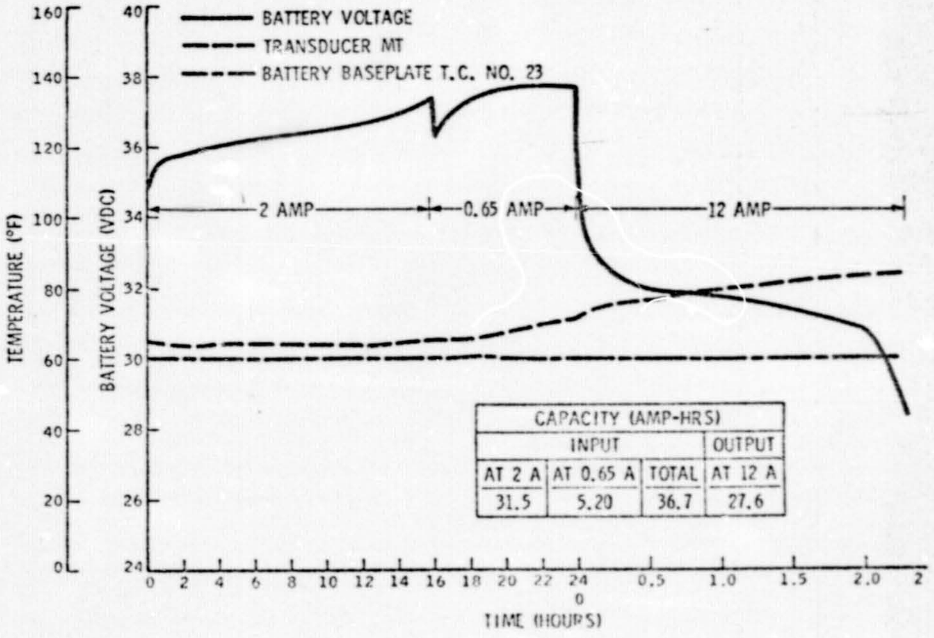
It is a little too early to tell if we are going to have the same problems that Steve has had and showed us this afternoon.

(Slide.)









CAPACITY (AMP-HRS)			
INPUT			OUTPUT
AT 2 A	AT 0.65 A	TOTAL	AT 12 A
31.5	5.20	36.7	27.6

I would like to quickly run through and this is what we are proposing to our management on how to handle the battery.

Briefly, we had three basic plans that we considered and I will go through and show our handling flow plan. You probably aren't interested in our schedule. Our flight battery lab operations -- in other words, what we do with the battery in the lab. Our selection-rejection criteria for the battery and constraints that we are going to attempt to impose on the project while the battery is on the spacecraft. And then briefly, some of the testing that we are doing in the lab to help characterize the batteries.

(Slide.)

Plan A. We would not install the flight battery until we get down to the Cape, and shortly before launch. This is the way we have handled it in the past. Of course, on other flight programs, we have flown silver zinc batteries and the life there is a little more critical, we feel, than it is on the nicad.

In this plan, of course, we would have minimum handling, and very little uncontrolled environment. And when I say uncontrolled, I don't really mean it is uncontrolled, but it is not controlled like you have in the laboratory.

The disadvantages of not installing this battery until you are at the Cape, is that you have no operational performance data of the battery while it is on the spacecraft and we don't feel it really takes advantage of the nickad capability.

(Slide.)

Plan B is going to the other extreme, and put the battery on the spacecraft the first opportunity we have when they first start testing.

The advantages there are a maximum test experience at the spacecraft level. And it takes full advantage of the nicad capabilities.

The disadvantages that we see in installing these batteries early in the program, is that the temperature environment is not really well controlled, although they do have air conditioning, every so often it kind of fouls up and is not working.

We have additional vibration at the spacecraft level which we feel would degrade the reliability. And this is a point I haven't seen too much in the literature on, that is how much vibration can you keep giving a battery or a cell, and when do you really find out that it is harmful. This is something that we don't really know.

We have danger of improper testing, putting the battery on the spacecraft early in the game. And also we feel that it would require tighter operational constraints on the spacecraft systems test people.

(Slide.)

The plan that we finally came up with here, is that the battery would be installed on the spacecraft for the solar thermal vacuum testing, and the final system testing at the Eastern Test Range of the Cape.

The advantage to this program we saw was that we get the most realistic test data during the solar thermal vacuum testing, because we are actually trying to duplicate flight conditions, temperatures, and we don't feel that this should hamper spacecraft testing. WE get more meaningful data from the battery and battery charger interface on the spacecraft. And it minimizes exposure to possible harmful environments.

The disadvantages, possibly, are loss of test experience on the spacecraft and we have considerably more handling of the battery, and you don't know exactly what happens when they are carting these batteries back and forth between the battery lab and the spacecraft. Although we attempt to have someone ride along with each battery.

We did lose out on a point here where the program management said they would like to see us put this battery on the spacecraft for its vibration test.

(Slide.)

This is our handling flow plan. We received the

MM 71 BATTERY HANDLING & TESTS

OUTLINE

THREE BASIC PLANS & CONSIDERATIONS

HANDLING FLOW PLAN

SCHEDULE

FLIGHT BATTERY LAB OPERATIONS

SELECTION/REJECTION CRITERIA

CONSTRAINTS WHILE ON S/C

CHARACTERIZATION TESTING IN LAB

MM 71 BATTERY HANDLING & TESTS

PLAN A

FLIGHT BATTERY INSTALLED AT ETR

- ADVANTAGES
  - SAME AS PRIOR JPL PROJECTS
  - MINIMIZES HANDLING & UNCONTROLLED ENVIRONMENT
- DISADVANTAGES
  - NO OPERATIONAL & PERFORMANCE DATA ON S/C
  - DOES NOT TAKE ADVANTAGE OF NI/CD CAPABILITY

MM 71 BATTERY HANDLING & TESTS

PLAN B

FLIGHT BATTERY INSTALLED FOR S/C TESTING

- ADVANTAGES
  - MAXIMUM TEST EXPERIENCE AT S/C LEVEL
  - FULL ADVANTAGE OF NI/CD CAPABILITIES
- DISADVANTAGES
  - TEMPERATURE ENVIRONMENT NOT WELL CONTROLLED
  - ADDITIONAL VIBRATION DEGRADES RELIABILITY
  - DANGER OF IMPROPER TESTING
  - REQUIRES TIGHTER OPERATIONAL CONSTRAINTS

MM 71 BATTERY HANDLING & TESTS

PLAN C RECOMMENDED

FLIGHT BATTERY INSTALLED FOR STV & FINAL SYSTEM TEST AT ETR

- ADVANTAGES
  - STV MOST REALISTIC TEST & DATA
  - SHOULD NOT HAMPER S/C TESTING
  - MEANINGFUL DATA BATTERY/CHARGER INTERFACE
  - MINIMIZES EXPOSURE TO POSSIBLE HARMFUL ENVIRONMENTS
- DISADVANTAGES
  - LOSS OF SOME TEST EXPERIENCE ON S/C
  - MORE HANDLING THAN PLAN A

batteries from TRW in July. We are storing them in the battery lab. AFter we get them in from TRW, we review the log book data. We have a hardware review at the project level. We perform a final leak test using the phenolpthalein leak test.

The batteries are cleaned. They go through a conformal coating of the terminals and all exposed surface. That is terminal encapsulation, not thermal encapsulation. And then it receives temperature control paint.

Steps 9 and 10 is charge and discharge calibration which I will mention in a minute, that we perform approximately once a month.

So we go through quite a bit of handling and back and forth between the lab and the spacecraft.

I will skip the schedule.

This is some of the work that we are doing in the lab, storing the batteries, performing conditioning cycling and then the final checkup and conditioning before flight.

(Slide.)

Storing the battery shorted, in the air-conditioned room where we have redundant air conditioning, because we have had problems there. So we keep the lab pretty close to 70 degrees.

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The batteries are kept in locked steel cabinets in their handling fixture, with connector savers on, and we have a minimum of mate-demates on the flight connectors, and then each time a battery is moved or anything is done to it, we keep a record of it and it is monitored by QA.

(Slide.)

This is a conditioning cycle that we perform on the batteries every four to six weeks. And it is performed on a heat sink where we control the temperature of the battery between 60 to 70 degrees. The charge and discharging is controlled by our bench test equipment. And the cycle consists of a 2-amp charge to 37.5 volts and then trickle charged for 24 hours.

Discharge cycle is 12 amps to one volt on the first cell.

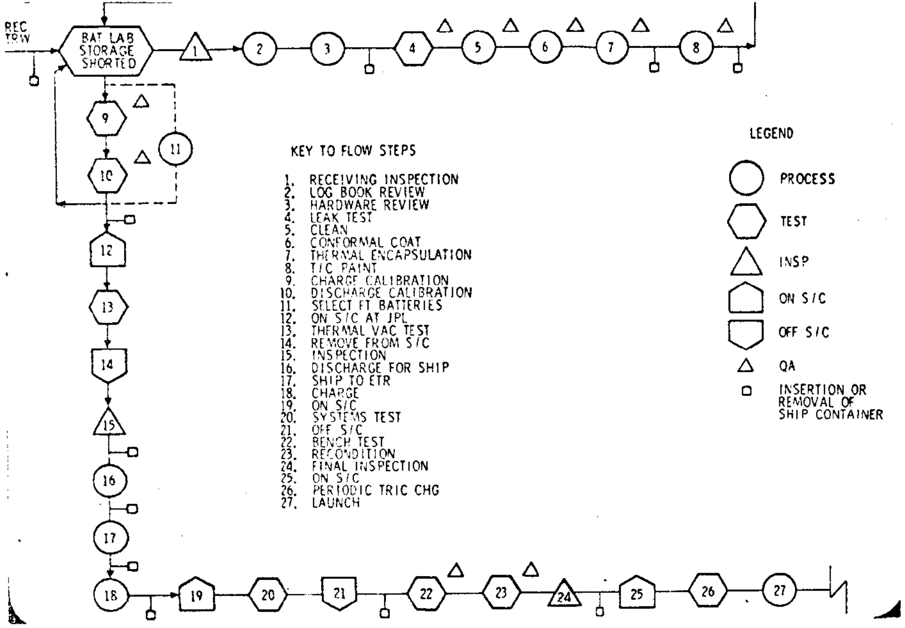
The battery is then shorted out and put back in storage.

And we keep a record, of course, of the temperature and battery cell voltages and the current.

(Slide.)

The final physical examination that we intend to give the battery would be, after it has been on the spacecraft through some systems test, and just before they take the spacecraft out to the explosive safe area, arm it, we remove the battery and give it a standard 12-amp discharge as received

MM'71 BATTERY HANDLING FLOW PLAN



KEY TO FLOW STEPS

1. RECEIVING INSPECTION
2. LOG BOOK REVIEW
3. HARDWARE REVIEW
4. LEAK TEST
5. CLEAN
6. CONFORMAL COAT
7. THERMAL ENCAPSULATION
8. T/C PAINT
9. CHARGE CALIBRATION
10. DISCHARGE CALIBRATION
11. SELECT FT BATTERIES
12. ON S/C AT JPL
13. THERMAL VAC TEST
14. REMOVE FROM S/C
15. INSPECTION
16. DISCHARGE FOR SHIP
17. SHIP TO ETR
18. CHARGE
19. ON S/C
20. SYSTEMS TEST
21. OFF S/C
22. BENCH TEST
23. RECONDITION
24. FINAL INSPECTION
25. ON S/C
26. PERIODIC TRIC CHG
27. LAUNCH

MM 71 BATTERY HANDLING & TESTS

FLIGHT BATTERY LAB OPERATIONS

STORAGE

CONDITIONING CYCLES

FINAL CHECK UP AND CONDITIONING

MM 71 BATTERY HANDLING & TESTS

STORAGE

SHORTED

AIR CONDITIONED ROOM REDUNDANT 189-2

LOCKED STEEL CABINETS

IN HANDLING FIXTURE

CONNECTOR SAVERS ON

RECORD OF EACH TIME BATTERY MOVED QA

MM 71 BATTERY HANDLING & TESTS

CONDITIONING CYCLE

CHARGE/DISCHARGE 4 - 6 WEEK INTERVALS

PERFORMED ON HEAT SINK

CONTROLLED BY BTE

CHARGE CYCLE 2A TO 37.5V THEN T/C 24 HR

DISCHARGE CYCLE 12A TO 1.0V 1st CELL

DATA RECORDED
- TEMPERATURE
- BATTERY/CELL VOLTAGES
- CURRENT

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from the spacecraft, see what kind of condition they kept it in, run a charge retention test for shorts, and then bench test, which consists of diode leakage, pin insulation resistance, wiring contininuity and chassis to battery leakage, give it a charge-discharge cycle, and final visual examination.

(Slide.)

This is a section rejection criteria that we use to pick the flight battery. We have five batteries. We will be flying two spacecraft, so we will pick two of the best batteries, we hope. Then we will have a backup battery, too.

The selection criteria, the capacity, the charge time is 37.5 volts. This should give us some measure of whether we are having the problem that Steve had where the voltage is going up on him. If it goes up on us, we should probably reach this 37.5 volts quicker than normal.

Cell uniformity, that should be delta V between the cells. And also uniformity from cycle to cycle.

And rejection criteria. I think most everybody would probably agree, if we have electrolyte leaks or internal shorts, battery to chassis shorts and mechanical defects, et cetera.

(Slide.)

Constraints that we will hold the spacecraft testing to is a maximum 60 percent depth of discharge on the spacecraft, for approximately 12 ampere hours.

Maximum temperature that we will allow them to see is 100 degrees F, at an end of a discharge, or they should not be over 80 degrees F if they are continuously operating.

We will trickle charge the batteries eight hours a day. This is about a C over 30 rate. Anytime they use a battery, we are requesting that they recharge it at the higher rate, before they switch to the trickle.

And any notification of any unplanned tests, and we require that they keep good records. We have a charge voltage versus temperature limits that we hold them to.

(Slide.)

Some of the tests that we are doing in the lab. We are running overcharged reversed discharge testing. Charged voltage limits. Extended mission tests.

One of these tests consists of an 80 percent depth of discharge. A 33 hour orbit. It is about a 3 1/2 hour discharge. The rest of the time is used for charging.

Performing storage tests which are in process, storing the cells shorted, discharged open circuit, and just plain open circuited charge.

On the batteries, we will be performing monthly cycling. Perform the battery, battery charge compatibility test, mission profile tests on two batteries, which we have

MM 71 BATTERY HANDLING & TESTS

FINAL PHYSICAL EXAMINATION

STANDARD 12A DISCHARGE AS RECEIVED

CHARGE RETENTION TEST FOR SHORTS

BENCH TEST

- DIODE LEAK
- PIN INSULATION RESISTANCE
- WIRING CONTINUITY
- CHASSIS TO BATTERY LEAKAGE

CHARGE/DISCHARGE/CHARGE

VISUAL INSPECTION

MM 71 BATTERY HANDLING & TESTS

SELECTION/REJECTION CRITERIA

SELECTION	REJECTION
CAPACITY	ELECTROLYTE LEAKS
CHARGE TIME TO 37.5V	CELL SHORTS INTERNAL
CELL UNIFORMITY V	BATTERY TO CHASSIS SHORTS
UNIFORMITY CYCLE TO CYCLE	CAPACITY MIN. 20 A-H
	MECHANICAL DEFECTS
	HIGH TEMPERATURE 100°F FOR 24 HOURS

DATA SOURCE: JPL & TRW TESTS

MM 71 BATTERY HANDLING & TESTS

CONSTRAINTS WHILE ON S/C

MAXIMUM 60% DOD 12 A-H

MAXIMUM TEMPERATURE

- 100°F END OF DISCHARGE
- 80°F CONTINUOUS

TRICKLE CHARGE 8 HRS/DAY REQUIRED

RECHARGE AT HIGH RATE

NOTIFICATION OF UNPLANNED TEST

GOOD RECORDS OF USE

CHARGE VOLTAGE VS TEMPERATURE LIMITS

MM 71 BATTERY HANDLING & TESTS

CHARACTERIZATION TESTING

CELLS

- OVERCHARGE/REVERSE DISCHARGE - 610-143
- CHARGE VOLTAGE LIMIT - COMPLETED
- EXTENDED MISSION - IN PROCESS
- STORAGE - IN PROCESS
- MISSION PROFILE EM 342-106

BATTERY

- MONTHLY CYCLING ALL BATTERIES
- BATTERY/BATTERY CHARGER COMPATIBILITY EM 342-120
- MISSION PROFILE 2 BATTERIES - INITIATED
- CHARGE VOLTAGE VS TEMPERATURE NOT STARTED
- BATTERY PERFORMANCE TEMP - LOAD - STATE OF CHARGE NOT STARTED
- ENGINEERING MODEL TEST REPORT

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just initiated. And charge voltage versus temperature and various battery performance data -- and I have to go through the data and look at the --

This is our test equipment -- bench test equipment that is capable of handling three batteries. It was built for us by TRW and is computer controlled. One of the nice things about this is you don't -- it doesn't spit out a lot of data at you. You can set it so that it only prints out a delta V, so much and saves a lot of paper.

These are the batteries in their handling fixture, and setting on the heat sinks, which are thermal electric heat synchs.

(Slide.)

This is just a bit of test data here on the cell level. These cells were on trickle charge at about C over 30 rate for six months, before this discharge was performed.

So the dashed line was a TRW data, where they scaled up the data from smaller cells, which falls in pretty close.

#2 tape

rt #3

Now their data was based on 70 degree F, where we have got data points at 80 degree F, which is approximately room temperature, and a 50 degree F chamber.

101 Now the cells themselves were probably running 3 to 5 degrees above the 50 and 80 degrees F. At 50 degrees F you don't see much degradation yet, and at 80 degrees you see considerable degradation where the cell capacity is only 15 ampere hours.

(Slide.)

This was the next cycle after the one I just showed, approximately 24 hours later we recharged it and discharged it again.

And at 50 degrees F you can see that we had very little degradation, whereas at 80 degrees, even after that last discharge, it didn't improve much.

So we are intending to fly these batteries in a temperature range of low 50's and low 60 degrees.

That is all.

(Applause.)

FORD: Thank you, Sam.

You have a question, Carr?

CARR: Carr of Eagle Picher.

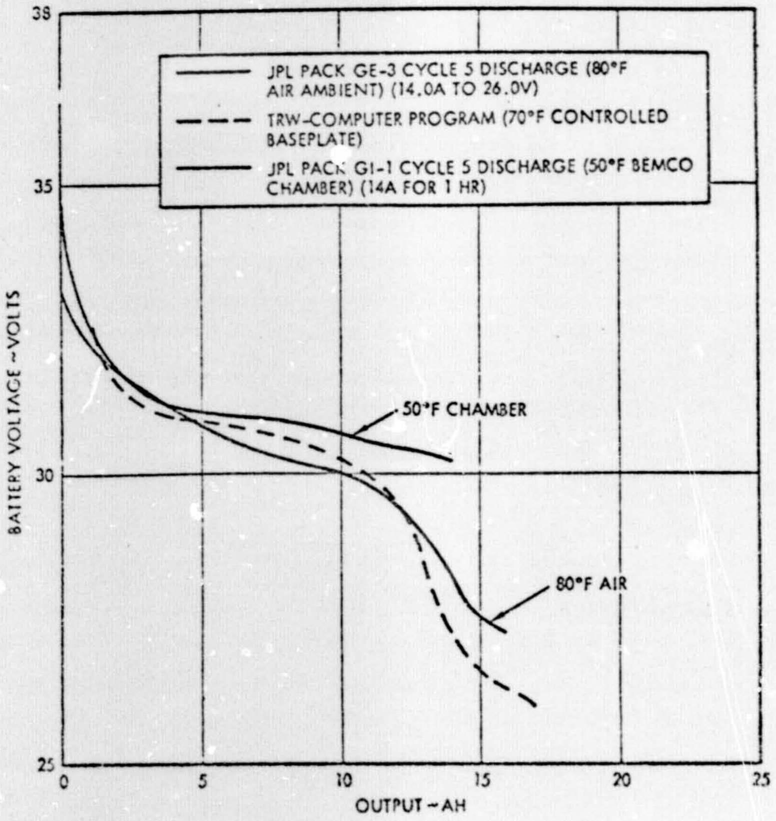
Sam what was the treatment of the cells before the test? Did you say they were trickle charged continuously?

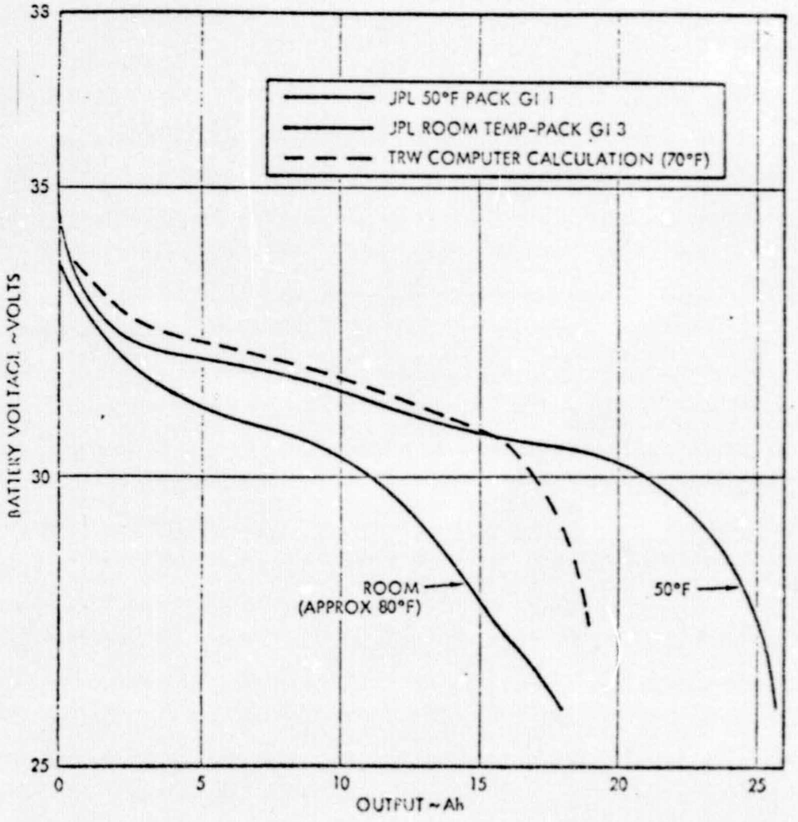
BOGNER: Yes, for six months.

CARR: What was the amps?

BOGNER: About 6.5 amps. 20 ampere hour cells.

FORD: Bob?


38
35
30
25
BATTERY VOLTAGE ~ VOLTS
0
5
10
15
20
25
OUTPUT ~ AH
JPL PACK GE-3 CYCLE 5 DISCHARGE (80°F AIR AMBIENT) (14.0A TO 26.0V)
TRW-COMPUTER PROGRAM (70°F CONTROLLED BASEPLATE)
JPL PACK GI-1 CYCLE 5 DISCHARGE (50°F BEMCO CHAMBER) (14A FOR 1 HR)
50°F CHAMBER
80°F AIR


38
35
30
25
BATTERY VOLTAGE ~ VOLTS
0
5
10
15
20
25
OUTPUT ~ Ah
JPL 50°F PACK GI 1
JPL ROOM TEMP-PACK GI 3
TRW COMPUTER CALCULATION (70°F)
ROOM (APPROX 80°F)
50°F

STEINHAUER: Steinhauer, Hughes.

Sam, I just wanted to comment that we have run similar propulsion tests to what you described earlier on Gulton 6 ampere hours cells for the TACSAT 1 program.

However, we pressurized through the vent tube. We used some cells that were gauged. These were run in the Surveyor lobster pot, which is a large steel vessel. We expected quite catastrophic results when they ultimately went, but unrestrained they went in a 300 to 400 psi range, and it was the stress relief collar around the metal ceramic that yielded.

And restrained, they went in the three to 4000 psi range, and it was rather unspectacular, sort of like a tire blowing out. It may have some systems implication in that what pressure restraint do you want to design your battery package to.

In other words, do you want the cell if it does go, sticking into the spacecraft or something less catastrophic?

BOGNER: Well, I guess the pressure the cell may burst at is probably dependent on the rate of pressurization. I am sure these might have blown lower if we hadn't pressurized them so rapidly. 50 pounds per minute, I think, is much faster than you would get in a practical use.

STEINHAUER: We pressurized much slower than that.

FORD: Another comment, question?

CARR: Carr of Eagle Picher.

Just as an aside to what Bob Steinhouer said, we took a larger cell, such as a 36 ampere hour,and you restraining it, we can have it yield at about 1200 at the weld.

And I think this is pretty much a function of the geometry. A small cell, like a little 6, would go to a higher pressure, I am sure.

BOGNER: Yes. Well, these cells, as you can see from the pictures there, burst at the top and at the weld, and right where the terminal seal was through the top of the cell.

FORD: Did anyone monitor for cell shorting before it burst?

BOGNER: These cells weren't any good before we blew them. They had been exposed to 250 degrees for about 48 hours, and they were shorted.

CARR: WE had a short cell at 300 psi did not have any short in it after it ruptured the wall. And it was like Bob Steinhauer said, it was like a flat tire, just opened the weld.

FORD: Any other questions, comments, on this presentation?

GEntlemen, it is a quarter of five. Jerry, do we have support here as long as we want it.

HALPERT: As far as I know, the gentleman in the booth will stay as long as we want him.

FORD: Well, let me give you the situation.

Why don't you all stand up while I am telling you. I think everybody should stretch their legs at a minimum.

We have four more presentations in the section that we can give, That is really up to the group and whether you would like to stay around for another 45 minutes, or -- we have a pretty full schedule tomorrow, I understand.

Does anybody object to hanging around a little while longer, and finish up the session?

We could take a break now for five minutes. Is that satisfactory?

(Recess.)

Is there anyone at the meeting here that has not signed this sheet of paper, the sheets of paper that were outside?

If not, why don't you come up -- or he will pass them to you right now. This is to assure that you will get a copy of the proceeding. If your name is not on here, don't expect to receive one.

Jerry, is this different from the book that you had outside for them to sign?

HALPERT: It is the same one.

N71-28670

FORD: The same one.

If you have signed outside, it is the same thing. Just make sure that you have signed your name on one of these sheets of paper, today.

Bob, I believe you had your hand up?

Okay, at this time, we will reconvene.

Our next speaker is Don Mains. Don is in charge of the NASA portion of the battery test facility at the Naval Ammunition Depot in Crane.

At this time Don is going to take about ten minutes to discuss some aspects of the Crane program.

Don?

MAINS: The overall program at Crane covers many phases of the testing and evaluating program, and as such, sometimes it gets quite confusing for people receiving our reports and data to assimilate all that we are doing. So I thought I might take this opportunity to review some of the various tests, reports, and give a little bit of the detail, a little bit of information on what we mean when we say we are running a particular test such as acceptance, life cycling, general performance, separator evaluation, storage, synchronous orbit, IMP battery evaluation, and some deep space probe tests.

To start out with, the acceptance tests consist of three capacity checks, which determine a baseline for the capacity for all of our future references.

Next the cells. Once we finish the capacity checks, the cells are then shorted out with a resistor for 16 hours until they are completely discharged. Then they are placed on open circuit in order to determine the recovery voltage as a part of the internal resistance, or internal short test.

Next, the cells are placed in a high vacuum for 24 hours. Then they are removed and sprayed with solution of phenol thaline to determine leaks.

This method we have found at the present time seems to be the best way of indicating small leaks. All the methods that we had previously used were unsatisfactory for one reason or another.

Following this, the cells were then placed on what we call an overcharge test, where we charge them up at C over 10 rate for 16 hours to get them fully charged. Then the rate is reduced to C over 20 rate for 16 hours. Then again raised to a C over 10 rate for another 16 hours.

By looking at the voltages at the end of each of these rates, we can see in what directions the cells are going. Are they stabilizing, or are they continuing to rise or fall?

Following this we then run what we call an impedence measurement test with a Hewlet Packard milli-ohm-meter. Sometimes we have been asked, exactly what does this mean? Does this show the exact impedence?

We are not real sure, but at least it gives us a more reliable baseline to work from. It is very repeatable, it is very simple, very quick.

A lot of other methods, the pulse methods, you get into all kinds of complicated equipment that is involved, and a lot of setup time, and when you are finished, you are not sure of the results any more than you were of any of the other tests.

So, essentially the acceptance test gives us: One, a method for removing any defective cells and supplies the data necessary for matching cells for further testing, and it also sets a base line for any future evaluations that might come along.

The most diversified program that we have going at Crane is the life cycling program. At present there have probably been somewhere in the vicinity of 2000 cells that have gone through this program covering such cells as new developments, charge control methods, precharge adjustment and numerous satellite programs such as OAO, Teeter, Nimbus, OSO, OGO, SQ, SAS.

The test parameters on this particular program consist of orbit periods of 1 1/2, 3, 8, 12 and 24 hours. And test temperatures of minus 20, zero, 25, 40 and one cycling temperature of zero to 40 degrees C.

The depths of discharge range anywhere from 10 percent to 60 percent.

Thus far the program has netted a large volume of data which has been analyzed by statisticians. It also has given some information as to life expectancy, weaknesses, and changes in the overall characteristics of the batteries, either those that are on test, or from one group of test samples to the next, which may indicate a change in materials used, manufacturing processes, or something else along this line.

It kind of acts as an alarm to some of the users that something may be amiss.

It doesn't always correlate with the use of the manufacturer, because the program and the test isn't exactly the same as your flight program.

Another extensive program that we run,and it is only run infrequently, which I would like to give a little bit more information on, is our general performance.

This test is run to determine the actual performance under various rates and temperatures. Normally we take 5 cells from any group that we select, start out with an environmental test of random vibration, sinosoidal vibration, mechanical shock and acceleration. All of the levels are consistent with those that are used for flight hardware.

During the environmental tests, the load is applied so that we might be able to get to detect any variations or abnormalities that might occur during any phase of the test.

Following the environmental test, the cells are then charged at rates varying from C over 40 to 2 C to 100 percent of the manufacturer's rated capacity. Then they are discharged at the C over 2 rate, to zero volts to determine the amount of actual capacity that was accepted.

After this sequence is run, the rate then is rerun at temperatures at 40 degrees, 20, zero and minus 20. Following all of these charge rate temperatures, we then determine the most efficient charge rate for each temperature. Following that, we then go through a similar sequence where we charge the cells at the most efficient rate, but then discharge at rates from C over 40 to 2 C down to zero volts. Again characterize the amount of capacity that the cells have accepted.

Following the charge, and discharge characterization, then we go into an overcharge which again starts out at a C over 10 for 16 hour charge rate at -- with one cell at each temperature of zero, minus 20, 20 and plus 40 degrees C. Charging at C over 40 until the voltage stabilizes and then increasing the rate up to 2 C, or until the cell voltage shows a decrease of .05 volts, or a temperature increase -- or the temperature reaches 77 degrees C,at which time the test is terminated.

And some of the results that we have found, is

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that the charging voltage starts out at minus 20, starts charging at about C over 10, at zero degrees at about C over 5, and coming all the way up to 40 degrees, the best or most efficient charge rate is the 2 C rate.

And a similar situation appears on the discharge rates. So that if you are going to operate a battery at high temperatures, you are going to want a high rate charge and a high rate discharge, according to these tests.

Other programs, the separator evaluation program consists of three individual tests. A 30-day stand, a constant potential charge test, a constant current charge test.

In this test, the cells are placed on charge and discharge on a 24-hour period. We charge them at a constant potential, and discharge them 100 percent depth, and continue this until the cells eventually fail, in order to evaluate various types of separator material.

I believe more will be said about this tomorrow.

Another program that we have been running, this is the start of the fifth year on it, is a storage program. We have two groups of cells, one group is on a trickle charge of C over 100 rate for a year. Another group stands on open circuitry for a year.

The results on this test are a little bit -- I might say confusing, in that there is no real trend as to one method is better than another. It depends on your application.

If you have to use the battery immediately upon the end of the one-year period, you better have it fully charged, because on the stand there is nothing left.

But if you have time to recondition it, you will come out with a little better capacity than if you have been trickle charging it for the whole length of time. Because the more use it gets, the capacity appears to drop off after the long trickle charge.

Another program we are running is a synchronous orbit program, where we are simulating the synchronous type orbit, the equatorial synchronous orbit of a stand period of 140 days, and then a charge-discharge period of about 43 days, starting with about a two-minute discharge, increasing to 72 minutes, and then decreasing back to two minutes, and then going on to the charge stand again.

Depths of discharge at the maximum time range from 60 to 80 percent over a temperature range of minus 20 to plus 40 degrees C.

These results have been reported out just recently for the Gulton 6 ampere hour cells, and we hope within the next month or so to have a report out on some Gulton 12 ampere hours cells with auxiliary electrodes.

One interesting factor of the auxiliary electrode is we found at minus 20 degrees, the cells could not accept any trickle charge at any rate.

We got it down as low as our equipment would go, and we still continued to get high voltage and high pressure. So we just stopped any charging. The cell stand during the -- more or less the sunlight period on open circuity -- and then during the shadow period, we charged them and discharged them. They seemed to work well under this type of criterion.

So this might be a new approach that if you get down into low temperature range, get the cells recharged, then just shut them off and let them stand. They might operate better if you can recondition them and then right before you go back into your shadow period.

Another program we are running is an IMP program where we actually simulate the program that is covered by the IMP battery. We are nominally about 30 to 60 days behind the launch. We receive the data back from the battery if it encounters discharge or any other conditions, we try to simulate these. The high vacuum and so forth.

So far we have been able to come up with fairly close correlatable information that helps occasionally that if some condition is expected to be encountered, we may jump the gun and run a discharge ahead of time to see how well the satellite will perform.

For example, about a year or so ago, the IMP satellite that was in orbit around the moon, encountered the eclipse of the moon. It was going to be in the shadow for approximately 6 hours, and the question was, how long would the batteries last?

To the best of my information, the results we obtained, said that it would last about 5 hours and 15 minutes or so. And I think we were off by 15 minutes by what the actual satellite information showed.

In the way of deep space probes, we have been running two programs for the Jet Propulsion Lab on silver zinc and silver cadmium cells, consisting of storage and cycling intermixed, ranging at storage from about minus 50 degrees all the way up to -- 50 degrees C up to about 40 degrees C.

And this program is still going. It hasn't come to a definite conclusion as to which is the best method, or gives the best results.

Another program that we have started is 100 ampere hour test program, that is just now underway. And I might say I was pleasantly surprised that the manufacturer had given us some results and said this is typically what you are going to get on these capacity checks, because doggone it, they were right, for a change.

(Laughter.)

The temperatures fell right in with the area that they had said. The pressures and everything worked just beautiful.

And when you see 100 ampere hours sitting there and expect that thing to blow, you don't want to be anywhere near it and running it a 100 amp discharge, you start wondering. So, all I can say, I am pleasantly surprised that they were right on the money this time.

Another thing that Crane is in the process of doing is procuring and installing a new data acquisition system.

This new system will have some unique characteristics, such as a uniform time interval for test control and data acquisition. A more precise timing sequence,will be able to record more data at more frequent intervals when it is necessary, will have more accuracy.

And maybe the biggest point to the new system will be the fact that people will be removed from most of the data recording. It will be done automatically. The recording on magnetic tape. And in this way, hope to come up with more consistent data, and less confusing and erroneous data, if there has been any in the past.

Thank you.

(Applause.)

FORD: Thank you, Don.

Are there any questions?

Yes, Bob Corbett. Lockheed.

CORBETT: I was curious Don to hear what you said about the impedance test.

I wondered what the conditions were? Does the millivolt meter come out with a five-volt signal, or is it -- (Inaudible.)

MAINS: The instrument we use is a Hewlett Packard model 4328A, and it reads out on the scale in actual milliohms that can be either recorded on a chart recorder, or taken and read by an operator.

Typically now we are getting results in the area of three to five milliohms which is not too far from the other methods we have been using, the impedance methods. But all the cells seem to be in this general area.

Now we are hoping in the future to be able to follow some of these cells now with this method on through life.

For example, we run acapacity check. Also include this impedence measurement to see, is the impedance changing? But the previous methods, it was pretty difficult to set up all the equipment required to run a pulse test at that time.

CORBETT: I might mention relative to that, we have been conducting a program for about three or four months now on battery impedance over a wide range of frequency, and we find that almost everything that you can do in nickel cadmium cells in terms of the charge or discharge states, the impedance is independent of over the range of, let's say, one to ten hertz. And this -- well,for example, if you take the cell almost into reversal, you don't see its impedance changing over that frequency range.

MAINS: I believe this instrument operates at around one kilohertz pulse. And again, we have run similar tests, where we run through a cycle of charge and discharge and saw very little impedance variation over the whole cycle.

CORBETT: Yes, I think that as an acceptance test, it is almost a worthless one, the impedance test.

MAINS:Well again, like I said, sometimes this isn't to accept or reject a cell, but to lay a baseline that we can look at in the future.

CORBETT: Sure.

In the tests we ran with the pulse test, the only informative value we got from the test is one that we compared the results for cells with the polypropyline separator. And of course there was a pretty significant difference in the impedance. The DC resistance, essentially.

FORD: I might comment that before Crane started using this, we had one meter in here -- we had one meter at Goddard for about one year, and we were very interested in any concept that would give you a quick, snap measurement.

resistance, that is C rate charge or discharge for a short period, square wave fashion, the fact that that isn't very different from the 1 KC method, that you have been using, would indicate that the reactive component probably is negligible at that 1 KC.

FORD: Yes, it is the capacity of the component that Hewlett Packard is questioning, and we can't give them it.

CORBETT: Yes. I think it is probably negligible at that frequency.

FORD: Yes, Dr. **Leuthard.**

LEUTHARD: The cells that were carried for the one-year period, those that were carried in the discharge state, what state of discharge were they taken to, and how many cycles were performed on the cells after this one-year period?

MAINS: ON the storage tests, both groups were fully charged at the beginning of each year, and then allowed -- the one group stood on open circuit from a fully charged state, and the other group was fully charged and then placed on a C over 100 charge state.

At the completion of the year, they follow the general outline of our acceptance test, where they receive the same three cycles of capacity and short test and everything else, right down the line.

LEUTHARD: That must be the same data I saw in a report that came out of Crane, then?

MAINS:Yes, there was one out last year, I believe. There is another one due out, it is in our print shop and should be out within a month.

LEUTHARD: All right, now. If I understand correctly, the cells that were on the trickle charge, or flow charge, showed a decrease with subsequent cycles, and the ones that were not carried in the trickle charge state, showed an increase.

MAINS:This is correct, and they have done that again this year. Similar trend.

LEUTHARD: Well, was there any data on cells that were discharged, say, to one volt and carried for a year, and then --

MAINS:No, these are the only two packs that we have on this at the present time. We don't have any others operating under conditions like this.

LEUTHARD:Thank you.

GROSS: Gross, Boeing.

We have made analyses of the Crane data, as I suppose lots of other people have.

One thing that you find out readily is that in attempting to take data on pack life, and to use this to get statistically meaningful information on batteries with the larger number of cells, there is quite a definite error involved to do this.

The only way this can be done is to go right back to the individual cell information and -- so in order to aid in statistical analyses, I would like to have it more easily available to get the data on the cells.

In the beginning of each annual report, you summarize all the prior history on the packs. It would be helpful to have this expanded a little bit so that we have the individual cell data as well as the pack data.

Now, one of the important conclusions on the work that I have done, is that there is a very significantly large Sigma on the failure distribution of the older packs. This is extremely important, if you are trying to make reliability predictions. We tend to think in terms of the average failure life, but you must have, in addition to average failure life, you must have good data on Sigma, the distribution of the probable error, in spite of extremely large expected lifetimes. If you do not have a reasonably narrow Sigma, all the work you have done is to no avail.

So, one of the things that I would like to see is some tests, some day, that are aimed at specifically pinning down what Sigma might be for a modern day cell. All you need is money.

MAINS: Right.

I might answer briefly on that.

All of the data that is gathered is available. The volume is so large that we haven't attempted to report out, like Sid says, all of the cell data individually. Anyone who is looking for results of this type, if they will contact us we will be glad to furnish them with the data.

If there looks like there is going to be enough interest, we could try to put out a volume or two covering all of these results. But the volume looks like it would be pretty large right now.

FORD: Don, would you comment on your microfilm program?

MAINS: This is something that we were just now getting pretty well perfected, and that is that all of our life cycling data that is on magnetic tape can now be microfilmed, and at the present time contained on about six reels of microfilm.

So that if you have the capability of reviewing microfilm, this might be one way of getting the actual test data that is being accumulated.

FORD: Would you care to comment on the cost of those?

MAINS: It is abour $4 a reel, I believe, is what the present cost is.

FORD: Jerry, do you have a --

HALPERT: Halpert from Goddard.

The point of Sid's is well taken. I would like to add to that.

I would like to see included in the reports, some of the manufacturer's data, or at least traceability to manufacturing plate lots, plaque lots and what have you, so that we can go back, if we see data on cells that have been worked for a while, go back to the original data on the plates and see how they were originally set up. This way we have got complete traceability from the beginning to the end.

MAINS: I might say, as this data is beginning to become available to us, we are trying to incorporate this, because a lot of people call up and say, is this the same cell that we are using? And a lot of times, I don't even know what the cell is.

So we are working real close with Goddard on this right now, to get this information fed to us so that we can include this with the rest of the data.

FORD: I would like to make a comment along that line, in view of the fact we have the manufacturer's representative here. We are considering the idea of going to an IBM format, and this would be very helpful if the manufacturers would look at their data recording techniques and see that you could not reduce your normal recording m123

when he gets his package of data, if he so chooses, can reduce it to IBM cards, which canbe put on magnetic tape. And once you have got in a format for IBM cards, I think it is pretty straightforward. It requires some man hours, but it would be up to each individual user to follow through on whether he wanted this or not.

Earl, I believe you had a comment?

CARR: That is about $20,000 worth, just as a quick response to your thing.

MAINS: Well, a lot of times you might think it is that much, but really you are recording the data on something right now -- we went into this. We used to record on straight spread sheets and then have to copy it over, or reassemble it for keypunch operators.

CARR: Oh, I agree. I think it would be real cost effective, if we could do this.

MAINS: Well, right now what we do is again record our data as if we were going to just tape the handwritten data, but use computer format sheets. This way then, if we decide to have it keypunched, the individual that wants it keypunched can have this done.

It doesn't mean that all the data has to be retransferred and that, because most of the data sheets that we had made up and I've seen others make up, cannot be readily transferred over to a computer format without really instructing the keypunch operator on how to punch it up and everything.

CARR: We think this is the way to go, and we are striving to get there.

FORD: We are not saying you have to put it on cards, Earl. We are just saying if you put it on format, we will take care of putting it on cards, if we so choose.

CARR: Well, really and truly, and this is offered for what it is worth, the optimum system for us would be to, during the manufacturing conditioning cycling, to have the equipment generate punchcards. This would be ideal for us, because we have the computer facilities available to then treat the data.

Our problems that we have so far with either manufacturing cycling, which we call conditioning cycling, or acceptance test or other tests, is that we suffer from a -- I don't want to use the term, but it is -- data diarrhea. And it is a very serious problem, and this is something that we have been trying to overcome, and I think that this is a step in that direction.

I would like to say one more thing, with regard to data, in response to Sid Gross' comment, and that is I think that you probably have the data to generate Sigma and other statistical information from your cycle life programs.

We have, and we have -- I wish I had brought that.

I have got the curves which were drawn from the regression -- in other words, we took the cell data, and like Sid said, we didn't just treat the fifth cell failure in ten, we used the individual cell failures to predict Sigmas for each of the operating temperatures and each of the depths of discharge. And I will show this in just a minute.

I don't have the Sigma, I don't have the regression analysis, but it is pretty straightforward statistical information. And I think it is real good.

So, once you have it on IBM format, it is pretty straightforward.

And then I have got one more thing, and this is in the terms of a question to Don, and that is: I think we have heard some information so far which relates to improvement of performance of existing batteries, like don't trickle charge them, seems to be a general good conclusion.

What other conclusions can you generally draw from your testing in the near earth orbit type of applications?

I mean, we hear lots of things, and this is one thing I definitely want to discuss in the workshop, and that is, how do we get to longer cycle life?

So I know that one thing that is coming out of your tests is that operate them at lower temperatures. And I was wondering what kind of reliability data do you have for the improvement of performance?

MAINS:I am not sure. I don't have all the data with me, but as far as -- like you said, operating at lower temperatures is one major improvement. By lower temperatures, this is around zero degrees C. You start going down much below this toward minus 20, you start running into other problems, pressure problems, that are difficult to get around.

Another improvement is a higher rate recharge with very little overcharge.

Most programs in that have been calling for 120 to 140 percent overcharge. WE have had real good results on a lot of tests where the overcharge has been limited to maybe 107 -- 105 to 107 percent of the amount of discharge. In this way it seems to extend the life. your capacity remains quite high, and all around better performance.

There are probably other conclusions, but I can't think of any right off the top of my head.

FORD: Bob Steinhauer.

STEINHAUER: Have you studied this cell resistance with respect to state of charge? And, over a large cycle life?

MAINS: We haven't studied it as far as we would like to. We just have been using the instrument for less than a year now. We have checked it over a charge discharge cycle like I mentioned previously, and saw very little variation.

This wasn't really a good test. It was some old test we had standing around there. We put them through a cycle or two, just to see if there was any major swings.

We have a couple of programs right now,and I don't have the most recent results as to how the impedance is changing with time. But it was set up specifically to answer this question, as to how long and how far can we go, and what kind of changes do we get on these?

STEINHAUER: We have run some tests on smaller cells that are sealed, but four ampere hour that seemed to indicate that you hit a minimum in resistance of about three-quarters of full charge and the quarter -- and full-charge points are about the same. A little bit higher.

IN other words, minimum is 20 milliohms, the full and quarter state of charges is about 30 milliohms, and then in a state of discharge it runs up to about 90 milliohms, but I don't know how that changes the cycle life.

FORD: Dunlop, and then Dr. Maurer.

DUNLOP: Just to follow up what Carr from Eagle Picher was saying, I would like to know what it is that you see that needs to be done, based on your test program?

I am going to put it in terms of synchronous applications. He used near earth application. What is it battery to extend the energy density to the use, to increase the lifetime?

MAINS: I guess one thing that has been brought out several times, and that is more consistency in the manufacturing of that. A more traceable process so that we can go back and see exactly what the problem areas are.

And one of them that is definitely known is the separator material. I think that is true in almost all the tests, and that is the reason now why zero degrees, or in that vicinity, we get the best operation, because the problems with the separator are minimal there.

DUNLOP: The second one is depth of discharge?

MAINS: The depth of discharge.

From our synchronous tests, we have gone up to 80 percent and again at the lower temperatures, the operation looks fairly good.

DUNLOP: When you say 80 percent, 80 percent of what?

MAINS: It is 80 percent at the -- this is 80 percent of the manufacturer's rated capacity at the maximum discharge time. This is at the 72-minute period, and we charge and discharge at the same rates, so that the first day the actual depth of discharge is considerably lower, and it continually increases up to the 80 percent.

FORD: Dr. Maurer?

MAURER: I would like to ask what kind of reliability you have with your test equipment itself?

How many failures of equipment occurred during the cycle life of the battery, and how much do they contribute to the life of the battery itself?

Do they lead to failure?

MAINS: On the cycling equipment we have -- I would say -- fairly good life expectancy. We may, in a year's time -- oh, the majority of our down time is considered, or due to commercial power loss. Actual equipment loss is very minimal. We have some equipment that has been running now for five, six, seven years with no down time other than power outage.

Most of our equipment we have enough duplication where we can slip another component in within one cycle, so that we lose very little time actually due to equipment malfunction.

Our biggest problem right now is in the data acquisition end of it. But we can't always record the data because of down times there.

MAURER: Does the malfunction cause failure in the battery? For example, go to a higher voltage than you intended or --

MAINS: Normally we have alarms to protect us either for higher voltage or lower voltage. And we have operators that are on duty 24 hours a day, so that they are checking this intermittantly, and are available any time an alarm would occur, so that very seldom do we lose a battery due to equipment malfunction.

Right off, I can't think of any that we have actually lost due to equipment malfunction.

MAURER: You stated that you are getting a computerized system with magtape output.

I just wryly comment that we have a system with 300 data pair positions on it with magtape output, and occasionally the magtape has times and voltages recorded as swear words. And computers being the straightlaced things they are, refuse to read these.

MAINS: Yes, this is a major problem.

Our system, as envisioned right now, will have approximately 2000 data inputs. We will have two magnetic tape recording systems. We are looking for as much reliability and redundancy as possible there. If one system does not record, or does not accept the data properly, it will kick it over to the other tape recording device. If neither device will operate, then the operator knows about it.

We are trying in every way to get around any of these problems. We have had them on the system we have right now, where we can punch paper tape and the computer won't accept it either.

With magnetic tape, you can't readily look at it and say, well, there is a bad spot right there. So we are trying to build the equipment with this reliability in it.

MAURER: That is the major problem you have, is that you can't read the tape after it has been written. There may be parody areas, or things of this sort that you don't find out about until the day that you take the tape off and try to read it.

MAINS: Right now we are looking for, probably, a system with a read after write capability, so that if it doesn't read what it thought it wrote, it will give us an alarm, if everything is working properly.

(Laughter.)

FORD: Do I have any other questions relating to the Crane test program?

Yes, gentleman here.

WILL: Will, General Electric.

WE have observed in studies of individual cadmium electrodes, which we have kept under constant voltage conditions rather than keeping them under trickle charge, that we obtained very beneficial results. Namely, we observed that we could keep the electrodes for months without any ill effects. And I wonder whether similar results have been obtained from nickel cadmium batteries, where the whole battery, in fact, could be kept under a constant voltage, which is just slightly above the thermodynamic voltage of the whole battery?

MAINS: At Crane we haven't done any individual cost potential stand tests of this type. Most of them have been the charge-discharge type, where the cell is cycled to a potential level for a period of 24 hours and then discharged. A cycling type test, rather than a storage test as we are running on the two packs we have.

FORD: Yes, Sid, just one more question.

GROSS: I just want to clarify, Don, isn't your C over 100 trickle only slightly above the open circuit voltage?

MAINS:They might be setting there. I haven't looked at the data for so long -- it doesn't give us any problems. But it is not controlled. It is a straight C over 100 rate.

GROSS: But you had concluded that the C over 100 trickle charge was not as good as the open circuit?

That there was degradation in the C over --

MAINS: If I remember correctly, we are getting some fairly high voltages there. By fairly high I mean for room temperature they are probably running 1.52 maybe to 1.55, something like this.--

GROSS: Well, that is pretty high.

MAINS: -- after the long charge. Now these are just off the top of my head.

Problems it looks like we are running into there is electrolyte distribution. After the long charge period, the electrolyte doesn't seem to be as well distributed within the cell. You see the dry spots and so forth when the cells are open, and at the end of each year we do open one cell from each group and make a comparative analysis to see what the variations are.

VERRIER: VErrier, SAFT.

I couldn't let this question remain in my head, and not come out.

If most of your problems in down time are equipment failures, have you ever considered emergency power using a nickel cadmium battery?

(Laughter.)

MAINS: I figure we couldn't justify the cost of it.

FORD: Bill Ryder?

RYDER: In answer to a question by Dunlap before when you were asked what you thought could be done to improve overall life of the nickel cadmium batteries, you said that uniformity of materials and methods and processes and so on.

Now this is a nice motherhood and sin statement. What, in your test data, which applies to individual cells -- what in the actual testing that you have done on individual cells -- leads you to that conclusion?

IN batteries, of course, it is obvious. If you don't have cells reasonably well grouped, you have a problem. But in your program, where does this point up? Where do you find failures that you can ascribe to lack of control and so on? Where is your failure analysis?

MAINS: Well, a lot of cells, when the fail cell is open, if you find a hole about the size of a quarter in a 20 ampere hour plate, for some reason this has gotten through. If these cells are hand-made, as most of the aerospace cells should be, or at least are claimed to be, this is kind of surprising. When you find cells that the edges of the plates are just sheared off, there is no coining, no attempt made to contain the material, they are ragged and rough, this type of process; we have gotten cells where the separator material was misaligned, where there would be as much as a quarter inch of the plate where there would be no separator material between them.

VERRIER: Well, the first one of those could happen in service and might not be noticeable during manufacture.

The other two are QC problems and should be caught before the cells are assembled and shipped. They are not wear rotted.

In other words, you are running rather essentially wear-rot tests. And all I am saying to you, what is there in the data that you are getting -- the results that you are getting -- that says, if you do control this better, or that better, you will indeed improve life?

MAINS: That is catastrophic, okay?

VERRIER: Right.

FORD: Okay, I think we will proceed on to the next speaker.

Thank you, Don.

I would like to say the NASA portion of the CRane program, I think one of the problems is we probably do not get the feedback from industry and from the users, and we are certainly open to criticism, critique and any suggestions that you people in scrutinizing the data may have to help us improve it.

I offer this right now. Most of you know what our telephone number is. Most of you are aware that you can get the data. But the one thing that I find missing is the fact that most people don't speak up when they feel like, that something additional should be done than what was done. You may hear about it through the grapevine, but you certainly don't hear it person to person.

And I, for one, and I think I speak pretty well for the group at Goddard here in this program, would be glad to hear from people that have complaints, that have suggestions, let's say constructive criticism type. We have all made mistakes in the past and we are going to continue to make them in the future. But we would like to benefit from what you found the mistakes to be.

At this time, I would like to introduce Earl Carr, Eagle Picher. I think you have all heard him a couple of times by now. He has a few comments and a few questions. I think he would like to discuss on the 25,000 cycle life battery.

CARR: Thank you, Floyd.

N71-28671

We, as a battery manufacturer, want to do and accomplish the things that, let's say in long life batteries, that you need.

We use the term 25,000 cycle life unit. I think we are talking in terms of a five-year battery in a near-earth orbit.

This seems to be one of the more difficult requirements that seem to be in the future.

We are spending a lot of time and a lot of our resources in exploring what we can do and what the problems are in attaining this kind of life.

I mentioned earlier that we have done some analysis on data we have on ourselves. I would like to just put these on the viewgraph. First of all show this page here. What you all can do is look at the difference in data. I hope this shows up.

(Slide.)

The first sheet, which is a table, and many of you have seen it. It is some data back from 1965. It represents the fifth cell failure in a ten-fail group at different levels of depth of discharge and different temperatures.

ANd as Sid Gross pointed out this is somewhat questionable whether you can use the data just like it -- you know, for what purpose.

(Slide.)

The next curve is a regression analysis treatment. I do not have the particulars on this, but I will see that Floyd gets some for inclusion in the minutes.

This is a log plot from the data of the other sheet,and which actually considers the particular cell failure number of the first five cells of each ten-cell group.

Now we extrapolate it up to something like 11,000 cycles for -- I think it is 10 percent depth of discharge, or something like that. Could you raise that up a little bit, Tom. I mean get the bottom up?

VOICE: That is all I can get.

CARR: Well, whatever it was -- This is like precharge. I thought I understood precharge when I came here, but I don't know what I understand any more after listening to this today.

Anyway, it shows an extrapolated point at 10 percent depth of discharge at about 11,000 cycles for each of the temperatures.

Now, Don Mains has pointed out that you can get better data, or get better results than this by operating in the region of zero degrees C, and by changing the type of charge regime that you use.

So this data represents essentially constant current charge and constant current discharge on the average current basis over a 90-minute orbit.

As I said, I will see that the data from the regression gets into the minutes for the meeting. It is a statistical treatment of the data, but it shows what you can do with, in this case, 75 failure points. The Sigma variation that we had was approximately 350 at the higher depths of discharges. We have it down to about a 500 Sigma at -- predicted at 11,000 cycles, which was a 10 percent depth.

Now basically, in trying to get to long-term life, I want to consider just the wearout modes. I am not really going to discuss quality control points. We are working with a lot of effort in these areas. Everyone is spending quite a bit of money to improve quality control, process control and so forth.

There are three things that I can attribute wear-out in nickel cadmium. One is separator breakdown, the second is cadmium penetration, and the third is the negative fading or the negative plate wearout, whatever you want to call it.

I really would like to throw this thing open for a discussion, although I want to say a few things, in that I would like to know from the test agencies and from users who have test data, what type of things can we expect at the current state of the art, based on your programs?

I would like to know -- or we would like to know -- what other work is being done in the areas of negative fading,precharge, and the cadmium migration problem? For example, we have shown in the analysis on fail cells, that the plate accumulates large inactive crystals that we identified as cadmium hydroxide.

Now we -- I think there is some other data available, which shows that there may be formations of carbonates or hydroxy carbonates.

We are wondering if maybe the problem is not -- is cadmium migration within the plate? Is the plate effectively being sealed by the materials, the cadmium materials themselves at the surface of the plate?

So these are the three areas that we look for as wearout modes, and I would like, maybe sometime tomorrow, if the chairman has time, to discuss these areas in more detail with anybody else' specific reference,

REGRESSION ANALYSIS OF CYCLE LIFE DATA FOR EAGLE-PICHER 20 AMPERE-HOUR SEALED NICKEL-CADMIUM CELLS

Earl S. Carr
Donald J. Doan

Cycle life data is typically shown according to Table Number I with failure of a group usually determined as 50% of the test sample. More data is obtained by review of actual cell cycle failure number as presented in Table II. However, assessment of reliability is not readily apparent, nor is reliability information at depths of discharge other than those tested.

This presentation illustrates the use of regression analysis as an aid to gain additional expected cycle life and reliability information from the data for cycle life tested cells.

Briefly, the procedure is to first compute the regression model or equation (see Draper and Smith, Applied Regression Analysis, Wiley) and then use this model to predict (Y (Pred)) the expected life with an estimated standard deviation or error (S. E. (Y)). The calculation of "reliability" from these quantities to meet a specified value of life is not presently satisfactory except to state that the reliability will be a function of the "K" value as defined as follows:

$$K = \frac{(\text{Pred. Life} - \text{Spec. Life})}{\text{Standard Deviation}}$$

The larger the "K" value, the larger the reliability number.

The analysis is presented on the following pages:

TABLE I	Summary of Cycle Life Test Results Eagle-Picher RSN-20 Nickel-Cadmium Cells
TABLE II	Cycle When Individual Cell Failures Occurred
Part A	Definition of Variables and Setting Up The Correlation Matrix
Part B	Determination of The Regression Equation
Part C	Use of the Equation to Predict Known Values
Part D	Use of the Equation for Prediction at Other Operating Parameters
Figure 1	Graphical Presentation of Results of Regression Analysis

TABLE NUMBER I

SUMMARY OF CYCLE LIFE TEST RESULTS
RSN-20 AMPERE-HOUR NICKEL-CADMIUM CELLS

GROUP NUMBER	TEMPERATURE °C	PERCENT DEPTH OF DISCHARGE	CYCLE PERIOD HOURS	CYCLES COMPLETED
1	-10	25	1.5	8544
2	-10	50	1.5	3225
3	-10	75	1.5	2075
4	5	25	1.5	9180
5	5	50	1.5	5593
6	5	75	1.5	2237
7	25	25	1.5	8413
8	25	50	1.5	3759
9	25	75	1.5	3291
10	35	25	1.5	8016
11	35	50	1.5	2579
12	35	75	1.5	1623
13	50	25	1.5	3449
14	50	50	1.5	775
15	50	75	1.5	35

NOTE: Tests conducted independently by Inland Testing Laboratory, Cook Electric Company.

Depth of Discharge based on 20 A-H, nominal capacity at 25°C is 27-28 A-H.

TABLE II - EP-20 AH Nickel-Cadmium Cell Failures

CYCLE WHEN INDIVIDUAL CELL FAILURES OCCURED BY GROUPS

GROUP NUMBER	FIRST CELL	SECOND CELL	THIRD CELL	FOURTH CELL	FIFTH CELL
1	6517	6929	8432	8527	8545
2	3226	3226	3226	3226	3226
3	1948	1967	1967	2076	2076
4	5022	5036	5069	9167	9181
5	2786	2816	3440	4916	5594
6	1933	2093	2205	2205	2238
7	7729	7927	8135	8247	8414
8	2979	3040	3376	3552	3760
9	1937	3020	3020	3292	3292
10	4624	6565	7953	8017	8017
11	881	2002	2577	2580	2580
12	1416	1549	1549	1549	1624
13	1744	2192	2821	3385	3450
14	755	775	775	776	776
15	36	36	36	36	36

PART A - DEFINITION OF VARIABLES AND SETTING UP OF THE CORRELATION MATRIX

The following information shows setting up the terms of the polynomial to fit the data of Table II. The method used is the least squares fit.

```
DEFINITION OF VARIABLES

X  1 = Z  1 = INPUT  1 *        0.0500
X  2 = Z  2 = INPUT  2
X  3 = Z  3 = Z  1 * Z  1
X  4 = Z  4 = Z  1 * Z  3
X  5 = Z  5 = Z  1 * Z  4
X  6 = Z  6 = Z  1 * Z  5
X  7 = Z  7 = Z  2 * Z  2
X  8 = Z  8 = Z  2 * Z  7
X  9 = Z  9 = Z  2 * Z  8
X 10 = Y  1 = INPUT  3
```

```
 AVERAGES, VARIANCES, AND STANDARD DEVIATIONS    N=  75

  X        AVG          VAR          STD
  1       1.0499       1.1503       1.0725
  2       0.5000       0.0422       0.2054
  3       2.2374       5.2534       2.2920
  4       4.5656      34.9600       5.9127
  5      10.1898     223.1028      14.9366
  6      23.4181    1433.7922      37.8654
  7       0.2916       0.0431       0.2076
  8       0.1875       0.0298       0.1727
  9       0.1276       0.0186       0.1365
 10    3621.9604 6872078.0117    2621.4653
 CORRELATION MATRIX

        1     2     3     4     5     6     7     8     9    10
  1  1.000 0.000 0.913 0.862 0.804 0.767 0.000 0.000 0.000-0.358
  2  0.000 1.000 0.000 0.000 0.000 0.000 0.989 0.966 0.940-0.743
  3  0.913 0.000 1.000 0.987 0.963 0.942 0.000 0.000 0.000-0.453
  4  0.862 0.000 0.987 1.000 0.993 0.982 0.000 0.000 0.000-0.475
  5  0.804 0.000 0.963 0.993 1.000 0.997 0.000 0.000 0.000-0.482
  6  0.767 0.000 0.942 0.982 0.997 1.000 0.000 0.000 0.000-0.482
  7  0.000 0.989 0.000 0.000 0.000 0.000 1.000 0.993 0.979-0.698
  8  0.000 0.966 0.000 0.000 0.000 0.000 0.993 1.000 0.996-0.651
  9  0.000 0.940 0.000 0.000 0.000 0.000 0.979 0.996 1.000-0.611
 10 -0.358-0.743-0.453-0.475-0.482-0.482-0.698-0.651-0.611 1.000
   8 IS OUT
   9 IS OUT
```

PART B - DETERMINATION OF THE REGRESSION EQUATION

The regression equation is shown in two forms as presented below. This equation represents the least squares fit of the data of Table II. The equation is derived by the steps presented in Part A.

The "B Coef's" are the respective variable coefficients and the constant (K) correspond to the following:

$$\text{LIFE} = K + X1\ B1 + X2\ B2 + X1^2\ B3\ \text{-----}$$

```
X   RSQR X       B COEF         SE(B)         T         ANALYSIS OF Y  1
1   0.9718     994.4013      661.0574       1.50
2   0.9795  -32216.2266     4053.1137      -7.94
3   0.9982    2181.7939     1232.5517       1.77
4   0.9998   -2748.9375     1823.2817      -1.50
5   0.9999     684.0258      879.3902       0.77
6   0.9995     -26.8975      155.9520      -0.17
7   0.9795   22735.6172     4011.5419       5.66
   CONSTANT       MULT F   DF1   DF2    RSQR,       RESIDUAL
 13383.35744      59.76     7     67   0.8611047695.37670 = S^2
```

S = 1024. = Residual Error

```
VARIABLES IN MODEL - Y 1
  X       B COEF
  1     994.4013
  2  -32216.2266
  3    2181.7939
  4   -2748.9375
  5     684.0258
  6     -26.8975
  7   22735.6172
  8       0.0000
  9       0.0000
CONSTANT= 13383.35744
```

The regression equation is used for comparison to the data in Table II. Of particular importance is the determination of std. deviations S. E. (Y) & the prediction (Y(Pred))

RESIDUALS AND PREDICTIONS

	DOD	OBS	Y(OBS)	Y(PRED)	RESIDUAL	S.E.(Y)	NORM DEV
°C	25%	1	6517.0009	7185.7353	-668.7344	312.6646	-0.653
"	"	2	6929.0009	7185.7353	-256.7344	312.6646	-0.250
"	"	3	8432.0019	7185.7353	1246.2658	312.6646	1.217
"	"	4	8527.0019	7185.7353	1341.2658	312.6646	1.310
"	"	5	8545.0019	7185.7353	1359.2658	312.6646	1.327
"	50%	6	3226.0004	3394.6118	-168.6113	312.6580	-0.164
"	"	7	3226.0004	3394.6118	-168.6113	312.6580	-0.164
"	"	8	3226.0004	3394.6118	-168.6113	312.6580	-0.164
"	"	9	3226.0004	3394.6118	-168.6113	312.6580	-0.164
"	"	10	3226.0004	3394.6118	-168.6113	312.6580	-0.164
"	75%	11	1948.0002	2445.4360	-497.4356	312.6589	-0.485
"	"	12	1967.0002	2445.4360	-478.4356	312.6589	-0.467
"	"	13	1967.0002	2445.4360	-478.4356	312.6589	-0.467
"	"	14	2076.0004	2445.4360	-369.4356	312.6589	-0.360
"	"	15	2076.0004	2445.4360	-369.4356	312.6589	-0.360
°C	25%	16	5022.0009	7094.9365	-2072.9360	312.5938	-2.025
"	"	17	5036.0009	7094.9365	-2058.9360	312.5938	-2.011
"	"	18	5069.0009	7094.9365	-2025.9357	312.5938	-1.979
"	"	19	9167.0019	7094.9365	2072.0649	312.5938	2.024
"	"	20	9181.0019	7094.9365	2086.0649	312.5938	2.038
"	50%	21	2786.0004	3303.8110	-517.8106	312.5917	-0.505
"	"	22	2816.0004	3303.8110	-487.8106	312.5917	-0.476
"	"	23	3440.0004	3303.8110	136.1894	312.5917	0.133
"	"	24	4916.0009	3303.8110	1612.1897	312.5917	1.575
"	"	25	5594.0009	3303.8110	2290.1899	312.5917	2.237
"	75%	26	1933.0002	2354.6391	-421.6387	312.5961	-0.411
"	"	27	2093.0004	2354.6391	-261.6387	312.5961	-0.255
"	"	28	2205.0004	2354.6391	-149.6387	312.5961	-0.146
"	"	29	2205.0004	2354.6391	-149.6387	312.5961	-0.146
"	"	30	2238.0004	2354.6391	-116.6386	312.5961	-0.113
°C	25%	31	7729.0009	7621.2168	107.7841	311.9898	0.105
"	"	32	7927.0009	7621.2168	305.7842	311.9898	0.298
"	"	33	8135.0009	7621.2168	513.7843	311.9898	0.501
"	"	34	8247.0019	7621.2168	625.7843	311.9898	0.611
"	"	35	8414.0019	7621.2168	792.7843	311.9898	0.774
"	50%	36	2979.0004	3830.0903	-851.0899	311.9760	-0.831
"	"	37	3040.0004	3830.0903	-790.0899	311.9760	-0.771
"	"	38	3376.0004	3830.0903	-454.0899	311.9760	-0.443
"	"	39	3552.0004	3830.0903	-278.0899	311.9760	-0.271
"	"	40	3760.0004	3830.0903	-70.0898	311.9760	-0.068
"	75%	41	1937.0002	2880.9165	-943.9161	311.9895	-0.922
"	"	42	3020.0004	2880.9165	139.0840	311.9895	0.135
"	"	43	3020.0004	2880.9165	139.0840	311.9895	0.135
"	"	44	3292.0004	2880.9165	411.0840	311.9895	0.401
"	"	45	3292.0004	2880.9165	411.0840	311.9895	0.401
°C	25%	46	4624.0009	6413.5810	-1789.5803	312.2114	-1.748
"	"	47	6565.0009	6413.5810	151.4199	312.2114	0.147
"	"	48	7953.0009	6413.5810	1539.4201	312.2114	1.503
"	"	49	8017.0009	6413.5810	1603.4201	312.2114	1.566
"	"	50	8017.0009	6413.5810	1603.4201	312.2114	1.566
"	50%	51	881.0001	2622.4555	-1741.4553	312.2170	-1.701
"	"	52	2002.0002	2622.4555	-620.4552	312.2170	-0.606
"	"	53	2577.0004	2622.4555	-45.4550	312.2170	-0.044
"	"	54	2580.0004	2622.4555	-42.4550	312.2170	-0.041
"	"	55	2580.0004	2622.4555	-42.4550	312.2170	-0.041
"	75%	56	1416.0002	1673.2834	-257.2832	312.2124	-0.251
"	"	57	1549.0002	1673.2834	-124.2832	312.2124	-0.121
"	"	58	1549.0002	1673.2834	-124.2832	312.2124	-0.121
"	"	59	1549.0002	1673.2834	-124.2832	312.2124	-0.121
"	"	60	1624.0002	1673.2834	-49.2832	312.2124	-0.048
°C	25%	61	1744.0002	4013.3989	-2269.3989	312.8485	-2.217
"	"	62	2192.0004	4013.3989	-1821.3986	312.8485	-1.779
"	"	63	2821.0004	4013.3989	-1192.3986	312.8485	-1.164
"	"	64	3385.0004	4013.3989	-628.3985	312.8485	-0.613
"	"	65	3450.0004	4013.3989	-563.3985	312.8485	-0.550
"	50%	66	755.0001	222.2715	532.7286	312.8789	0.520
"	"	67	775.0001	222.2715	552.7286	312.8789	0.540
"	"	68	775.0001	222.2715	552.7286	312.8789	0.540
"	"	69	776.0001	222.2715	553.7286	312.8789	0.540
"	"	70	776.0001	222.2715	553.7286	312.8789	0.540
"	75%	71	36.0000	-726.9122	762.9122	312.7540	0.745
"	"	72	36.0000	-726.9122	762.9122	312.7540	0.745
"	"	73	36.0000	-726.9122	762.9122	312.7540	0.745
"	"	74	36.0000	-726.9122	762.9122	312.7540	0.745
"	"	75	36.0000	-726.9122	762.9122	312.7540	0.745

PART D - USE OF THE EQUATION FOR PREDICTION AT OTHER OPERATING PARAMETERS

The regression equation is especially valuable for determining reliability information at untested operating temperatures and depths of discharge.

Standard Deviation Data (S. E. (Y)) are obtained in addition to the predicted cycle life.

The following example provides 25°C cycle life prediction at depths of discharge of 11%, 15%, 20%, 30% and 35%. Standard deviations are also provided for each of these depths of discharge.

```
OBS      Y(OBS)       Y(PRED)      RESIDUAL         S.E.(Y)   NORM DEV
  1      0.0000     6635.6357    -6635.6357        287.8416     -6.432
  2      0.0000     5763.7324    -5763.7324        287.8288     -5.631
 76      0.0000    10985.6113   -10985.6113        562.7181    -10.732
 77      0.0000     9933.4140    -9933.4140        464.3477     -9.704
 78      0.0000     8720.4765    -8720.4765        370.3591     -8.519
```

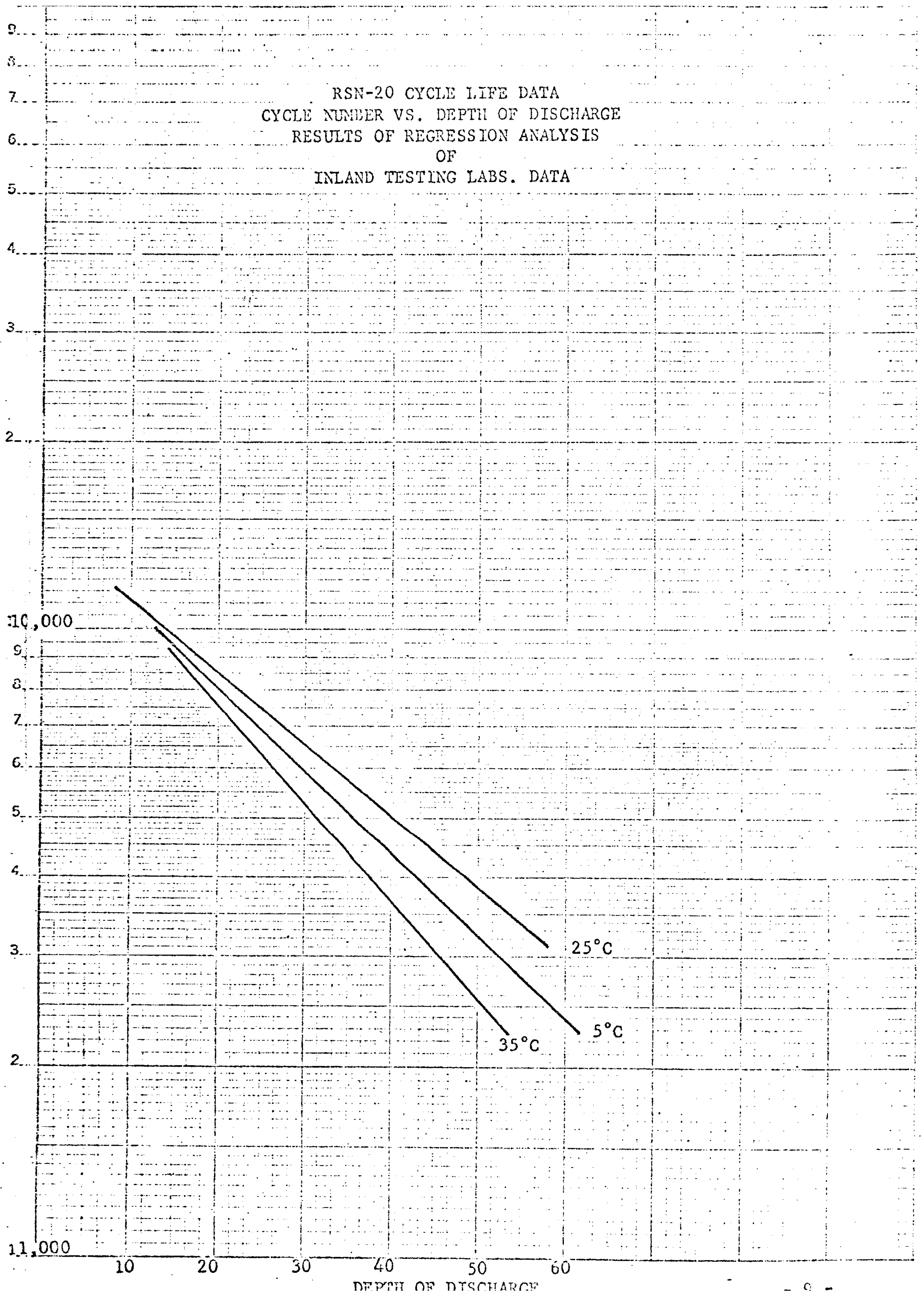
A note of caution should be expressed concerning the predictions in Part D. Those for 30% and 35% are interpolations while those for 11 to 20% are extrapolations. The latter are, of course, less accurate as shown by the larger standard error (S. E. (Y)).

Also, charge control methods are not included in this analysis. However, we believe that the data are conservative as there are techniques of charge control that can extend nickel-cadmium battery life.

Earl S. Carr
Donald J. Doan

EAGLE-PICHER INDUSTRIES, INC.
NOVEMBER 18, 1970

RSN-20 CYCLE LIFE DATA
CYCLE NUMBER VS. DEPTH OF DISCHARGE
RESULTS OF REGRESSION ANALYSIS
OF
INLAND TESTING LABS. DATA



FORD: Thank you, EArl.

Jim?

DUNLAP: I have one comment.

I have just recently read a report by Dr. Scott, who happens to be here, from TRW, and I think that the first thing he picked out as a failure mode was the positive electrode. At least he mentioned it.

And I do think that we -- I, in my own testing -- have seen a loss in voltage, particularly with the trickle charge type of storage. I am not sure it is not in any type of storage you might also see this type of loss of voltage. And I think this is a loss in voltage at the positive electrode, and I didn't hear any comments made yet in terms of wearout modes or failure modes with respect to positive.

And I just wondered, have we solved all of the problems of the positive?

CARR: I don't know Jim, whether we have or not.

The failures that we observed on the data that I just presented, were failures of the negative plate by and large.

I guess really that is it. As far as we know, the cells failed negative limited on long term cycling. This is in a near-earth type application.

It may be a completely different matter in synchronous orbit.

DUNLAP: Okay.

FORD: Bob Corbett?

CORBETT: Regarding what Jim just said about cell failures, and recalling what Sid was saying about the undesirable format of the Crane data, I was going to point out at that time that there is a lot more that is undesirable from the statistical standpoint in the Crane test, as regards the criterial for cell failure. Because dependent upon your specific system and the voltage regulation that you require, for example, and the rates at which you operate, your criteria for failure could be quite different.

For example, in the in-house tests that we have run, Ihave attempted to look at cycle life from the standpoint of how long can the cell survive as an energy storage device? But if you look at it from the spacecraft standpoint, I think from most of the spacecrafts that you have got up there now, 1.1 volt, for example, is considered failure or an improper operating mode. Or perhaps 1.05 volts.

I think there are some articles in literature which I can't think of off hand, which -- in which there is a correlation made between the lost of valency on the positive electrode and low voltage phenomena.

But of course, getting a low voltage on the positive needn't be a system failure. It depends upon your design.

I would like to suggest that from the testing we have performed, it might not be a bad idea, and I guess TRW is on to something like this -- it might not be a bad idea to have a battery that is allowed to go down to eight-tenths of a volt per cell or something equivalent to that. Perhaps this is a more optimum design.

FORD: That is certainly one approach to get a longer life.

Dr. Scott?

SCOTT: Scott, TRW.

I believe that there is becoming clear, a greater and greater distinction between the important failure modes applicable to a short orbit, that is a 90-minute close earth orbit, and those applicable to a synchronous orbit whereby by the nature of the beast, one is pretty well forced to operate at much higher maximum depths of discharge during the cycle.

We are pushing 80 percent depth of discharge, for example, in one program, and I am -- I believe that the effect of operating at that level on the positives is much different than operating at 25 to 40 percent depth of discharge in a 90-minute cycle.

And it was primarily in relation to the higher depth, 24-hour type cycling appropriate to a synchronous orbit

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that we have observed primarily failure of the positives, and relatively little failure of the negatives under the conditions that we have been using.

And that is why I mentioned that in that report that Jim referred to. Here again, I guess it is relative to the question of tailormaking cells, also. I think that that is the way the thing is likely to go. I believe that the optimum design of cells for synchronous orbits are likely to diverge more and more from the optimum design for a 90-minute close earth orbit.

FORD: Thank you.

EArl, and then would you pass it over to Bill Ryder.

CARR: Carr of EAgle Picher.

I would like to pass on one more data point. We di some testing at 100 degrees F where we deep depthed the batter We discharged the battery to one volt or so average. It is very difficult cycles on the battery, just continually to cycle the battery.

We noticed the capacity dropped off from, let's say a nominal 36 ampere hours down to 25 to 27 ampere hours. It dropped almost linearly each cycle, and it seemed to bottom out at about 25 to 27 ampere hours.

And by using the case as a rough reference, we determined that it was the positive, so that I am sure this is some substantiation of this type of deep depths.

And with regard to deep depth, I would like to pose a question to the users. We are asked many times for a ten-year near-earth orbit battery, or what can you do toward that?

Is this really a true application?

Are there applications for low-earth orbit satellites for ten years? Or, are we really looking for deep depths of discharge to increase the effective watt hours per pound?

FORD: What is wrong with both, Earl?

(Laughter.)

I think the answer to both questions is, yes.

CARR: You guys want everything.

FORD: I believe Bill Ryder had a question?

RYDER: I just want to say that the question I asked before, perhaps unfairly, of Don Mains, is appropos to this discussion, and if I heard Mr. Carr's little presentation first, it really expressed it very much better.

In other words, we tend to live with what, in the Army they used to call SOP, Standard Operating Procedures.

Standard Operating Procedure today on any questions that has to do with battery performance or life, is tighten all your controls. Weigh your plates to a gnat's eyebrow, control this, control that and control the other thing.

I am not against this, and I think that these things are necessary. But we have talked today, and Bill Carr has pointed out some points here, that aren't necessarily related to this at all.

So my question is, still is, and I don't expect to have a pat answer to it. What does the Crane data -- Crane has done the greatest amount of testing on these cells -- what does this really point up, if you analyze it, in the way of overall improvements or changes that could or should be made in nickel cadmium cells?

Thank you.

FORD: I would like to take a stab at that, Bill, in a couple of areas.

One, I think we have pretty well gotten most of the problems resolved. Maybe for the five-year. I am not sure there is a ten-year seal available yet.

I think in the areas of the seals, some of the deficiencies have been pointed out previously and are now -- most of them have been corrected.

I think one of the things that disturbs me most when I read some of the reports coming out now, that polypropylene separator is going to be the solution to all our problems.

And I don't think it is. Particularly when you talk about designing right now, you are both familiar with the requirements of the space station batteries, zero to 20 degrees C. Polypropylene I don't think is going to solve the problem. The cells are going to start failing because of cadmium migration before the separator deteriorates.

The separator is the one area right now is the major weakness in our system that we are working with.

Are there any other questions?

WILL: Will, General Electric.

I would like to make a few remarks in regard to the questions raised by Dr. CArr from Eagle Picher, which refer to cadmium migration, and the formation of cadmium hydroxide crystals.

We recently completed a study under the sponsorship of NASA Research Center in Cleveland, which was done under conditions of oxygen freedom and carbonate freedom. In fact, simulating all the conditions in a cadmium battery plate, we were able to look at the phenomena occurring in this simulated battery plate under the microscope. And we did observe that conditions of high rate charge favored the formation of small cadmium hydroxide crystals, while conditions under low rate discharge -- did I say charge before -- I meant to correct that to discharge -- high rate discharge favored the formation of small crystals of cadmium hydroxide. Low rate discharges favored the formation of very large crystals of cadmium hydroxide, which then are obviously very

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difficult to recharge.

However, if one now charges and allows sufficient time for the charging, then the cadmium hydroxide does dissolve, and subsequently forms dissolved species without cadmium ion, $cd(04)_3$ or, $cd(0H)_4^=$ minus, [illegible], which are then electrodeposited in fact, on this cadmium plate, and on subsequent discharge, this becomes again available in the discharge capacity.

So I believe that some of the questions which are being raised with regard to some of the phenomena occurring in cadmiumbattery plates, we were able to understand by these studies on simulated plate under the microscope.

FORD: Has this been reported in the final report or are you still --

WILL: The final report is being completed and will be submitted to NASA shortly, probably still within the month of December.

FORD: Other questions?

We really have one more speaker scheduled to talk on accelerated testing. Seeing that it is such a late hour, I think we should try to hold that and probbably pick it up and work it sometime tomorrow.

Jerry, is this acceptable. I think 6 o'clock is a reasonable time to ask anybody to stay here.

So, if there are no further questions, we will