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Goddard Space Flight Center

1971 NASA/Goddard-Aerospace Industry Battery Workshop

Second Day

Greenbelt, Maryland
18 November 1971

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Goddard Space Flight Center

Greenbelt, Maryland

1971 NASA Goddard-Aerospace Industry

Battery Workshop

(Continued)

Chairman: Gerald Halpert

Room 231, Building 7,
Goddard Space Flight Center,
Greenbelt, Maryland.

Thursday, 18 November 1971.

The meeting was called to order at 9:15 a.m., pursuant to adjournment.

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P R O C E E D I N G S

HALPERT: Gentlemen, can we take our seats, please?

Good morning. Welcome, all, back to the third session on the nickel-cadmium batteries, the NASA/Goddard Battery Workshop.

If you have not signed the sign-in sheet, if you were not here yesterday or if you were here and did not sign the sheet, we would appreciate you signing it to make sure that we have recorded all the people who are here for this meeting.

At the sides of the room we have some additional material. Bill Webster brought over three samples of 100 ampere hour cells from Eagle Picher, GE, and Gulton for you to inspect during the break time if you have a free moment. Their weights are listed.

Tom Hennigan would like to say a couple of words before we get going with our materials section.

HENNIGAN: Recently at these meetings we've been talking more and more about the company's products and identifying them, which is good. But I noticed yesterday there has to be some clarification on some of these things: did you treat them or did you do something to them, because this is not really the same product any more if you did something.

I guess in the separator area this becomes particularly touchy because as far as I know, all fibers have a lubricant on the surface so that fibers can be handled in the machinery. It just so happens that lubricants are usually good wetting agents and if you remove them before you put it into a cell, you're going to change the characteristics of that material and no longer can you identify it by the manufacturer's number unless you put some kind of a subscript after it like I used on mine, "AR" for "as received," "W" for "washed," and "T" for "treated."

I couldn't go into all the things we did but at least you knew we had changed it. To go into all the treatments and washing would take quite a long time.

I think we have to do this to protect those who gave us or sold us the material.

Thank you.

HALPERT: If anyone would like to make corrections in their parts of the paper, if they'll contact me within the next week I'll be glad to insert the proper subscripts so that it is recorded properly.

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For our first speaker this morning on materials, Bob Howard from Eagle Picher is going to talk about machine processing for dry sintered plaque.

Bob Howard.

xxxx

HOWARD: The purpose of this paper is to present some of the work accomplished on the NASA process variable study, contract number NAS 521159. This presentation pertains to the development of the semi-automatic process for the dry sintering of porous nickel plaques.

The authors of this paper, Mr. Walt McCarter, Dr. Don Crabtree, and myself, wish to acknowledge the technical assistance of Mr. Floyd Ford, Goddard Space Flight Center.

The design concept basic to the program was to develop a machine system to manufacture dry sintered nickel plaques. The target specifications were plaque thickness plus or minus 1/1,000 of an inch anywhere on a plaque and from plaque to plaque; plaque porosity of .4 of one percent anywhere on a plaque and from plaque to plaque. Yield weights were 85 percent of all plaques produced were within plus or minus 2 grams on a 100-square-inch plaque area.

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The design concept dictated close machine tolerances, machine stability, reproduceability of machine operations, and no hand labor which would directly influence the forming of the nickel plaque.

A machine system which satisfactorily met all of the foregoing criteria evolved during the development program. Figure 1 presents a photograph of the final configuration of the plaque-forming machine.

Floyd, would you turn the lights down, please?

(Slide 109.)

To the right beneath the control panel is shown a typical carrier platen which is used in conjunction with the machine. The platen is approximately 1 foot square and is fabricated from 031 thick nickel 200 sheet.

Located in the center of the platen is a nickel substrate screen. Prior to joining the screen to the platen, the platen is flattened in an impact press with an automatic feed. The screen is processed through a neophrene-faced press during which a series of 60 each, 1/8th inch diamter embossed studs are formed in the screen.

The embossings hold the screen approximately 7/1000ths above the platen thus assisting in positioning the screen in the center of the plaque.

The platen with the screen is inserted into the machine underneath the two parallel bars and a ground steel table possessing a circumferential O-ring is activated upward and firmly holds the carrier platen against the underneath side of the parallel bars.

A vacuum is pulled over the entire lower side of the carrier platen. This vacuum flattens the platen against the vacuum table.

Next, the storage hopper containing the nickel powder lowers and a pre-determined quantity of nickel powder is automatically dispensed at the upper end of the platen. The hopper automatically retracts and there is a narrow pile of nickel powder immediately in front of the crossbars shown in Figure 1.

This crossbar is mounted at each end to bushing blocks which are carried on precision-ground shafting. The shafting is protected by shaft boots and each shaft is positioned on an adjustable weigh mount.

The shafts, crossbar, parallel bars, vacuum table, and carrier platen are thus located precisely to one another, insuring the required dimensional control.

Carried beneath the crossbar are two semicircular polished rods mounted parallel to one another. The rear bar determines the final thickness of the unsintered plaque. Upon command of the machine operator, the crossbar assembly is actuated forward. This motion pushes the nickel powder across the platen and screen forming the unsintered plaque.

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After the plaque is formed, the vacuum table lowers, the operator removes the carrier platen and places it on a belt of the sintering furnace.

The crossbar is returned to the rear position and the operator removes any nickel powder from the vacuum table.

The machine is controlled employing a pneumatic logic system which is interlocked with various mechanical motions of the machine. The machine is housed in a temperature controlled room adjacent to the sintering furnace.

Several problems were incurred during the development, some of which deserve comment.

Ground ceramic plates were tried as carrier platens. These ceramic plates lead to an excellent quality plaque but repeated passes through the sintering furnace resulted in grain growth and eventual fracture. The ultimate solution was the nickel plate used in conjunction with the vacuum table.

Dimensional control on the nickel carrier platens is as good as that determined in early use of the ceramic platens.

The first method of distributing the nickel powder was to sift it onto the carrier platen and substrate screen. This procedure resulted in porosity variations as high as plus or minus 2 percent and in non-reproduceable weight of nickel powder laid down per unit area.

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The present method of drawing a pile of nickel powder across the substrate screen proved to solve both of the above problems.

Figure 2, please, Bill.

(Slide 110.)

Figure 2 presents a comparison of the sift method and pile-and-draw method. Shown as the thickness of the final center plaque as a function of the final net weight of nickel powder laid down on a 2-square-inch sample, the result reveal a clear linear correlation between thickness and net weight of nickel powder laid down for the pile-and-draw method.

The sift method has no clear correlation.

Figure 3.

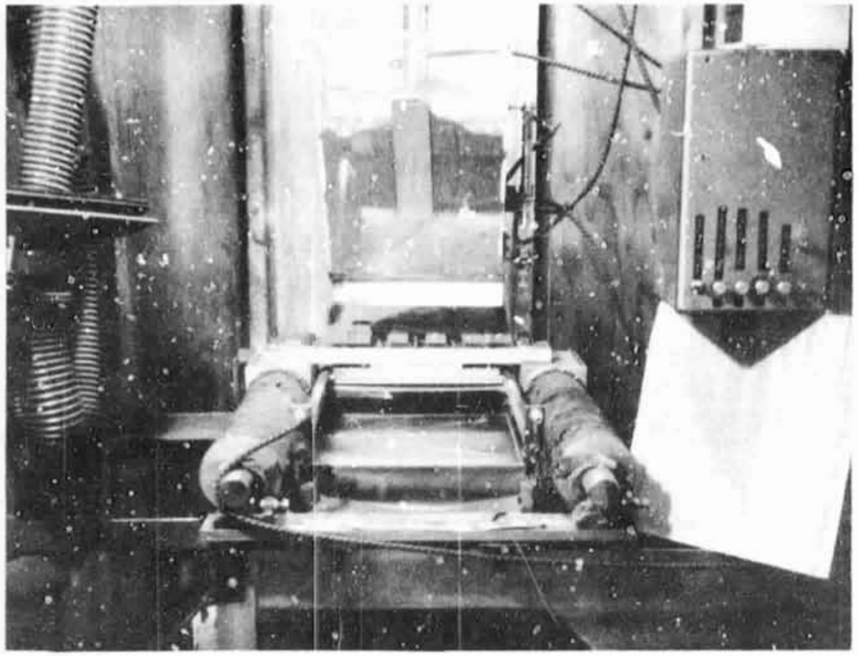
(Slide 111.)

Figure 3 presents plaques 100 square inches in size as a function of plaque weight for two groups of plaques produced on this machine. Of 1,010 29-mill plaques, 89 percent were within plus or minus 2 grams. Of 403 each 21-mill plaques 97 percent were within plus or minus 2 grams.

All of the plaques were 100 square inches in size.

This uniform weight characteristic is a direct result of the mechanics of the aforementioned pile-and-draw method.

The day-to-day production yield of plaques within plus or minus 1/1,000ths of a desired thickness is approximatel



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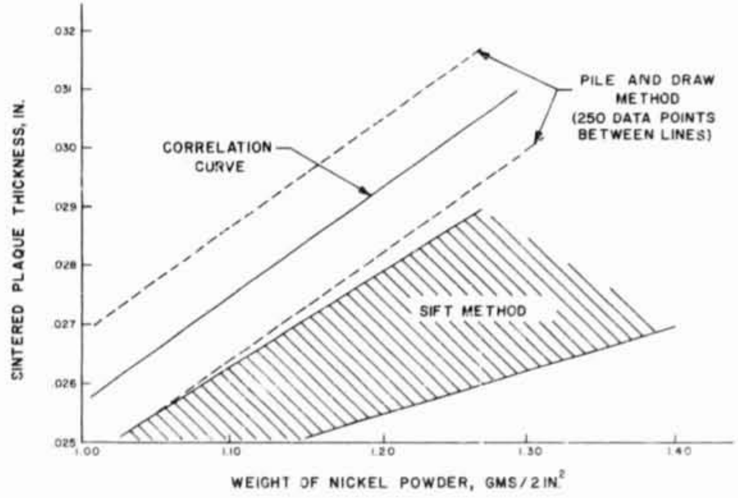

Figure 110 NUMBER OF PLAQUES AS A FUNCTION OF PLAQUE WEIGHT

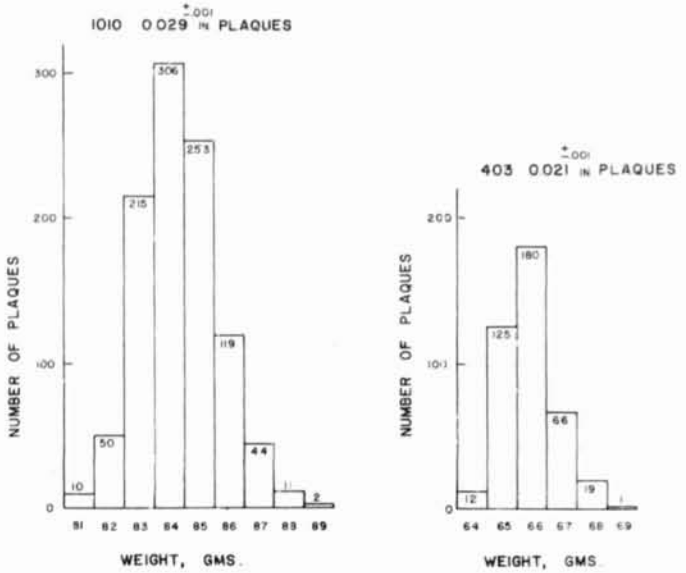

Figure 111 NUMBER OF PLAQUES AS A FUNCTION OF PLAQUE WEIGHT

Figure 109

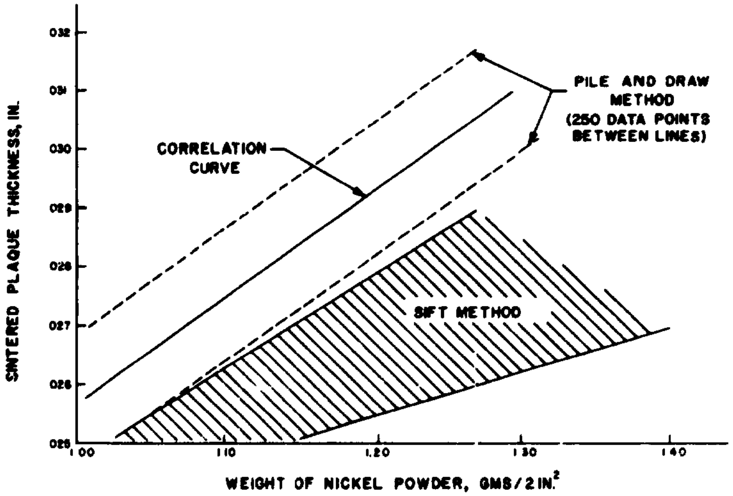

Figure 110 NUMBER OF PLAQUES AS A FUNCTION OF PLAQUE WEIGHT

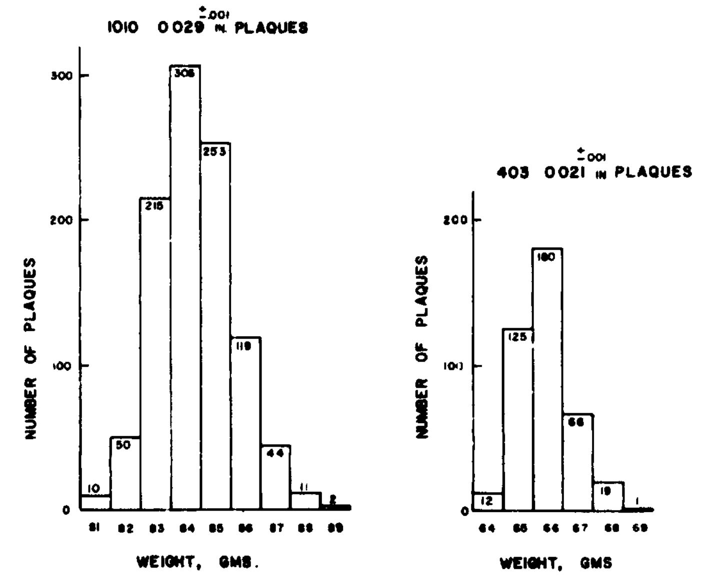

Figure 111 NUMBER OF PLAQUES AS A FUNCTION OF PLAQUE WEIGHT

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90 percent. The porosity variation of 1,010 29-mill plaques previously mentioned was from 85.0 to 85.7 for the particular furnace conditions of the same process.

The strength of the plaques as determined by a standardized break test exceeds the normal requirements applied to similar products manufactured by the manual method.

From our data we reached these conclusions:

We concluded that a dry sintered nickel plaque can be produced by a machine system, and such a procedure yields desired characteristics of thickness, porosity, and weight per unit volume of area.

We might add that this process has been incorporated on the following programs:

Philco-Ford SMS program, Grumman 100 ampere hour program, NASA/Goddard 6 ampere hour program for separator study, and Boeing cells for the United States Air Force.

May we have the lights, please?

(Slide off.)

HALPERT: Are there any questions for Bob about this process?

John?

PARRY: Parry, Arthur D. Little.

Is there any tendency for the nickel powder to stick to the nickel platen?

HOWARD: Yes, sir, there is.

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PARRY: Does this cause any real problem from the point of view of the production process?

HOWARD: The carrier platen -- nichel carrier platen is treated in such a way that this sticking is only around the edges of the platen. The plaque is then trimmed and this area is cut off.

PARRY: What is the treatment?

HOWARD: Zirconium oxide.

PARRY: Thank you.

HALPERT: Any other questions?

Okay, thank you-- Oh, sorry, one more back there.

BACHER: Are there any problems with porosity variations through the thickness of the plaque?

HOWARD: This was investigated with a weight determination of various areas over the plaque wherein areas were punched from the plaque and carefully analyzed for weight. We have found that the distribution of weight per unit area is very good in this dry sintered plaque.

BACHER: I don't mean from an area point of view but is one side of the plaque denser than the other side of the plaque?

HOWARD: Predominantly the substrate structure is on one side of the plaque. This would possibly limit surface area on that side, yes, sir. Is that the question?

BACHER: Yeah. Well, could this affect the surface

eb10

area that the opposing negative plates see -- you know, the opposing plates?

HOWARD: I think Earl Carr is just chomping at the bit to answer that question.

CARR: Earl Carr, Eagle Picher.

The reason that the screen wire is predominantly on one side is because in order to maintain something similar to previous qualified designs we intentionally put the screen wire off center on one side.

Now this procedure is so good that you can literally laminate the screen on one side of the plaque and then all you see is the screen and the plaque almost looks like it's separated -- like it's glued on, but that'a a deviation from our process.

Now we're continuing on to investigate putting the screen in the precise center of the plaque. Again, this is a change to what has been used in the past so we have to proceed a little bit slowly.

But I have a question, and that is I understand your question in that the variation, say, over the thickness, whether it's a 20-mill plaque or a 30-mill plaque, what is it at one point and what is it at another.

We really don't know a good way to measure this and if anyone has any comments about this we would really appreciate any input as to how you would determine the uniformit of a cross-section like that.

HOWARD: Also in response to your question, we have analyzed fixed areas of an impregnated plaque and the net weight per fixed area is consistent over different areas of the plaque However, analyzing for which side and how deep the impregnation is -- I'm not sure I can answer your question, sir.

CARR: Also, regarding the effective area of the plaque, if you were to take the plates and when you orient them in the cell you will find that the screen side of the positive always opposes the screen side of the negative so that you always have the like side opposed to like side in a design.

I think you can work this out. It's a geometrical thing. The plates are all the same so when you turn the negatives against the positives they face the same type side.

HALPERT: You're telling your secrets.

Any other questions of Bob?

GROSS: Sid Gross, Boeing.

Have any measurements been taken on the strength of the plaque?

HOWARD: Yes, sir, there has been.

GROSS: Do you have any comments on how strength is changed as a result of modifying the processes?

HOWARD: I would say that the strength is more uniform over the given area of the plaque. As far as

eb12

mechanical strength, this is determined by the sintering elements of the process, not by the interaction of the long nickel fiber and any matter that would be just deposited on the substrate structure.

As far as the strength determination, we have the designer of this machine, I believe when he was with Tyco Labs. If you have any questions about the elements of the machine or the method of determination of strength, he would be glad to answer those, I'm sure.

VOICE: Thank you, Bob.

HOWARD: That's fine. I'll just shift a little of the responsibility around.

Yes? One more question?

RUBIN: Rubin, Tyco.

You mentioned some weight distribution over a hundred-square-inch plaque, 85 percent of them fell within two grams of a certain net distribution. What is the smallest area that you measured and what was the weight distribution on that smallest sample?

HOWARD: Weight distribution for a given area?

RUBIN: In your method you distribute a fairly consistent amount of powder over a large area, but have you measured the uniformity over smaller areas and if so, what was it?

HOWARD: Yes. The measurements mentioned were over a smaller area. They were two-square-inch samples, to about one inch effectively, and these were cut from the same areas of different plaques and then compared with each other on plaques and with each other, plaque to plaque --

RUBIN: And this gave --

HOWARD: -- by thickness and weight.

RUBIN: And what percentage deviation did you find in those small areas from plaque to plaque?

HOWARD: I'm sorry, I don't think I have that data with me. I don't really know.

CARR: Earl Carr, Eagle Picher.

The reason we went into this work was as a result of the first two quarters of the NAS 521159 contract. We found variation within-- We were working to plus or minus 3/1,000ths which is reasonably typical and we found variation within this range and we identified it.

And we found some surprises during the first two quarters in that we took the data and we compared within a plaque nine samples, as Bob mention, two-square-inch samples taken in nine places from a plaque. Then we compared those nine samples to each other; we compared them to the next plaque in the sequence. Then we compared them to the next day at the same setting, and then we compared them to the next week; in other words, different types of reruns.

And the surprise was -- and this data is presented in the first two quarterly reports -- was that we found that the variation in the plaque is in any one single plaque. Something like 80 percent of all the variation we ever experienced you can find -- or we used to be able to find in a single plaque, so that it became very obvious that, if you have a plaque, a single plaque, that does not have any variation, we have immensely improved the process, and this, indeed, is what we did.

The means by which we did it were to lay a plaque which, when it is introduced into the furnace, is uniform because, if it is introduced into the furnace uniformly, it comes out uniformly. So this is why the emphasis was placed on the equipment to lay the plaque in a uniform manner.

To maybe add one more point on your question, in Figure 2, I presented the weight of nickel powder in grams per two-square-inch sample. This was on 250 data points cut from various plaques, possibly from -- I would assume maybe five samples per plaque or something along that line so there would be an analysis across approximately 500 square inches of plaque area.

It appears that there may be less than maybe or .2 of a gram variation among the samples pulled from 500 square inches of plaque material.

MAHATO: Mahato, from Globe Union.

ebl5

Is that variation any way related to the particle size?

HOWARD: I'm sorry, I didn't understand the question.

MAHATO: Is that variation any way related to the particle size?

HOWARD: The particle size of the nickel powder?

MAHATO: That's right.

HOWARD: An analysis on the individual size of each nickel fiber laid down wasn't done but the bulk density of the powder prior to its laying on the substrate was analyzed. Other than the bulk density measurement, I'm not sure I can answer your question about particle size of the nickel fiber.

However, there are two types of carbonyl nickel powder. Both were investigated and both can be satisfactorily laid in the dry process.

BELOVE: Belove of Marathon.

Was the bulk density of the various cells maintained at a constant?

HOWARD: Yes, sir. The bulk density does come in in a varied range within one particular type of the carbonyl powder. I believe that your carbonyl type 287 might run from .8 grams per cubic centimeter to as high as 1 gram per cubic centimeter.

The dry process allows us to control bulk density. We can select our bulk density to any desired final plaque e516 characteristics, both within the 255 and the 287 range.

BELOVE: You select the bulk density. That means you select barrels of material and reject other barrels?

HOWARD: We may use all barrels received but bulk density can affect porosity of your plaque on a unit area -- weight or thickness unit area.

BELOVE: Thank you.

2 HOWARD: I would like to also point out this is one advantage, we feel, in the dry sinter process, is the ability to control bulk densities. It selects rather nicely to whatever you want to get out the other end of your furnace.

FORD: Ford, NASA/Goddard.

Gerry, I would like to ask one question.

Bob, if I understand what you're saying you're saying that the variable is in the bulk density but by controlling some of the variables in the process, you can account for this in the final plaque?

HOWARD: Do you think you remember that well enough to repeat it?

(Laughter.)

FORD: Okay. I'm trying to clarify a point because I'm a little bit confused now.

You acknowledge there is a variable in the bulk density of nickel powder.

HOWARD: Yes, sir, there is.

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FORD: And the implication of what you said is that you allow this variable to come into the sintering process but you can counteract it somewhere in the process to give the same plaque characteristics in the end product.

HOWARD: Yes, you can, Floyd. It is possible that you can change your furnace setting to allow for deviations in bulk density, --

FORD: Okay.

HOWARD: -- but I'm not sure that is what you'd want to do. I think I'd rather know what bulk density I'm starting with and leave my furnace where I had it and take the sacrifices on the higher end of the bulk density and porosity.

PARRY: Parry, Arthur D. Little.

The work we did at Tyco,I think we found that if there were variations in bulk density with the starting powder, that if you did change either the sintering time or the sintering temperature you could end up with a plaque with the characteristics that you wanted.

We would need some exploratory work to find out what you had to do to get the characteristics you wanted but in general, the porosity, the resistance, the mechanical strength of the plaque all move together so you could get the plaque with the characteristics you wanted just by changing the sintering conditions.

HOWARD: I think Sonotone is going to have something to say.

BELOVE: Belove of Marathon.

I didn't want to pursue this thing but now that it has been taken up, the powder variation -- the powder as we receive it varies practically from barrel to barrel, and probably within the barrel. The question here is-- There are several ways of maintaining uniformity of the finished plaque if the bulk density of the powder is found to vary.

The point we're trying to get here is: How do you obtain uniformity in the plaque, when the barrel -- the bulk density of the various barrels vary?

One method of course is to mix the powder and obtain a uniform or at least a practically uniform bulk density. Now the other method would be, as we just mentioned, by changing the parameters which would be a rather tricky job because it would mean experimenting on every barrel of powder, practically.

Now the question is: How do you do it in a practical regime?

HOWARD: Day by day I control my bulk density. I don't blend to a bulk density.

BELOVE: You don't blend. You control the bulk density?

HOWARD: Yes, sir. I utilize bulk densities within a range that I find acceptable.

BELOVE: That means that you reject barrels of powder back to the vendor?

HOWARD: I haven't lately.

(Laughter.)

BELOVE: Then Eagle Picher must have a contract with Inco that's special.

HOWARD: We have a working relationship with those people.

BELOVE: That's good to know. Now I've learned something. Thank you.

(Laughter.)

PARRY: Parry, Arthur D. Little.

Again my experience was that within the barrel, the bulk density was pretty uniform. We used to sample the barrel at various levels in the course of doing our work and for us, a 200 pound barrel would last maybe three or four months for the work we were doing, so this was over quite an extended time period.

BELOVE: I would out that for you that's all right.

PARRY: This is true. I think you have a very valid point, that you have to experiment for each bulk density if you want to control the characteristics of the final plaque.

There are variations from barrel to barrel, but I would like to mention, too, that blending powders is not the

eb20

solution to the problem because these nickel carbonyl powders are relatively fragile and any blending process you go through actually changes the bulk density.

BELOVE: That depends on the quantity.

HOWARD: I might add that that's my experience, also. I have had no luck in blending nickel powders.

BELOVE: Again, it depends on the technique used.

HOWARD: I'm sure that's true.

CARR: Carr, Eagle Picher.

We made a little booboo a long time ago on doing the work, the same mistake that John just stumbled into. His powder lasted him three or four months.

When we set up the first regression models for the sintering process we did not consider, just as an oversight, the bulk density. Lou Belove has made a statement that it's very tricky. It can be done a lot easier than most people think by regression analysis techniques to establish precisely the variations in furnace setting to compensate for a change in bulk density.

But these things are related to things like furnace atmosphere, dew point, like you wouldn't believe, so it is tricky but it is within the state of the art to precisely know what settings will give you what porosity.

BACHER: Joel Bacher, RCA.

To change the subject slightly, among the plaque

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parameters that you measured you mentioned porosity, weight and thickness. Do you have any means of determining degree of fusion or sintering or some strength?

HOWARD: Yes, sir, we do. It's a four-point band tester developed by -- or designed I guess originally by Tyco. And the designer, the original designer of that machine is with us today, and he'll be glad to comment on that if you'd like.

(Laughter.)

I think he is going to refuse to comment right now.

PARRY: Parry, Arthur D. Little.

I just want to make one comment to Earl Carr. I didn't --

HOWARD: This is the designer, by the way.

(Laughter.)

PARRY: The four-point band test works and it's fully written up for anyone who wants to look it up. I make no further comment on that.

I would like to say to Earl Carr that I didn't exactly stumble onto the problems of blending nickel powders; it was a specific study on our part, and is also written up in one of the early quarterly reports.

CARR: Earl Carr, Eagle Picher.

Sorry about that, John.

One thing else I wanted to say in answer to the

eb22

question from RCA is there is another technique for studying bonding and this is also reported in some of our early quarterlies and that is scanning electron microscope pictures -- I can't say that word. But SEM photographs are fantastically revealing as to the properties of the plaque. You can literally look at it and see pore bonding or pore fusion or uneven fusion in the photograph.

And also I think these photographs are useful in determining such things as pore size distribution. It's a very powerful technique.

HALPERT: Thank you, Bob.

Earl, I'm glad you brought that up. I just happen to have a series of three conglomerate photographs on plaques, using the SEM and I'll just show you. One is an experimental model. One is a special version. Another one is a commercial product, and I will just show you the three to give you some idea of the variations you can get between plaque materials.

(Slide 112.)

This is the experimental model. You see it's a conglomerate so that it covers quite an area. I think it is, as I recall, at 250 X. Each slide, each photograph in the conglomerate was taken at 250 X. This is a 250 X pattern of a significant area of this plaque.

You can see a fair amount of porosity but quite a bit of nickel powder bonding.

(Slide 113.)

Here's a second version. This was made more for aerospace use. This particular dark area here is a problem with the SEM. That particular part did not come out. It is not a hole area, as you can see.

The other areas that are porous tend to show up rather well but that's kind of blurred. But here you see slightly greater porosity; still quite a bit of nickel.

Both of these have been made in the slurry process.

(Slide.114.)

And the third is one which was sent to us as a commercial item and it is from the dry process. You can see here greater porosity. It's hard to talk about uniformity when you talk about plaque materials and I don't want to say and I can't say which is better for what purpose.

I think we have found that if you sinter them long enough, as John Parry and others have been saying, at different temperatures you can get the overlapping even greater, but this particular one seems to have greater porosity than the others. But as Earl has mentioned, it is a valuable tool for looking at these various plaque materials.

However, the mechanical strength test does give you the degree of bonding that you have between the nickel particles.

Are there any other questions? Oh, I'm sorry.

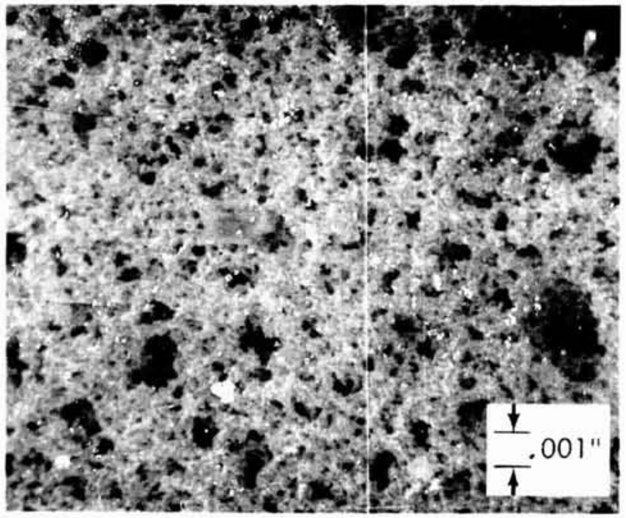

Figure 112

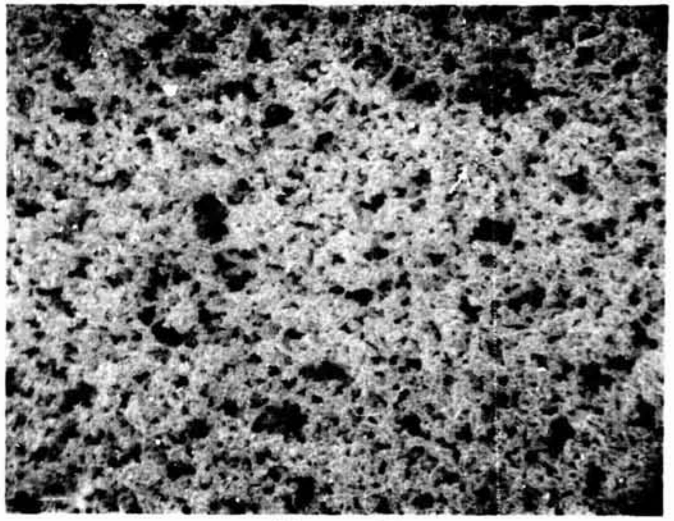

Figure 113

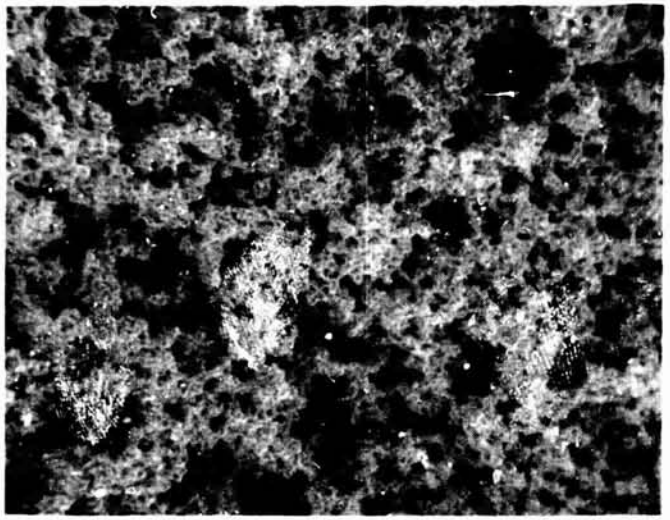

Figure 114

WT. BEFORE IMPREGNATION (grams)	WT. AFTER	NET GAIN
9.2222	16.9090	7.6868
9.3916	17.4829	8.0913
9.3192	17.2953	7.9761
9.2522	16.3804	7.1282

Total Wt. Gain = 30.8824

(Corresponds to 8.93 A-h the O. Cap.) 0.030 in, 83% porosity plague 3" × 3", coined 0.010"

Figure 115

Tom Hennigan -- I'm sorry, Tom -- wanted to ask a question.

HENNIGAN: I'd like to ask this of Ed Rubin, who used to work for TI, and this question came up before, can we get the grid in the center of the plaque?

If I remember right, TI's grid was on the side. It had to be on the side because of the process. This appeared to be satisfactory.

Do you have any comment? Were there any problems with this plaque with the grid on the side?

RUBIN: Rubin, Tyco.

In most of the plates that TI had worked with, they were under 30/1,000ths thick; and restricting ourselves to that thickness, we did not run into any difficulty in terms of swelling of materials or warpage of the plates.

I believe once you get into thicker plates than that you will run into some difficulty, especially with warpage.

Of course when it comes to making cylindrical cells it is desirable to have a screen on one side.

HALPERT: Are there any other comments or questions regarding plaque materials?

(No response.)

HALPERT: Okay, if not, then we'll go over to the next step, that is in the plate materials themselves, impregnation, and David Pickett of the Aero Propulsion Lab., Wright-Patterson, wants to talk about nickel hydroxide electrodes fabricated from the Bell high temperature electrochemical impregnation process.

PICKETT: One of the first presentations at the battery workshop last year was given by Dick Beauchamp of Bell Labs on a new high temperature electrochemical impregnation process for a nickel-cadmium electrode. In this process a sintered nickel plaque is impregnated by making the plaque cathodic and immersing the plaque into a boiling solution of nickel or cadmium nitrate between two inert annodes and passing a current of about a half amp per square inch of electrode surface through the plaque.

The pH of the solution was initially set at about 4 and was controlled by an initial addition of sodium nitrate to the impregnating solution.

Electrodes made by this process showed a substantial increase in capacity over electrodes made by conventional vacuum impregnation techniques. In fact, performance of the electrodes was quite impressive in general.

Since this time we at the Air Force Propulsion Lab, especially Dr. Lander and I, have been investigating the process in one of our in-house efforts. I would like to present to you today some of the data that we have obtained from this. It is by no means conclusive but I think some of it is rather interesting.

Since the original presentation by Dr. Beauchamp, Bell Labs has introduced papers, in particular at the Electrochemical Society in Cleveland, where they use various additives in the process for the positive plate such as cobalt.

In the original impregnation solution, two molar nickel or cadmium nitrate and .2 molar sodium nitrite solution was used and impregnation was carried out on inch and a half by inch and a half plaques. We deviated-- Well, excuse me. These were connected in series in beakers so if you wanted to impregnate several plaques at a time you merely connected the beakers in series.

We deviated from this original procedure by carrying out our impregnations in a large Pyrex vessel, connecting all of the plaques to be negative of a power supply and all of the annodes to be positive so essentially we have the whole thing in parallel -- plaques connected in parallel in the large bath.

Our solution contains 1.8 molar nickel nitrate, .2 molars cobalt nitrate, and .2 molars sodium nitrite. The current we used varied from .3 of an amp per square inch to .5 of an amp per square inch, and in most of our successful runs we have impregnated plaques as high as -- using currents as high as one amp per square inch.

I would like to show you some of the gains that we have obtained on these.

(Slide 115.)

These are 30 mill plaques, dry sinter variety, made by Eagle Picher, and you can see that the total weight gain varies between 7 and 8 grams. This corresponds to roughly 8.9 ampere hours theoretical capacity, on the theoretical.

We formed plates of this type by combining in particular these four plates with five negatives taken from a standard 22 ampere hour aircraft cell that were cut to 3 by 3 dimensions. All nine plates were made up in a formation cell and the cell was given an initial formation charge at C over 10 of the theoretical capacity with about 20 percent overcharge.

Discharge at the one hour rate to .9 of a volt showed 6.55 ampere hours capacity. The cell was then charged at the one hour rate and discharged at the one hour rate to .9 of a volt for 27 more cycles and eventually showed a capacity of 10.4 ampere hours.

Positive plates from this cell were removed, placed with four other positives formed by the same process and the resulting cell placed on cycle life at 120 degrees Fahrenheit with nine negative plates, again the plates being taken from conventional ni-cad batteries.

The cell was sealed with a 26 psi release and initially charged at 20 amps for one hour. The first discharge showed 17.1 ampere hours to a cutoff voltage of .9 volt. Cycling was then carried out by charging at 33 percent overcharge at the one hour rate based on capacity from the previous

eb28

discharge to .9 volt.

A typical example of some of the capacities obtained:

At cycle No. 109, 19.7 ampere hours were put in and 13.8 ampere hours were obtained on discharge to .9 of a volt.

After 152 cycles, the cell shorted. We have made other cells by this method and have run them at these high temperatures. Eventually in some of these electrolyte was dried out but we have obtained much higher cycle life than these. But this is just a typical example of some of the work that we have done.

I think the most impressive thing about it is the charging efficiencies for this high temperature. We do not get near as good charging efficiencies out of conventional aircraft batteries at this temperature. In fact, they are well below 50 percent.

We are still doing investigations on cells of this type and are making negative electrodes by the Bell process. We hope to have some data on complete cells in the near future.

That is the essence of my presentation. Are there any questions?

LACKNER: Lackner, Canadian Defense Research.

You mentioned you got good performance at high temperature. What temperature and for what number of cycles were you operating out of?

eb29

PICKETT: All these cycles were carried out a 120 degrees Fahrenheit.

LACKNER: Charged and discharged at 120 degrees?

PICKETT: At 120 degrees.

LACKNER: For how long?

PICKETT: One hour. We measured the capacity to .9 of a volt on the previous discharge and then put in the same capacity with 33 percent overcharge at the one hour rate.

LACKNER: For the 150 cycles before it shorted out?

PICKETT: Right.

LACKNER: What kind of separator did you have in there?

PICKETT: We had a layer of cellophane and a layer of nylon.

LACKNER: Good enough.

PICKETT: Gerry asked if these were flooded. Yes, these are flooded cells.

MAURER: Maurer, Bell Laboratories.

Did this short occur because the electrolyte had dried out?

PICKETT: Apparently so.

PARRY: Parry, Arthur D. Little.

Dave, do you have a figure for the specific capacity of the positive plates as operated in the cell, the ampere hours per cubic inch?

PICKETT: Well, based on the figures that I've given you and after 28 or 29 formation cycles, the capacity was roughly 10 ampere hours per cubic inch of void volume available in the plaque.

PARRY: Are all your capacities on the basis of void volume or volume of the plate?

PICKETT: We usually calculate them on the basis of void volume in the plaque but these can easily be converted.

FONT: Font, of SAFT.

What can you say about the aspect of the positive plates compared to plates which were impregnated in vacuum condition with standard plates, if you will, the aspect of the positive in such process after such cycling?

PICKETT: Well, we --

FONT: Did they --

PICKETT: In terms of what? Cycle life or capacity?

FONT: Yes, cycle life and the flake of the plates, for example.

PICKETT: Well, it's really hard to compare cycle life here with other cells that we made because this is one of the first experimental cells we've made and tried, and it would be I don't think justified to really compare it with any other cells, but of course the other cells do get much greater cycle life.

As far as capacity goes, I would venture a guess --

eb31 I don't know exactly, but I assume that conventional state-of-the-art aircraft battery electrodes have about four to five ampere hours per cubic inch of electrode and that these would be roughly between eight and nine.

FONT: Thank you.

BELOVE: Belove of Marathon.

Dave, I heard you say you formed for 29 cycles. This formation occurred before you began testing the battery?

PICKETT: That's correct, yes.

BELOVE: What does the formation cycle consist of?

PICKETT: Our first cycle was a C over 10 charge based on the theoretical capacity of active material we had in the cell. This was then discharged at the one hour rate to .9 of a volt.

The subsequent charges were made at the one hour rate and discharges made to approximately the one hour rate to .9 of a volt.

BELOVE: In all cycles thereafter, they were charged at the one hour rate?

PICKETT: That's correct.

MAURER: I would like to comment that at Cleveland, Beauchamps presented a paper on additive effects to improve cycle life on the electrodes made by these processes and one can get cycle lives of several thousand cycles, deep discharged when cobalt is present in the electrode.

eb32

FONT: Font, SAFT.

Have you performed the chemical analysis on either content -- hydroxide nickel content on your electrodes?

PICKETT: No, we have made no analysis as yet. We are in the process of doing that now and the results just weren't available for this presentation.

FONT: Thank you.

SULKES: U. S. Army Electronics Command.

After you finished the cycling did you take any physical data? In other words, particularly on these high utilizations did the plaques swell or have cracks or that type of thing?

PICKETT: There was some swelling, yes, but there were no cracks in the plaque.

SULKES: Would you have an idea of what, say, the actual ampere hours per cubic inch ended up after the swelling? In other words, I've had plaques from various manufacturers that, say, started out at 9 but by the time they finished swelling and growing, they were back at 6-1/2 and 7 where everybody else's plaque is.

PICKETT: Well, no, we didn't measure the thickness of the plaques after the 150 cycles, no. After the 29 cycles we did. We showed no substantial increase after the 29 formation cycles.

SULKES: Well, usually it would occur right away

eb33

so you may have something.

BACHER: Bacher, RCA.

Getting back to the original plate processing, what were the inert electrodes?

PICKETT: In the Bell process they use platinum electrodes or platinized titanium. We do not use electrodes of that type and I don't guess you would call our electrodes inert. We use 200 nickel and there's substantial corrosion to the electrode.

HALPERT: Any further questions?

(No response.)

HALPERT: Thank you very much.

For the next subject, I have a short presentation on some negative plate materials that we've looked at from four ampere hours cells on test at Crane. One set of cells had a teflonated negative and another was non-teflonated, and Floyd I think has some background data that I think it might be helpful to present before I show the photographs that I have.

FORD: In the early stages of the SAS-A program, APL, which is the prime contractor on this program to Goddard, procured cells from two different manufacturers. For identification purposes, if you are interested in following these tests further at Crane where the cells are still on test, Pack 1-C, "C" as in "Charlie," the manufacturer is General Electric; Pack 18-D, Gulton Industries, and one correction to what Gerry said, these are 6 ampere hour rated capacity cells.

These cells were put on a life cycle program for the SAS-D using a charge control system simulating that of the spacecraft. They were run in a 90-minute orbit. The depth of discharge was approximately 21 percent and they were run at 25 degrees C. The charge current is limited at 3-1/2 amps until the voltage limit is reached, at which time it goes into a taper.

The voltage limit is 11.4 volts at 26 degrees C. This is a temperature compensating voltage. They were placed on life cycling on July the 22nd, 1970 and exactly one year later, one cell in each pack was removed for analysis. These are the cells Gerry will now discuss.

HALPERT: I don't have any chemical results at this point. These are really photomicrographs of samples of the materials, of the plate materials in the cell.

The first ones are from both cells. I'll try to get both of them in here at the same time.

(Slides 116, 117, 113.)

The left one seems to be a little out of focus.

All I wanted to show here: All are positives. There was little or no difference. The bright parts that you see are the nickel plaque. These are cross-sectioned and mounted in sample holders. What you can see -- The grey area, the active material has come to the surface of the plate and

Figure 116

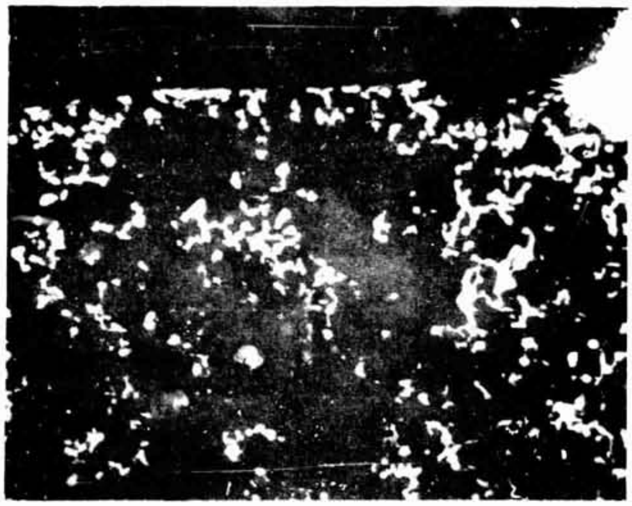

Figure 117

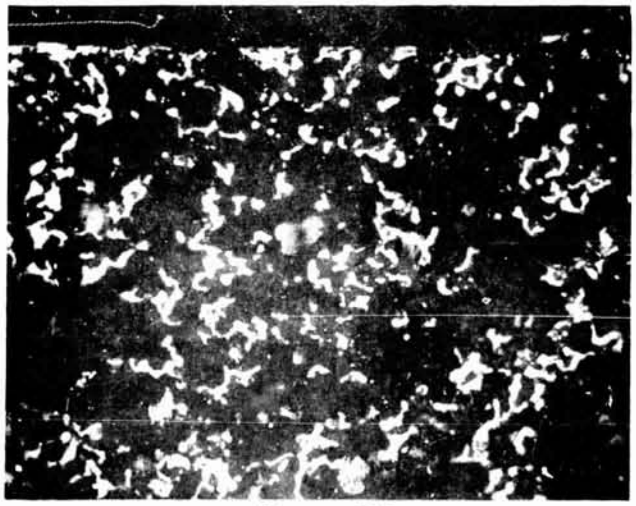

Figure 118

MV-6

it actually is not as clear in this partiular photograph but it's the same. The active material has come to the surface of the plate.

I have put in one of an unused material and I think here hopefully you can see that the active material is completely covering rather uniformly within the entire surface -- within the entire area of the plate rather than just accumulating at the surface.

So I would say as far as deposit is concerned, in both cases we have -- Neither one was, of course, teflonated but in both cases the major change was the actual material near the surface.

(Slide 119.)

At the negative we tended to find in the non-teflonated large, fairly large crystals of negative material coming from the surface of the plate. I've got this first as a negative now at the surface, and that's a fairly large crystal. These photographs are all 250 X (corrected from the 500 X cited by speaker.)

The very bright spots in this area are the nickel material for plaque. The gray area is the cadmium hydroxide, and then the shiny dots within the cadmium hydroxide is the cadmium active material.

You can see on this piece now that seems to be away from the surface of the plate that we have not only the cadmium hydroxide growing in a crystalline shape away from the plate but some cadmium metal also embedded in it.

MV-37

We found that at times removing a cell or removing a plate in the charge condition and wiping the surface of the plate, quite a bit of powder came off. We analyzed the powder and it was mainly cadmium metal and we did the same thing for discharge plates. The power was still very loose. We wiped it and took that material for sampling and almost all that material was cadmium hydroxide, which means that even though this powder is coming away from the surface of theplate, it is very loosely attached, it is still -- quite a bit of it is still electronically connected to the plate so it can be oxidized and reduced.

(Slide 120.)

You can see these two are the same or similar. What we've done is taken the sample and dipped it into the famous mussprat solution, affectionately referred to by our metallurgical people as muskrat juice, and tried to remove some of the cadmium hydroxide, hopefully leaving some of the cadmium behind.

But, as you can see -- This was only a very short dip, as a matter of fact, but you can see that some of the cadmium has been removed, as well as the cadmium hydroxide in this dip process.

(Slide 121.)

This further photograph is one in which we used polarized light and here now you can see back in the area

Figure 119

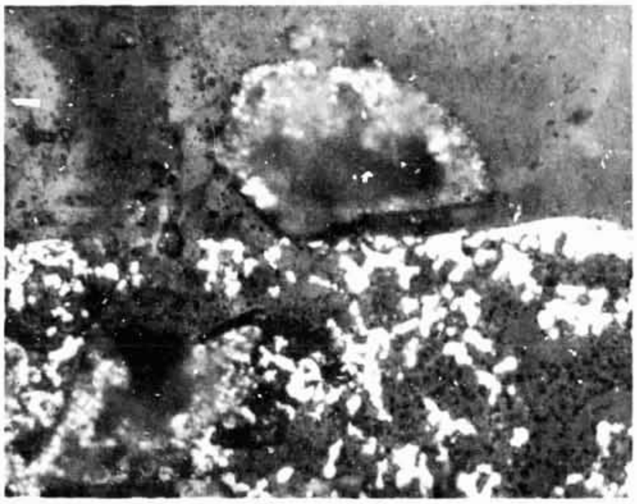

Figure 120

Figure 121

MV-3

here what looks like a small crystalline area. It comes out very bright and you get a kind of a 3-D effect in the crystal.

Up in here, you can see actual crystal into the mounting material away from the plate.

I have a couple more of these I can show, but, what it does do is bring out the crystals with greater detail.

(Slide 122.)

Okay. Now, looking at the separator material just adjacent to a sample of the plate, we found this -- As a cros sectional area we found this type of a structure in which you can actually see some of the cadmium and cadmium hydroxide particles.

These lighter gray spots are the nylon separator coming through but you can see both cadmium metal and cadmium hydroxide in those particles.

(Slide 123.)

This is another sample that was similar, actually dipped for a few moments in the musspratt solution.

(Slide 124.)

A further sample in which we dipped it in mussprat solution and you can see now these holes where some of the active material was that has now been removed, but if you look at a polarized light photograph on the same sample, you can actually see the 3D effect.

(Slide 125.)

You can see the 3D effect in which you see the crystals right down into the separator material. Again, this darker area here is the nylon. These lines here are due to the nylon separator. What comes out-- Everything else is dark except the crystal material.

This is as I say in the non-teflonated one. We had similar results with the teflonated ones.

(Slide 126.)

This is a cross-section of the teflonated electrode in which again we see the nylon separator here and some of the crystalline material at the top. Now one of the things is, no matter which plate we used, we were able to find areas where there were large amounts of cadmium at the surface of the plate.

(Slide 127.)

In this particular case we found some further cadmium hydroxide by doing a polarized light.

Let's see if I've got the right direction. Yes, this is the same photograph in polarized light. You can see the crystalline material coming through very nicely, and we still have some crystalling material down in here although it seems to be lesser.

Another aspect, we find areas of large amounts of

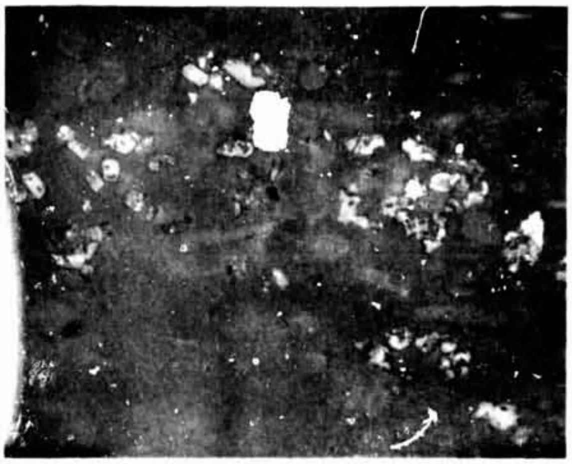

Figure 122

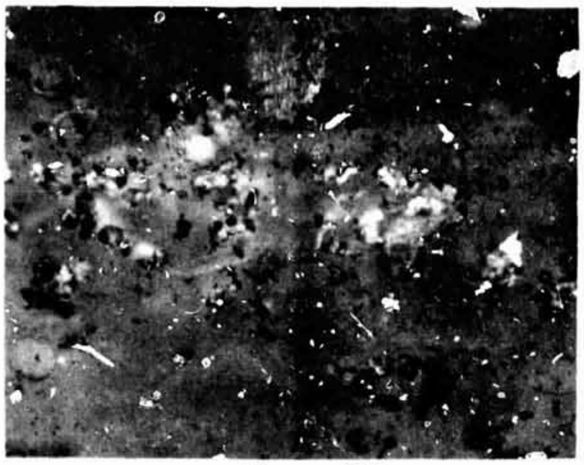

Figure 123

Figure 124

Figure 125

eb39

cadmium or small amounts of cadmium on the plate, on both types of plates, regardless of what it is teflonated or not. The major difference that we did find is the following:

Using the scanning electron microscope, we looked at only the surface properties of some of these materials and here we have a couple of photographs --

(Slide 128.)

-- of typical areas within the non-teflonated structure which seem to be larger and fairly irregular types of structures.

We can see here one of the nylon strands being embedded in that particular plate, but as I say, the major difference here was in this teflonated one-- That's the next one I can show you.

(Slide 129.)

You see a more regular shaped, smaller particles. We don't know what the reason is yet. We do know that the separator pulls very easily from that negative electrode while in the case of the non-teflonated one we find that it takes quite a -- it does not come off easily. It can be washed off, of course, but it's more difficult. It seems to come off the negative.

In both cases we have some cadmium in the separator. In the non-teflonated one we have a little bit more cadmium. We found negative material on both positive plates in both cells so that the cadmium is getting through.

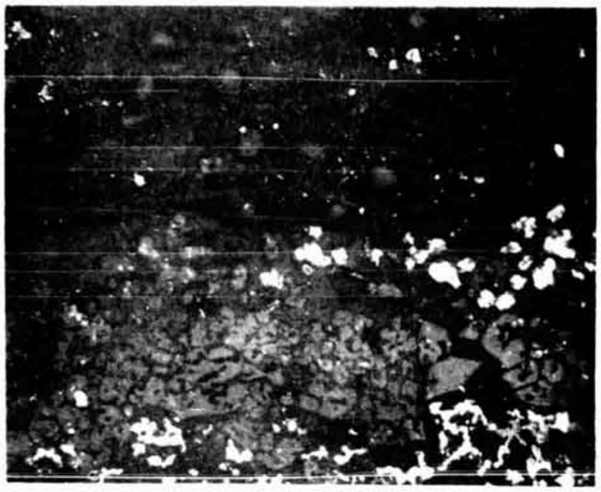

Figure 126

Figure 128

Figure 127

Figure 129

MV-9

It does appear in some of the samples we looked at to be lesser on the teflonated one that the non.

The main points at this time are two things: First, the separator came off very easily and, secondly, that this type of structure, another example of which is here --

(Slide 130.)

-- was fairly regular on the teflonated one while the larger, more irregular type crystal structure was available on the non-teflonated one.

Okay, that's it.

Are there any questions?

LACKNER: Lackner, Canadian Defense Research.

What do you mean by "teflonated" negatives?

HALPERT: I am told there are cells built which have teflonated negatives -- negatives which have teflon coatings on the plate.

Now, we did do an electron microprobe analysis to see if we could find the chlorine or the fluorine from the teflon on the surface of the plane and -- Since it was such a thin film and, since the plates may have been used for some time, it was very difficult to find where that teflon was and how uniformly it was put on, whether it had migrated into the center of the plate, or what.

So, thus far, we still don't know where the teflon is

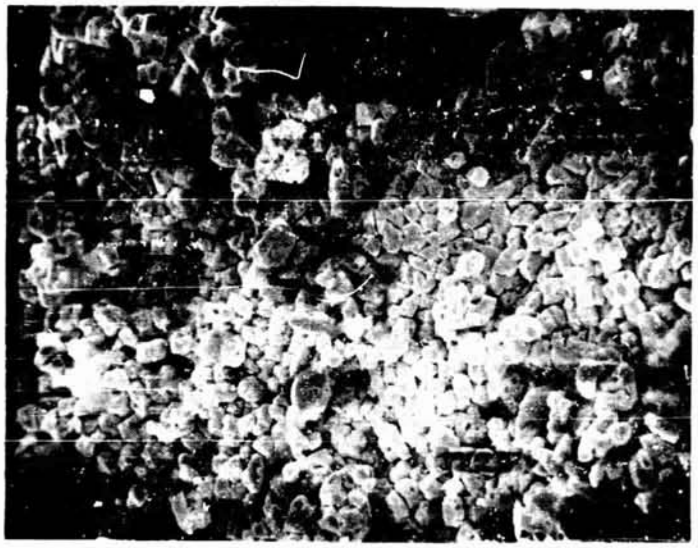

Figure 130

or what actual purpose it's serving, other than to have that different crystal structure and remove the separator from the plate.

But what the process is in putting the teflon, I myself do not know. Maybe there is somebody here who might want to comment on that.

LACKNER: Who put it on?

HALPERT: The manufacturer put it on. These were cells that were prepared and have been under test for what? -- a year, Floyd said.

FORD: Yes.

LACKNER: Who was the manufacturer?

HALPERT: General Electric was the manufacturer.

FORD: General Electric.

BELOVE: Were they sintered plates?

HALPERT: Yes, sintered plates made in the normal GE production as were the plates from the Gulton cells that were compared with it.

HAINES: Defense Research.

Would you like to comment on the effect that teflonating has on the absorption of electrolyte and on what effect it has on the oxygen recombination reaction?

HALPERT: I can't. Unless Floyd has some data on pressure, I don't have anything on that yet.

Do you have anything?

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FORD: I have no data prepared for this meeting. I will say this, that all these cells, both groups of cells, went through the acceptance test in which we have certain maximum pressure requirements and certain overcharge test, and all these cells met these requirements and they were acceptable as flight hardware.

BACHER: Bacher, RCA.

A little more, Floyd, for you. Has the teflon-- Does it affect the electrical performance or cycling performance?

FORD: We haven't seen any degradation in capacity of these cells that we can attribute to the fact that there's teflonated negatives in the cells.

RAMPEL: Guy Rampel, General Electric.

I'll volunteer the information to that gentleman over there from the Canadian Defense that teflonated negatives in cells do require a little less electrolyte and pressures are lower.

HALPERT: Any further questions?

(No response.)

HALPERT: Okay, I think at this point we'd be due for a coffee break and we'll meet back about eleven o'clock.

(Recess.)

B/5 ebl

HALPERT: Gentlemen, will you please take your seats?

I did want to make one comment with regard to my last presentation and that is I did say that the musspratt solution removes the cadmium and cadmium hydroxide. It doesn't attack the cadmium; it only attacks the cadmium hydroxide but since the cadmium hydroxide may be surrounding small particles of cadmium, the cadmium is removed at the same time.

Okay, as we continue on through this manufacturing materials session, our next speaker is Ed McHenry from Bell Labs who is going to talk about the scale-up studies of the Bell High Temperature Impregnation Process.

Ed McHenry.

xzxzx

MC HENRY: This is a report on some of the process studies we have done as a background toward a continuous impregnation process. We were just trying to gather some data and find out some of the problems we're going to have if and when we do attempt to scale this up and make a continuous process out of it.

The first slide, please?

(Slide 131.)

This is just a schematic of the process. Depending on whether you're making a nickel or cadmium plaque you use cadmium nitrate solution or nickel nitrate solution. The center plaque is cadmium or nickel hydroxide deposited by

eb2

cathodic precipitation, washed, dried, and then put into formation.

Next slide, please.

(Slide 132.)

These are the compositions of the impregnating solutions that we used during this work. The nickel solution was a two molar nickel nitrate, tenth molar and cobalt nitrate, .3 molar and sodium nitrite, and the pH of 4.

Now this is the starting point when you first start your impregnation. What happens, as you impregnate your nickel is deposited as nickel hydroxide so your nickel concentration is going down. The nitrate-- Presumably the reaction is not well understood but the nitrate would be reduced at the cathode and then at the annode, some of your nitrite is oxidized to nitrate. Possibly some of the nitrite is also reduced at the cathode.

The cobalt co-precipitates with the nickel and pretty generally precipitates in the same ratio as it exists in the solution. In other words, if you have 5 percent cobalt in the solution-- In other words, 5 percent of the nickel, the weight of nickel, is cobalt, so that they will then precipitate in the same ratio. All that you are doing is precipitating by raising the pH, and all the hydroxide in that area, all the ions which -- where the hydroxide is insoluble will simply precipitate so it doesn't really matter what the electrode potentials are for deposition of these metals. You aren't depositing; you're simply raising the pH and so they just precipitate.

In the cadmium solution of course the nitrate is being reduced at the cathode and the nitrite is being oxidized at the annode.

In general, the nitrate concentration remains reasonably constant, the nitrite is going down, and the nickel and the cadmium are going down, and the cobalt is going down. The pH has a tendency to rise a little but as you run out of nitrite then the pH begins to go down.

Next slide, please.

(Slide 133.)

This is the impregnation jig that we used in this work. We used a 4 by 4 inch plaque as you can see in here, the black part. We used these platinized titanium counter-electrodes. This was for economic reasons. Oh, it's a factor of 10 cheaper to buy this type of material.

The jig that holds the electrode is made such that the working electrode is masked so that you have the current flow, the potential gradient, is perpendicular to the surface of the plaque so you get a uniform current density over the whole surface.

The next slide, please.

(Slide 134.)

SCHEMATIC OF ELECTROCHEMICAL IMPREGNATION PROCESS

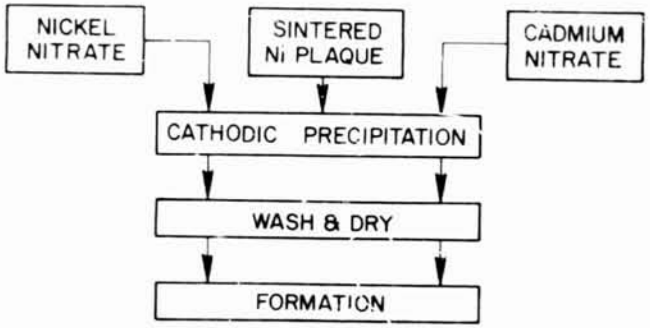

Fig. 131

IMPREGNATING SOLUTION COMPOSITION

Ni	Cd
2.0M $Ni(NO_3)_2$	2.0M $Cd(NO_3)_2$
0.1 M $Co(NO_3)_2$	0.5M $NaNO_2$
0.3M $NaNO_2$	pH = 4
pH = 4	

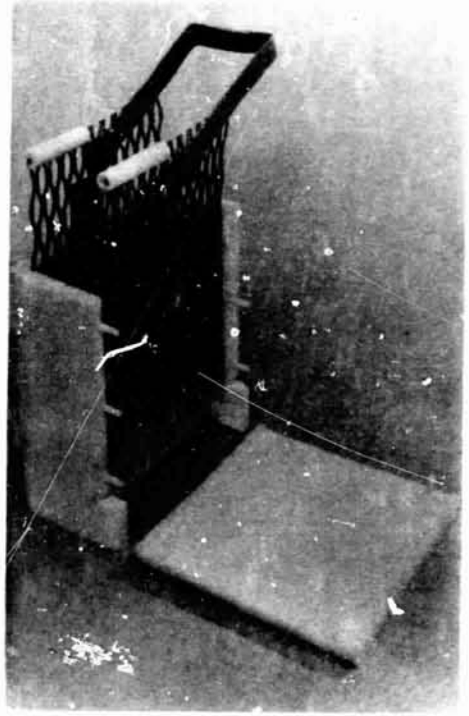

Fig. 133

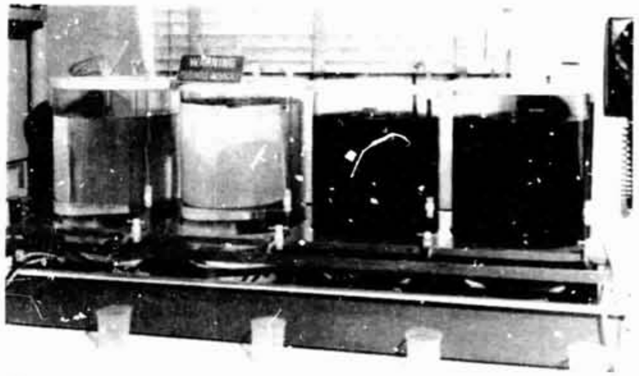

Fig. 134

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Here we show the impregnating solutions that we use. We had two of each so that we could use the first one and then while we were analyzing and adjusting this solution, we used the other one, and we'd run on alternate days.

We ran-- Let's see--

Next slide, please.

(Slide.135.)

Here we show the setup. We ran 18 of each electrode each day so there were 18 positive and 18 negative. They were all run in series in one operation.

These are 2 liter beakers. Each beaker contains one of those impregnating jigs, as I showed. We have three hotplates to keep these solutions boiling. Here's our power supply down here.

This just gives an idea of the extent of our operation.

The 4 by 4 electrode is a scale-up of about seven to one over what we had done in the previous laboratory work.

Next slide, please.

(Slide.136.)

Here we show the forming equipment that we used. Each electrode is formed individually in one of these cells here. We have two large-centered counterelectrodes. They are just regular centered electrodes which have a great deal more capacity than the working electrode so that-- They are charged

eb5

at C over 2 for four hours and then discharged and we have protection circuitry there so that the voltage can't drop below about .6 of a volt, so you discharge down to .6 of a volt. This is essentially 100 percent discharge.

Next slide, please.

(Slide 137.)

Here are the analytical methods we used in maintaining our solution. The nickel, cadmium and cobalt were determined by X-ray fluorescence. This is accurate to about 1 percent which is perfectly good for control of this solution. It's very quick. You just dilute your solution down ten to one and put it in a little sample holder, put it in the X-ray machine and within a minute or so you have the result, what the concentration is.

The nitrite was determined by permanganate nitration. This is a standard textbook method and is accurate to about half of a percent.

I used the specific ion electrode on sodium and the nitrate ion. This is not a very accurate method but fortunately these two ions-- One, we don't do anything about them anyway. In other words, if I knew they were too high or too low, I'd use it anyhow. And two, they have very little effect on the solution.

We've run as high as 4 molar sodium nitrate addition to our solution and find essentially no effect at all,

eb6

so that the only reason why you'd monitor this is that on a continuous basis, eventually you're going to build up so much sodium nitrate that you've got to do something about it. It's going to start precipitating. Actually, it's the cobalt and cadmium and nickel nitrates which will precipitate.

So presumably on a continuous basis you would bleed off some of your solution and precipitate out your nickel and recycle it and then I don't know what you'd do with the sodium nitrate solution. Maybe you can sell it or use it.

I don't know how you make sodium nitrite. Possibly you can reduce nitrate, but in any event, that will eventually have to be taken out of the solution, but we haven't done anything about it as yet. You can stand a very high concentration without any effect at all, and the pH was measured by glass electrode.

Next slide, please.

(Slide 138.)

Here we show electrochemical precipitation of cadmium hydroxide. This just gives you impregnation time versus theoretical capacity.

Now before anyone challenges me on the subject, theoretical capacity on either our positive or negative is determined by simply weighing the electrode and subtracting out the substrate weight. We have run experiments and others have and there is very little corrosion of the center so that--

C2

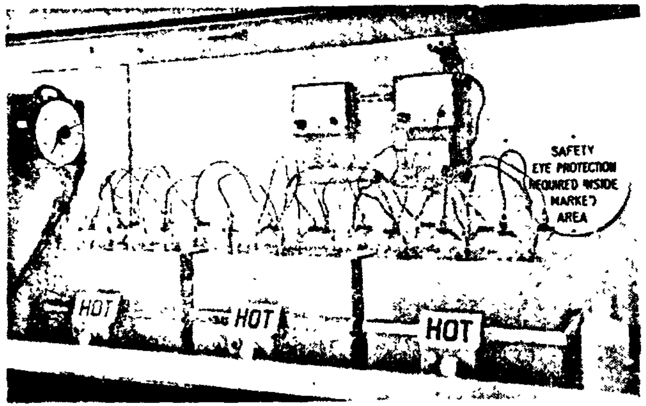

Fig. 135

Fig. 136

ANALYTICAL METHODS

ION	METHOD
Ni, Cd, Co	X-RAY-FLUORESCENCE
NO_2	PERMANGANATE TITRATION
Na, NO_3	SPECIFIC ION ELECTRODE
pH	GLASS ELECTRODE

Fig. 137

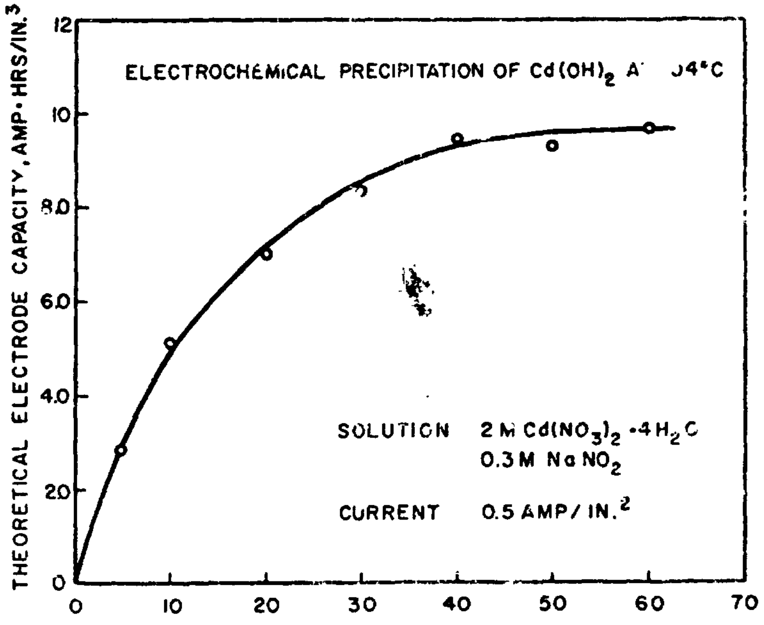

Fig. 138

eb7

It's maybe one or two percent of the capacity would be corrosion.

So that you can simply subtract the two numbers and get your weight of material.

I have assumed that cadmium goes from cadmium zero to cadmium plus plus, from cadmium to cadmium hydroxide and therefore, theoretically you should get something like .477 ampere hours per gram. So this is simply the weight multiplied by a factor, and this is in ampere hours per cubic inch and if you go long enough, you can get about ten ampere hours per cubic inch.

We were going for a loading of 1.8 grams per cubic centimeter of void volume in the plaque which came to around six or so ampere hours per cubic inch and we did run to 25 minutes on these. We stopped in the middle of the curve.

You could probably get more uniformity by going to the top. Then if you make a little error it doesn't matter because it isn't changing much anyway.

Next slide, please.

(Slide 139.)

This shows the concentration of nitrites as a function of time. We had six electrodes and we ran one for ten minutes. Well, we ran them all for ten minutes and then we kept picking one out every ten minutes and then we took the solution and analyzed the nitrate.

eb8

The rate of loss of nitrite is a little higher in the cadmium solution but I think this is because you have not only electrochemical decomposition of nitrites but you also have a chemical decomposition. Nitrite is somewhat unstable, especially in a hot, slightly acid solution.

So the higher the concentration, the higher will be the rate of loss. So one would expect that the two lines would be -- the cadmium would have a slightly higher slope to it. And you see at the end of the run in the nickel we're getting rather thin in nitrite. In the cadmium we still have sufficient.

Next slide, please.

(Slide 140.)

This is an electrode, a 4 by 4 electrode which was cut into 1-inch squares. The tab was up in that corner there and we kind of figured that particular square doesn't count for much because I have a tab on it. You add the weight of the tab but then you subtract the weight of what you would have impregnated there. Actually, this should be discounted altogether because by chance it comes out about the same as the other.

But what I did was weigh all the electrodes, get the average, all these little squares, get the average and then I calculated deviations and this is simply a percent. This one was 1.4 percent higher than the average, and this is

.6 percent lower.

But we see that the deviation from highest to lowest is plus or minus 2.5 percent and this includes the error that you would get from the plaque itself. They are within about a percent, and then the error that you get from me cutting the thing. I have to cut it n little shears and if I miss by a hundredth of an inch, that's 1 percent.

So essentially this thing is quite unform across the whole area of the plaque. This is an impregnated plaque.

Next slide, please.

(Slide.141.)

We then took one of the 4 by 4 electrodes and we cut it up into little squares and put little tabs on them and ran them as four 1-1/2-inch electrodes. That comes to about half the area of the original plaque but the 1-1/2-inch squares were cut out of the four corners, and these were cycled at a very high rate. I think it was 10 C rate.

As you see, they are quite uniform and they all tend to go out together. They're within 10 percent of each other in the capacity over -- which comes to -- let's see, at two, three, about four hundred cycles they begin to bend down. Well, they're only down about maybe 20 percent at the end of the thousand cycles.

Next slide please.

That's all there is? Okay.

I have here-- This is a Vu-graph.

(Slide 142.)

This is a summary of the data that we gathered over essentially 300 positive and 300 negative electrodes. We find a theoretical capacity in the cadmium of 4. -- No, that one is a mistake. This is about 3.219. It's about a 74 percent utilization on that.

This is what you get for having these things typed up the minute before you go.

The standard deviation is about 5 percent on this large number of electrodes. If you take one string of 18-- They're made in strings of 18 -- the better ones will run down to a little less than 2 percent standard deviation on that group.

The nickels will run in two groups. We had one battery with a little bit higher capacity than the other, so we increased our-- We were running a 30-minute deposition and a 40-minute deposition, and so we get a higher capacity in the second group.

Here we're getting I think pretty good standard deviation on these electrodes of essentially three, and in the measured capacities we're getting approximately, well, 4 to 5 percent standard deviation. So it's quite a uniform process. This considers a whole bunch of electrodes made on a semi-production scale sort of, and we do have a higher measured

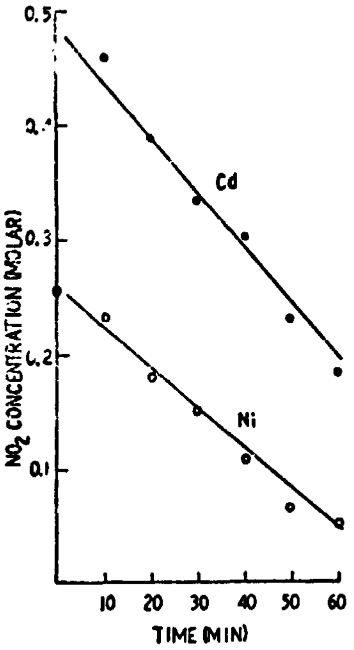

Fig. 139

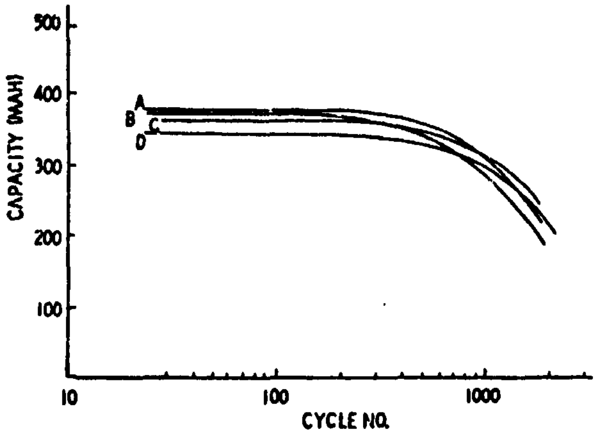

Fig. 140

ELECTRODE WEIGHT DISTRIBUTION
% DEVIATION FROM MEAN

+1.4	-1.3	+0.3	-2.5
+2.1	+1.6	+2.8	-0.6
+2.0	-0.3	+0.7	-0.4
-0.7	-0.3	+1.9	-2.5

Fig. 141

ELECTRODE PERFORMANCE
AH CAPACITY AT C/2

	Cd	Ni	
		Group 1	Group 2
Theoretical			
Mean	4.401	1.613	1.786
SD	0.219	0.046	0.058
%	5.0	2.7	3.1
Measured			
Mean	3.287	1.935	2.082
SD	0.204	0.104	0.069
%	6.2	5.4	3.3

Fig. 142

eb11

capacity than theoretical and this is explained by saying that the reaction is not a one-electron transfer.

In other words, if you overcharge a nickel electrode you get more capacity than would be dictated by a nickel 2 to nickel 3 oxidation.

And this is essentially a conglomerate of all the electrodes we got and it shows I think a fairly good reliability. I don't have these things as a function of time. There was no degradation with time in our solution. As the solution aged there was no variation with aging.

We had had troubles in the past when we were using a polyvinyl chloride storage container. We leached some kind of garbage out of there which had a tendency to slowly poison the cadmium solution for some reason. So we have stuck to glass, teflon, platinum and titanium in this work.

We are working on other materials to see if we could get away perhaps with a 410 stainless but-- For economic reasons we would like to do this but for practical reasons we don't want to use anything we are not sure of at the moment. We have to test out the other material.

And that's the whole story.

HALPERT: Thank you, Ed.

Any questions for Ed?

O'ROURKE: Joe O'Rourke, Grumman.

In that slide you had, the checkerboard type one

eb12

where you had weight distribution of each one, you talk about the weight deviation per square, about a mean. Now is that the mean of each square? Is that the average deviation, about the average weight of each square, or about the weight of the whole plaque?

MC HENRY: I just took the average weight and then took the percentage deviation of each square from that average weight, and then that is a real number on each, and the spread is not a standard deviation. Plus or minus is the range; it's not a standard deviation.

The standard deviation I suppose would be about a half -- it would probably be plus or minus 1-1/2, something like that.

HALPERT: Thank you, Ed.

We'll continue with more discussion on the Bell process. Dean Maurer is going to talk about sealed nickel-cadmium cell design for Bell systems service.

xzxzx

MAURER: Yesterday you heard quite a variety of methods of charging control, all based on quite a lot of electronic circuitry. There was pulse charging and there was PPC's and PCC methods. What I would like to present here now is a minority report, a charging control method that we use which we'll call ZCC, for zero charge control.

(Laughter.)

It requires the use of a resistor and a diode and

eb13

you simply charge continuously and the major difference is that you get a lot of overcharge as opposed to a very limited amount.

The problem with this type of method is that it requires a cell with some peculiar design features which I will talk about.

(Slide 143.)

The performance is something of this sort, in which we've plotted the measured capacity to one volt versus the charging current ranging from C over 20 to the 2 C rate, giving these capacities and pressures shown on the lower curve.

In the right-hand axis you will notice that at 2 C, we're somewhere around seven pounds absolute pressure, not gauge.

And to give you the callibration, since everyone who talks uses a different set of units, we have the theoretical capacity of the positive electrodes, again based on one electron transfer shown here, so that we are above theoretical capacity when we charge at rates higher than about C over 5 or so.

This theoretical line, in terms that Steve Gaston used yesterday, would correspond to the 267 milliampere hours per gram of active material -- 287, rather, at this point, so these points are up around 340 milliampere hours per gram of active material, just as a cross-calibration.

So that now we can design cells which can be rapid charged at the 2 C rate if we like without worrying about overcharge. We can turn them off on the basis of a thermal sensor if we like, just to keep the rest of the package from getting too hot.

The way one designs cells like this--

(Slide 144.)

Now before I go further, these are the two cell designs that I'll be talking about. This one is a cell whose performance I just showed. It's about 100 mills thick and it has two modified Ziegler seals on it; it's a prismatic design.

This is a 23 ampere hour design, again with Ziegler seals.

The key to the performance of a cell on continuous overcharge, either in reserve use in terrestrial environments which are quite severe, temperatures from typically minus 20 Fahrenheit to plus 140 Fahrenheit, and also the problems of making cells capable of rapid recharge all boils down to the same point: You want to keep the pressure down, whether it's the oxygen pressure during rapid recharge or whether it is hydrogen or the lack of hydrogen pressure, during low temperature operation especially, or the accumulation of hydrogen on life, and it is all related to the negative electrode.

First I'll consider the oxygen problem.

If you plot the oxygen pressure, the equilibrium pressure, versus the negative loading --

(Slide 145.)

-- I've plotted it here as percent of the negative plaque volume that's filled, but you could consider it a variety of other ways if you like.

But you get a curve for different levels of electrolyte that break upwards fairly sharply. The usual negative loadings that you see in commercial cells tends to be up toward the 40 percent region and consequently the pressures are relatively higher and sensitive to the volume of the electrolyte in the cell, a relatively unstable type of a region. And we feel that the best place to operate is down near the knee of this curve where there is little variation in pressure with electrolyte quantity and one can get the theoretical capacity out of the positive and still maintain low pressure.

And of course things like state of charge will affect these curves. In essence, as you increase the state of charge on the negative you make it more porous, so a given curve will more further towards the right for a given loading; when you increase the state of charge you'll get a lower pressure.

And again, down in this region it won't make very much difference, but if you're up in this region, out in this area, it will make a substantial difference.

What this means then is if you plot the oxygen pressure versus the charge rate, -- there's a log charge rate

(Slide 145A.)

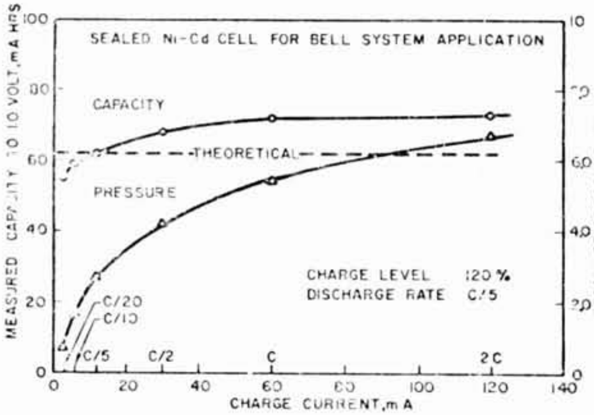

Fig. 143

EFFECT OF NEGATIVE LOADING AND QUANTITY OF ELECTROLYTE ON STEADY STATE OXYGEN PRESSURE

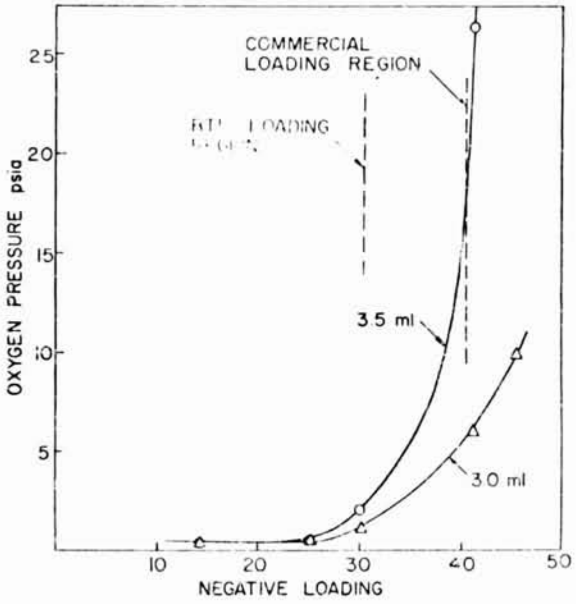

Fig. 145

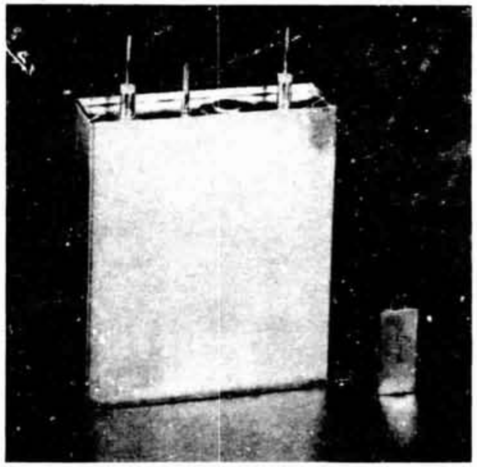

Fig. 144

EFFECT OF CHARGE RATE ON STEADY STATE OXYGEN PRESSURE

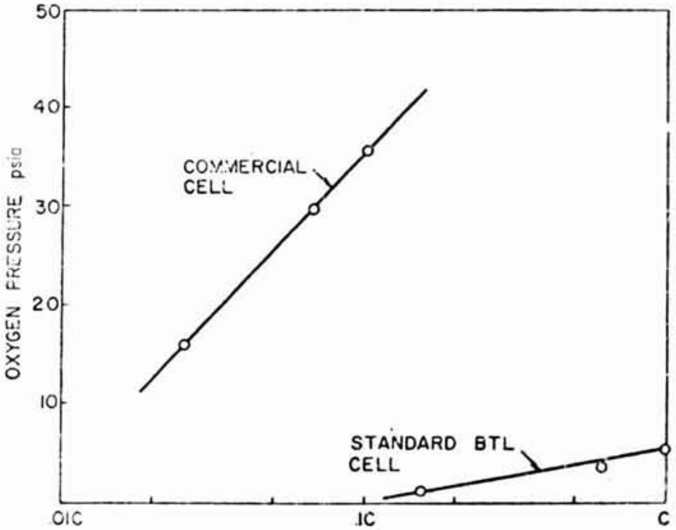

Fig. 145A

and a 10-hour and 1-hour rate -- cells operating down in the 30 percent fill region give you very low oxygen pressures whereas those operating up in the 40 percent region give relatively higher pressures.

So now, using just this consideration, you can make a cell then that can be recharged -- charged continuously at the 30-minute rate.

(Slide 146.)

Now let's talk about the negative electrodes.

Looking at the negative polarization versus the charge return on a negative electrode you get a typical curve looking like this: a constant potential region where the negative is charging. This then breaks to a higher potential region where you get hydrogen evolution, and if this were a sealed cell or if oxygen were present, then the oxygen depolarizes the negative and the voltage drops to a lower level, you do not get hydrogen evolution and in fact further charging of the negative ceases.

So one normally then designs a cell with a positive lower capacity than the negative, as you all know, and you get the oxygen coming over before the negative becomes fully charged and things are great.

Now if you look at these same curves at either higher rates or lower temperatures or both, the curve shifts like this. The charging region comes up in voltage. There is

(Slide 146A.)

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an initial high voltage on a charging curve in which you get some hydrogen evolution and the point of hydrogen evolution toward the end of the charge has moved substantially to the left at the lower temperature and/or higher rate.

And just where this shifts to depends first on the conditions you're talking about and also the previous condition or history of the electrode.

So then what you want to do to design a cell is arrange to have the positive capacity operate within this band between the preliminary hydrogen evoluation and the final hydrogen evolution region.

I've marked here-- This is the range of the safe positive theoretical capacity if you have electrodes which generally give you less than theoretical capacity but as we were discussing yesterday, some cells which are continuously charged, especially at lower temperatures, give higher and higher capacities and in fact we've found in most cases this approaches the theoretical capacity of the electrode, especially around zero degrees Centigrade.

In the positive electrodes that we make by the electrochemical process this has to be 120 percent of the theoretical capacity, something in that vicinity.

Now one can plot-- For a given charging temperature one can plot the hydrogen free capacity, that is, the capacity in before this hydrogen evolution ever occurs,

eb18

(Slide 147.)

-- and that looks like this, on which I've plotted the hydrogen free charge return in terms of percent of the rated capacity of the electrode versus the charge rate in terms of percent rated capacity, and looking at it for different preconditioning cycles and different charging temperatures.

So that here are a set of data in which the electrode was equilibrated at 77 degrees F. at the five-hour rate first. Then it was lowered in the discharge phase to zero and charged at one of these rates, and we generate a curve that looks like this.

Now if in fact we had gone to a lower temperature than zero, minus 20 for instance gives a curve that has dropped all the way down to this region. If, on the other hand, the electrode is equilibrated at 140 Fahrenheit first and then lowered to zero, the curve shifts from this position to this position.

Now these are not such outlandish conditions as you might think at first off. Zero degrees followed by equilibration at 140 is simply the cold winter following a lot hot summer in a piece of pole-mounted telephone equipment. The equipment is in a box in the hot sun. The temperature gets up in the 120, 140, even 160 region. And in the winter of course it drops.

So that if one does not have enough excess negative capacity to keep out of this hydrogen region, you will develop hydrogen gas and the cell will vent.

Also, for a reserve battery with perhaps a two to one negative to positive ratio, at the 20 hour rate of charge, that's a 40 hour rate on a negative so one is talking about something down here very close to the axis, so these effects are not all that drastic but they are present.

If you wanted to design a cell for rapid recharge, however, you have to take these into account and have quite a substantial excess capacity for rapid charge at very low temperatures.

Now that takes care of the time zero negative condition. The negative doesn't stay in that state throughout its life. You have to worry about some other things happening, fading, for example.

(Slide.148.)

These were shown last year, the theoretical capacity of the electrode and the electrochemical electrode, and here a particularly -- a rather bad commercial electrode with a fairly sharp drop with cycling in capacity.

Now this electrode-- A cell designed on the basis of that electrode would have to have much larger ratios in order to keep you out of trouble later in life.

Now I want to emphasize that cycling in the flooded state on negatives is not the same as cycling in sealed state,

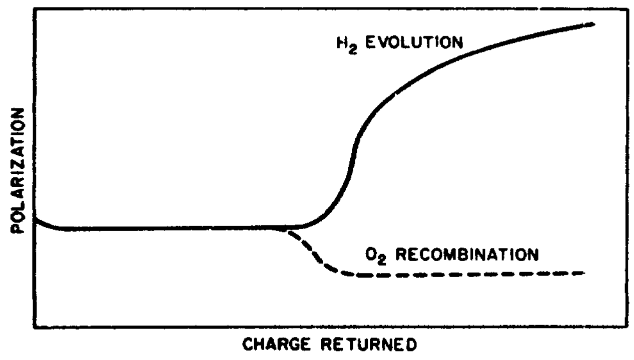

Fig. 146

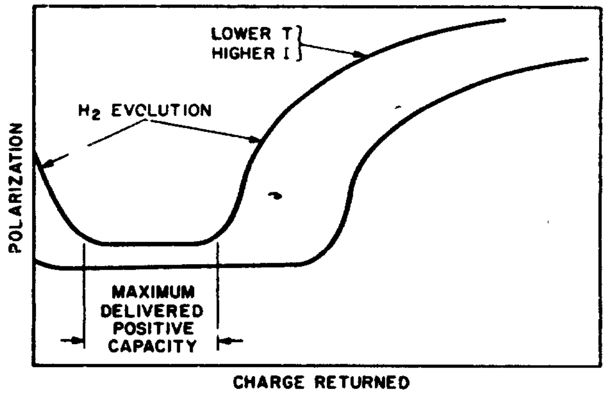

Fig. 146A

H_2 FREE CHARGE RETURNED vs CHARGE RATE FOR VARIOUS PRECONDITIONING TEMPERATURES/CHARGE TEMPERATURES

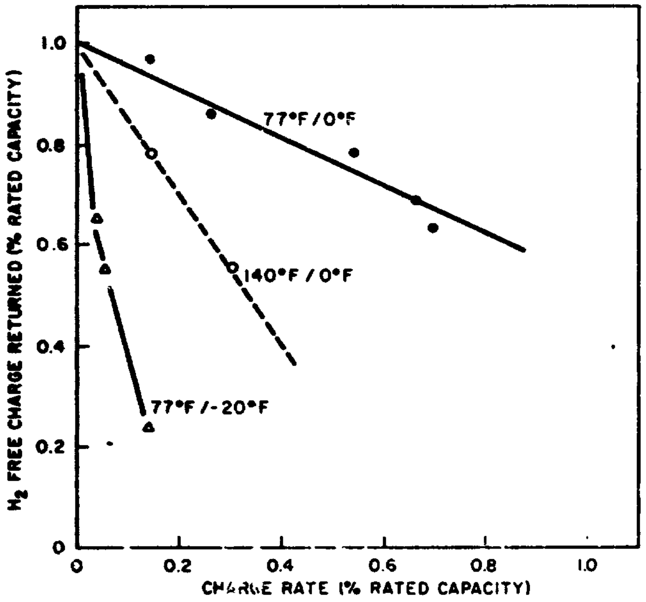

Fig. 147

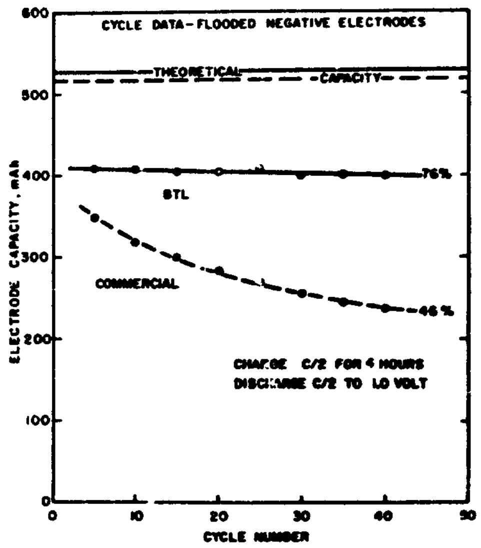

Fig. 148

and just what the relationship is I don't know, but one gets longer life, cycle life on negatives in the sealed state. Part of this of course is due to the fact that you don't cycle them through nearly as great a range in the sealed state.

Now while this material is electrochemically inactive it is still present as a chemical species within the sealed cell and has to be contended with, and we propose the following things going on.

(Slide 149.)

First, we represent the positive battery by this block, the negative by this block. It's divided up into the black area representing the electrochemically active material and the red area representing the inactive material which I think you will generally agree is usually cadmium that's isolated, and most chemical analyses show this to be cadmium metal and not hydroxide.

Then this is divided up into the working capacity which matches the positive, some excess negative cadmium hydroxide to account for the low temperature charging. You have an amount here now-- You design the cell to have an amount there that matches -- to give you the hydrogen free performance for the highest rate and the lowest temperature you intend to design the cell for.

You have a certain amount of precharge material and basically all that we're concerned with in the design is cb21

the precharge to keep you out of that preliminary hydrogen evolution region that I showed earlier. Then some things can happen.

(Slide-150.)

On overcharge, oxygen in the cell can oxidize this cadmium metal. It is not isolated chemically, just electrochemically. So the cadmium plus the oxygen and water will give you some cadmium hydroxide but since the other half of the electrochemical couple has to be satisfied, some cadmium hydroxide gets reduced at the same time.

So one transfers active cadmium hydroxide to active cadmium in exchange for inactive cadmium to something that I'll admit is questionable. This can be either active or inactive, but I would assume that it's quite a bit inactive, let's say.

So one needs to design for this and allow enough extra cadmium hydroxide present on the negative to match the amount of inactive material that you have because it is potentially capable of being transferred to active cadmium at the expense of cadmium hydroxide which you need for the low temperature operation.

So then what this says then is that you have the over-all design of the cell now. You have the working cadmium capacity which is equal to the requirements of the cell design. If you want a 12 ampere hour cell you have a 12 ampere hour

eb22

working cadmium capacity.

Then you make the electrode some maximum thickness, probably around 30 mills, and you load it to the 30 percent point so this gives you the amount of cadmium area, cadmium electrode area that you require-- I'm sorry, you add enough cadmium preharge and hydroxide to account for the effects that I've been talking about.

Then you match this total area with a positive electrode.That usually winds up to be a very thin electrode because you don't need very much capacity per square inch to match the cadmium. Then you make the positive loading as high as you can to maximize the energy density of the cell.

We've made the cells in this form. I showed you the data on the small cell initially, capable of rapid recharge.

(Slide 151.)

Here are some data on some -- on one of our cells on continuous overcharge. Here we have a C over 20 overcharge over 20 degrees Fahrenheit but these cells had been previously conditioned 35 days at 110 Fahrenheit on overcharge, so again this is the winter following the hot summer.

Now I plotted pressure in pounds per square inch absolute versus time and the cell has shown low stable capacity. And for comparison I have three different other cell designs on the same plot that were not designed to take all these

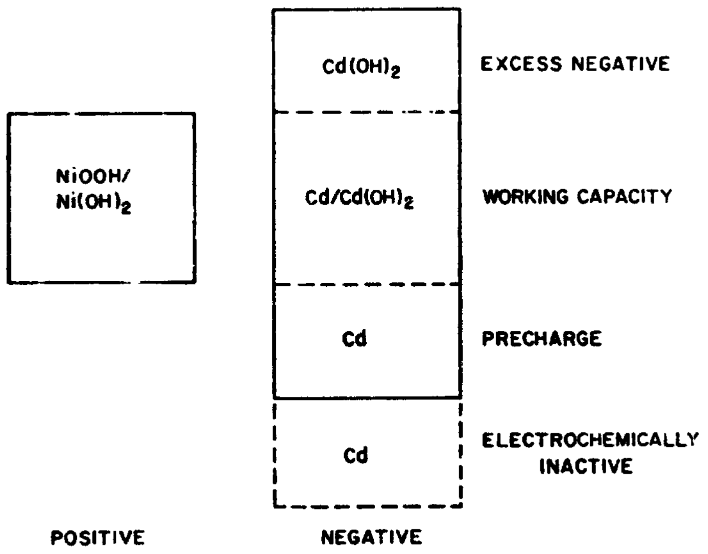

Fig. 149

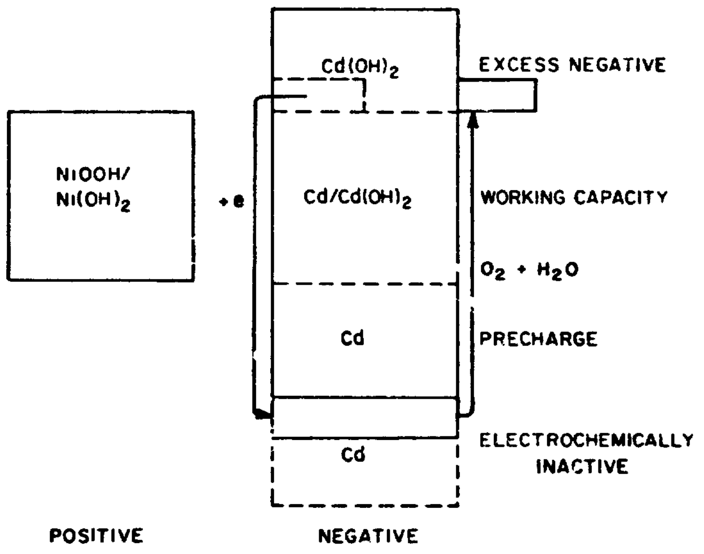

Fig. 150

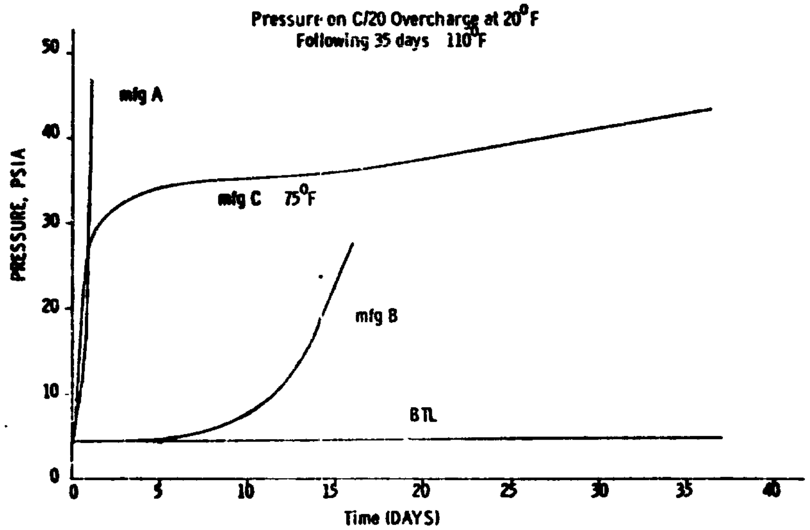
Pressure on C/20 Overcharge at 20°F
Following 35 days 110°F

Fig. 151

factors into account.

One of these fell out right at the start. Another one went for a while but then started to generate hydrogen, presumably because of the exchange effect that I spoke of.

And another guy that really doesn't belong on this plot *per se*.At 75 Fahrenheit it started to generate hydrogen after several weeks on overcharge.

So that by taking all these into account, one can design cells that can be used on continuous overcharge. I think that the aerospace industry might consider some of these facts in their cell design, especially the effects of overcharge on the electrode performances and perhaps opt for a little more overcharge at least than is presently being used.

Thank you.

HALPERT: Are there any questions for Dean? Any comments?

FORD: Ford, NASA-Goddard.

Dean, would you care to comment on-- You mentioned how the hydrogen free capacity changed with life. Have you had any experience or observed any difference in cell potential through which you can get hydrogen as a function of life at these steady or these constant current overcharge rates?

MAURER: No, I don't think I could quote numbers off the top of my head on that specific thing. We have observed voltages and you can get hydrogen evoluation to vary over quite a wide range from safe operation above 1.6 to hydrogen generation at 1.55.

Of course we have observed hydrogen generation as I pointed out here even at room temperature even though the voltages were not very high. As I remember it, the voltage was probably in the range of 1.45.

FORD: Gerry, do you have another question here?

DUNLOP: Jim Dunlop, Comsat.

Do you have any observed mechanism for hydrogen recombination once you get it generated?

MAURER: No, but I'd like to have some.

(Laughter.)

LACKNER: Lackner, Canadian Defense Research.

On the hydrogen free charge return, are we talking of negative-to-positive plate balance or ratio? You haven't given us a figure for that.

MAURER: What we finally used?

LACKNER: Right.

MAURER: We use a ratio of theoretical positive capacity to measured negative capacity of 2.2 to one-- I'm sorry, negative to positive of 2 to one. And that, in theoretical terms, theoretical negative to theoretical positive, is 2-1/2 to one.

LACKNER: The other question is facetious. If your precharge, which I think we're on record we don't like, prevents the onset of hydrogen evolution, why don't you have a larger percent of precharge so you have a one-to-one ratio?

MAURER: All you need is enough precharge to get out of that initial region, and that only amounts to something like 10 percent of the negative capacity. This depends on the particular electrode that we're talking about. All you need to do is get out of this region and that in general is perhaps only 10 percent of the negative capacity so you just put in enough to get you out of that area.

LACKNER: Does that mean that if you started with a totally discharged negative and a totally discharged positive, you would evolve hydrogen at the beginning?

MAURER: It would if you did it at a low temperature and a high enough rate.

LACKNER: At normal rates of, say, C over 20, C over 10 at minus 5, would you evolve hydrogen?

MAURER: Again, it depends on the electrode and its preconditioning. I would guess that if you would equilibrate it at 140 degrees first, and you're talking about minus 5 and C over 10 on the negative capacity then you might very well get a burst of hydrogen.

LACKNER: You're making a generalization and you're taking specific cases here of preconditioning electrodes and what-have-you. As a general electrochemical phenomena, you don't evolve hydrogen from the negative until you get into the

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overcharge region, so I'm asking:

If you start with a fully discharged negative and a fully discharged positive, what causes hydrogen to be evolved?

MAURER: You get hydrogen evolved-- On the negative process there is in general three polarizations to concern yourself with. One is the polarization for hydrogen evolution on nickel surfaces; another, the polarization -- activation polarization for cadmium reduction; and the polarization -- concentration polarization; and the polarization for hydrogen evolution on cadmium.

Now on the very start of the charge on a completely discharged electrode there are exposed nickel sites available and one can have a condition in which they hydrogen polarization on nickel takes over and you get some hydrogen off before cadmium covers these areas during part of the charging process on cadmium. So it's a burst of hydrogen; it's not a continuous evolution that continues throughout the cell charging.

But if you're talking about cycling the cell under those conditions, then you can accumulate some hydrogen, but just where the process occurs depends on each particular cell design and all I'm saying is that one needs to take all of these factors into account in designing the cell.

Maybe for your particular application, your particular conditions, this won't be a problem that you have to worry about at all. In our set of conditions we have to worry

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about it a little bit.

LACKNER: It's been our experience that the less precharge you have the better off you are, but it's hard to convince anybody else.

MAURER: I agree with that in the sense that you want the excess cadmium in the form of cadmium hydroxide so that the ratio doesn't have to be any higher than you absolutely need, because the higher the ratio the lower the energy density becomes and so on.

I don't think you need precharge for the purpose that many people put it in, namely to lower their oxygen pressure. I don't think it's especially necessary for that. If you load the electrode low enough you can have low enough oxygen pressure.

And the other reason that some people put it in is because of fading of the negative on some types of cycling regimes. I think that's accentuated when you have very limited or no overcharge. Then one tends to get into negative fading more -- in a more pronounced way than you would if you had overcharging.

STEINHAUER: Steinhauer, Hughes.

Dean, would you say then-- I noticed you ran a long-term 35-day overcharge test -- that if you don't have the opportunity to have fully instrumented cells, say for gas partitioning or for pressure, would a long-term low temperature overcharge test be a reasonable indication of adequate overcharge protection or cadmium hydroxide upstairs, along with voltage?

MAURER: No, not just in itself. You need the overcharge. You also need something in the way of preconditioning to the worst case condition. And then you have to have some idea how the negative might be fading in capacity with life and account for that as well.

Because what you want, you want to eliminate all of these factors as failure modes so that what you do is look at what the negative is going to be looking like far out in time and allow for enough excess capacity and enough excess cadmium hydroxide way out in time so that you won't get into trouble.

Otherwise, this might very well become the failure mode itself.

HAINES: Haines, Defense Research Establishment, Ottawa.

I'd like to come back to this hydrogen evolution. If I understand what you said correctly, it's when you have your negatives completely discharged, you have nickel sites where you can possibly get the evolution of hydrogen.

Now are you stating that when the thing is partially charged, these nickel sites are covered? And if they are not, then how come you don't get hydrogen evolution every time you start to charge?

MAURER: Well, I think it's a matter of degree. I think that once you've started to charge you cover enough of them that you get out of the problem to some extent.

HAINES: I just can't see how the charge cadmium will cover these nickel sites.

MAURER: Well, the charging action goes through a soluable intermediate and the cadmium will sit down on any electrically active site available, and there are probably more nickel sites available initially than anything else.

In fact, if you can think of a pristine state, and I'm not sure you ever really have this, depending on the method of impregnating, where you have cadmium hydroxide presumably throughout most of the -- covering much of the area in the cell and nickel -- there isn't any cadmium initially -- and then as that becomes reduced it has to go down on some substrate, conductive substrate within the electrode.

GINER: Jose Giner, Tyco Laboratories.

I think there probably may be another explanation, and I want to suggest a look at the old papers of reduction of oxides by Ohse and Nagel and many other people have shown that when you have a completely oxidized substance like cadmium oxide or silver oxide, you have always an overshoot of potential to reduce the beginning because you have to create some nucleation for the further reduction.

So it is possible that if you have only cadmium oxide the potential overshoots in order to create these.

So, in the overshoot you may evolve hydrogen.

Therefore, I think that probably you want to have the cadmium, free cadmium, to avoid the potential overshoot that you get when you nucleate.

MAURER: Yes. So that you are saying that, instead of nickel sites per se, you now have some cadmium sites as well?

GINER: You need them for the cadmium oxide reduction.

DUNLOP: I want to comment on that, too. This overshoot that you look at, you normally observe when you completely discharge the cell for a long period of time and that's the reason why almost all the battery manufacturers recommend that, if you have cells that are shorted in your laboratories for a long period of time, that you exercise a great deal of caution when you initially start charging.

Now, after you've cycled the cells for a while, it seems that you don't really have this problem, and our results would indicate the reason you don't have this problem is that you now have more actively charged cadmium available to you.

MAURER: That's true, at room temperature.

GINER: At room temperature.

The other point that we have observed in the cells that are being made for us using the normal SAFT process is that when they make the cell initially they're going to have this 10 percent charge cadmium in there because they can't get it out of there. It's there, and there is no way initially to discharge it after the cell plates come out of the formation cycle.

So it's really not something you have to put in; it's really in there anyway, and they really can't, unless they change the procedure, the current procedure, they can't get it out anyway.

MAURER: What you say is partically true and would be true at room temperature operation but if you take those electrodes that have been completely discharged electrochemically at room temperature and dropped to low temperatures, you get this effect again anyway. So that amount of precharge isn't enough to account for, let's say, 20 degree or zero degree operations.

SEIGER: Seiger, of Heliotek.

Dean, in the first part of-- During that period of hydrogen evolution, what's happening to the temperature of the cell? Is it getting very hot, or is it staying moderately cold?

MAURER: It's moderately cold.

HALLECK: Halleck, Tyco Laboratories.

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I have a question pertaining to the fade of the cadmium electrodes. Do you know anything about whether it fades faster or less fast if you have a high rate, a continuous high rate of overcharge?

MAURER: No. I have a few generalizations, [illegible] that's all they are at the moment. We're going to do some of these studies, look at the effect of overcharge and rate or lack of overcharge at all on the negative.

But in general, I think the higher the rate, the worse the fading is.

HALLECK: You mean the higher the rate of overcharge?

MAURER: The higher the rate of discharge, the more fading one accumulates. As far as charging, I'm not sure. I don't have any real feeling for that.

FORD: Ford, NASA/Goddard.

I'd like to make two comments, one in regard to Bob Steinhauer's point on the low temperature overcharge test for long periods. It is my belief that that only is a status indicator of the present condition of the cell and as Dean indicated, that will change on a day-to-day basis.

But I think we are missing the major point here. Dean showed a curve labelled "commercial plates" of the degradation in ampere hour capacity of the negative electrode. I can show you data in NASA reports of commercial aerospace plates that look essentially the same. So you might draw your own conclusions from that.

But my point is simply this:

I think we are basing negative capacity total in a cell -- this is measurable capacity as required in the specification, the ratio test, and parity capacity. We are basing our ratio on an early point in life. We are not taking into consideration this degradation, and I am proposing today, and I think you will see it very shortly in future NASA specs, that one of the requirements for qualifying a group of negative electrodes for a cell is to run the cycle test to demonstrate capacity stability, and I think this is something we should be looking at very hard.

HALPERT: Any other comments on this point?

One more.

THORNELL: Thornell, ESB.

What are the energy densities on these cells?

MAURER: I'm not sure what it is for the 23. For the little one it's in excess of one watt hour per cubic inch. I don't know what it is in terms of weight.

HALPERT: Okay.

We're going to start our pre-charge session. I guess we're going to have to do that directly after lunch. We have one more paper for this morning, and that is by Will Scott, who wants to present some analysis data from the state of the art plate materials.

SCOTT: I'd like to present some data that has been generated to date on a program that is supported by in-house resources at TRW directed toward determining the fundamental limitations to operating cells at very high utilization factors or very high depths of discharge, whatever you wish.

The orientation of the work is toward applications at the moment in synchronous equatorial orbits where one has the freedom at least, let's say, of choice because of a relatively low number of cycles, at least compared to what is required in a low earth orbit.

This work is in support of, at the moment, of various other hardware and development programs at TRW directed toward long-term synchronous orbit type applications.

Now most of you have seen various kinds of analytical data for plate material in the past and I'm not going to show you, I hope, the same kind of data that you may have seen before. What I would like to show you is some data for some plate material made under a special set of conditions but not necessarily any different basic process conditions than is ordinarily being used today.

The main difference is that the material was -- the data that I'll show you today was taken from plates all taken from a single spiral during the production cycle and therefore, it represents in a sense possibly -- "possibly," I say, a

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higher distribution or a more single-point type of data than may be ordinarily available when one cannot have available to him a single spiral or a single small lot of plate material made under controlled conditions.

What we did was to isolate this spiral of material, follow it through the manufacturer's process and obtain samples of the material at various points in the process, including the samples of the unimpregnated plaque material at various stages of the impregnation and of the final plate material prior to formation, final formation and after final formation.

I will not make any attempt to show you all the data that we have but I do want to show you some selected data which is typical and point out some interesting results that we are beginning to see.

First of all I would like to show you our own version of electronmicroscope photographs of two stages of plate material. One is the unimpregnated plaque and the other is the finished plate after formation.

(Slide 152.)

This is a scanning electronmicroscope photograph of the unimpregnated sinter used to make the positive plate.

This is at 100 X as it was printed on the photograph as you see it there.

I might point out that to me this looks like it is

[illegible]

near the same magnification as the photos that Gerry showed you earlier when he mentioned the figure 500 X. Now I'm not sure what the difference is there but I believe I'm right when I say that this one is at 100 X.

(Slide 153.)

This is the same material, positive plate, unimpregnated plaque at 1,000 X. Now again here this looks much larger than the photos that Gerry showed that were mentioned as 500 X so I'm not sure why there seems to be that difference.

But here you can see even more graphically than you can in the smaller magnifications the type and degree of variation of void spaces and sizes and shapes and you can appreciate the problem of trying to evaluate and characterize the nature of the void spaces in these sintered structures.

Next is a photograph, a scanning electron microscope photograph at the same magnification of the completed positive plate.

(Slide 154.)

I'm not sure exactly how yet to interpret the photograph on your right, what it all means, but one of the interesting points that I'll point out which I haven't completely evaluated is the -- are the plateaus that you can see there where it appears that the high spots have been flattened or sheared off.

This plate material is made by a process which involves compacting the positive material sinter prior to impregnation.

By the way, the photograph on the left is of a material that had been compacted and doesn't appear to be -- doesn't have that appearance, so I'm not quite sure yet why these two figures don't correlate better than they do.

The other photograph of that type that I can show you is a finished negative plate which is roughly similar in appearance to that of the positive plate.

(Slide.155.)

There are considerable areas that appear to be flattened.

Now what in general we are trying to do is to -- We're doing two things with the analytical approach to this plate material. As part of an Air Force-supported program we are going to do extensive life testing of cells containing this plate material. This life testing will be under various conditions and will extend over a period of a minimum of two years and possibly longer.

We expect to be analyzing the condition of the plate material at intervals during the life test and so the analysis we're doing now is the reference point to which we are going to be comparing the additional analyses as time and cycling progresses.

The other thing we're doing is on the internal-

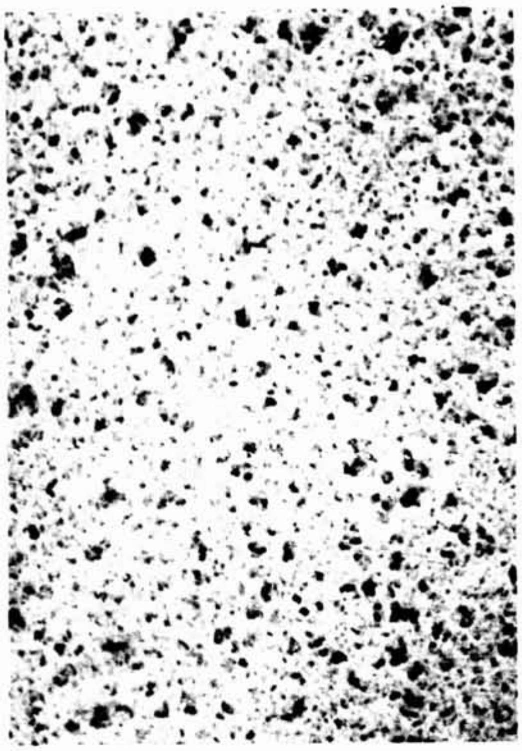

Figure 152

Figure 153

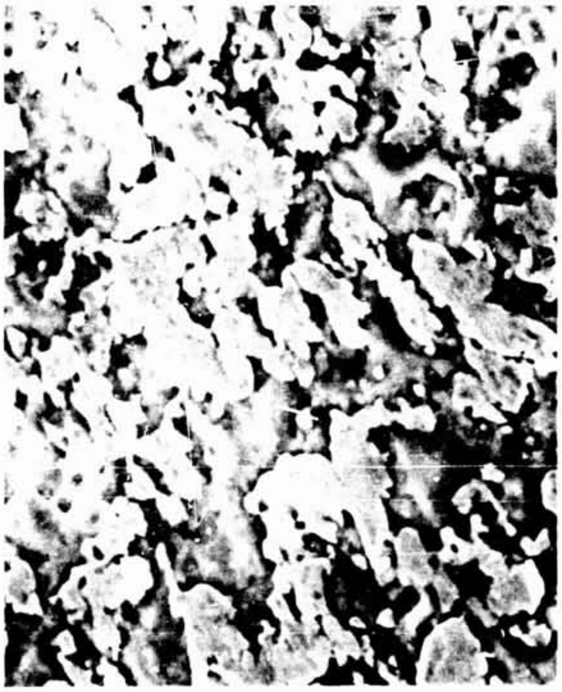

Figure 154

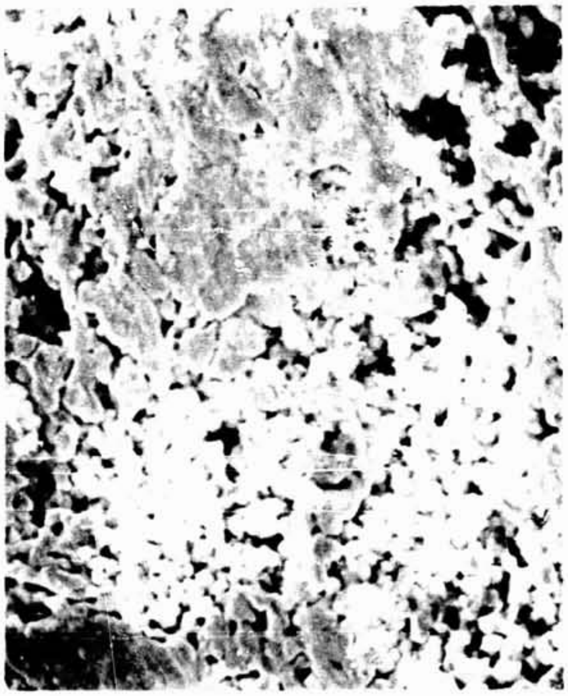

Figure 155

funded program is that we are building some special cells in-house under laboratory conditions containing this plate material, among others, and we are going to be cycling those cells under conditions of 80 percent depth of discharge over a period of time to determine basically what the mechanism of degradation is in terms of actual changes in the physical and chemical conditions of plate materials.

We're not restricting ourselves to plate materials; we are going to be analyzing changes in separator materials also. So this data is the forerunner of that effort which will be extending over a period of time.

(Slide 156.)

I just want to show you a list of the types of analyses that we are going to run for unimpregnated plaque. I've put the word "surface" in quotation marks because I am not quite sure exactly yet what we're going to be able to tell of the surface by the scanning electron microscope. We're still investigating that.

We are measuring void fraction by absorption of water. Thickness and weight are of course very simple characteristics, and purity content involves analysis for carbon and for various metallic minor constituents by spectrographic analysis.

The plate characteristics are essentially those that most people are thinking about and looking at these days.

I don't think I'll need to comment further on that, but I'd like to show you quickly if I may -- if the gurggling of stomachs doesn't drown me out -- one set of data for carbonate analysis because I would like to make a point here.

(Slide.157.)

Two points.

Now first of all, the two items at the top of this are for plate material after it is finished with its complete processing just prior to insertion in a cell.

Now notice that the positive plate analysis -- this is on weight percent -- is higher than the negative analysis. Now this is interesting because the consensus of a number of people seems to have been that the problem of carbonate is always worse on the negatives than it is on the positives and our data don't seem to bear this out.

Now down at the bottom, I have four sets of data from what I call our negative plate study. This was a set series of analyses tracking the plate material-- This is negative plate only in this case. I don't have the data for the positive yet -- through the process.

Now these are slightly out of order at the bottom but the first line gives the analysis for carbonate prior to formation. The second line gives you the data for the values after formation but prior to washing where the plates were vacuum dried and not contacted with air except for a very few

CARBONATE ANALYSIS DATA
(FIGURES IN WT. PERCENT)

	AVERAGE*	RANGE*
IN FINISHED PLATES		
POSITIVE PLATES	1.12	0.88 - 1.26
NEGATIVE PLATES	0.73	0.64 - 0.78
FROM NEGATIVE PLATE STUDY		
BEFORE "FORMATION"	0.80	0.68 - 1.08
AFTER "FORMATION," NO WASH, VAC. DRY	0.89	0.80 - 1.00
AFTER WASH, VAC. DRY	0.35	0.32 - 0.37
AFTER WASH, AIR DRY	0.85	0.71 - 0.96

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*Data from 3 samples selected at random.

Figure 156

PLATE CHARACTERISTICS TO BE DETERMINED

UNIMPREGNATED PLAQUE

"SURFACE" BY S.E.M.

VOID FRACTION

THICKNESS

WT./UNIT AREA

IMPURITY CONTENT

FINISHED PLATES - BEFORE AND AFTER CYCLING

"SURFACE" BY S.E.M.

"SURFACE" AND CROSS-SECT. BY E.M.P.

VOID FRACTION

THICKNESS

WT./UNIT AREA

ACTIVE MATERIAL (CHEMICAL ANALYSIS)

CHARGED POSITIVE ACTIVE MTL.

CHARGED NEGATIVE ACTIVE MTL.

ELECTROCHEMICAL CAPACITY

CARBONATE

NITRATE

IMPURITY CONTENT

Figure 157

minutes required to transfer them to the vacuum drying equipment.

The last line should be the next one in order. It's the analysis for negative plates after completion of the normal processing including air drying and that figure is really comparable to the one up at the top. They were plates taken from a different point in the spiral, and I'm not quite sure why the range and average is not the same between those two.

But that second line and the bottom line are comparable points in the process.

VOICE: Excuse me, could you read those numbers? We can't see them.

SCOTT: Yes. The four numbers at the bottom, the average is .80, .89, .35, and .85.

The second line from the bottom is a special situation where after normal washing, the plates were vacuum dried rather than air dried.

Now the point is here that it appears that during -- in this particular case, during the process of formation which involved cycling in concentrated KOH solution, there was essentially no change. In fact, there appears to be a slight increase in the carbonate level in these plates.

From there to normal air dry, there was essentially again no change in the carbonate level in the plates. However, if, instead of air drying, the plates are taken at that point eb41.

and are vacuum dried, there is a significant reduction in carbonate level down to .35 percent, so this would tend to indicate that people should give some attention to the exact method of washing and drying and handling the plates at this point in time.

Just to give you an orientation, the .8 percent level would give you, if it was all extracted into the electrolyte in a normal cell containing a normal amount of electrolyte, would give you a carbonate concentration of the order of 90 grams per liter, which I consider to be excessively high.

HALPERT: I want to apologize to Will for moving him a little bit faster than he planned. He had some other data to show.

The cafeteria is expecting us at this particular time so we'll take a break, and since we have the pre-charge work to start with this afternoon, I'm sure there is going to be a great deal of discussion, and I wonder if we could make it back here by 1:30.

(Whereupon, at 12:30 p.m., a luncheon recess was taken.)

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AFTERNOON SESSION

(1:35 p.m.)

HALPERT: If there is anybody who is going to be going to National Airport after this meeting, we have someone who is interested in getting a ride. I'd appreciate it if you would let me know and I'll be glad to pass on the information.

For this afternoon's session I'm going to turn the session over to Dean Maurer, Bell Labs, who will introduce our speakers and handle the afternoon session.

MAURER: We have a special treat for the first thing this afternoon. We have some movies and Charles Thomas, Chrysler, is going to show us how to fire up a silver-zinc battery.

THOMAS: This film that we will see documents the results or partially the results of a program that we are conducting for the NASA/Marshall Space Flight Center to define the hazards associated with silver-zinc batteries.

The hazards documented by this film are the ones that are the most spectacular, that is, of spontaneous combustion due to certain abnormal conditions.

Now we have had some problems with silver-zinc batteries in the past and NASA felt that we should evaluate more thoroughly the conditions that will cause spontaneous combustion. We have evaluated such things as -- the effect of such things as insufficient electrolyte, short circuits in

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cells, overloads of batteries, and overheating of cells.

The film that you'll see has been partially edited. It does not include the results of all the tests. It documents, though, first the results of a short circuit in a 350 ampere hour cell, then second, the effect of overload on a battery containing 350 ampere hour cells, and third, the effect of overload on about a 35 ampere hour battery.

In the case of overloads, the actual discharge current for this test was something like, oh, six times rate maximum current.

In the case of the short circuit in the cell, the resistance prior to activation of the cell between the positive and negative terminals was 75 ohms. Now that's one of the things that was very interesting. The resistance of the short circuit need not be low in order to cause this problem.

Do you want to start the film?

(Whereupon, a film was shown with the following commentary.)

The first part of the film shows activation of the cell. The cell that is under test is in the chamber right under the clock.

The electrolyte was put into a reservoir through which a vacuum was pulled. The vacuum was then removed after the air had been evacuated from the cell and the electrolyte is now being drawn into the cell.

Now the short circuit is directly underneath the cement that holds the thermocouple on.

Now you see the electrolyte beginning to boil in the vicinity of the short circuit. The temperature -- well, it's about 150 degrees Fahrenheit.

It looks like the editor didn't leave enough of the temperature gauge.

The time to combustion for this cell was about 45 minutes.

Now you can see at the bottom light and discoloration, smoke, and it appears from the glow at the bottom that maybe combustion has actually started on the back side or on the bottom, although you'll see shortly a bright spot just to the left of the thermocouple.

The temperature at combustion was just about 325 Fahrenheit.

Now once these things start burning, combustion is quite vigorous because of the --

(Laughter.)

Now this is a single cell. Think of what you'd have with 21 cells.

What happens is that oxygen is liberated by a breakdown of the silver peroxide on the positive plate. This oxygen supports combustion. Now this is one of the problems which you have with a silver-zinc battery fire. It's very difficult

-eb4

to extinguish, or impossible.

This was a pretty good test of that clock, too.

(Laughter.)

Incidentally, the clock is still running.

There's some more of the film. The clock is still operable. This is the same clock used for battery test, battery overload test.

Now let's see. Watch closely. This is the one that explodes.

Now that was a 35 ampere hour operated at about six times normal rating. The internal pressures were so high that a very large contact in the output connector was actually blown out like a bullet and the lid, the cover, blew off. The cover has 20 screws and about half of them were broken off; the other half were just pulled out, the thread stripped off.

We've got another test. This is a 350 ampere hour battery. Now combustion occurred but was not sustained in the case of this battery because the peroxide had been apparently virtually all depleted before combustion started.

We started discharging this battery at a relatively low current and did not get up to a current of sufficient magnitude to cause internal overheating until we had consumed most of the capacity.

Now this battery was being discharged at 350 amps.

That is smoke. It's not electrolyte vapor. It had

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a distinctive zinc odor that you get from a burning zinc plate.

Incidentally, the mode of combustion here appears to be thatthe zinc plates start burning first at about 325, 350 degrees Fahrenheit. Of course after they start to burn, oxygen is liberated and this raises the temperature to the point where everything inside the battery burns.

(End of film.)

Any questions?

MAURER: Any questions?

GROSS: Sid Gross, Boeing.

Did you deliberately create a short in the cells before you --

THOMAS: Right.

GROSS: -- filled with electrolyte?

How did you do that?

THOMAS: We drilled a hole through the side of the plastic case between two of the plates, and of course the hole went down into the area between the plates. We then inserted a stainless steel pin that fit rather loosely. We wanted to have a fairly high resistance short.

GROSS: A stainless steel pin between all the plates?

THOMAS: No, between just two of the plates.

The short circuit-- It appears that you have a greater tendency for combustion when the short circuit area is small.

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GROSS: Had you ever seen or heard of any similar fires occurring naturally?

THOMAS: Yes. Afterwards you might correct my memory on this but I know of at least three cases in which batteries of the type used in the Saturn launch vehicles have burned spontaneously due to problems that we were never really sure of.

MAURER: Any other questions?

We have a slight reorganization-- We have another question for you.

PASCHAL: I might add a little bit to this. On the batteries that had failed previously we had an estimated unit battery that had been a spare unit for one of the launches. After the launch, this battery was brought back up to Marshall and was put under vibration test. It was then pulled to a laboratory and was sitting in the laboratory, and of course the shelf life of this battery wet is about 120 hours, so obviously the shelf life had long been exceeded.

As a result, the cell failed through failure of the separator system. This was one of them that Charlie Thomas is talking about.

A second battery was an S-4-B stage battery which failed during test operations on the West Coast. This particular one failed as a result of a controller, heat controller that stuck and caused the heater to fail to turn off. This

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heated the battery up-- There's a heater blanket in the bottom of this battery and of course with the controller turned on, the heater remained on until it was able to heat the battery to such a temperature as to cause the battery to catch fire.

MAURER: We had a reorganization of the program slightly. This afternoon was originally scheduled for thermal properties and so we'll actually adhere to that.

We have one or two papers on thermal properties. That will get rid of all the fires and get the smoke out of the room. It'll get the heat off and then we can get down to business and have the rest of the day and into the night to haggle over pre-charge effects.

So the next speaker will be Bill Webster on the design and development of the heat flow calorimeter for measuring thermal properties of aerospace cells.

WEBSTER: The co-author of this paper is a fellow by the name of Sid Teller, also a Goddard employee, and any questions that you might have, if you cannot reach me, I'm sure you could also get ahold of Sid. His number is 5379.

The development of the calorimeter was decided because people are unable to predict from theory the amount of heat that will be generated by a nickel-cadmium battery. This is extremely important to the spacecraft manager and to the battery engineer since, as we know, a battery's operational

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life is proportional to its temperature.

For instance, at 15 degrees C. we might expect a five-year life out of a cell. At 35 degrees C., this life would diminish to one year.

For a period of over 60 years, scientists have been building coulometers, so why did we build another one? Well, we thought that of all these coulometers that appear in the literature, about 400 of them, none of them were particularly suited to an aerospace cell.

The problem is further complicated by the fact that in the next decade, NASA will be using at least seven different sized cells in their spacecraft ranging from a 6 ampere hour to a 100 ampere hour sized cell, so what we wanted more than just a coulometer, which we've had before -- I did some work at American University on one; Joe Cherfee has done some work on it, and quite a few other people -- is we wanted a universal coulometer, one instrument bought one time that could handle all size cells, and that's what we got.

We had a six-month contract with Rocketdyne which called for the calibration of the instrument at Goddard, the design and construction of the instrument.

I would like in my first slide to show you a comparison between a 6 and a 100 ampere hour cell, and discuss the design problems confronting an instrument maker.

(Slide 158.)

eb5

In case some of you have forgotten, a 6 ampere hour cell only weighs 250 grams, and the 100 weighs almost 4,000 grams, so the first problem that you have is one of geometry, thermal mass, and response.

For instance, we might anticipate that the 6 ampere hour cell would rate one watt where the 100 ampere hour cell -- we didn't really know but we speculated as high as 25 watts. Also, as you know, you have to bring leads into and out of the cell. This could cause two sources of error in the coulometer. One would be I^2R heating and the other would be conduction heating.

Again as you are aware, cells operate in a constraint manner so that if a designer were to operate a cell on a coulometer in the same manner in which he would operate one in a spacecraft or on your lab bench, you would have some kind of massive constraining plates, especially on that 100 ampere hour cell.

This would be extremely bad insofar as it would slow down the thermal response of the cell.

Also, we wanted this coulometer to be capable of operating at minus 10 degrees Centigrade through to plus 40 degrees C., have an accuracy and reproduceability of 1 percent, and a response time of less than five minutes.

All these criteria were met and in my next slide I'd like to show you the philosophy of design that met this.

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(Slides 159, 160.)

This is just a schematic and the detailed drawing of the coulometer appears on that chart over there. It is so involved that I think the schematic is all that we can show.

First of all, we have an adiabatic shield which isolates the instrument from the environment. This, through differential thermocouples, maintains a temperature equilibrium of approximately 5/100ths of a degree Centigrade.

Then we go internal to the calorimetry vessel itself. Now this is where the first design criteria was met.

This is a pressure vessel. We filled the vessel with helium. Helium has excellent thermal properties and eliminated the need for constraining points on the cell.

How would the coulometer operate? All right, if you would like to look at a cell, you would place it on a silver platform in the coulometer and if you'd like to investigate it at, say, 25 degrees C., that would be T-2 in this equation on the left.

Then coming down from the silver tray you have a pair of copper rods. They go down to a heat sink. This heat sink can contain many materials but for the purpose of this discussion we used liquid nitrogen. That's T_1. That is a fixed temperature.

The next thing that we have is K which is the conductivity of the copper rod, A, the cross-sectional area, ebll and X, the length.

Now the first thing that is done is that you go through a calculation here that says you need so many watts. You apply the wattage. In this case it would be 30 watts to the automatic heater at the top. There is a thermister circuit there which senses the temperature and keeps the bridge in balance.

Now once equilibrium is established at that temperature you initiate your cell reaction and the amount of heat that is liberated or absorbed by the cell during this reaction is detected by this thermister bridge and that quantity of heat is either added or subtracted to the automatic heater, and this is a direct measure of the rate of reaction that takes place in the cell.

Now I'd like to point out some of the unique features of this design.

This is actually two copper rods separated by a thin mylar film. They serve as your positive and negative terminals. They are sized so that you have no I^2R heating even at 100 -- well, at 50 amps was the requirement.

Also, the heat conduction is working for you. It is one direction. It is from the coulometer to your heat sink.

Additionally you'd say, well, what happens if you want to look at a 6 ampere hour cell on this same coulometer instead of a 100? You would simply use a different eutectic

eb12

material here. You'd use something like ice water.

Ice water would then give you T_1 here. The amount of wattage that you'd need to maintain that equilibrium condition at 25 degrees C. would be, instead of 30 watts,-- I haven't gone through the calculation but it would be considerably less, like 5 watts.

Also, something I would not recommend but another thing you could do, you could adjust the sensitivity by adjusting the length of the rod.

There are a lot more details on the picture, on the poster over there which are omitted from this drawing. For instance, there is a pressure vessel which goes around the outside which has cooling coils so that your adiabatic shield is always applying heat to isolate the system from the environment.

There are other things to take care of radiative heat losses. The pressure vessel is completely gold-plated. In addition, the copper rod coming down is protected by several radiation shields plus a vacuum chamber so that you don't have heat losses there.

We have been using this coulometer here at Goddard in support of the Houston program with Grumman. We've been looking at the 100 ampere hour cell.

One of the first things we did was Grumman furnished us with a heater cell which was made by Eagle Picher

eb13

Corporation which-- It removed one positive and two negative plates and substituted an expanded nickel material in there.

We used this cell to measure the response time of the calorimeter.

Slide off, please.

(Slide 161.)

And this is what we found.

Now there is a calibration heater in the calorimeter located at the base of that silver tray. This was used to calibrate the instrument without a cell in there and we found that it met the design criteria of less than 5 minutes.

Now this is what happens when you add a large thermal mass, like a 100 ampere hour cell. You can see that it takes approximately 90 minutes for 90 percent of your signal to come out. Now this was done at 25 degrees C., and a constant 20 watts was put in the coulometer. And then 100 percent of your response requires 140 minutes.

Next slide, please.

(Slide 162.)

The next thing we did is we took a General Electric cell in this case, a 100 ampere hour cell, and we subjected it to a near-earth orbit, a 90-minute orbit, 110 percent recharge and 25 degrees C. What we were setting was the effect of thermal output versus depth of discharge. The percent recharge was fixed; the temperature was fixed. It was 10 percent, 15

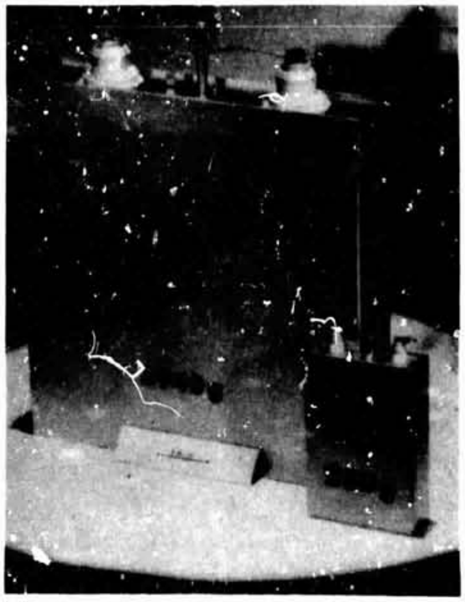
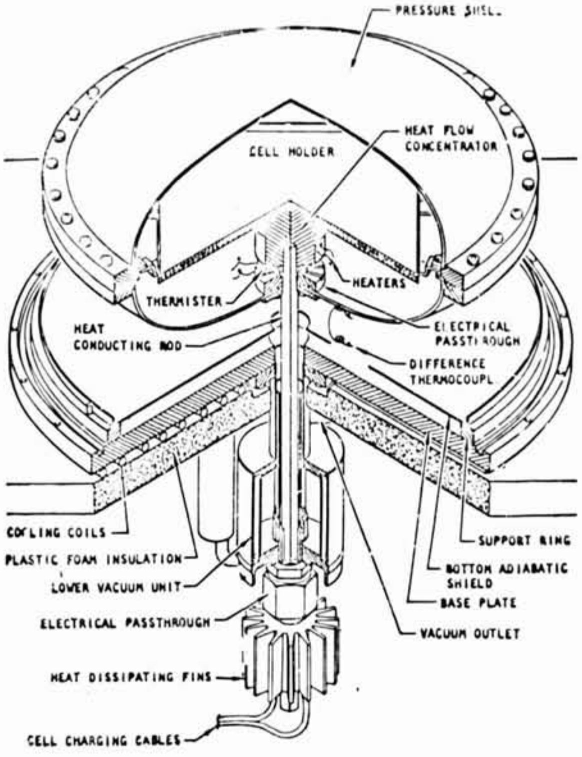


Figure 158



Quarter Section Drawing of Calorimeter

Figure 159

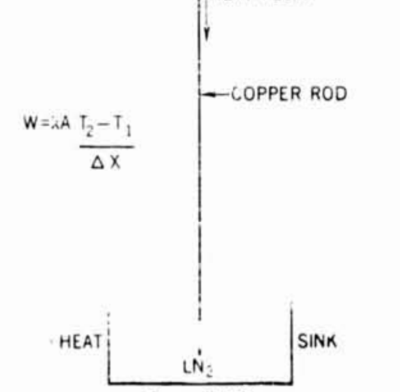


Figure 160

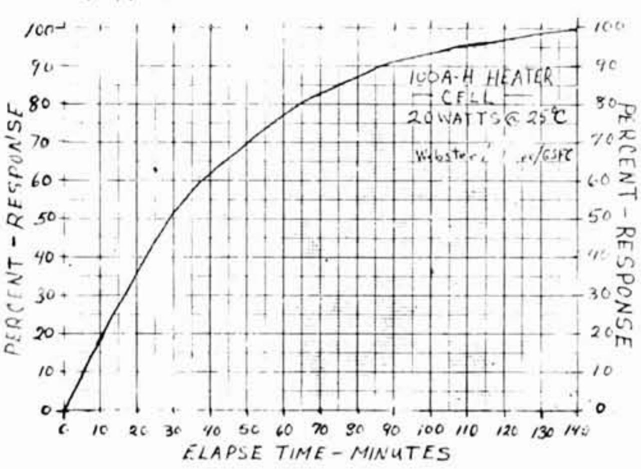


Figure 161

percent. 20 percent, 25, 35, and 45 percent.

Now remember, this is a 30-minute orbit so that 45 percent, we're talking about 90 amps.

You will also notice that the curves are changing shape. This seems to be following a trend so that you could predict possibly what was going to happen. Then at the higher current rate something else happened.

We ran a check of the instrument to make sure it wasn't instrument error by using a copper bar across the output terminals and applying the same amount of current and there was no error associated with that amount of current.

My next slide.

(Slide 1637)

What I did was I plotted what I call inefficiency where I took the peak thermal output versus the integrated watt hours during discharge and you can see what is happening. At a discharge rate of 20 amps with 10 percent depth of discharge, we're talking about an inefficiency which people talk about on OAO, about 15 percent.

But as your rate goes up, your inefficiency goes up and when we get up to 90 ampere hours, we're up as high as 32 percent. Now this actually I would think is almost common sense. It's a current density problem that we're probably running into here.

Another consideration, though, and that may be more

eb15

important to a thermal engineer, would be what is the average bay temperature, so I integrated the total heat out during that 30-minute discharge, put that over the electrical wattage, and we end up with a completely different picture. We're talking about a range from about 6 percent to a maximum of 10 percent.

Not being a thermal engineer, I don't know which one of these figures would be more significant and I don't know in the past, when people referred to the thermal inefficiency was typically 15 percent, which figure they were referring to, but it's a distinction you have to make. If you're interested in peak output, it's considerably different. It's as much as 25 percent higher.

Next slide, please.

(Slide 164.)

Then of course everyone always says, "Well, what happens during overcharge," and we thought we'd take one more look at it, and it happens just the way everyone always says it does.

What we have here is we have a continuous overcharge at various rates, C over 10, C over 20, C over 40 and C over 80, and we find in each case that once the cell has become fully charged and you've hit an equilibrium condition, your thermal energy and your electrical -- your thermal and your electrical are exactly the same; that is, you multiply your

eb16

current rate times your cell voltage and you're right on.

The little discrepancy here is probably due to the fact that when we get down in this range we should have changed the sensitivity of the coulometer. We were up at the 30 watt baseline; we come down here; we're looking for less than two watts out of 30.

✓

Next slide.

(Slide 165.)

This is the last slide. This is looking at the thermal output as a function of the percent recharge. Here we kept the depth of discharge constant. We kept the temperature constant and we put in different amounts of energy, 105, 110, 115 percent. And you can see that there is definitely an increase also with the percent recharge, but the order of magnitude is much less than that that I had in the first slide where we were talking about the effect of the depth of discharge, so it is a factor.

Of course, if we continue to overcharge the cell then it would become a very predominant factor but we are not in this particular experiment; only up to 115 percent.

We have right now-- We've been running this instrument on a continual basis since January. We have about 125 pages here of raw data that we're reducing and we intend to come out with out next report but to be honest,it will probably be spring before it comes out, so if anyone is interested in

C3

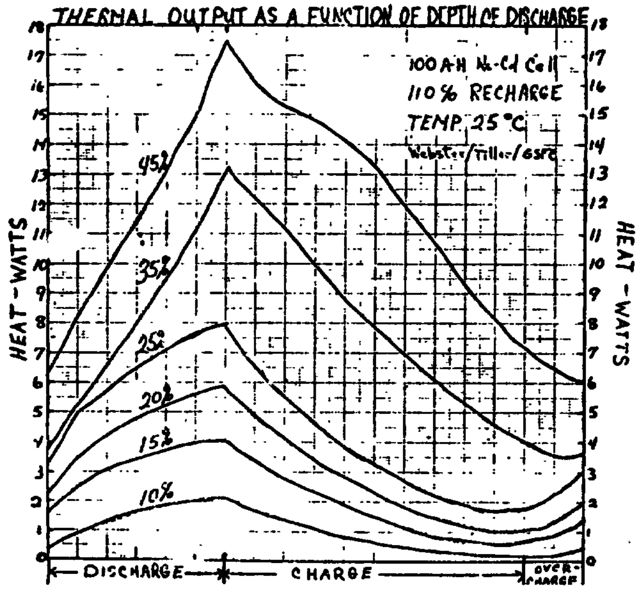


Figure 162

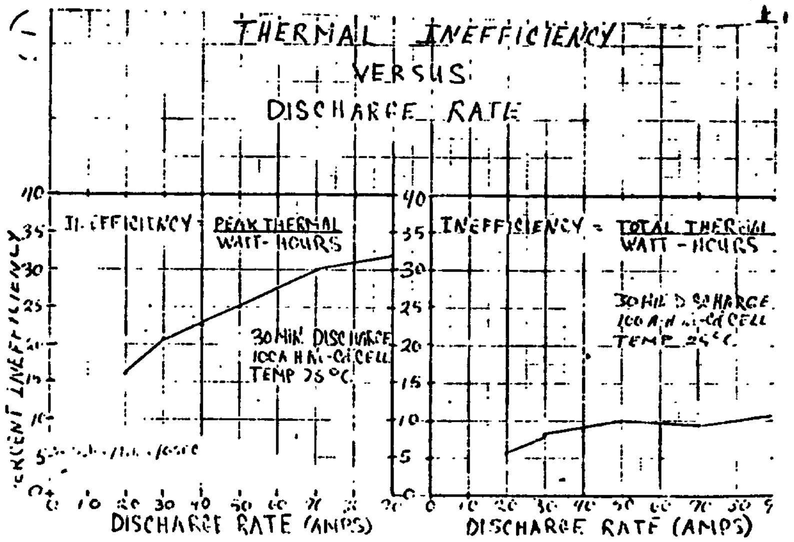


Figure 163

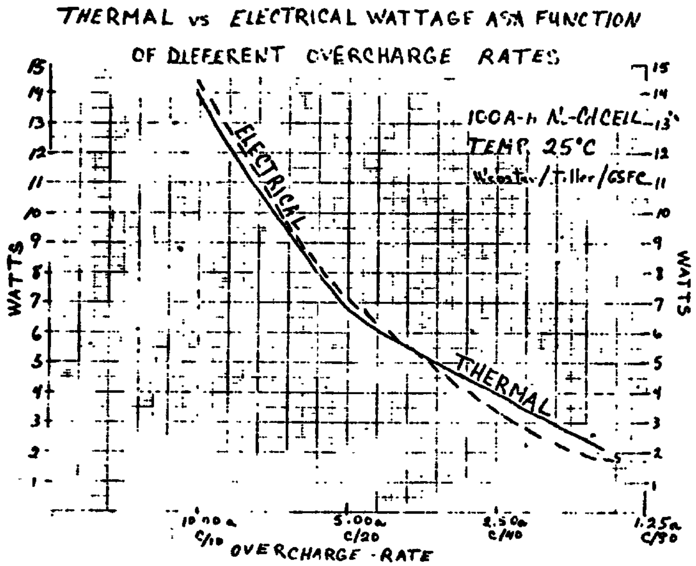


Figure 164

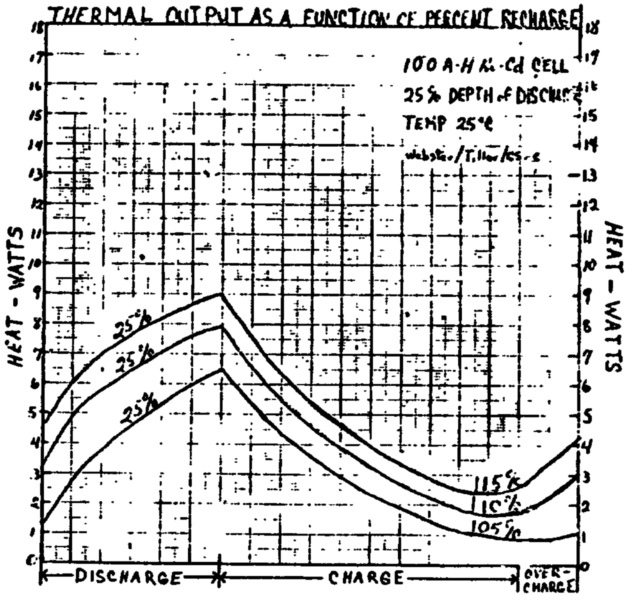


Figure 165

eb17

obtaining more information, we have it here and we just haven't had time to get it published yet.

MAURER: I have a question to start off, Bill.

In some of the curves that you showed it would appear that the time constant of this system was something on the order of an hour and yet you were showing heat flow data that was considerably less than an hour, like 30 minutes. How do you know whether what you're measuring is controlled by the system or whether it is controlled by the cell?

WEBSTER: Your observation is correct. We cannot do anything about improving the response of the system since the thermal mass of the cell governs that. However, the system is an equilibrium system. It operates at 25 degrees C., and on the C over 2 discharge to one volt where we are going for a period of two hours, the curve of our heat output follows exactly the curve that we obtain from a heater cell.

The only thing I could say regarding this, and it's probably not really answering your question, is that if at the end of 30 minutes you were to go back to your calibration curve and you'd see this represents some percentage of the total output, maybe 60 percent, if you were to continue at this rate to one volt which would take maybe two hours or longer, you would see that these two values concur.

So I don't think the instrument is influencing it and it is a valid criticism, though, that you're not seeing all

eb18

the heat, but it is due to the mass of the cell.

GROSS: Sid Gross, Boeing.

I've calculated the thermal response of cells, not that one but others, quite large, approaching that, and it's on the order of four or five minutes so therefore, the one hour time response of your instrument appears to be mostly due to the design of the instrument and not the response of the cell.

It is possible to closely approximate the thermal response of the cell with other design approaches.

WEBSTER: Sid, a question on that. What order of wattage are you talking about and how did you run your experiment?

GROSS: Thermal response is calculable and it's not a function of the heat rate. It's the time required to approach one over pi on the final asymptot of the result.

WEBSTER: And you think a cell of this size has a thermal response of less than five minutes?

GROSS: Well, I haven't calculated that but you could easily calculate it. It's quite straightforward.

WEBSTER: What size cell are you talking about?

GROSS: I've calculated it on a cell about an inch and a quarter thick.

WEBSTER: That's the same thickness. But what about the rest of the geometry?

GROSS: Well, I think this dimension turns out to be the most important.

WEBSTER: We're talking about 4,000 grams of weight here.

GROSS: Well, the thermal response is a function of the thickness squared and the thermal diffusivity and the conductivity, and you can do it fairly straightforward by calculation and get a pretty close estimate of what the response of the cell is.

Or I guess you can actually run an experiment where you separate the cell from the coulometer in an experiment designed specifically to measure the thermal response of the cell --

WEBSTER: That's right.

GROSS: -- and that would confirm or get a more accurate value. And I think if you do this that you will be able to identify most of your one hour time response as a built-in design feature of the coulometer.

WEBSTER: I will certainly look into this. I think it has been looked into. I will have to look back into the reports. The fellow who did this is Dr. Bill Johnson, who is internationally known for his work in Coulometry.

He did go through such a calculation. I believe it appeared in the first report concerning the design of the instrument, and we have operated it without the cell in there and the response time has been less than several minutes, and

eb20

with the cell in there then the response time has gone up to the times indicated. And the servo loop for the coulometer has a response time on the order of seconds, so I don't really think --

GROSS: The calculations I've made on this kind of thing, the heat transfer between the cell surface and the heat sink is the critical step.

MAURER: Bob?

STEINHAUER: Steinhauer, Hughes.

Bill, your data is 25 percent at the discharge and I assume you are concentrating on that for obvious reasons, but will you be generating or are you in the process of generating data for deeper depths, namely geared at synchronous?

WEBSTER: Yes, in the near future here we're going to be supporting the ATS and OSO project here at Goddard, and the ATS is a synchronous orbit program. We'll be looking at 15 ampere hour cells, 50 percent depth of discharge, and various other depths of discharge, and supporting also the SMS program here at Goddard.

I might also mention that this instrument is available for uses by private industry insofar as requesting us to run some cells for you in it. And sometimes we might not be able to accommodate this by schedule and we might be able to take a cell which we have in there, like for instance the 15 for ATS, and approximate your regime while we have that cell in there.

MAURER: Our next speaker is Joseph Yuen who will talk about controlled battery temperature in satellites with Berlon and Berlox.

YUEN: We all have heard about batteries. Since we are the space satellite battery user, I'm going to give you some information and results from the battery that is now on the satellite in orbit.

Most of our battery packs are 918 F size polypropylene triple-sealed cells. The size of the pack is roughly 5-1/2 inches by 7-1/2 inches in diameter and weighs about 15 -- 11-1/2 pounds.

All cells are supported by an echo form mode and in the early part of our program we put this mode with the battery pack inside of a sealed container. In the last two launches we have witnessed a rise in battery temperature and this is the configuration of our battery pack.

(Slide 166.)

Here is the battery pack, the F cells inside with the nylon insulator and this whole pack is inside a sealed container. And we monitored the battery pack with a temperature sensor that was buried inside of the echo form. At that time we did not monitor the temperature on the cell itself.

So a year ago our battery pack witnessed a high temperature on the payload. We were not able to command the

eb22

TM on so we're guessing the temperature is a little bit high.

So on our last launch, solar F-10 which launched from Wallops Island in July of this year, four months ago, we feel that the battery problem-- The battery was kind of hot so we used another method of trying to conduct the heat away from the battery pack.

We are also monitoring the temperature on the cells, on top of the cells. On the battery pack we have two rings of cells, an inner ring and an outer ring. We also monitored the cells, each cell on the inner ring and the outer ring.

The battery pack is also supported the same way with echo form but we add an aluminum plate underneath with the nylon separators. But we also did away with the cover -- I mean the hermetic seal cover because we feel that the cells themselves are hermetically sealed so why launch the battery pack with a sealed cover?

So instead of insulating it with the nylon we used a Berlon -- Berlox disk, which is a ceramic disk, beryllium oxide filled ceramic, and the glue the ceramic onto the bottom of the cell and also onto an aluminum substrate. We glued it with beryllium-filled oxide RTV Berlon. They call it Berlon. These two items are made by National Beryllium Oxide up in Haskell, New Jersey.

We've got temperature from the payload now, so it's a very comfortable temperature.

(Slide 167.)

At 62 percent sun the battery pack ranged from 21 to 24 degrees C.; at 63, from 25 to 28; at 90 percent sun it's 34 to 36. And I just got word from the office a while ago that this payload now is in 100 percent sun and the battery has only gone up as high as 38 degrees C.

The rest of the payload is pretty cool.

I think the battery pack sits on a support tube that mainly supports the rest of the electronics in the payload and the support tube is also mounted to a thick plate of honeycomb, and that's what the electronics are on. And the honeycomb plate is only seeing about 21 or 26 degrees C. And this method we used to carry heat away shows very good results.

Now I would also like to mention something about the rectangular cells. This was on the round cells.

On the rectangular cells I have now worked out a method using annodized shim to go between each cell. As we all know, hard coat annodized aluminum is a good insulator but it is also a good thermal carrier. So in between cells we have a thin film of annodized shim and we clamp them this way. We have to clamp them anyway so we might as well clamp them and carry heat down to another heat sink plate and it will be mounted into our honeycomb substrate by that method to carry heat away.

(Slide 168,169.)

On the side of the cell we will also clamp it to another annodized shim to carry heat away further. We feel that this method of controlling the temperature in the battery in the payload has been quite successful. This is the method we have hoped to carry on.

That's all.

Any questions?

GROSS: Sid Gross, Boeing.

I didn't understand how you get the heat out from the bent shim to the bottom. Is it bonded on?

YUEN: The bent shim is this one right here, actually, and this is another-- You have another heat plate which is right underneath the bent shim.

GROSS: The two are bonded then?

YUEN: This is also bolted to another big plate that is also a support plate of the payload.

GROSS: This shim then is bolted to something underneath it?

YUEN: Right.

GROSS: On the outside, on the outside flange?

YUEN: No, no. These flange are the bolting flange and also hold the cell down to the plate.

GROSS: Okay.

One comment on the use of annodizing aluminum -- annodized aluminum for an insulator. This is kind of an iffy

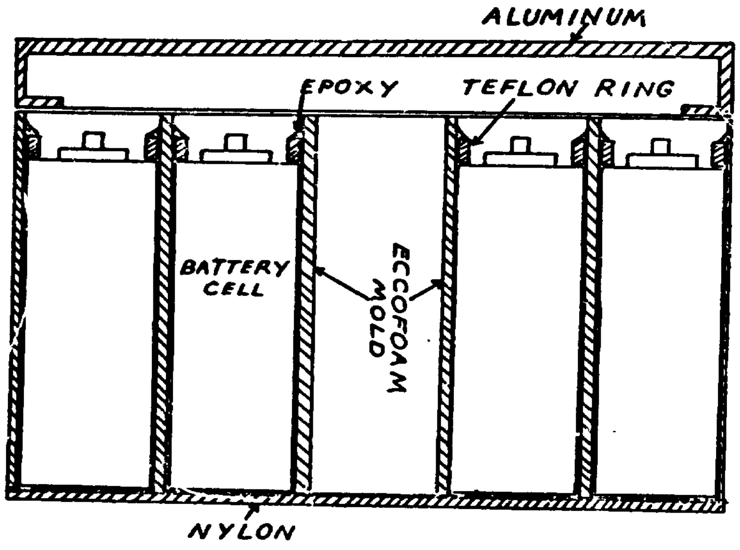


Figure 166

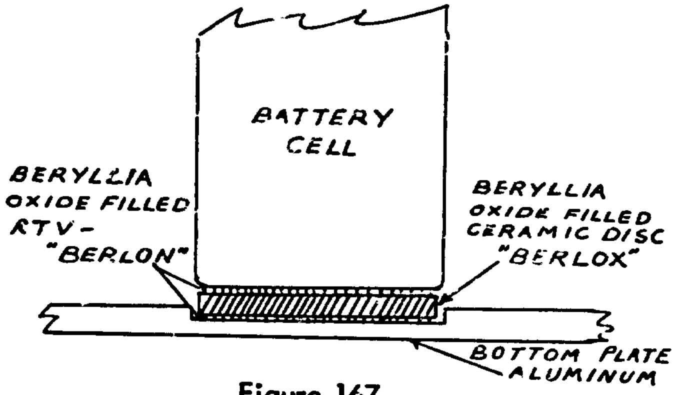


Figure 167

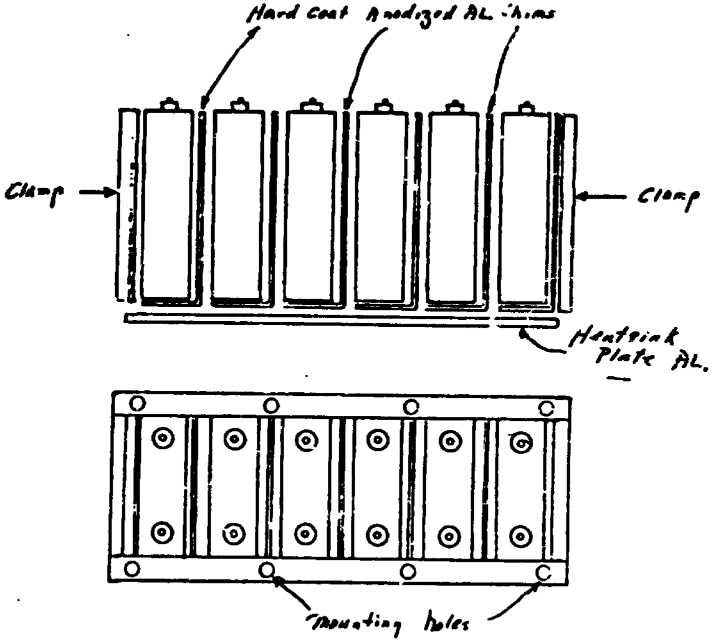


Figure 168

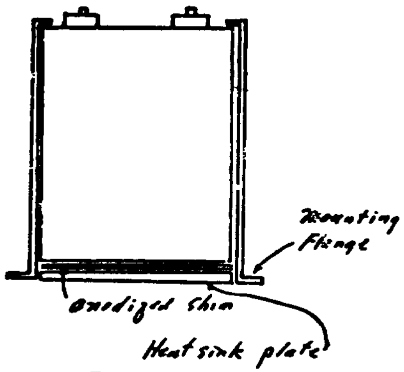


Figure 169

thing sometimes and it might warrant looking into. It is hard to depend on consistent protection at battery voltages.

YUEN: We plan to use a two-terminal cell and so I figure the voltage between the case and the inside won't be too great.

GROSS: As I recall, the annodizing films break down around 15 volts.

YUEN: But I'm quite sure you'll have about maybe a tenth of a volt in between.

GROSS: I guess it would be worth looking into. Sometimes you can get a whole battery voltage across the insulator in certain failure modes.

MAURER: The highest plate voltage in the cell will be sitting between the cell case, inside the cell case and the case in contact through this aluminized plate to the ground?

YUEN: Yes, but we also have insulation inside the cell.

MAURER: But that's in contact with the electrolyte so-- Insulation inside the cell can will be in contact with electrolyte and that can only stand 1.2 volts per cell until you get hydrogen.

CARR: Earl Carr, Eagle Picher.

It seems to me that probably the spacecraft is grounded so that whenever you have a series string of cells you have built up a potential and you've got voltage to that

eb26

case through the electrolyte path and you can have a breakdown of electrolyte and that is a single point failure.

YUEN: We have measured hard core annodized. Hard core annodized they claim is roughly about 3 mils thick and I used an ohmmeter with two scribes in my hand and I couldn't even break through to read any kind of a resistance.

STROUP: Gene Stroup from Goddard.

Joe, it seems to me I recall reading some reports from TRW Systems regarding an attempt to annodize on the OGO battery, I believe it was.

Would anybody from TRW like to address the subject of your annodizing on that particular project?

I don't know what the annodizing-- I don't know how you did that or what the thickness of it was. That might clarify this point that Joe has brought up.

SCOTT: Scott from TRW.

Since you've put me on the spot, Gene, I have to say something, --

(Laughter.)

-- and that something is that I wasn't around when that was going on.

(Laughter.)

But I'll say one other thing and that is that I concur with the people who are concerned with the high voltage available at the positive end of a multicell series string battery and also there is another potential problem and that is during ground handling or if you have any -- especially if you have any electrolyte leakage -- perish the thought -- you can get high conductivity through the pores of some of these annodized films. That will be an accelerated point of breakdown of the annodizing and you can really have problems.

But I don't remember anything-- I don't have any knowledge of what the story was on the OGO program, Gene. Sorry.

STROUP: One other thing on that. TRW did use a fiberglass sort of insulating material between the annodized structure and the cell, the annodized heat transport fin and the cell. It seems to me-- I did not measure the depth of the annodizing itself but it seems to me that it was thinner, much thinner than what you described, Joe, and it might be worth looking into.

I believe I may have some of these in the lab.

YUEN: Yes, but when you're using a fiberglass insulating you're defeating the purpose of that annodized can carrying thermal conductivity.

STROUP: Yes, but I understand it was necessary in this particular case.

MAURER: One more question before we go on to the next, and coffee after that.

GASTON: Gaston, Grumman.

eb28

I have a comment. On the OAO batteries we have certain similarities to your packaging and certain differences. We do have a hard coat annodized heat fin, L-shaped, but before we take the cell we wrap it in a layer of Kapton, about one mil Kapton to insulate it. Then we embed it in a Dow Corning potting material to smooth the surface of the cell so we get a good thermal contact.

So we do have more than one insulation. We do have the hard coat that's an insulation and we do have the Kapton and additionally, we have the Dow Corning potting.

And at the bottom of the L shape that is mounted directly against a heat sink, again we have an insulation there. I think it is also Dow Corning, where it is mounted against the heat sink.

So you have various numbers of insulation and additional electrical leakage path protection.

YUEN: One more thing I forgot to mention.

/69

(Slide 169.)

Besides the annodized we were also anticipating a surface that would be not flat so we were also going to use some of these in between so that will probably still further carry the heat away and take care of any voids that there is.

MAURER: One more question from Steinhauer.

STEINHAUER: Steinhauer, Hughes.

Without telling tales out of school, I do recommend that you look carefully into insulating of cells electrically.

One other possibility is if a cell case does get grounded, what is the potential of that case with respect to the electrodes in that cell and what type of gases could be generated.

MAURER: The next presentation will be by Dan Lehrfeld, whom Steve Gaston had mentioned would tell us about the thermal design of the Grumman 100 ampere hour battery.

LEHRFELD: I have requested some time in this session to provide some additional background information on a subject that Steve Gaston first introduced yesterday, and that is the work we've been doing at Grumman on the design of a 4-cell module for a manned orbital space station.

I'll present some of this additional material and then perhaps if there are any questions, even left over from yesterday or that may arise today, I'll be happy to answer them.

Basically the goal of our work at Grumman is to design a 4-cell module which can be a building block to a space power system for a 25-kilowatt manned orbital space station. I have some notes here that perhaps I could project on the screen. It might help familiarize some of you with the manned space station program if you are not already so familiar.

(Slide 170.)

The space station program being studied for NASA by McDonnell Douglas and North American-Rockwell considers a manned system with an average power level of 25 kilowatts. What this means to the battery system and to backtrack, the power system for this station is foreseen as a solar cell nickel-cadmium battery system.

A typical battery system would consist of 148 of our 4-cell modules or 672 cells. This corresponds to an average 30 percent depth of discharge in orbit.

To give you some feel for the size of the system, that number of 100 ampere hour cells weighs approximately three tons and we're talking about a total module weight of on the order of four tons, allowing about 35 percent for packaging.

The battery voltages in the system and the actual system configuration varies with the study. The different contractors are looking at many different systems. Typically we have seen systems described as 21-module batteries, eight such batteries comprising the total system, or 28-module batteries, these modules strung in series, six such batteries comprising that particular system.

So you can see that we're talking about a fairly large number of cells and the battery system does represent a significant part of the over-all space station program.

(Slide 171.)

BACKGROUND INFORMATION ON MANNED SPACE STATION PROGRAM

POWER LEVEL: 25 KW (average)

POWER SYSTEM: Solar array/Ni-Cd battery

BATTERY SYSTEM: 168 -4 cell modules (672 100 AH cells)
(based on 30% average DOD, 94 min. orbit)

BATTERY WEIGHTS: 672 cells (@ 8.5 lbs./cell) 3 tons
168 modules (@ 33% packaging wgt.) 4 tons

BATTERY SYSTEM CONFIGURATIONS: Vary with electrical system concept

TYPICAL CONCEPTS:
- a) 8-21 module batteries in parallel
- b) 6-28 module batteries in parallel

Figure 170

100 A.H. MODULE DESIGN REQUIREMENTS

MECHANICAL:
- a) 0 psia to 100 psig internal cell pressures
- b) Saturn type vehicle launch loads

ELECTRICAL:
- a) 4-100 AH Ni-Cd cells connected in series
- b) 12 to 50% orbital DOD
- c) Case to case (and case to ground) electrical isolation

MAINTAINABILITY & HUMAN FACTORS:
- a) Module removal (and installation) without breaking coolant lines
- b) Target Weight: 45 pounds

THERMAL:
- a) Heat removal via a circulating water cooling loop
- b) 32 to 55°F inlet water temperature @ 30 lb/hr. flow rate
- c) 0 to 14.7 psia compartment pressures
- d) 0 to 1g gravitational field
- e) Allowable cell (case) temperature range 32 to 68°F (0 to 20°C)
- f) Minimize cell to cell temperature gradients

Figure 171

This next page will outline some of the requirements that have been defined for us in the design of this module.

Mechanically we've designed it for internal cell pressures ranging from zero psia up to 100 psig and additionally we've designed for the type of launch loads you would expect from a Saturn-type vehicle.

Electrically we have four 100 ampere hour sized cells connected in series. Our orbital regime varies from 12 to 50 percent depth of discharge over a 94-minute orbit.

Additionally, we must provide case-to-case isolation and case-to-ground isolation within the module.

We also have maintainability and human factors considerations because each of these modules is replaceable in orbit. The entire battery system over the life of the space station system will probably be replaced many times. That is the reason for packaging this four cells as the basic unit.

Two requirements which we thought of putting down here just off the top of our heads were the target weight in our program which is approximately 45 pounds, and that's come out of human factor studies which have been done which have shown that that's approximately the maximum weight that an astronaut in orbit should be required to handle.

Additionally, we just design our module to mount with a cooling system and to be removable without breaking any fluid lines in that system.

eb32

Some of the thermal requirements that we have to contend with are we are designing for heat removal via a circulating water system. There is a water system aboard the space station in the baseline studies through which all electrical equipment dissipates its excess heat.

We are designing for a range of inlet coolant temperatures from 32 up to 55 degrees F. at a flow rate of 30 pounds per hour available per module.

Additional requirements are that the modules be mounted in crew-habitable compartments which can be up to 14.7 psia environment or during a depressurized operation could be zero. And the gravitational field in the space station can be either zero G or up to one G.

The requirementson our cells are that the package must maintain cell temperatures no higher than 68 degrees F. or 20 degrees C. while the package is exposed to the maximum environment. Our minimum temperature is 32 degrees F. although in the space station that requirement is automatically met.

What I have down there is cell case temperature. When we speak of cell temperature we refer to the temperature on the cell case; that's our reference temperature.

Additionally, because we have four cells packaged and we have a moving coolant system picking up the heat that we're rejecting, there will be some variation in temperature from cell to cell, and we've tried to minimize that variation

eb33

so that the four cells are as nearly isothermal as possible.

(Slide 89.)

I have a Vu-graph which we'll put on now that shows the 100 ampere hour module that we've constructed for engineering evaluation tests. The picture was taken during fabrication; it's not complete but I think it can illustrate the design to you.

We call this the flat-pack design. I should backtrack to say that in our studies we have considered many different geometric arrangements and we've looked at alternate possibilities in packaging the module. However, the thermal requirements are pretty stiff; that is, we've got to maintain the maximum cell case temperature at 68 degrees with a coolant inlet temperature of 55, so we've only got a total thermal gradient of 13 degrees allowable.

So some of the more traditional packaging methods that we've looked at such as packing cells broad side to broad side with thermal conduction fins in between and channeling heat down to a base plate -- we've looked at those but those resulted in very large, massive thermal conduction plates because of the size of the cell.

We're talking about a large amount of heat and the height of the cell being approximately 7-1/2 inches high, that heat has a long distance to travel to a typical base plate mounting system. That would result in a very large gradient

eb34

over the face of the cell and to counteract that you would require very massive plates.

The design that we've come up with here is lighter in weight. It meets the requirements. It comes very close to our goals, and we think it's a very simple package because it is easy to fabricate; it doesn't require internal heat pipes which is one of the things we did consider in our program but the fact that we do not require them we think is a plus for this design.

To describe it for you, we have the four cells end-to-end, resulting in a very long, narrow package. The heat dissipated within the cells primarily comes out the broad faces of the cells across an interface which consists of Kapton tape and capsulate material, a hard anodized coating, to the side walls of the module.

It is conducted down the side walls to the mounting flange. This is the mounting flange, one on each side of the package. The heat is channeled to this mounting flange. It's rejected through a bolted interface to a cold rail.

This cold rail typically would be a long aluminum extrusion which provides a passage for a flow of coolant past the module and it also provides structural support for the module in a typical system.

The cannister itself is made out of 6061 T-6 aluminum. This side plate you see here, 30 inches by

eb35

approximately 8 inches, is one integral piece of aluminum that has been machined out. These are stiffening ribs required to constrain the cell pressures that we're designing for.

The module mounts to this cold rail via captive hardware which is not shown in this drawing, and this is early in its fabrication. The captive hardware consists of bolts which would be installed here. They move with the module and they simplify the ease of installation of the module in that the module just has to be slipped in between the two cold rails and a normal Phillip's head type screwdriver used to fasten the module to the cold rails.

We use a silicon grease interface material between the cold rail and module to enhance the film performance of the interface.

What's shown-- Structurally, let me say this:

We provide-- Our basic cannister provides for containment of the cell on five sides. This top cover which is installed last is bolted down and constrains the sixth side, so we do constrain all six sides in our design.

It is hard to see in this picture but each of the cells is in an individual compartment. There is a base plate. There are end plates, and there are cross pieces separating these into four separate compartments.

What is shown here are tabs which are welded to the side plates. They structurally connect these cross pieces to

eb36

the side plate making it a one-piece, rigid construction.

To speak just about the fabrication techniques, the way the module is built up is after assembly of this basic cannister, we would take a premeasured amount of potting material. We did study various potting materials. We selected one which has very good heat transfer properties. It has a K of 0.5 btu per hour per foot, and very low viscosity which was important, as I'll get into later.

We would measure out predetermined volumes of this potting material. After it is catalyzed we would pour it into the bottom of each one of these cannisters. The cell would then be taken-- The cell is potted with an internal vacuum in the cell. It would be taken and placed down into the cannister to sit on top of that layer. Then it would be allowed to sink under its own weight, allowing the potting to rise around all four edges of the cell.

Then we apply pressure to the top of the cell until it is fully seated. By that time the potting will have flowed up all around the cell and we guarantee that we are encapsulating the entire cell.

The final step after that potting hardens,we would top pot and then install the cover.

Let me just mention, the cells that are shown here are the heater cells which were constructed for us by Eagle Picher. That's these two extra set of terminals you see here.

eb37

Those are the terminals by which we energize that heater cell.

(Slide 172.)

This Vu-graph just summarizes the status of our program, where we've actually gone to.

We've designed, fabricated. We've assembled an engineering test module with four actual cells. We've selected our configuration which is the flat pack; it has been optimized. We do feel it is the optimal consideration based on weight, thermal performance, maintainability, and the structural requirements.

We have run an engineering evaluation program of both thermal tests to demonstrate the design the proof pressure tests. These have been completed and the module has performed within our expectations.

MAURER: Thank you.

I think in order to keep within our time frame -- A few people have flights to catch earlier -- or later, rather, in the afternoon -- let's not have questions now. In fact, let's have coffee --

(Laughter.)

-- and perhaps the thermal discussion can go on in small groups.

(Recess.)

D ebl

MAURER: We've finally made it to the star attraction of the session, the pre-charge session. And the first speaker will be Dr. Font from SAFT, who will speak on a study of different pre-charge levels in 20 ampere hour cells.

xzxzx

FONT: I will try to present to you some results on the pre-charge study performed on the 20 ampere hour cells under a contract program or contract study.

In the preliminary study we have determined that after formation cycles on the plates, cadmium remains on the plates and this has been determined by chemical analysis to be from four to seven ampere hours on our 20 ampere hour cells.

I have to state that we have negative to positive ratios in these cells, theoretical ratio, theoretical capacities of 2.0 which is real capacities are about 1.7.

We have performed three different levels of precharge in three different groups in these cells and we have performed this pre-charge using a venting technique. I will show you the results.

(Slide. 173.)

On oxygen evoluation on all these cells of the contract, we see in this table that the rate of oxygen evolution is about twice between all the cells from 300 cubic centimeters to 600 cubic centimeters.

(Slide. 174.)

This table represents results on pre-charge

eb2

measurement. We have made in all the study two different measurements, one by chemical analysis and one by electrochemical measurements.

You see on the first table there the results on ampere hours of the cells -- ampere hour determination of cadmium, inactive cadmium on the plate. We have put on these cells, E group, four ampere hours corresponding to oxygen; ten in F group, and 16 in group G.

So before doing anything else, in each group we have total pre-charge of 1 to 11, 14 to 17, and 20 to 23. In these cells we have performed a cycling test, 30 cycles and each cycle's duration is 12 hours, 11 hours charge at zero-10 and one hour pre-charge at zero-2 rate.

(Slide 175.)

Here are the pressure evolutions expressed in absolute pressure versus the time. And we see that in the group of higher pre-charge, the pressures are lower than they are in the other pre-charge adjustment. This is on cycle 2.

(Slide 176.)

And we have another sheet where we see on cycle 29 it is almost the same. We have to notice a little difference in the end of charge pressure, more senstive in G group than in any other; very little change.

The last pre-charge cycle on these cells shows the

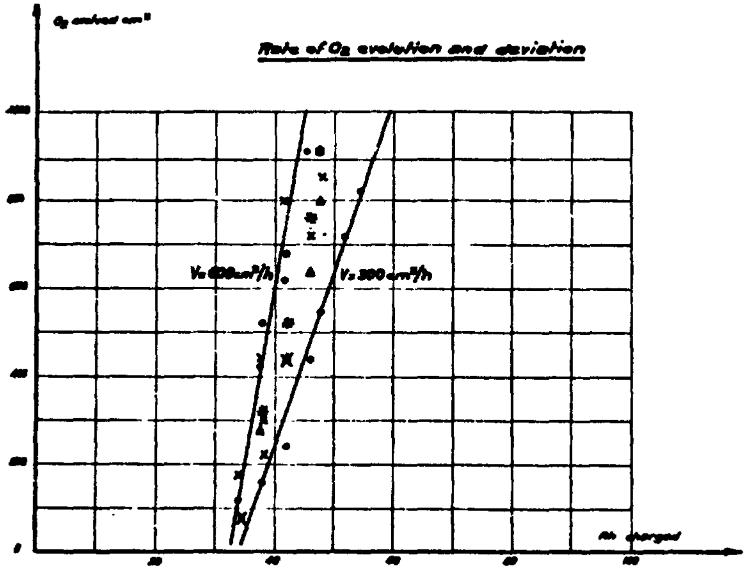

Rate of O_2 evolution and deviation

Figure 173

PRECHARGE ANALYSIS

	E	F	G
Precharge adjustment			
Chemical analysis after formation	4-7	4-7	4-7
Precharge by venting technique	4	10	16
TOTAL PRECHARGE	8-11	14-17	20-23
Measured precharge before cycling			
Electrochemical	1.8	4.8	10.4
Chemical analysis	11.3	11.0	9.2
TOTAL PRECHARGE	13.1	15.8	19.6
Measured precharge after 30 cycles			
Electrochemical	9.6	14.0	20.0
Chemical analysis		in process	

Figure 174

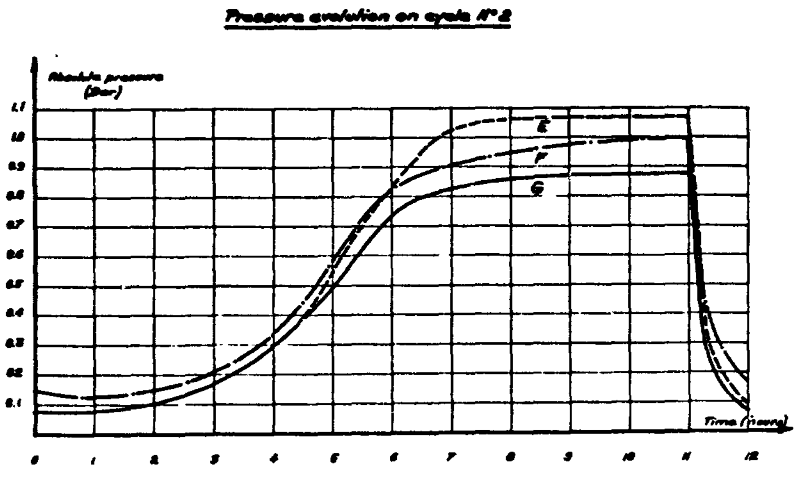

Pressure evolution on cycle N° 2

Figure 175

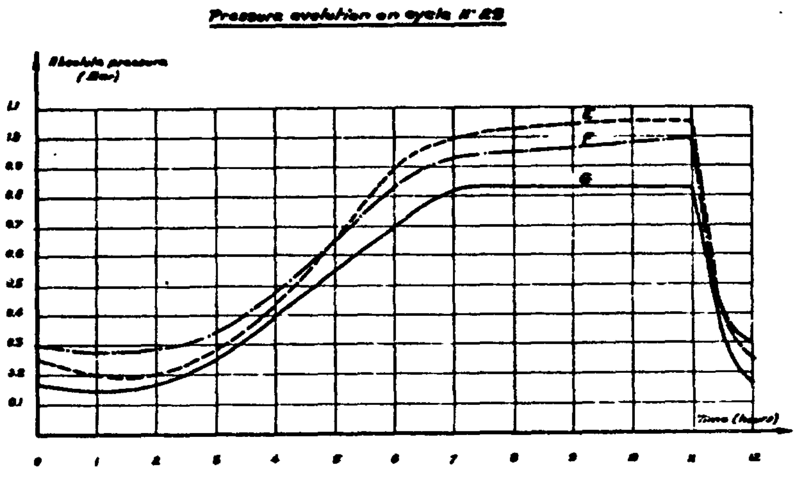

Pressure evolution on cycle N° 29

Figure 176

eb3

following curve.

(Slide 174.)

We'll see this later, another time.

I will present the first result here.

Before doing these cycles, we have measured the ampere hour electrochemical measurement on each group, and we have found the following results which are less than the ampere hours we have put at the beginning on these cells.

We have performed chemical analysis on the same cells and found the following results. This is that electrochemical measurements show it's less than what we have put on the cells but that chemical -- cadmium has increased. But we have to note that the total amount of pre-charge is about the same as we had before, except perhaps on this group which is a little higher, but we have to take into account the accuracy of measurements, both electrochemical or chemical.

Now we are on the step of measuring electrochemical and chemical pre-charge in these cells after 30 cycles and we see that electrochemical has increased in each of these groups from 1.8 to 8.6, 4.8, 14, 10.4, 20. We have not yet performed the chemical analysis on these cells. The test is running.

The important point is that you have an increase in electrochemical measurement on each group and this increase can be explained in the following ways.

(Slide 177.)

First of all, we can explain it by the same explanation that Dean Maurer said this morning about the activation of chemically determined inactive cadmium.

The second point, cadmium oxidation of separator.

And the third point, nickel attack on positive electrode by oxygen.

So we have not performed the chemical analysis on the cells after the cycling. We are not able to say exactly what are one of the many possibilities here.

But I have to go back to the discharge curve after cycling in which we see that the capacities on the high pre-charge group is higher to one volt -- is higher for the high pre-charge level and they follow on the pre-charge measurement.

(Slide 178.)

So seeing this curve, I should say several points.

First of all, our pre-charge level, considering the end of charge pressure and capacity after cycling tests seems to be good for the cell -- yes, for the cell.

A lower pre-charge level gives lower capacity and higher pressure but if we consider the increase in pre-charge measurement, electrochemical pre-charge measurement, we see that high pre-charge levels are very dangerous for the cell because we need either for long-lifetime cycling overcharge protection which is discharged cadmium.

And as we have not all the results on the chemical

POSSIBLE MECHANISMS FOR INCREASING ELECTROCHEMICAL PRECHARGE

1. ACTIVATION OF CHEMICALLY DETERMINED INACTIVE CADMIUM.
2. OXIDATION OF SEPARATOR.
3. NICKEL ATTACK ON POSITIVE ELECTRODE BY OXYGEN.

Figure 177

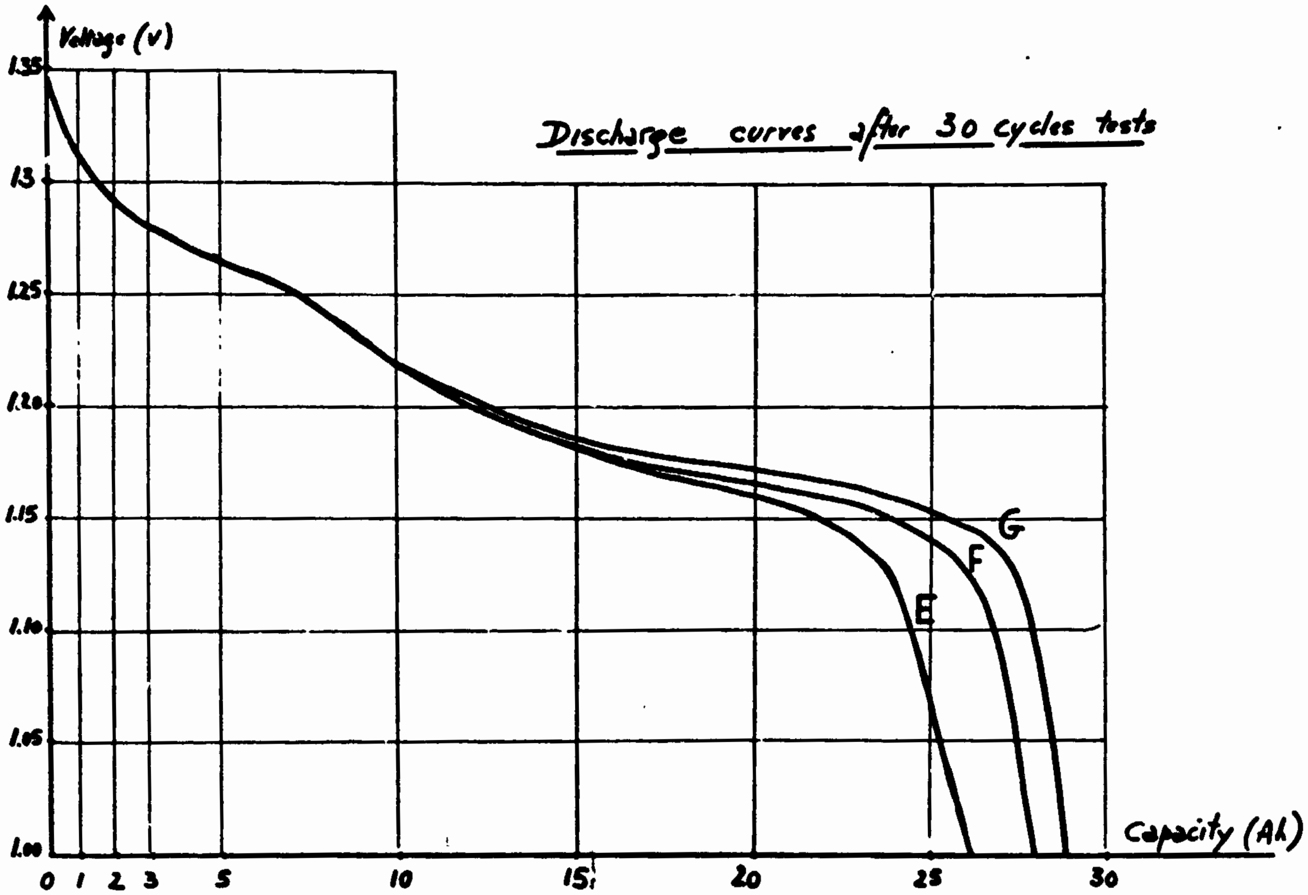


Figure 178

eb5

analysis from these cells, we cannot make a further statement or hypothesis on this point.

Thank you.

MAURER: Exercising the privilege of office, I will ask the first question.

(Laughter.)

How did you measure the electrochemical capacity of the negatives in the cells?

FONT: We measured the electrochemical capacity-- We drilled a hole on the cell after discharging it to one volt and we put the cell in open condition in potassium hydroxide and we reversed it versus the mercuric reference electrode and we measured the capacity to minus 0.5 volts

O'ROURKE: O'Rourke, Grumman.

I have two questions I want to ask you.

You said on the one chart you had up there that you had put a certain amount of pre-charge in the cell. Did you determine this by a rate/time method or did you measure the amount of gas coming out of the cell or --

FONT: Putting on the pre-charge, we measure the amount of oxygen. In the slide I have shown only the beginning until 1,000 cubic centimeters which is the same extrapolation for the highest pre-charge level. It's about 3,000 cubic centimeters at pre-charge.

O'ROURKE: How many cubic centimeters of oxygen per ampere hour? What was the relationship you used?

FONT: We used one gram of oxygen, one gram of oxygen, 3.3 ampere hours.

O'ROURKE: Okay.

The other question I had was what type of time period elapsed from the time that these plates or cells were immersed in electrolyte from the time that you made the actual electrical pre-charge measurement? Was there any attempt to control that time?

FONT: After formation cycles? After formation cycling through the electrolyte?

O'ROURKE: Did you take a pre-charge measurement directly after the pre-charge adjustment or did they go through formation cycles first?

FONT: After pre-charge adjustment we closed the cell and we performed two cycles at C over 10. The pre-charge measurement was made immediately after the first pre-charge, after pre-charge. Immediately after pre-charge using venting technique, we closed the cell. We performed a decharge to one volt and at this time we determined the electrochemical capacity.

O'ROURKE: Okay.

The reason I bring this up is I'm going to present something in a minute. I've found the correlation between the soaking time, in other words, the time you actually fill the cell with electrolyte, to the time that you do the pre-charge

eb7

adjustment. I've found out there is a relationship between the amount of pre-charge a cell will have, and that's why I was just wondering whether that time was either controlled or measured.

FONT: Going into details, after which -- after formation cycles we assemble the cell and we fill with electrolyte. Between performing any charging cycle we keep them 72 hours in that state after we perform one preliminary cycle in a closed condition and after we perform the pre-charge adjustment.

CARR: Earl Carr, Eagle Picher.

I couldn't see all the numbers but just simply:

Were the plates all the same before you set pre-charge? In other words, was there the same amount of cadmium in all of the cells?

FONT: In all this contract the plates were of the same lot.

CARR: Okay. Very good.

And then the next thing is what was the voltage difference during the overcharge for the three levels of pre-charge?

FONT: We didn't perform overcharge, a long over-charge time in these cells but the end of charge --

CARR: Well, what I was referring to is you presented some pressure data and corresponding to that pressure

eb8

data, what was the difference in voltage between the cell that was pre-charged?

FONT: I think it was not higher than 10 millivolts, 10 to 20 millivolts between the different groups. We had to state that the end of charge pressure are no very different, too. There is only 200 millibars.

KIPP: Ed Kipp, Gulton.

Can we assume these are starved cells?

FONT: Yes.

DUNLOP: Jim Dunlop, Comsat.

One point, partially in answer to the gentleman's question in front here, that Dr. Font and I had talked about before his presentation. I think I'm going to add something I think he meant to say.

These pre-charge measurements that he is talking about were made -- the measurements were made after the pre-charge was set. He got different results-- If you'll notice the first time he set the pre-charge he put in four -- in one case he put in four ampere hours of pre-charge and only measured 1.8 electrochemically.

In answer to your question, he also did a chemical analysis and he found that the remaining -- he found that it was essential for him to determine the total amount of pre-charge that he had in that cell at any time to do both the chemical and the electrochemical analysis. And by doing just the electrochemical measurement he could not determine how much pre-charge he had in those cells at any time.

STEINHAUER: Steinhauer, Hughes.

Dr. Font, could you tell us what method of chemical analysis was used? Was it complex symmetric titration or calometric?

FONT: It was titration by EDTA method.

SEIGER: Seiger of Heliotek.

Could you tell us whether you have the same amount of electrolyte in each of those groups before you set the pre-charge?

FONT: Before we set the pre-charge we have exactly the same amount of electrolyte.

BETZ: Betz, from Fairchild.

The initial chemical pre-charge that you showed there for the seven ampere hours, that's the valuability from the end of your formation process?

FONT: This is the difference on all-- We have performed these measurements on about 20 plates and this is the total deviation of the measurements.

BETZ: Coming out of formation?

FONT: Immediately after formation.

BETZ: Okay.

The second question: After your discharge to one volt, do you resistively load the cell to zero volts before you measure your pre-charge? That is the Goddard technique --

FONT: At what stage?

BETZ: After discharge to one volt, the technique for pre-charge measurement has included an intermediate step of resistively loading the cell until it goes to zero volts.

FONT: After discharging to one volt, we have discharged at C over 10 rate from one volt to zero.

BETZ: Then C over 10 from one volt to zero.

FONT: And after, from zero to minus 0.5 C over 10, too.

BETZ: C over 10 also. Thank you.

LACKNER: Lackner, Canadian Defense Research.

You mentioned you didn't have too much of an overcharge period; is that correct?

FONT: Yes-- Well, not performed especially an overcharge measurement on these cells.

LACKNER: Our experience has been that if we had too much of a pre-charge that we would get into hydrogen generation and the way we tested it out was to put the cells on 120 hour overcharge at minus 5, and if you had any hydrogen generation it most certainly would come out.

We feel that you have to tie in the pre-charge with a long overcharge as a screening out test.

FONT: It's not understood exactly --

LACKNER: We find that there is a definite cbl

dependence of pre-charge and overcharge capability and particularly if you are getting into synchronous orbit where you may have to be charging for long periods of time. I'm not saying you have to, but you may have to.

FONT: You may, yes.

LACKNER: We would like to have a cell that could stand the overcharge capability for a long length of time.

FONT: Yes. In this case you have not to put too much pre-charge.

LACKNER: In most of our past experience with a bare minimum pre-charge you get very good results by stringing out with a long overcharge period.

FONT: Yes.

One point here is that I think for synchronous orbit or a long-life cycling program we have to consider immediately on the discharge curve that if we have too low pre-charge the end of charge will be lower in that case. If we see that curve, --

(Slide 178.)

-- this curve is only for 30 cycles, and we see that mostly if you cut here, you have less capacity with lowest pre-charge.

So I think we have to have some compromise between no pre-charge and high level pre-charge which-- Perhaps for commercial cells high level pre-charge is good because you have

eb12

good capacity but no time duration guarantee.

But in this case we have to do some compromise and I think Mr. Dunlop will tell you about this following this program to determine what amount would be necessary.

HALPERT: Halpert, from Goddard.

Were these your aerospace grade or aerospace quality materials that were used?

FONT: We used our space quality plates which all were high ratio-- We used exactly the same materials, nickel, but we have the space definition with high ratio on these cells.

HALPERT: And what kind of separator was it? Nylon or polyprophylene?

FONT: Until now we used nylon but we are studying the eventual change to polyprophylene.

BELOVE: Belove, Marathon.

What is the difference in capacity of those cells with the low pre-charge and the cells with the higher amount of pre-charge to one volt?

FONT: There is on this curve -- Immediately after discharge the difference is about two or three amp hours.

You have your 26 to 29, about.

BELOVE: Thank you.

KIPP: Ed Kipp, Gulton.

Have you been able to generate enough data so that

eb13

you could establish a relationship between the amount of pre-charge measured electrochemically and that measured by chemical analysis?

FONT: What kind of-- For example, I think an important point would be the chemical measurement after cycling tests.

KIPP: What I'm getting at is could you-- If you could establish a definite relationship by that measured electrochemically and that measured by chemical analysis, you wouldn't have to do the second, or the first.

FONT: Yes, or maybe. You have to point out here that these two total measurements are pretty close and then the order of accuracy, but we have to consider this measurement also, and the possibility of extra pre-charge such as the nickel attack of the positive electrode by oxygen evolved and oxydation of the separator with life.

So you cannot only consider-- For instance, you cannot only consider electrochemical pre-charge measurement. You have to perform the chemical analysis.

RAMPEL: Guy Rampel, General Electric.

I would like to ask Joe Lackner this question:

You mentioned that you have a screening overcharge at minus 5 for 120 hours. At what rate is that, Joe?

LACKNER: C over 10.

RAMPEL: Thank you.

eb14

FORD: Ford, NASA/Goddard.

To what do you attribute the inability or the lack of being able to measure that pre-charge in an electrochemical or in your reverse mode?

FONT: Really, I don't know. For the moment we don't know enough to attribute something. Perhaps-- I don't know.

FORD: I'm sure there are other people here who have experienced the same results. I'd like to throw the question to the floor.

BETZ: This is Betz at Fairchild, and I'll sit for this one.

I'm going to make some general comments. We at Fairchild are buying cells right now and are experiencing a very similar type of data. Our test technique for pre-charge, as I indicated previously, is slightly different so that the electrochemical measurements of pre-charge we'd be getting would be less than yours by the difference between perhaps one volt and zero volts. The one-ohm technique of getting down there takes out I think a reasonably large amount.

We had used initially two ampere hour oxygen pre-charge and got zero measurable electrochemical pre-charge. In addition to that, the cell capacity at zero degrees C. was less than specification.

Increasing the pre-charge to four ampere hours of oxygen, we again were marginal on measurements. This is fairly -- not directly after the pre-charge operation but downstream a little bit; a fairly marginal, approximately zero measurable pre-charge. However, the capacity was quite satisfactory,up in the order of 125 percent of nominal at room temperature, 25 C. and 110, 115 percent, on that order, at zero degrees C.

Overcharge at zero degrees C., extremely uniform voltages at C. over 20, something on the order of 400 percent of capacity input; the first 120 percent or 200 percent goes in at about C over 10 at 25 and then the temperature is lowered to zero and continued at C over 20.

So we found uniform voltage characteristics on over-charge, and we do have the over-charge test, and capacity improved with the increase in pre-charge.

Then we had some mavericks which, although we did some tests on them and I believe that the oxygen pre-charge is on the order of 6 ampere hours, and those cells had the highest capacity, again compared to the others.

But the interesting thing was that the highest capacity cells had the least variability in capacity. Maybe we don't have a large enough sample yet but it appears to be that there is a variability of capacity factor, also, involved. You may get some negative limiting influence so you're not really measuring your positive in every individual cell due to the variability of pre-charge perhaps or the individual nature.

It takes a lot of effort to look into these type things.

I might make one other comment:

Going back a while when I was a manufacturer, not on the user end of the stick, or working in the manufacturing area, we were able to use a technique to measure pre-charge after a starved reversal to one volt and that is by oxygen addition, pressurizing the cell with oxygen and observing recombination.

Unfortunately, it took something on the order of 20 days or more before it began to indicate we were not having any significant oxygen recombined, but it might be simpler than a chemical analysis.

FONT: Simpler, but perhaps less accuracy.

DUNLOP: Jim Dunlop, from Comsat.

Dr. Font didn't include some data here that we had fed in in response to something he said.

In the program he actually tried three different ways to do this before he set the pre-charge and one of them was to put a resistor across the cell. One of them was to run it down at a C over 10 rate like you described. And one of them was just to quit at one volt.

Now the reason I make all this-- I'm just saying the reason we didn't present the data is that in essence, it does make a difference-- Like you point out, where you put a one ohm resistor on something and take it all down, it does take out some capacity, so if you do this, it would change your pre-charge measurement that you would measure electrochemically.

The point is here that it didn't really significantly change any of the-- In other words, what we do anyway is completely discharge the cell on down to minus .5 a volt before we do the analysis and in discharging the plates on down to minus .5 volt and then doing the analysis -- and that's a very important point -- in that case, there wasn't any difference.

The number you mentioned, which was three or four ampere hours or five ampere hours of charged cadmium remaining after that plate had been completely discharged electrochemically, was there whether we use method A, B, C, or D.

CARR: Earl Carr, Eagle Picher.

I would like to interject one more thing. I think we had the same or a similar experience and that is that with the one-ohm load placed on the cell prior to the reversal to determine pre-charge, we had tests which indicated no precharge and yet we were somewhat confident that there was precharge there.

The test on a limited number of cells was run without putting the one-ohm load and in this case continuing

eb18

the discharge in the starved state at a C over 2 rate-- You mentioned you used C over 10 -- on to zero volts and then on to minus one volt, and we got the pre-charge that we had intended to put in the cell.

So what we have done -- and this is on the SMS program with Philco-Ford -- is we have concurred that we will do the pre-charge measurement under these conditions; in other words, starved, going at C over 2, all the way through zero and to minus one volt.

FONT: In your measurement to minus one volt, do you take into account the positive capacity in the negative plate?

CARR: I don't know the answer to that. No.

MAURER: Maurer, Bell Labs.

The negative plate, because of corrosion, has a substantial positive capacity, nickel capacity; by "substantial," several percent, maybe 10 percent, depending on what impregnation method is used. And if these negative plates are reversed during their formation at all, that material becomes reverse-charged or converted to nickel plus three.

Then if you make a cell from those plates and start to charge, the first thing you do is charge the nickel and you charge your positive electrode and you charge the nickel part of your negative electrode and so you build in an automatic reduced negative charge which you will observe on

eb19

the subsequent discharge as a negative limiting cell.

So what you need to do is on your last formation cycle, stop before you reverse the electrode at all.

CARR: When you say "referse the electrode," reverse it against what?

FONT: Against the counterelectrode.

MAURER: Against the counterelectrode.

CARR: Okay. Well, we don't do that under normal circumstances so that we don't think that we have reversed the negative.

MAURER: Well, if you are reversing your cell in the cell state now to look at pre-charge and then charge it back up again, you'll go through this problem all over again.

CARR: Right. But on the first time down, measuring pre-charge, you would not.

MAURER: No, unless you had done it in formation.

BETZ: Betz, Fairchild.

Just to comment, between Carr and Jim Dunlop, and that is that the difference in measuring techniques has a large tendency to affect the data so that when we all talk the same language I think the standardized test technique-- Really, we have one but if it is not the best then another one should be evolved so that when we come to talk, we can all talk the same language.

The other comment, that I didn't mention, is that

eb20

I'm sure that we had the same residual initial material from formation in our cells, and that this is something else.

CARR: Earl Carr, Eagle Picher.

I concur, Fred, very much. The thing that I was going to say but I forgot a minute ago and that was the reason we selected C over 2 was that in this particular application, which was synchronous orbit at a 60 percent depth of discharge, this is the rate. So we thought well, this is as close to being representative of whatever we're going to do while we're in orbit, and so therefore we're going to use these conditions, starved, C over 2.

We don't put one ohms on them in orbit.

MAURER: Maurer, Bell Labs.

Another effect I wanted to mention was that a positive electrode is diffusion limited. Once the voltage drops below about -- well, below about let's say two volts with respect to mercury oxide reference, it becomes diffusion limited and follows the diffusion limiting discharge; that's diffusion of the protons in the lattice.

And this is a very long time process and if you put a resistor across the cell, as you know, the voltage that you measure on the resistor indicates a substantial current still flowing that lasts for, well, the order of 10, 12 hours at values perhaps above 5/100th of a volt, and it continues down in a logarithmic fashion which looks like a series --

exponential expansion with slopes in the ratio of 1 to 9 to 27, and so on.

And the capacity available under these conditions is substantial, perhaps 10 percent of the theoretical capacity of the electrode, so that if you discharge electrochemically below one volt on the cell and then immediately reverse, there will be this amount of positive capacity still there, and that will be this charge material on the negative.

If you put a resistor across you need to leave the resistor on for a long enough time, perhaps 24 hours, to get all of this material back out.

RAMPEL: Guy Rampel, General Electric.

I think the important part of this thing here in measuring the negative capacity residual charge is to say that the whole thing really is relative and that it depends -- no matter when it's done, it depends on the amount of cadmium that is available, because there is a ratio down below, an equilibrium between active and inactive cadmium, and this equilibrium shifts from one direction to the other, depending upon plate design, previous dod temperature and so on.

So I think that the electrochemical measurement of negative pre-charge can be viewed as a measurement indicative of what is available then and there, but it should not be used as a quantative measurement to indicate anything except the part of the cadmium that happens to be available at that moment.

eb22

MAURER: There ought to be comments on that.

BETZ: Just a quickie.

In response to that, that's the way we look at it. In our specification we spec uncharged excess negative but in order to determine that you've got to get a measure of precharge somehow and the electrochemical technique is used to reverse the cell, then recharge, and then a measure -- then recharge flooded and a measure of the total negative. So you can get a measure of excess uncharged.

RAMPEL: Fred, going beyond the reversal and then adding electrolyte to do the flooding measurements, there are two problems there, too-- Well, there's another one down below. Let me get to that one first, and that is rate dependent.

If you go, for example, at C over 10, like SAFT, you run into a serious danger of shorts and parallel resistances which can throw that whole result off considerably and you can find more cadmium in the cell than you have theoretically in some cases.

I only point that out to indicate that there are problems there, too, and maybe C over 2 is a little bit better, but nevertheless it's still relative.

Now going the other way, when you want to find out how much positive electrodes you have, you flood the cell and then according to NASA you charge at C over 10 for forty hours. Okay, that's good but depending upon the activity of

eb23

the cadmium electrode you can charge the negative electrode perhaps, or you think it may be fully charged when you get to 152 but there is some error there, also.

As a matter of fact, we have found it absolutely necessary to take the cell apart for that part of the analysis.

Now the next thing I want to point out is now you are taking a sealed cell and you're flooding it and you're getting a positive capacity under flooded conditions. Now if you run ECT or that kind of data flooded, you know that generally .82 percent -- 82 percent of that can be counted upon for a sealed capacity, sealed positive capacity. So that ought to be taken into account also.

BETZ: I think your comments are well taken. The test is not necessarily an absolute measure of the things that are happening.

Incidentally, I found, oh, somewhere around 40 or 50 ampere hours at C over 2 in reversal, also, in a nine ampere hour cell.

BAER: Baer, Goddard.

I guess this could be directed at Guy.

You said you ran -- checked the electrode capacities; you ran it flooded. How about if you ran it starved in that condition also? If you ran the pre-charged starved and also the check the electrode capacity, if you ran that starved?

RAMPEL: Well, I think we're probably getting away

eb24

from the true capacity of positive electrode anyhow, but that is not at room temperature and as Dean Maurer pointed out this morning, the charging efficiency of the positive electrode, besides being related to charge rate, it's also temperature-related and you have to take these things into account, so there is no use kidding ourselves.

I think we had better just get the absolute amount of positive capacity that you can get and take that into regard. I think if we do it sealed we're going to get a lower value which is fine, but we'll be kidding ourselves.

SCOTT: Scott, from TRW.

I think underlying some of this discussion is the presence of an electrochemical procedure for measuring pre-charge and so forth as it now is in print in the NASA interim hi-rel spec. From what I hear, I think there is cause to possibly reconsider that procedure and possibly even set it aside until -- pending further work, until we know more about exactly what we're measuring.

The other point I have is that also what I hear is the possibility that the only incontestable measure that we have right now that we know of of pre-charged cadmium is the chemical analysis and if that is so, I am wondering whether -- what the relationship is between a chemical determination of excess negative and electrochemical performance or expectation in the cell.

I don't know what that is. I wonder if anybody could comment on that?

DUNLOP: It may be my procedure that is in that spec; I'm not really sure whether it is or not.

VOICE: No, it's mine.

(Laughter.)

DUNLOP: Are you talking about chemical analysis, Dr. Scott?

SCOTT: No, I thought you were referring to the electrochemical --

DUNLOP: We were talking about chemical analysis here a minute ago.

SCOTT: And I thought you were just referring to the electrochemical procedure in the NASA spec.

DUNLOP: Unfortunately I don't know what's in the NASA spec right now. The last NASA spec I looked at didn't have-- I don't remember that it really mentioned a measurement procedure for pre-charge, frankly.

I'm not really at all clear what you're talking about.

SCOTT: I'm talking about the original interim spec issued in '69 or '68.

DUNLOP: The procedure for discharging down to minus half a volt; is that what you're talking about?

SCOTT: Yes. That's the one that I think people are still trying to use because it is there and it had a certain degree of legitimacy because it's there, --

DUNLOP: Okay.

SCOTT: -- regardless of whether it is any good or not.

Okay?

DUNLOP: Okay.

SCOTT: That's the one I was referring to.

DUNLOP: Okay. I just wanted to clear that up. Thanks.

FORD: Ford, NASA/Goddard.

Then we still have a basic question: Why can't you measure pre-charge electrochemically? What is it in the cell that prohibits you from doing this?

I have had it suggested that this is influenced by the mechanical pressure exerted within a cell.

MAURER: Maurer, Bell Labs.

I'd like to suggest a method that we've used and that is to reverse the cell and measure the gas coming off, confirm that it's hydrogen, and measure its rate. And then when the cell voltage goes over the knee, indicating that it would appear that the negative has completely discharged, then you compare the electrical current or capacity back through with the amount of hydrogen that you've collected. If they agree, I think you can be reasonably sure that that was the pre-charge.

However, if they don't agree, then you're in trouble.

(Laughter.)

HALPERT: Halpert, of Goddard.

In response to Floyd's question, we've got to learn how to measure it, I think we've got to learn how to put it in before we can learn how to measure it, put it in reliably and uniformly every time.

BELOVE: Belove, Marathon.

The question there, Gerry, would be how do you know what you're putting in, if you can't measure it.

(Laughter.)

But I have another point here. Do you have to have the absolute measurement of pre-charge? I believe that any method you use is only going to be an approximation. The electrochemical tells you how much cadmium you have, but again we have this question of percentage of inactive cadmium and a certain amount of it in the form of cadmium hydroxide.

In every way you measure it you will have certain factors, as Guy pointed out, the rate of discharge, the temperature. All of these factors can come into the absolute value that you determine, and what I say is that this is not necessary.

What is necessary is to obtain a relative -- an accurate measurement of the relative amount of pre-charge and to see what effect this has upon cell performance.

SCOTT: Scott, TRW.

I wonder if this afternoon we cannot come to one tentative conclusion, or whether we cannot, that electrochemical measurement is not likely to give us a reproduceable measure of pre-charge. And then we can go on from there.

I've heard several comments to the effect that variations on maybe one certain way are able to measure pre-charge reliably. I'm not sure whether that's the message or not. But I wonder if somebody would want to comment on that?

DUNLOP: Let me comment. I'm sitting here kind of like a cat on a hot tin roof because I'd like to go up and make a presentation --

(Laughter.)

-- which is very relevant to all this discussion, frankly, because we've been making these measurements for two years and we'd like to show what we have, and I think they might lend some light on this whole discussion as to what -- how repeatable these type of measurements can be.

And frankly, to tell you the truth, we've been measuring GE cells and the measurements we get show that the results are very consistent. As a matter of fact it shows their process is in very good control. As a matter of fact it shows that this method of running it in reversal gives you very repeatable results after about the first 30 or 40 cycles.

MAURER: Let's get on with the data and save some of the philosophy until later then.

Jim will give a dissertation on some of his measurements.

zxzxzx

DUNLOP: Dr. Font just got done describing to you about an hour ago --

(Laughter.)

-- his method for adjusting the pre-charge at three different levels, measuring it and what the effects were initially and after some 30 cycles on the pre-charge in terms of the pressure level and ampere hour capacity.

I might say that the reason that we entered into this contract starting about a year ago, I guess, was that we wanted to evaluate exactly what Dr. Font has done, what SAFT has done, and we're very pleased with the results. And I think finally-- You know, the problem for a long time was that nobody would really discuss this very openly because it was in some kind of a proprietary category or something, and now it seems that everybody wants to discuss it in depth.

We planned to take those cells from SAFT with the different pre-charge levels and operate them in synchronous application and try and determine what the effects of the different levels are over long-term periods of time. What they have done is show what the effects are over a short period of time.

We have as a background for this program a considerable amount of experimental data from our Intelsat-4 effort. We started a program in 1969 to simulate the Intelsat-4 mission. with the only variable being this storage mode. We picked three different storage modes at that time.

The storage modes we used were trickle charged continuously during storage; open circuit charged with reconditioning every 30 days; and open circuit discharged.

Now we decided in the course of that program that we'd pull a cell out from each of these storage modes every six months, every eclipse season, and analyze that cell and we had to pick a couple of years ago the procedure that we would use to analyze it.

At that time, the procedure we used was the procedure that was recommended by Dr. Flasher, being used at Battelle for analyzing the negative. The only thing that we added to that procedure, frankly, was our approach to doing i in what we consider a little more consistent manner. And I don't necessarily want to go into the fine points.

We have documented that procedure and described it, I thought in some detail, last year. Gerd Van Ohmring and I made our presentation last year along with Dr. Parry who described the positive analysis that he was using at that time.

What I'd like to do today is show some of the results from that program. And when I show these results, I want to say that I believe, based on these results, that we are getting ourselves in the position of being able to make some measurements which do make sense and can be used to evaluate or estimate what the lifetime expectancy of those cells is going to be in a synchronous application and that under the type of operating conditions we are pretty sure we expect to see in a synchronous application.

It may or may not be germane or relevant to the 30-60 minute cycle.

With that in mind, I am going to start with my first graph here.

(Slide.179.)

The data that I'm presenting here is data on the pre-charge cadmium variation with time determined for cells that were trickle charged during the storage mode.

The zero reference point here is actually a measurement made when the cells have gone through a normal acceptance testing program either at Hughes Aircraft or at Comsat so they have already been through at least 30-60 cycles. At that point in time we found that all the cells that we've looked at -- and I'm only showing three on this graph, but we must have looked at approximately 10 or 20 with this method. In all the cells that we've looked at so far, the total pre-charge determined by both chemical and electrochemical analysis, has

eb32

been 12 ampere hours plus or minus one ampere hour.

Now I think that indicates that their process is in pretty good control when they set the pre-charge.

The amount of pre-charge determined electrochemically is also fairly uniform at this point in time. It has been about six ampere hours plus or minus one ampere hour determined electrochemically. That's the electrochemically measured pre-charge at a C over 2 rate, no one-ohm resistor or anything else.

And we use the C over 2 rate, just like everybody else does, because that's the way we're running them in orbit. We're using about a C over 2 rate, so we discharge it down right through on reversal. We puncture the cell and we also measure the gas so that the amount of gas that escapes has to correlate with the number of ampere hours that we measure.

After we completely discharge that cell to half a volt we cut it open with that famous Goddard cutter and put it in a nickel soxlet and extract the electrolyte, and then we take the plates out, dry them, and perform the famous muskrat analysis to determine how much charged cadmium is remaining.

The charged cadmium remaining has been something between 5 and 7 ampere hours at this point in time so that the total, adding together the amount of charged cadmium remaining and the amount of charged cadmium measured electrochemically comes out to be this 12 plus or minus one ampere hours.

Now the interesting thing about this data is that we continued doing this analysis after one eclipse season, two eclipse seasons, three eclipse seasons and up to four. That represents cells on test since two and a half years now, and what we are observing is that after one eclipse season, the amount of electrochemical measured pre-charge increased from the initial value of about six up to about eight. In the second season it was still about eight. In the third season it was still about eight; actually it was dropping off a little bit, but this kind of variation, seven and a half to eight.

So that the amount of pre-charge that we are measuring up to two years now electrochemically is fairly consistent for the cells that we're looking at.

And if we take the amount of pre-charging that we measured electrochemically -- Each time we also determine the amount of pre-charge from a chemical analysis and we continue to come up with-- Actually it looks like this pre-charge is increasing slightly with time.

Now we actually expect that to happen because of the level of carbonate buildup that we're observing in that cell, and this line that I put on right here is a line which just relates the level of carbonate buildup that we're observing with time to what we would expect that to do in terms of changing the pre-charge level.

C 4

eb34

These particular cells are made with the pellon separators.

(Slide 180.)

This data shows the carbonate buildup observed with time. At the same zero point in time or after the cells have been through the 30 cycles of burn-in, we measure about five grams of carbonate in that electrolyte and we measure five grams of carbonate -- it's really about five and a half, and it's very close-- All the cells that we've analyzed have something very close to around five or five and a half grams of carbonate initially.

As a matter of fact, the SAFT cells have a carbonate level in their cells, too, and percentage-wise it is almost the same. I really don't know why they have this problem but I think this has been discussed earlier and I think it is coming from the plates.

We notice that as we run these cells and do this analysis again six months later -- The X's here represent cells that are trickle charged -- you will notice that the carbonate level is increasing; you're up to about-- After one eclipse season, about six and a half, seven. You're up here about seven and a half, eight, or seven and a half grams of carbonate with time.

Now there's some spread on this data, obviously, but you do see that there is the increase in the carbonate level for these cells and that if you go to a different storage mo. , if you go to a storage mode where you're not continuously charging, where you only have an oxygen environment or your oxygen environment in your cells is much lower, or as Dean Maurer pointed out, there is maybe not a chemical-reducing effect but an electrochemical reducing effect-- I didn't hear that paper but I heard about it yesterday.

Either way, you would expect that the cells that were trickle charged continuously would have a higher rate of carbonate buildup with time.

Based on these results we sort of estimate that if you are storing cells with a pellon separator in a trickle charge mode, you are going to have a buildup of between 1.4 and 2 grams of K_2CO_3 per year in these cells. If you relate that-- You really need to relate that to the total amount of electrolyte in your cell.

I believe that the initial carbonate level on a percent weight basis is about 25 percent of the KOH and so you can get an idea. At this point in time we're up to about 30, 35 percent by weight carbonate of your KOH.

(Slide 181.)

Again, in this test program we were running we were-- As we analyzed these cells after we got done taking the cells apart, we did take some of the plates and run them in a flooded bath to determine what their utilization was.

You will notice the utilization is running-- It starts out as high as 80 percent when we first receive them; it drops down to about 75 percent after the burn-in; after the first eclipse season it's to 71, 72, 73 percent, 71, 72, 73, 69 percent.

So most of the change in utilization appears to be occurring in the first six months to a year and thereafter, these cells appear to have, at least in the flooded electrolyte, a very consistent utilization of the cadmium material and it's about 70 percent.

Now that number is not too different from the number that Dr. Maurer presented this morning. I think he was showing about 74, 75 percent utilization for the Bell Labs plates.

By the way, I want to make one more comment here.

This utilization that we get here is pretty good and I do think that Dean Maurer has possibly the right idea. To get this kind of utilization I do think that you do need to exercise and overcharge that cell somewhat. And the reason I say that is that of the three storage modes that we have -- and I'm not going to present all of the data today -- but the one mode that we threw out already was the mode in which we stored the cells passively during the entire eclipse season. And those cells, by the third eclipse season, started to generate overvoltage potential and indicating no overcharge protection, indicating that you couldn't utilize that cadmium for overcharg

eb37

protection when you were storing those plates or those cells passively.

But the other two storage modes, the one in which you exercised it every 30 days and the one in which you continuously trickle charged, we have almost identical voltages at the end of charge, identical voltage performance from discharge, and they seem to have very similar characteristics, and I think we have very similar utilization of the cadmium, too.

So it does require some amount of overcharge and some amount of periodically exercising those plates to maintain that utilization.

(Slide 182.)

Finally, in a bar graph fashion somewhat similar to the bar graph again that Dr. Maurer presented this morning, we have looked at the cadmium electrode after burn-in, one eclipse season, two eclipse seasons, and three eclipse seasons and three storage periods, to determine how the cadmium material appeared to be distributed.

The bottom portion here represents unusable precharge determined from the chemical analysis. The second block here represents the usable pre-charge determined electrochemically by discharging the cell in the reversal and C over 2 rate to minus half a volt.

The third block here represents the positive cell

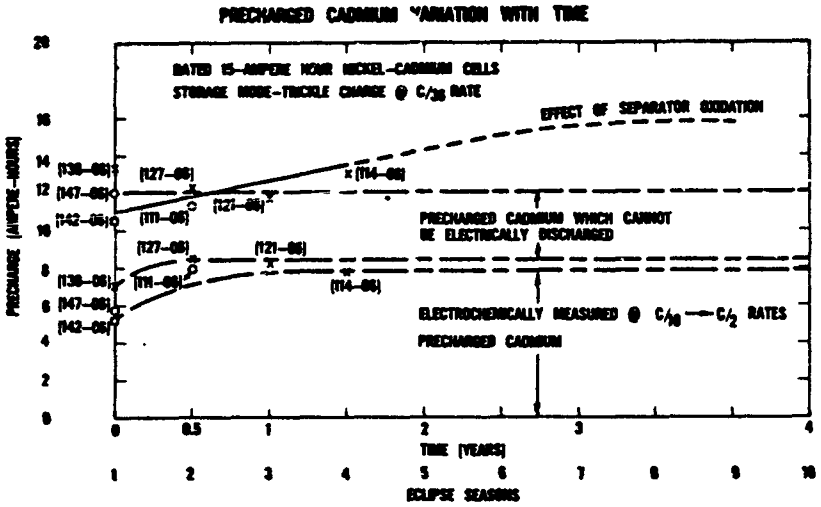


Figure 179

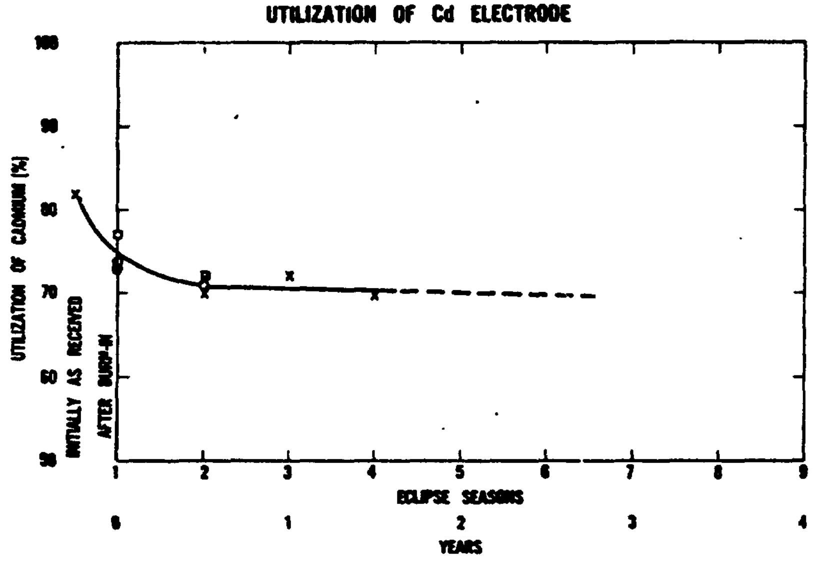


Figure 181

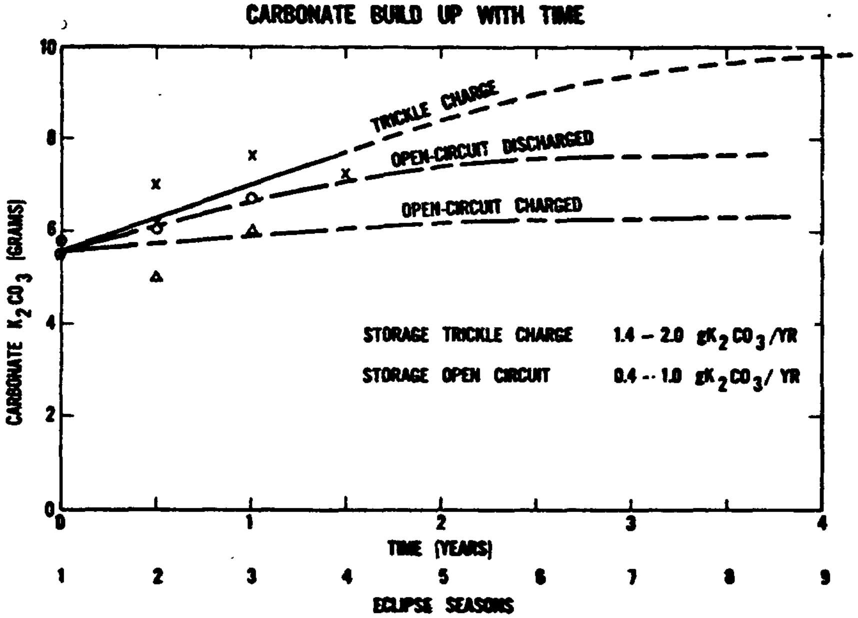


Figure 180

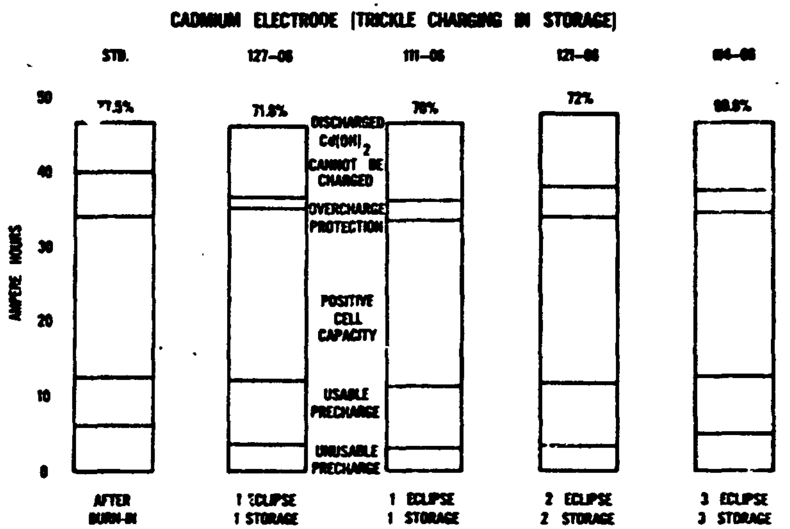


Figure 182

capacity where the portion of the cadmium hydroxide is being used in cycling.

The fourth block here represents overcharge protection.

And the fifth block here would appear to be discharged cadmium which can no longer be charged.

The total pre-charge as we define it appears to remain fairly consistent or be on a slight upgrade here. The amount of non-usable pre-charge seems to be staying relatively constant. The amount of usable pre-charge, again relatively constant; only slight changes.

What primarily concerns us for a seven-year mission is the amount of cadmium which appears to be there for overcharge protection. We are beginning to make predictions based on the kind of results that we are observing as to how long cells will last. We're making these predictions, based on the kind of measurements that we can take at this point in time and using data of this type to extrapolate out.

What we're predicting is that after one year, the utilization of the cadmium electrode will be about 70 percent; that you will have at least 65 percent utilization of the amount of pre-charge material that you used. After one year, there will not be a significant change in the pre-charge.

So whether you measure it-- If you look at the electrochemical measurement, it really is immaterial to me

eb39

whether you make the chemical measurement at that point in time. All I'm saying is that after one or two years of time, there isn't going to be any change here.

The amount of overcharge protection is going to remain about the same after one or two years with one exception. As you have any method in that cell which is going to allow either oxidation of the separator as has already been described, such that there is going to be the shifting in the pre-charge level, or any method which is going to cause positive method to increase due to attack of the nickel, as Dr. Font described, or any other slight change in the amount of cadmium hydroxide which becomes non-usable, as Dr. Maurer described, all these procedures tend to cut into the overcharge protection.

None of them really affect anything down here but all of them affect the amount of overcharge protection.

We estimate that after you get by one or two years that you need about one to two percent per year cadmium overcharge protection so from that kind of an argument you can hypothesize how much overcharge protection you need to get to four-year life, five-year life, and six-year life.

On top of that one or two percent you've got to have some variation due to the amount of cadmium that you have in there or the amount of pre-charge that you put in there and as I have pointed out, in these particular cells that

eb40

variation is relatively small.

In summary, I'd just simply like to say that we would like to see in a specification some type of procedure standardized to be used to evaluate cells for synchronous application and I believe that we, based on the kind of information that we presented here, we are getting closer to being able to make that kind of a prediction based on the kind of test program that we're proposing to run.

In essence, what I'm saying is that I think there can be a test written that will answer the question of how good is a cell and how good a chance does it have in meeting a five-year life, based simply on the type of measurements that you can make when you receive the cell and run it through a 30-cycle burn-in test.

STEINHAUER: Steinhauer, Hughes.

Jim, I'd like to comment on the discharge/storage mode in that I think you can't use it without some low rate reconditioning. The question I would like to ask is:

I think I've been listening carefully but Dean Maurer made a statement this morning that inactive cadmium is predominantly if not all in the charged cadmium mode. You have exhibited a very large portion of inactive material in the cadmium hydroxide upstairs.

Do we have a controversy here or did I hear wrong?

DUNLOP: We have a controversy to some degree. I think you saw what Dr. Font presented. Now let me review that for a moment.

When we went through the formation cycle, the results we got in that program I think are very similar to the kind of results we got from any other formation cycle. In other words, we get about a 1.7 to one ratio of negative to positive materials.

That 1.7 to one ratio of negative to positive means that there is not enough completely electrochemically utilizing that negative plate at that time because you're putting into that negative plate about a two to one ratio.

When SAFT does the analysis they show a two to one ratio. They show that in that 72 ampere hour plate, for example, that Dr. Font described, there were three or four ampere hours of charged cadmium that couldn't be discharged in the analysis and there were six to eight ampere hours of discharged cadmium.

Just using those numbers, that means that there's something like five, six, or eight ampere hours of discharged cadmium initially in the formation cycle which cannot be utilized.

Dr. Maurer this morning made a statement that if you converted some of this cadmium in a charged state to discharged cadmium, then it may become nonusable. A portion of it or all of it will become nonusable.

eb42

STEINHAUER: Was that a firm statement or an uncertainty?

MAURER: That's an uncertainty.

FORD: Ford, NASA/Goddard.

Jim, in your-- You indicated your overcharge capability had diminished because you cadmium you could not charge. Have you tried to find out why it can't be charged, what form it's in.

DUNLOP: Well, the analysis says it's discharged cadmium that can't be charged. You know, it's cadmium hydroxide that can't be charged.

FORD: Why? What ties it up?

DUNLOP: Of course there are a lot of arguments here. We don't know the right answer. There were some pictures that Halpert showed this morning, very interesting. He showed, for example, some kind of a glob -- excuse that word -- of cadmium hydroxide and cadmium in which he showed that-- He pointed to the darker and lighter areas and he showed that the outside of this ball was cadmium hydroxide and the inside was cadmium.

Now, if that were the case you would not be able to discharge that cadmium inside there. That would explain discharged cadmium that could not be charged.-- I said it the wrong way.

SCOTT: Scott, TRW.

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At the risk of being repetitious, I don't think that I caught your experimental method of distinguishing inactive from active discharged cadmium. Analytically, how do you do that?

DUNLOP: Do you want to know the discharged cadmium? How I did it on-- Okay.

SCOTT: You have a bar chart showing-- At the top you have two forms of discharged excess cadmium or discharged cadmium. How do you experimentally determine those two blocks?

DUNLOP: Okay. For all the data that is presented here we started our analysis by fully charging or charging at a C over 10 rate for 16 hours the cell, then discharging it down, running it in reversal, and then opening it up.

We then took the cell apart and measured the flooded capacity of the negative plates and we assumed -- and this is, by the way, if anything I think probably an optimistic assumption, that that represents the amount of cadmium that can be -- The flooded plate electrochemical measurements indicate the amount of cadmium that can be used in the cell.

If that's the case then you simply go from here to here. That's the difference from here to here.

Now if the actual dry -- in the starved condition -- utilization of the cadmium is less than that, this level is going to move down. What we intend to do next time-- We've had this question raised before, so what we intend to do next

eb44

time around is sacrifice the measurement of the pre-charge by charging the cell up and then venting oxygen and measuring the quantity of oxygen that we vent until we get to an overvoltage condition, and do it on that basis to confirm the measurement that we are currently making.

GROSS: Sid Gross, Boeing.

Jim, you said you had three methods of charge, three methods of storage, two on open circuit and the one that was open circuit discharged didn't charge up very well whereas the one that was open circuit charged and reconditioned periodically worked out all right. I presume that's correct?

DUNLOP: No. What I said was that the one that was stored discharged developed high voltage characteristics during the eclipse cycle, went to overvoltage, went over a 1.5 volts, went up to 1.5 volts at 75 degrees F.

GROSS: And the one that was open circuit charged and periodically reconditioned, how did that work out?

DUNLOP: Fine.

GROSS: Okay.

Do you attribute this to the discharge part of the conditioning process or to the overcharge that probably followed it?

DUNLOP: I attribute it to the fact that we were storing the cell almost completely discharged. In other words, this would all be cadmium hydroxide and when we tried to utilize the cell after normal reconditioning by the normal procedure that we proposed to use -- that's by a couple of cycles of reconditioning before the eclipse,but during the eclipse season by the 30 or 40 cycle -- over 50 percent of these cells were beginning to go to -- had pulled out from what the other cells with the other storage modes overvoltage potential was had pulled out to the hydrogen evolution potential.

GROSS: Well, I understood you to say open circuit charged for that second mode. Was it open circuit charged or open circuit discharged?

DUNLOP: We had an open circuit charged which we reconditioned every 30 days. That mode is behaving okay.

We had open circuit discharged with no reconditioning, or what I mean by that, no conditioning during the storage period. We didn't condition it every 30 days; we reconditioned it before going into the eclipse.

RAMPEL: Guy Rampel, General Electric.

On the storage mode that gave you overvoltage, I think you said that in that particular case the cadmium hydroxide that was there was not available.

DUNLOP: It would appear so because we generated high voltages.

RAMPEL: Okay. So likewise on the upper bar chart there where you indicate discharged cadmium hydroxide which

eb46

cannot be charged.

And now, going back to the discharge mode of storage, apparently as we are all aware, the cell can be reconditioned and that cadmium hydroxide be made available again, so what I wanted to suggest --

DUNLOP: Guy, you're talking about a different mode of storage. If you're talking about shorting a cell with a wire, that's a different mode than leaving the cell discharged open circuited. That's a rather fine point but it is a little different.

RAMPEL: Okay. What I'd like to suggest though nevertheless is that there is an equilibrium of available cadmium down below between the active and inactive and perhaps at the top there is likewise an equilibrium situation. Particularly the charts we're looking at right now determined statically flooded and in the sealed cell, there may be a ratio. The availability may shift.

SCOTT: Scott, TRW.

Jim, you're talking about this discharge storage mode and the results you got when you started cycling that in a normal eclipse season. Did you-- Have you taken apart cells stored in that mode and then measured the actual amount of discharged negative material or characterized it in any other way to corroborate your theory that it's inactive discharge material.

eb47

DUNLOP: We have done that and there are a couple of things we've found out.

First of all, I have only shown here the data that we have from the trickle charge mode. In the modes where we store passive we-- Actually you lose utilization of the pre-charge cadmium, in other words the charged cadmium that can't be discharged, as well as the discharged cadmium that can't be charged. I didn't bring any graphs along to show this point but by the third eclipse season we find, using this same method of reversing and electrochemically trying to measure pre-charge that we are only able to measure one or two ampere hours rather than the eight ampere hours that I'm showing here. That's the first point I want to make, Dr. Scott.

So we're showing that during these passive storage modes we are not able to utilize the cadmium -- pre-charge cadmium. That's the first point.

The second point is that we're not able to utilize as much of the discharged cadmium. One of the problems that we didn't do and that-- See, the correct way to measure this if you really run into a problem is going to a venting technique. Then once you already are at the hydrogen evolution potential, there is no longer any point in going to a venting technique; you're already at the point that you started venting to get to.

SCHULMAN: Schulman, Gulton.

Jim, did you ever attempt to measure the pre-charge by one-ohming them rather than by discharging a minus .5 at C over 2 rate?

DALTON: No.

FORD: Ford, NASA/Goddard.

Jim, I can't let you pass one point that you-- Perhaps it was a subtle point but I don't think it is quite so subtle. In the difference in storage modes where your discharged open circuit are truly stored in a shorted condition, as was presented last year by Steve Gaston, some experience on the OAO program comparing cells that had been stored for a period of one year in a shorted condition, we saw no significant change in the overcharge voltage at room temperature or at zero degrees C.

We have seen similar tests recently as was mentioned yesterday, but we also have some data from the ITOS battery, two of them, in fact, that was used as backup batteries -- These were GE four ampere hour cells that were manufactured -- I'm recalling from memory now, but I think it was early or some time in 1968. These cells were fabricated, built into batteries, the cells went through the acceptance test, the batteries went through acceptance test, and then they were put in a storage mode.

The storage mode called for the cells to be discharged and shorted but it was an oversight and the cells were

eb49

left open circuit.

This summer we were asked to evaluate those batteries as far as flight worthiness to be used again in a backup spacecraft. The only change we observed on those cells from the initial capacity that we had was the change in the overcharge voltage at low temperature. Those cells could not be overcharged at zero degrees C.F. and incidentally we had manufacturer's data that we were repeating a test that the manufacturer had conducted at the cell level when he made the cells.

Those cells could not take an overcharge as low as C over 40. In fact, it is safe to say those cells couldn't be overcharged at zero degrees C. at C over 100 without exceeding a voltage of 155 volts per cell.

So I'd like to point out that I think the storage mode gets critical even when you talk about discharged open circuit or a shorted mode.

DUNLOP: Well, Floyd, maybe I missed the point. The discharged cells were the ones that gave us the problem.

FORD: Yes, that's the same experience we had, discharged but not resisted down and shorted out.

DUNLOP: I didn't mean to pass that over as the right point.

I wanted to add one thing to Dr. Scott's comment.

Let me add one thing more, Dr. Scott, to this comment about the amount of cadmium that can be used.

In the cells that we have stored in the passive modes, both of those groups, we were not using our normal method of discharging the cell down. We were only able to measure one or two ampere hours electrochemically of cadmium in a pre-charged state.

We followed exactly the same analytical procedure and measured 10 to 11 ampere hours of cadmium remaining in a charged state from the chemical analysis so that the total measurable pre-charge adding the electrochemical measured value to the chemically measured value gave the same total that we would expect to get.

FORD: Ford, NASA/Goddard.

One other point I'd like to make-- And let's go back to the basic question. Why are we trying to measure pre-charge? Is it in fact to establish the overcharge capability of the cell? That was the original intent, back when we first got interested in this.

So perhaps the technique is to let's just try to come up with a technique to measure the overcharge margin that we have in the cell and forget about measuring pre-charge.

DUNLOP: Well, Ford, look, maybe that's fine but when I buy a cell from a battery manufacturer -- and this is what I think is germane to the point -- I'm going to specify a certain positive to negative ratio. I'm going to go ahead

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and I'm going to specify a certain amount of that ratio of excess cadmium that I'd like to have for overcharge protection.

Based on what Dean Maurer said, I am also going to specify at least 10 percent of that cadmium electrode in a pre-charge state because I don't want hydrogen to be evolved initially when I start charging and actually we've seen this kind of problem can happen. You do need a small amount of pre-charge in there, something like about 10 percent, and that's exactly--

I didn't make any comment here but I think if I were going to make a cell today and specify today with a positive to negative ratio of 1.7 to one measured electrochemically and two to one chemically, I would request that the battery manufacturer put 10 percent of his cadmium in an uncharged state so that he has the capability to achieve the seven-year mission.

And I have to do something in order to be able to determine this, to make this measurement.

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There are a number of points being brought up here, and I would like to spend a moment to expound on the issue of hydrogen-free capacity on cadmium electrodes.

The charging process on the cadmium electrode consists of cadmium hydroxide going into solution to cadmium hydroxide ions which are then electrochemically reduced to cadmium on the electrode. This is a soluble intermediate step, it's a chemical step and it has nothing to do with the electrochemistry.

So that the voltage, or the polarization on the negative electrode is controlled not by this stuff but by the concentration of this in the electrolyte.

So that if you have a lot of very small cadmium hydroxide crystals the quantity of cadmium hydroxide in solution is high and the polarization for this reaction is low, and proceeds nicely.

When you have big crystals, or when the electrode is mostly charged, and you have a few large chunks remaining, the rate at which this reaction can go now will be the rate limiting one, so that the concentration of this in the electrolyte will fall and consequently the polarization for this reaction will go up.

Now as it goes up it reaches the point where the reactions going on at the electrode compete strongly with the water going to hydrogen reaction, whose polarization is normally lower than this one. --is higher than this one. But when this concentration drops, this polarization comes up. And then this one takes over.

So that the concept of cadmium hydroxide which is electrochemically inactive is perhaps a little bit misleading. What we really mean is that it's functionally inactive; that if you put the electrode in a flooded state and charged it for a long time, I think you could get it all charged: there would be no cadmium hydroxide remaining on the electrode at all.

But the point is that most of it would have been charged -- or some of it would have been charged with the evolution of hydrogen; which we don't want in the sealed cell.

So that when we've been talking about inactive cadmium hydroxide, what we mean is cadmium hydroxide existing in such a state, such as in large crystals; and these could result from high temperature storage or high temperature overcharge, or a whole variety of ways; these crystals now provide too little cadmium in solution to sustain this reaction without hydrogen evolution.

So that's what we mean.

This is why it's rather indefinable, or why measurements of it are many times misleading. Because just what you call "inactive" depends on just what conditions you

wb3

have and what conditions you're trying to measure.

If you try to measure it on very rapid charge characteristics, you'll find you have a lot of inactives; if you do it very slowly you'll have less. And so on. So I think we have to bear that in mind.

The reaction is: CdOH taken twice, going to CdOH taken three times, with a minus sign. And then this is followed by electrochemical step in which Cd-zero is formed.

STEINHAUER: Steinhauer, Hughes.

A two-part question. First, Dean, the cells you described this morning for Bell Telephone service, are these shallow depth use or deep?

MAURER: Well, they're designed for deep, 100 percent discharge.

STEINHAUER: I was just wondering, then, on this amount of pre-charge necessary for long life, how much that percentage might be. Andthen I wanted to ask Jim if he would put that 10 percent in an inactive form or in an active form?

MAURER: I'm not sure that I understand what the first part of your question is. But we would put about 10 percent pre-charge in an active form. We would start with the electrode as it's formed in the cell, and remove enough oxygen to give us an additional 10 percent, roughly.

wb4

GASTON: Gaston, Grumman.

I have a question to Jim. I believe one of his first comments was in the pre-charge adjustment that the procedures were controlled and repeatable.

What is the pre-charge adjustment procedure? I don't believe you commented on that.

DUNLOP: I don't want to answer for G.E., and I really don't know, so I really shouldn't say. But I do know that they do a certain amount of oxygen venting; and I don't know how much, and I don't know anything else about it. But I do believe it's an oxygen venting technique that they use.

And the only point I made was not how it was done but the fact that our measurements show that the amount of precharge that they're putting in there is repeatable from cell-to-cell and from lot-to-lot.

GASTON: My comment to that is, I believe we would like to look for procedures which we can specify, which are repeatable. I'm just wondering if that procedure can be made know, or is that a proprietary proprietary.

DUNLOP: There's another point here. I want to make very clear this particular point. For the particular cells that we receive in this program we were able to measure a very consistent total pre-charge, and after cycling a fairly consistent electrochemically measured precharge using the procedure of a C/2 discharge into reverse, which is a destruct test.

If we got another size cell, or another lot of cells from G.E. today I do not believe we would get the same ratio of electrochemical to chemical pre-charge, because I made some measurements on some other cells, and they don't give you the same ratio. And the same thing applies to SAFT, by the way.

One of the major points that we have been making to date is that if you want to know how much pre-charge you're getting in your cells, you're going to have to use some method of determining it by both electrochemically and then by some form of chemical analysis to determine what 's remaining.

RAMPEL: Rampel, General Electric.

Jim, you mentioned before that possibly what you may do on some cells later on in orbit to determine the amount of chargeable cadmium hydroxide at the top is to continue the pre-charging sort of technique, and so on. I only want to point out, that's a good idea. But keep in mind that at that stage of the game the separator has become much drier, the recombination rate has increased, and it may be quite difficult tc perform that perhaps without adding a lot of electrolyte, or something of that kind.

And in some cells, even adding electrolyte and

wb6

maintaining the close spacing that you have in the cell, it still may be somewhat impossible to fully charge up the cadmium hydroxide.

zx

DUNLOP: What utilization do you expect from a G.E. plate after two years of operation?

RAMPEL: What plate?

DUNLOP: Let's take the program that we're talking about here. The plates that we have appear to have a 70 percent utilization after about one or two years of operation. It seems to remain fairly constant after that.

Is that about the number that you would expect these Intersat-4 plates to give?

RAMPEL: Now you're talking about the cadmium plate. Yes, I would expect that utilization to continue.

MAURER: I think we have a little more data here to show. Joe O'Rourke has some things he wants to show before it gets too late.

I would like to make one other comment, however, and that is that in doing these various manipulations of reversing and so on, we're upsetting the balance of the potassium hydroxide concentration. So we have to worry about that, too. We lose water and we change the reactivity of OH and water.

zxzx

O'ROURKE: It's getting kind of late, and possibly the data that I have to present might confuse things. But

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I'll present it anyway.

Up until now most of the discussion centered on getting reliable, or consistent pre-charge measurements after some type of a burn-in period is first performed. The data that I have found shows that you get quite a variation in pre-charge depending upon when the actual pre-charge adjustment is done relative to the time from when these cells were filled with electrolyte.

This data was obtained on the OAO serial number 34,35 battery build. These two batteries are the ones that are in the OAO satellite right outside the room there.

Essentially what we did -- we did this at Gulton -- we measured the oxygen that was being vented during the cell build. This is with Gulton's standard pre-charge step. And we collected the gas generated, which was nearly entirely oxygen, into 1-liter graduated cylinders which were filled with water. And initially we had the tubes set in the bottom of the graduated cylinder such that the oxygen will bubble up through. And we ran into some difficulty.

Apparently some pressure had been formed at the top of the rubber tubing. And this created enough of an obstruction to prevent ready flow of gas out of the cell. And we're not too sure about some of the gas measurements we obtained that way.

After we changed the procedure and put the rubber tubing up near the top surface of the graduated cylinder while it was inverted, in such a way that there was a small air pocket there, so that when the gas came out it simply forced the level of the water down, we obtained a lot more reliable gas measurements.

(Slide 183.)

Okay. Some of these points may be hard to see. They're relatively close to the axes.

The x's represent the gas generated for the Gulton third electrode cell; they call it the anhydrode. And the o's represent the amount of gas that was evolved for their standard cell. And the 'x' axis is the hours of stand time from the time that the cell was filled with electrolyte until the time that the pre-charge adjustment was made.

And, as you can see, these points here -- I believe the one closest to here was one hour stand time before the pre-charge adjustment was made. And these here were six hours soaking time before the pre-charge adjustment.

You can see that the gas that was evolved, the oxygen evolved, was very high and very transitory during this period, and that after about approximately ten hours or so of soaking time we got a very uniform amount of oxygen evolution.

Possibly what was occurring was, if the negative

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electrode wasn't sufficient wetted, most of the gas, instead of recombining with the negative, just vented right out of the cell.

(Slide 184.)

What I did here was, I plotted the actual pre-charge negative capacity which we measured for the battery build prior to the one I just showed you. And we're seeing the same type of trend. Those cells which had the pre-charge adjustment relatively shortly after the cells were filled had higher pre-charges than those which were adjusted roughly a day after they were filled.

(Slide 185.)

This just shows a plot of the gas generated, the oxygen obtained versus the actual measured pre-charge for the 34,35 battery build. And the dotted line is the theoretical 220 milliliters of gas oxygen per ampere hour of discharged negative capacity. As you can see, there's quite a bit of variation about the line but yet there is a strong correlation with the points also.

Some of the actual TN-1 measurements we made, as you can see the cells did gas. --referring to the points on the bottom, the cells did gas. And yet, as was mentioned earlier, we didn't have any electrochemical measurement obtained. This was obtained relatively shortly after the pre-charge adjustment.

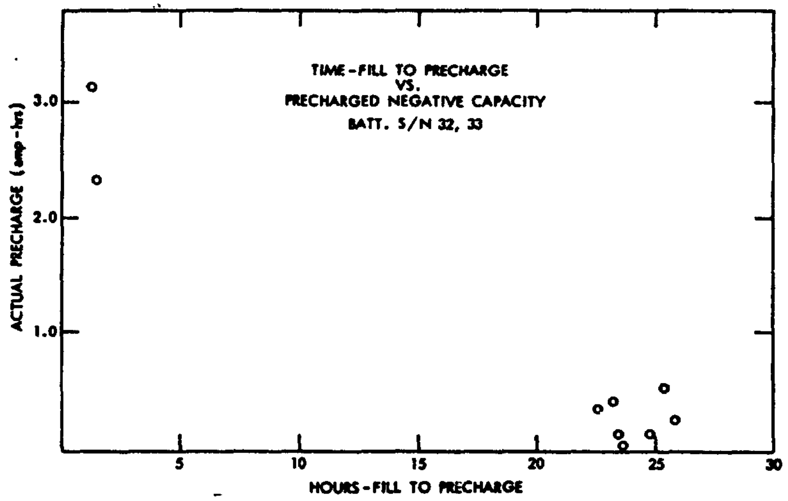

Figure 184

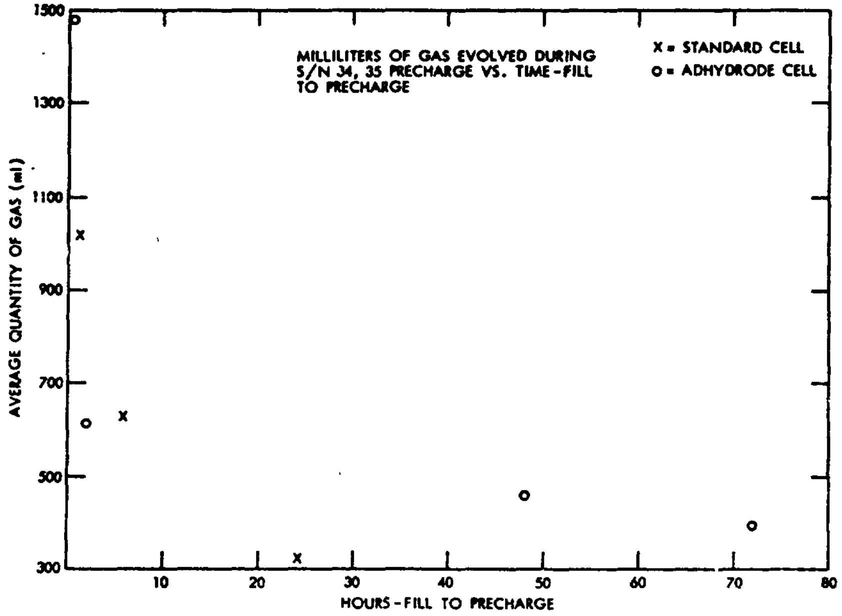

Figure 183

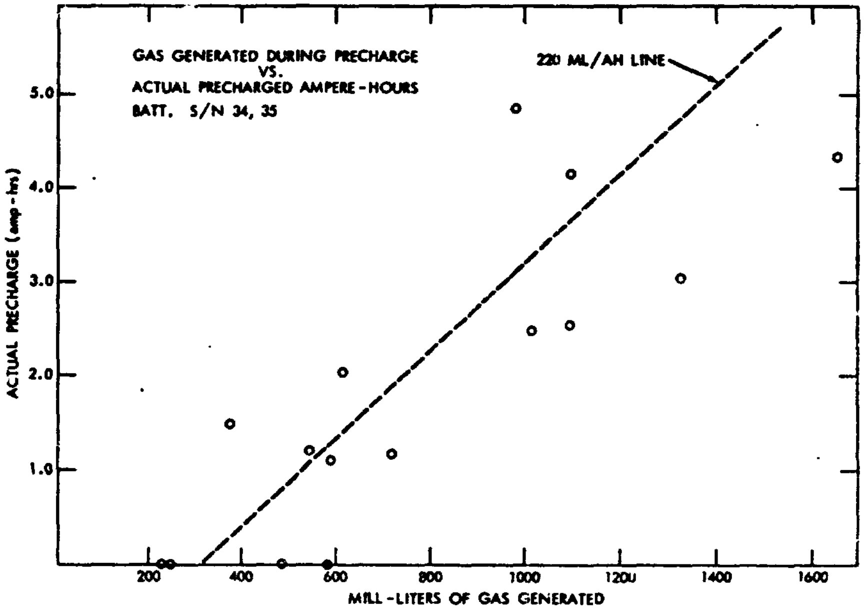

Figure 185

wb10

Essentially I'm saying it wasn't much of a burn-in.

That's all I have.

MAURER: Any comments?

BETZ: A number of things-- In my previous employ I lived through a number of these problems along with you guys. I might mention a few things.

On cells very similar to the -- or pre-charged in a manner similar to OAO, that particular lot of OAO, normalizing the pre-charge we found a sigma of about six minutes and a mean of about thirty minutes. Unfortunately that -- they were all charged relatively soon after pre-charge, or after activation.

Also I might mention that the reason there was a 24-hour lag was because there wasn't enough equipment to handle all the cells so that you could measure the oxygen.

Secondly, at the time of this OAO build there was a different technique available for providing pre-charge. In fact I might mention it was 20-ampere-hour cells, and they're in Mariner Mars 71 out there right now. The pre-charge had an average of about 18 minutes, which would be about three ampere hours on a 20-ampere-hour cell. The standard deviation was about three minutes, as I recall, which would be comparable to Dunlop's plus or minus an ampere hour on a 15. There were relatively large samples

wb11

here of three to five cells per 40 for a couple of hundred cells in both cases.

What I wanted to say, though: the technique for measuring pre-charge will produce fairly reproducible results with reasonably large sample sizes.

Also, it's much better if you have some measurable pre-charge there electrically. For instance, as I indicated recently, ATS has now achieved the ultimate: we have zero pre-charge and zero standard deviation; measurable, as you found.

I think the interesting point on your curve also is that there is a threshold. And in Dr. Font's data it was the same thing. That you must permit a certain amount of oxygen to escape from the initial state before you're going to measure anything. And it looks to be, in the 20-ampere-hour size cells here that he had, something maybe in the order of 4 to 6 ampere hours. I think that agrees with my recollection of what the oxygen offset was, from utilizing a baseline, actually a reversible baseline.

But depending on the technique of pre-charge certainly there are more uniform ways available today that everybody knows about, for setting pre-charge, than what you're using on OAO. And they were available a few years ago. And I think Grumman chose not to use them.

KRAUSE: Krause, JPL. There has been a lot of

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concern expressed over pre-charge this afternoon. And perhaps I would like something clarified, that being where does this concern really lie? Can anyone make any general comments about failures that have occurred in application of batteries due to pre-charge problems specifically? Can anyone pinpoint that?

Secondly, can anyone answer if there is a type of cycling regime -- temperature, cycle life, lifetime in general -- where pre-charge is or is not a critical item? And are pre-charge techniques that are presently being used sufficient for a great number of applications, and are we getting worried over something for nothing; or is there really a problem?

FORD: Ford, NASA Goddard. I would like to answer that one.

Stan, as you, and 'most everybody here, are aware, one of the problems that led us down this path that we're currently pursuing today was back in 1968. It was involving a spacecraft battery for the OAO program.

We had been running cell tests, and we did observe through cell test at Goddard out of a flight lot, that after-- I remember particularly it was approximately 1300 cycles in a near earth orbit at about 15 percent depth, we begin to see a cell voltage divergence on charge. This naturally did not concern us. But then as we watched it progress it got worse with time, or with use.

To make a long story short, we resolved then that the situation that we were observing was one due to cells becoming negative limited with cycling. And I think this is attributed to -- if you look at some of the data that has been presented here and elsewhere, that when you build a cell and you look at it in the early life of it, you got good utilization in the negative, or better utilization than you do get six months downstream.

As you cycle the cell, the utilization in the negative falls off, and perhaps reaches some steady state value. Although I have seen data from a NASA program where certain lots of negative plates do not necessarily stabilize with cycling.

Now let's take the two cases.

If you assume that the negative plate capacity stabilizes with cycling, then all you have to worry about is having sufficient overcharge capability on Day-1 to allow that degradation in the negative electrode.

But then you take the second situation, which I don't have an answer to, that the negative electrode does degrade and continues to degrade; it does not show stability after a burn-in period. And I'm not sure anyone knows what a satisfactory burn-in period is.

We did not fail cells in the test because we had pressure gauges, we took cell samples, and we were able to identify the problem.

We carried it one step further. We got involved and built another battery. But we know today we didn't resolve the problem in building that battery either, because we got those cells in-house from that lot, and we tested them approximately a year. This data is documented in the next document that I have left on the table, and part of it was reported in the 1970 Power Sources Conference.

We did observe, after about 4000 cycles on those flight cells for the A-2 spacecraft -- the one we've been talking about during this two-day meeting -- that one of those cells began to diverge in voltage. --divergence meaning increase. And after a period of time, approximately 1000 cycles if I remember correctly, this cell began to show a gradual pressure increase with cycling. No change in test conditions, just a gradual build-up in the charge pressure. And on a cycle-by-cycle basis this is not obvious, but on a day-by-day, and particularly a week-by-week basis, you begin to see this pressure build-up.

Now on that cell, by using a technique of -- we discharged the pack down, we reversed that cell; it was a C/10 rate; and removed some pre-charge, and then put the pack back on cycling. And we did indeed bring the overcharge voltage, or bring that cell back into line with the other

wb15

packs.

Something I haven't mentioned that is pertinent to this, because I mentioned that was a group of cells out of a flight lot. Well, we have observed characteristics on that flight battery today, or earlier this summer, that lead us to believe that we have the same symptoms now in flight.

I hate to bring this up, because it can get quite involved, but, as most of you know, we have one cell in each battery that has a third electrode. And, incidentally, there is some correlation in the data -- looking back through the manufacturing data -- that third electrode cells going through the manufacturing process, have a certain tendency to come out with higher levels of pre-charge. And I think, without going into details, I could show you data to verify this.

So what we observed back during the early spring of this year, that under similar operating conditions the flight battery, the third electrode we started observing what we called an anomaly on one of the third electrodes in the flight batteries, of which there are three. We became quite concerned because we had had about two and a half years of operating time on this battery, and we saw something here that we had never really observed on ground testing -- or perhaps it's better to say we had never really looked at it in detail on ground testing.

What we observed is, in fact, as if the third electrode was losing sensitivity; even though we were charging, cycling, as we normally do, the third electrode on one battery just ceased to come up during charge. The other two performed as they had been in the past.

This went on, and we began to analyze the data. And in about another month we noticed another third electrode dropping out of the normal range of operation.

So as we looked further into this we set up a series of tests to try to find out from ground -- and this is pretty difficult to do because you have very limited data to look at. But we arranged a series of tests where we tried to analyze what the problem was.

Essentially we found out that if we reduced the overcharge on the battery by lowering the BVLS level control, which lowers the voltage point at which you're controlling the battery and, consequently, lowers the recharge, and stayed that way for two or three days, and then recycled back up to a high overcharge condition, the third electrodes all showed a very healthy response and all come back to near-normal condition.

We stayed there at a medium to high overcharge, in a range of 120 to 130 percent. And one of these -- possibly two of these third electrodes would then, over a period

wb17

of days, start decaying again and dropping out.

We did this on two different occasions. By that time we had done extensive investigation into the test data that we had. And we began to realize that one of the things that will kill the third electrode is the presence of hydrogen in a nickel-cadmium cell.

Now I can't explain all the ramifications of this, other than the fact to tell you that the test data we have shows that as you get high cell voltages and begin to generate hydrogen you can observe an apparent decrease in the sensitivity of the third electrode in the same relative oxygen environment.

We have seen further indications of this some time early in the program when some cells were reversed, and we noticed that on initial conditioning cycles, trying to rejuvenate the cells, that the third electrode stayed negative for quite a while, and it finally recovered over a period of two or three days. At that time we knew there was hydrogen pressure in the cell.

As a result of all this, we have imposed additional operating restrictions on the spacecraft. We're operating at a much reduced voltage level. We are not suffering any degradation in capacity because of this. We have reduced our recharge in the range somewhere below 110 percent; in fact, we have followed this with ground tests and demonstrated that we could maintain this battery with 105 percent recharge.

So I think the data that Joe O'Rourke presented yesterday adds additional information on this when he shows a chart that showed that what we call our shunt charge time had decreased by approximately about ten minutes.

Now the implications are simply this: We are convinced that in those flight batteries today we have considerable cell voltage divergence if we're allowed to overcharge. And when I say "overcharge" mean put in a respectable overcharge but not excessive. By maintaining a very marginal overcharge on the battery we have been able to keep the third electrodes back, and they are functioning what we consider properly.

But all we have to do today is to allow the battery to go to a relatively higher overcharge condition, and we will indeed see one or two of these third electrodes begin to drop out again. And it's pretty clear-cut now. This is a distinctive pattern that we have established.

GASTON: Gaston, Grumman. I would just like to go back to Mr. Betz' remark before, to bring it into proper perspective.

He somehow -- and I hope I don't misquote him: he said that there were various other pre-charge techniques available, and Grumman chose to stay with one. Well, for the record, until 1968 Grumman did not know what the pre-charge procedure is; it was proprietary; and the other pre-charge techniques became, I would say about the last year or year and a half. By that time the program was qualified. And we would much rather like to stay with the one which we had before, try to control that, before we go to other techniques.

MAURER: Jim?

DUNLOP: Jim Dunlop, from Comsat.

I would like to address that question about pre-charge and why we have pre-charge.

It's necessary in a battery apparently to adjust the positive with respect to the negative. And the methods that are currently being used are to adjust the stated charge of the positive with respect to the negative by pre-charge. But the reason that you do it is not really-- It's not really as important how much pre-charge you put into it as how much overcharge protection you have, I believe.

Unfortunately, we've been talking about "pre-charge" and I think what we're really discussing in terms of the synchronous application is how much overcharge protection we really have.

And the second point we're discussing is how to measure the amount of overcharge protection we have. And, unfortunately, as was mentioned earlier, it doesn't seem that there is -- it seems that there is some concern about the best way to measure it. And what we were proposing in this, or presenting in the work that we have, is a method just to measure both the overcharge protection or the amount of protection you have before you 're going to start getting into a problem with hydrogen evolution.

And to do that it seems necessary to measure pre-charge.

KRAUSE: Krause, JPL.

I agree with you, Jim, and that was the point I was really driving at, that we keep talking about pre-charge and it has become apparent today that measuring pre-charge does not help you really determine what your actual overcharge protection is.

DUNLOP: I don't agree with that.

KRAUSE: Well you aren't really correlating the two, because there seems to be some inactivated species at one end that have no correlation with what is going on at the other end. And I think you've got to talk about both and not just dwell on pre-charge here.

I agree with you , we've got to look at both ends of this thing and not just dwell on pre-charge.

It seemed like there was a great concern over that one word and that one concept, and I think they are two things.

wb21

FORD: Maybe we've been trying to grab the donkey by its tail and we should be trying to lead him by his head.

LACKNER: Lackner, Canada Defense Research.

I agree with some of the comments that Mr. Dunlop has been saying.

Now he's saying we should have an effective positive to negative ratio, if I read him right. Now we have stipulated this in our satellites as being an effective 1.7-to-1. We write "effective." So if there is any pre-charge it goes above that.

Now the way we get the effective is by matching plates. So we match the capacities of the plates, not by pre-charge.

So a very simple thing would be if you had a 1.7 amp hour negative against a 1 amp hour positive; which you can measure in an open vat before you even put the plates together. --instead of trying to play games using pre-charge.

DUNLOP: Just put them together; is that what you're saying?

LACKNER: Yes.

DUNLOP: You don't do anything to them; you just put them together and seal them up?

LACKNER: Yes.

RAMPEL: Rampel, General Electric.

Ten percent pre-charge has been mentioned, and if I remained silent it could be construed that I am in agreement with that level; so --

(Laughter)

And I take it to mean total pre-charge, when we're saying 10 percent. Okay.

Going back to Dr. Font of SAFT, with his various pre-charge levels, he summarized it and said, Well, the level of pre-charge is a compromise. I agree with that. It's necessary to have pre-charge, and I feel that we need far more than 10 percent. But by that I'm not suggesting that we go out the other end.

But I'm saying here that we need more than 10 percent in order to sustain problems coming from losing levels of voltage on discharge with time.

DUNLOP: Guy, I think I would agree with the fact that you do need some pre-charge. And the amount that you need seems to be one of the arguments.

There seem to be two arguments: the amount that you need, and how to measure it.

Now taking the amount that you need: in that program that Dr. Font described, interestingly enough the levels that were used there are 2 percent, 20 percent and 30 percent, approximately. You notice that the amount of pre-charge in the case of the lowest one was about 8, 7 or 8 ampere hours in a 72-ampere-hour cell. That's 10 percent. The second case was about 15, and the third case was about 20 ampere hours of pre-charge.

Now we don't really know-- We do know that the pressure doesn't seem to be a factor. We also know -- I think what your comment is -- that there is an effect, an apparent effect on the measured capacity initially, ampere hour capacity of the positive plate.

Is that the point that you were making?

RAMPEL: No, sir. The point I'm making is that the cell at the 10 percent level of total pre-charge will rapidly become negative limiting with life.

DUNLOP: Well, Guy, the only comment I can make is that your cells that I have been testing would not have become negative limited based on the results that we presented today.

FORD: Are we talking about 10 percent of Day-1 negative capacity, or 10 percent after burn-in?

DUNLOP: Floyd, as I show on this graph up here, and I'm going to repeat this many times, I guess, today, the ampere-hour capacity of those plates didn't change from Day-1 to Day-20 in terms of the total measured ampere-hour capacity of that negative plate. It was 46 ampere hours on Day-1 and it was 46 ampere hours three years later. The total measured ampere hour capacity of those plates had not changed over that entire three-year period.

We didn't even see it change due to this effect that you're talking about of the soluble cadmium. We were measuring plus or minus 1 ampere hour, 46 plus or minus 1 ampere hour.

FORD: Yes, Jim, I acknowledge that. But when we say "total",I'm concerned not with the total but with the electrochemical. And that's what I'm saying: should we base it on what the electrochemical capacity is after this burn-in period, and make it 10 percent of that? Then will we have sufficient pre-charge to prevent the problem that Guy has mentioned of fading?

DUNLOP: Okay, Floyd, I go back to the data that we presented today. In that cell we had a total measured electrochemical capacity, total determined. That's measured chemically and electrochemically. 46 ampere hours. We had 4 ampere hours or less of cadmium charged that could not be discharged. And we're operating that cell not completely discharged; we're operating that cell between the full charge condition and the 50 percent discharged condition. We're nowhere near the point at which we might become negative limited. And we had no indication from the data that we saw that that cell would have ever become negative limited if we would have put into that cell a large -- if we had put wb25.

into that cell-- There was no reason to put into that cell more than 4 or 5 ampere hours pre-charge, based on our results to date.

MAURER: I would like to make a comment.

There seems to be a tendency among one faction here to say, Should the pre-charge be 10 percent, 20 percent or zero? I think the pre-charge should be what you need for your particular application.

Some of us are exposing the cells to a whole lot of overcharge, and under those conditions the amount of pre-charge can be relatively smaller. But for somebody who wants to use the cell, where he cycles it to essentially no overcharge, or even cycles it down almost upside down, then the amount of pre-charge might need to be quite a bit higher.

So I think we have to bear that in mind and tailor these to the application we're talking about.

RAMPEL: I agree, Dean.

And, in addition to that, pre-charge levels required may also vary between vendors' different plate properties.

FORD: Dean, are you saying we've finally come to the realization that we've got to design a cell for each application?

MAURER: Essentially.

FORD: Agreed.

STEINHAUER: Steinhauer, Hughes.

Does it also mean we have to develop an analytical technique for each vendor?

(Laughter)

MAURER: Well, I will comment.

I think you need to make measurements on each vendor with one particular technique in which you have some faith and confidence personally, and then be consistent and apply a certain set of numbers to one vendor and another set of numbers to another vendor, depending on his particular properties.

RAMPEL: One more comment.

As far as the necessity for a given level of negative pre-charge, well, we did say application. But I want to emphasize that relative to temperature, high temperature, one needs a heck of a lot of negative precharge.

MAURER: Well I think we've nearly run out of questions now, so maybe we should break up and go off the record into corners and various other suitable places.

LACKNER: Lackner, Canada Defense Research.

I just have to get this title in. We talked about separators and we talked about polypropylene and wetting agents. Now in February 1970 there was a separator symposium in Columbus, Ohio, put on by the Columbus Section

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The Electrochemical Society, where separators were exhaustively covered for nickel-cadmium, silver-zinc fuel cells. And Dr. King presented a paper on "QC Procedures and Measurements, Polypropylene Separators for Sealed Nickel-Cadmium Batteries." This is available in the standard abstracts of the Columbus Section of the Electrochemical Society meeting.

It covers our point of view on the separator, that a wetting agent is necessary. It goes through a whole series of tests on how we test the separator. It goes through a table which shows that air permeability does lower the pressure within the cell. And short of giving a dissertation on the separator, I will just put it on the record.

MAURER: Very good.

I'll turn the meeting over to Gerry.

SCOTT: May I have the last word, please?

In my view, the question of a satisfactory method of testing is a much simpler one than how much you need or don't need. I would hope it was one that we would have resolved a little bit more, possibly, today.

But, in addition to that, I would like to say that in general if one has to burn in a cell for 'x' cycles before one can get any present method of measuring pre-charge to work, then that method is suspect and not very practical, in my view. Because today in the real world of purchasing cells it is generally not practical to include burn-in in acceptance testing in order to purchase cells from a supplier. And, therefore, what we need is a method which could be applied by a supplier without having to go through a burn-in procedure, in my opinion.

Now, whatever the user would like to do after he gets the cells is his own business. And he may be able to, indeed, make a better final determination after such a burn-in. But we still need a procedure that the supplier can use prior to that.

MAURER: Well I would say really that the procedure is all right, but the stated charge is really changing during that period of time.

SCOTT: The same question then comes back again: is it better -- can we anticipate that possibly a strictly chemical method is, in the long run, going to give us something that is not so dependent upon all these conditions that we could lean on as far as some indication of what the manufacturer is doing for the purpose of quality control, and leave electrochemical measurements until sometime later on? Is that a feasible approach?

MAURER: Do you want to comment?

DUNLOP: I would like to make this comment: that I think it may require both, with the present technique, unfortunately, Dr. Scott.

The reason I say that is this: In that presentation that Dr. Font from SAFT made, you will notice that the amount -- that it wasn't really complete because the electrochemical analysis wasn't complete at the end of the 30-cycle test. But initially the data seems to agree very well.

If you notice, if you added together what he measured electrochemically to what he measured chemically, the result agreed with what he expected to get.

Did I make myself clear there?

In other words, it was a consistent -- the results were consistent, but that if you tried to use either, just the chemical or the electrochemical, by itself, you would have seen a variation in the results. So you have to use both.

And, unfortunately, in our data to date -- and let me repeat this: I think I said this once before: in the chemical analysis it is necessary for us to first completely electrochemically discharge that plate before we can make a good chemical analysis.

Do you understand the last point? You have to electrochemically discharge that plate.

SCOTT: Why?

DUNLOP: Because if you leave charged cadmium in there that can readily oxidize. It seems difficult to make a chemical -- not to oxidize in the process of doing the chemical analysis.

SCOTT: You mean if you take the cell apart in an inert environment you're going to oxidize the cadmium?

DUNLOP: I will just say that if we on purpose charged the plate, or if you don't completely discharge it, you don't seem to get a consistent result. The only time you get a consistent result is when you completely discharge the plate electrochemically. Because the material remaining, you know, does not react either electrochemically or with oxygen at a very high rate.

There are other ways to discharge it, by the way, just by putting in oxygen.

I think there are some other people in the room that can answer that question. This has been observed not by just us but by Battelle, by SAFT, and by many people who have worked on this procedure. And it's actually documented that the best way to do it is the way I just got done describing.

SCOTT: If that is true, then I agree. However it would be worth while, I guess, being more sure that, for example, you could not perform a reliable chemical analysis after discharging the cells to plus 1 volt, rather than having to go through an electrochemical step.

FORD: I would like to make one last comment, Gerry, if I could. I've got to go on record with this, because I will have to say that with the exception of the data that Dunlop has presented I have seen no data, since we started looking at this, that tells me that the electrochemical method of looking at ampere-hour pre-charge is satisfactory. Consequently, the only alternative we have today is just to make sure the procedure used for precharging or putting that charged cadmium in the cell is satisfactory and acceptable to us. That I have to go on record for.

And the only one that I know that is acceptable to me today is the one of a controlled oxygen venting technique.

DUNLOP: True; but how do you know how much to put in?

FORD: I have as much confidence in knowing that I did that and measured, say, 'x' number ampere hours. Now you're going to ask me how do I know what 'x' number ampere hours should be. For that I'll have to rely on experience. That's the only type of thing I have confidence in today in running a flight hardware program.

I cannot rely on the test technique and the numbers that result from the way it is now specified in the interim model spec in subsequent Goddard specs.

DUNLOP: Okay, Floyd. I agree with everything you say. But I guess I want to make just one more comment.

We've presented data, SAFT has presented data, and Battelle has presented data on a procedure to measure the pre-charge. And, for some reason, you don't want to accept it.

Now all I'm saying is that all these procedures, all these groups that have used this particular procedure that we're describing today, have come up with a relatively consistent result. And that's the only point I'm making. Battelle, SAFT, and Comsat to date have used a procedure that we've documented, that you have access to, that says that you can measure it, and that the battery manufacturer can measure it. He can use the same procedure. They do use the same procedure. And they can measure it.

So it's not the fact that you-- You made a comment that I challenge, and the comment was that you haven't seen any data that shows you that you can measure the pre-charge. As a matter of fact, I think there has been a lot of data presented that says that you can measure the pre-charge; not just by me, but by Battelle and by SAFT today.

FORD: My comments still stand.

STEINHAUER: Jim, if you're measuring these things, pre-charge and overcharge protection, maybe you can measure them on a relative basis. My question is, Relative to what?

In other words, it seems like we have to establish

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correlations, either chemical or, you know, electrochemical to chemical, or whatever we choose to use as the standard.

But I'm kind of worried, after listening to all this, and seeing members of the Spec Committee in the room, as to how long the things we heard today are going to take to get into the spec.

HALPERT: Let's leave it at that. That's a good question.

I think our questions about whether we were going to have a good meeting here this year have certainly been answered. I think we have had a good meeting. I think we look forward to next year's meeting. And I think a lot of people say they're going to do a lot of testing. We have recorded in the notes all the things that they're going to do, and we're going to expect them to report on it next year.

We will have material, more specific data to talk about, and more specific tests, and we can identify more material.

I think we've gotten a lot out of this, and I'm very happy that you all attended. I want to thank all the people who have helped in chairing and in helping with the microphones, and so on.

I hope you all have a good trip. And we'll try and get the information to you within a month, as I said.

Thank you all for coming.

(Whereupon, at 5:35 p.m., the meeting was concluded.)