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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

BATTERY WORKSHOP

CASE FILE COPY

October 6 and 7, 1966

Room 62012-15

Federal Office Building 6

400 Independence Avenue, S. W.

Washington, D. C.

FOREWORD

During NASA's Battery Program Review of April 7, 1966, a number of topics relating to battery R&D were discussed that appeared to merit further deliberation. The most important of these themse constituted the basis for the neeting of October 6-7, a transcript of which is presented on the following pages. Thanks are due to Thomas Hennigan of GSFC for arranging the program.

In view of the fact that this was a work shop and was intended to provide information for subsequent action, no emphasis was intended to be placed on formalism of presentation, nicety of expressions, etc. The importance of this document resides in the thoughts expressed by the participants, regardless of the form used to express them. The value of this volume will decrease with time, perhaps exponentially. It was decided, therefore to make it available to interested parties as quickly as possible, without taking time for editorial changes or revisions. The reader is asked to consider the produce in this light, i.e., as a working paper rather than a literary contribution.

Ernst M. Cohn

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON 25, D.C.

IN REPLY REFER TO: RNW

On April 7, 1966, NASA held a battery program review for the prime purpose of acquainting designers of space power systems with available batteries, components, circuit designs, and test results, all in the area of secondary, alkaline batteries. The second purpose was to determine whether our R&D in this field is responsive to the needs of system designers.

As a result of discussion at this meeting and of later correspondence, it has become apparent that we should concern ourselves with accelerated battery testing. Other topics, now in the program but perhaps deserving more emphasis, are failure analysis and parts inspection. Lastly, the question of standardization was raised again, but no conclusions were reached.

Before proceeding with new work in any of these areas, we want to make sure that we have the best thinking and suggestions available. Accordingly, we are planning to have a

Secondary Battery Workshop

Dates: October 6-7, 1966
Times: 9 a.m. - 5 p.m. (6th) and 9 a.m. - 1 p.m. (7th)
Place: Federal Office Building 6, 400 Maryland Ave., S.W., Washington, D.C.
Room : Auditorium (62012-15)

A tentative agenda is appended. You will see that most of the available time is reserved for discussion rather than for formal presentations. The meeting is unclassified. A verbatim transcript will be distributed afterwards.

You or your representative are invited to attend and requested to present your views on these topics. You may show 35-mm, $3\frac{1}{4}$ x 4-inch, or transparent Vugraph material. If such illustrations are shown, we request that you let us have, at the time of the meeting, 8 x 10-inch glossy black-and-white prints, with your name and the figure number and title written on the back of each sheet. This will speed distribution of the proceedings.

Please inform Mrs. Betty Burton, Code RNW, 600 Independence Ave., Washington, D.C., phone (202) 962-0121, on or before September 23, 1966, if you or one of your associates plans to attend. To get as wide representation as possible at the workshop, it may be necessary to limit attendance from each organization. We are looking forward to an interesting and productive meeting.

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P R O C E E D I N G S

MR. COHN: I would like to welcome all of you and to thank you for coming here today to our pseudo-le chance commemorative meeting, the second NASA battery meeting of 1966.

Some of you were here in April when we also almost got thrown out of this room, as almost happened today again. But fortunately it happened neither time.

In April we presented some of the recent results on secondary batteries to you and asked you to let us know what problems were bothering you that we weren't doing anything about. As a result of that, we had several topics that were brought up at the last meeting. Tom Hennigan and I and others went over these and decided that we would pick the most important ones and make them the topic of our next meeting that is today's meeting, to get as many good ideas from you as possible.

This time we have a brain-picking session. We would like to get your ideas so that we can use them to do the kind of work that you think we should be doing, and to it as intelligently as possible.

We have a full program today. So we will have to keep things moving.

As you may remember, we asked you to bring in glossies photographs of all the slides that you are going to

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use and to put your name and the figure number on the back of the glossy. This is so that we can get the transcript together in a hurry and get it out to all of you.

I hope you have done so and you will let me have the glossies during the meeting.

Furthermore, I would like to ask all of you who haven't done so already, to sign one of the attendance sheets. I have about 10 or so sheets around here on which I would like you to print your name, affiliation, and address. The reason for that is that we intend to send out the proceedings to you, to the addresses you give us, as soon as they become available. It is to your advantage to print your name and address on these sheets. Also please be sure that I get all the sheets back during the course of the meeting. If you see anybody come in who hasn't signed them yet, and you have a chance to tell him to sign, please do so.

With this introduction I would like to ask Dr. Fleischer to chair the morning session and to keep it as much on time as possible, with the presentations kept to the pithy minimum and the questions phrased pithily, and the comments likewise.

Dr. Fleischer.

DR. FLEISCHER: There is a discussion period allowed after every third paper. If there are any questions and we have time, a brief question to clarify any point, we will

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probably be glad to entertain them.

We are going to start our session today at pH of zero. Dr. Willihnganz will speak on accelerated testings in lead acid battery experience.

STATEMENT OF DR. EUGENE WILLIHNGANZ
C&D BATTERY CORPORATION, SPEAKING ON
ACCELERATED TESTING, LEAD ACID
BATTERY EXPERIENCE

DR. WILLIHNGANZ: I would like to start off by saying that I was gotten here under false pretenses. I was told that a workshop was going to be a meeting of a small group of people sitting around a table to discuss life testing, that these would be people I already knew, this would be extremely informal, and there might even be a pitcher of something in the middle of the table we could fill our glasses with at times. That would give us a nice, relaxed, easy meeting and we could talk really informally. The meeting looks halfway between what I visualized and a full session of the United Nations with Ambassador Goldberg giving a speech.

The only trouble is that my speech is not formal. I got together a few notes and it is going to be very informal. If I make some mistakes in presentation, by all means interrupt. It is still informal.

This represents the tail end of roughly 30 years of talking life testing with various engineers on automobile

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batteries. If I don't quote some of the people correctly, it is all my fault. But we can't blame these other people, so I won't even give their names. This is a general discussion and I don't claim that this is my work. This is general information.

Before we go into it in too much detail, let's show what we are talking about.

Here is a grid. And a lead casting which supports the active material. If you have an automobile which has a battery guaranteed for 30 months, and the battery fails on the first day of the 31st month, it has corroded away to where it no longer carries current.

Item 1.

Next, this is a finished plate. The holes in this thing have been filled with active material. If you are driving a golf cart, this active material tends to soften and fall to the bottom of the jar. My friends tell me that in normal country club service one of these plates will last something just under two seasons. So the normal thing there is to use it for one season, throw the whole thing away -- The battery -- and buy a new one in the spring of the following year.

Item three is the separator. You have active material, lead peroxide and sponge lead in alternate plates. You put this in between to keep them insulated. The

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separator is a little bit more involved story. In some cases you eat holes through the separator. In some cases I believe this is particularly characteristic of parts of Canada where they have a rutted dirt road and the automobile you drive bounces all the time. That vibrates and makes holes in the separator.

So we have really several different problems here. If you are going to run an accelerated life test it might be rather difficult to have one test to bring out all three problems -- grid corrosion, disintegration of active material, or holes in the separator.

If you are going to set up a life test method, it might be a good idea to know why the battery is going to fail and make your accelerated tests cause the battery to fail by that same fashion.

My introduction to the battery business goes back quite a ways. We were having some trouble with negative accelerating material. When I was a boy every fall you drove your car into the garage, put it up on blocks to take the load off the tires and left it there until spring. Sometime later than that people found you could still drive your automobile in the wintertime, but it was a little hard to crank the engine.

Then sometime after that somebody found you could add things to that negative plate and improve its cranking

ability very remarkably. This was done using the first life test.

You took a battery and at this time, at the starting point you put it on discharge for one hour, at a constant rate, more or less. Then you put it on charge. Here is the zero current. You put it on discharge for 30 minutes then on charge at a much lower rate. Pardon me, I am wrong. You do this for one hour and that for five hours. That gives you a six hour cycle. You do that four times a day. And if you keep this going on and on and on, after 250 or 300, or maybe 450, your battery isn't good for much.

This test was used for evaluating the negative active material. Back around 1935 to '38 some pretty good negative materials were developed which worked nicely in a battery. Then some hardware merchant took the battery from under the car, under the floor where it belongs and set it up right next to the engine where it got good and hot.

Then we learned some surprising things. Some of these organic additions which gave us good behavior no longer worked. So we had to modify the test method and run the test hot in order to get a decent negative plate. This is our first lesson, which is when you have a life test method which works, and somebody using the battery changes the conditions of use just a little bit, you may be in for trouble, and you may have to modify your life test.

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The next lesson. After that was under control these positive plates were shedding. That is, active material was falling to the bottom of the jar in an automobile. This was the result of using a so-called third brush generator. The generator would charge the battery and the rate of charge was controlled by the position of a brush on the commutator. You moved that to make things work right. If you set it a little too low the battery wouldn't stay charged. If you set it a little too high, the battery would use too much water and would have a short life.

There was just one place to put it, and you had to change that from winter to summer even.

Then these hardware merchants I was talking about came around with the voltage regulator. This automatically took care of this problem. It gave the battery just what it needed and the batteries worked very nicely. The loved it. But they stopped shedding active material. Then the failure was grid corrosion. When you got into the grid corrosion problems that cycle life test, which was causing shedding, was no longer valid. With a better amount of disagreement among various people, we took the batteries and put them on a continuous charge test. Set it out on a table, put through 10 amperes and let it ride. Once every week or two run a capacity test to see how it is going. When the battery is no longer capable of cranking an engine it is worn out.

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This gave a beautiful test. We were all happy about it. It seemed to tie in with service, it gave the right kind of failure, that is batteries in the lab that failed looked just like the ones that failed in the field. And the people who are responsible for quality control -- some of them at least -- thought it was a pretty good test.

In this period there were some diehards who wanted that first test, the shedding test. One of the battery engineers did a nice trick. He took a whole factory and changed it over to make a battery which had a life of about a fourth of normal on that shedding test, set out a whole month's work out of one factory and watched return reports. It didn't make a bit of difference. His poor batteries on this test were just as good as the good batteries he was making.

So we had an invalid life test which was on the way out, and a new one which was perfect because it gave exactly the result we wanted.

Unfortunately, another snake in the grass. One of the battery companies found a new grid metal. It gave somewhere between two and three times the life of what everybody else was using. And there was great anguish among those of us who were told or asked why didn't we develop something like that. We complained there would be a tremendous change in field service.

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Then another skeptic in the battery industry went ahead and got himself a bunch of these batteries made with this fancy alloy and put them out in a field test along side the ordinary grids and after three years when all the reports were in his answer was simple and to the point: it doesn't make a bit of difference.

Lab life test says these new grids are much better than anything we have. The field test says it doesn't make any difference. Once again we have a life test which we like and everything else, but it didn't tell us the truth. This is the next important lesson. If you have a life test that looks good, keep a watch on what is happening in the field and make sure that field service is predicted by the lab tests or you are in trouble.

Those of us who are involved in this thing took a very careful look at what goes on, including one of the members of this audience. We came to the conclusion that in an automobile you were testing the battery of a voltage regulator. It was a constant potential charge in a hot location, and the lab was a constant current charge and a cold location.

The recommendation has been made that the proper thing to do is to change our lab tests and see what happens. That is where we stand on this thing. I don't know what the results are. I have been away from this long enough that I don't know what has been done, but I think it is an interesting

problem.

Now we have a third item. All the way through here I am talking about the accelerated life test which accelerates the thing you are looking for. There is an entirely different approach now which is possible. Instead of trying to run the plate under some rough conditions you can run them under more nearly normal conditions and then increase the accuracy of your method of test.

Suppose we have our grid corrosion problem and instead of corroding this grid until there is no metal left, we just corrode it for a short time and then pull the battery apart and measure the corrosion product. This isn't particularly difficult.

You take the finished positive plate, soak it in certain kinds of plastic, of which there are several, harden it up, cut it apart, then polish the edge and look at it with a microscope. And the corrosion product has an entirely different appearance from the active material so you can look at it, see it, and with a micrometer eyepiece on a microscope you can measure it. And you can spot a film a ten thousandths of an inch thick very nicely. And if you can spot a film a ten thousandths thick nicely and find one three thousandths, you have worn away quite a bit of the grid.

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We tried doing this on some great big telephone

batteries. The results were nice and interesting. We loved them. Until we took a look at the numbers. It said that our grid was corroding at a rate of about two ten thousands of an inch per year. Since we had a grid that was a quarter inch thick, the battery life should be close to 500 years. That is a ridiculous result. It says that the test method is no good.

There is something wrong. So we went ahead and looked at our test method.

We are in the middle of that kind of test now which I would like to explain very briefly, or diagram very briefly. You can make yourself a chart -- temperature and life. If you plot instead of life in years, make it on a logarithmic scale, a tenth of a year, one year, ten years, a hundred years, a thousand years, and on up if you want to, and across the bottom instead of plotting the temperature cold, make it one over temperature, one over the absolute temperature now.

Under those conditions the line does this sort of a thing. You get a nice straight line. You can measure some points here. If they fall on the straight line you can legitimately extrapolate it up to here and say at 77 degrees that battery should last so long.

VOICE: Shouldn't that go the other way?

DR. WILLIHNGANZ: At the lower temperature longer

life.

VOICE: You have one over it.

DR. WILLIHNGANZ: But we plot that this way (indicating).

(Laughter.)

What we actually do is calculate our scale and put us in our points and give them a normal label here of 77, 100, 115, 130, and so on.

MR. COHN: However, it seems to me you ought to plot the reciprocal of life, rather than life, on the logarithmic scale.

DR. WILLIHNGANZ: If you plt the reciprocal of life, it is still a straight line. Besides this is the way I have been plotting it and that is the way I have to think.

You see this is an informal talk. We want some conversations like this. Mistakes sometimes do get made.

This on telephone batteries appears to be working out quite well. Keep your fingers crossed.

VOICE: Have you tried to calculate to determine the significance of the slope of that line which is essentially an Arrhenius plot?

DR. WILLIHNGANZ: It is an Arrhenius plot. The slope, I would say this point is just a little bit in doubt. When the thing is done under conditions which appear to predict service life, the slope turns out to be 14 degrees, which cor-

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responds to heat of activation of something or other which I will let you figure out. If you do it at the wrong voltage, that is outside of the normal operating range, that slope does this (indicating). It says the batteries we now have in the field failed three years ago.

(Laughter.)

However, if you do it in the normal range, that is the kind of curve you get.

This is a reasonably good test. We are talking here about batteries which last 20 years. As far as this test goes, it says that we are going to last 25, 30, 35 or maybe even 40, depending on how we build them. Most of us don't live long enough to run very many tests of this kind on field experience, so we have to do this accelerated test.

What we are running into now is at this end of the curve, if this is up at 180, our slope has change a little bit. I see we are at the end of our life here. This is essentially what I had to say. I was going to go back over it and emphasize each of the things that go wrong on batteries in a different way.

I would like to add just one sentence, which is that there is nothing in this world that is quite as expensive as an accelerated life test method that doesn't work or gives the wrong answer.

DR. FLEISCHER: Thank you Dr. Willihnganz. I

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hesitate on being the one that has to stop him from talking. I think that he set the tone of the entire conference in telling you that life tests must have a direct relationship to service conditions.

Our next speaker is Dr. Royce Biddick, manager of the development section of Gould National Battery Company, head of the research and development department of Gould National Battery, who will talk on accelerated testing of lead acid and sealed nickel-cadmium cells.

STATEMENT OF ROYCE E. BIDDICK, MANAGER,
GOULD NATIONAL BATTERY COMPANY, INC.

MR. BIDDICK: Thank you Dr. Fleischer.

Gentlemen, I would like to talk this morning about two types of accelerated tests and expand the entire pH range.

The first test I would like to discuss is the one which Dr. Willihnganz was describing at the end of his talk, the one on the accelerated growth of the positive plate in stationary lead acid cells.

In this case we increase the degradation rate by means of an increase in temperature. The other test which I would like to describe very briefly involves an increase in the degradation rate of nickel-cadmium cells, by means of an increase in current during cycling.

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As Dr. Willihnganz has discussed, the usual mode

of failure in the stationary cells which are originally used for emergency power supplies in case of power outage, is by corrosion of the positive plate. When the lead grid of the positive plate corrodes, lead dioxide is formed. This occurs because the normal potential of the cell which is held on float, the normal potential of the positive grid is the PPO_2 potential and therefore the lead grid wants to become PPO_2.

As it does corrode, the lead which becomes PPO_2 increases in volume and therefore the outer skin of the grid tends to stretch the entire plate.

Therefore we find that as the cell is floated in service, the positive plates tend to buckle because of uneven growth, they tend to become longer and wider, and the elongation in length tends to break the cover seal and actually elevate the cover above the cell.

This happens of course over a period of five to 20 years, depending on the particular cell.

Bell Telephone Labs have been very interested in this phenomenon because it is vital to their business. They began a test in 1948. And this was described by Dr. Turner at the fall meeting of the ECS in Buffalo last year.

In 1948 they placed about 50 lead calcium stationary cells on test and they observed the growth of the positive plate over a period of nearly 20 years. They found that this

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growth is a minimum at a certain polarization which amounts to 75 millivolts above the equilibrium potential.

In an effort to develop an accelerated test they studied the rate of growth as a function of temperature and they found that the rate approximately doubles in ten degrees C. At a temperature of 180 degrees F. the growth rate is increased 60 fold and therefore they can conduct a 20 year test in 120 days.

They found further that the mode of failure is the same. The cell which is tested by the accelerated method looks after failure like cells which have been in the field for 15 or 20 years. The plates buckle, the covers lift, and the cases buckle where the bulging plates push on them.

Using the foundation which Bell Labs had built, we carried out some tests in our own labs. The apparatus is shown in the first slide.

We carried these tests out on nominally 50 amp hour stationary cells. These cells have two positive plates about six inches square and three negative plates.

(Slide.)

To accommodate the experimental paraphrenalia we had to put the normal limit in a slightly oversized case, about 50 percent oversize. This gave us somewhat larger quantity of sulfuric acid. This appears to have had no effect on the

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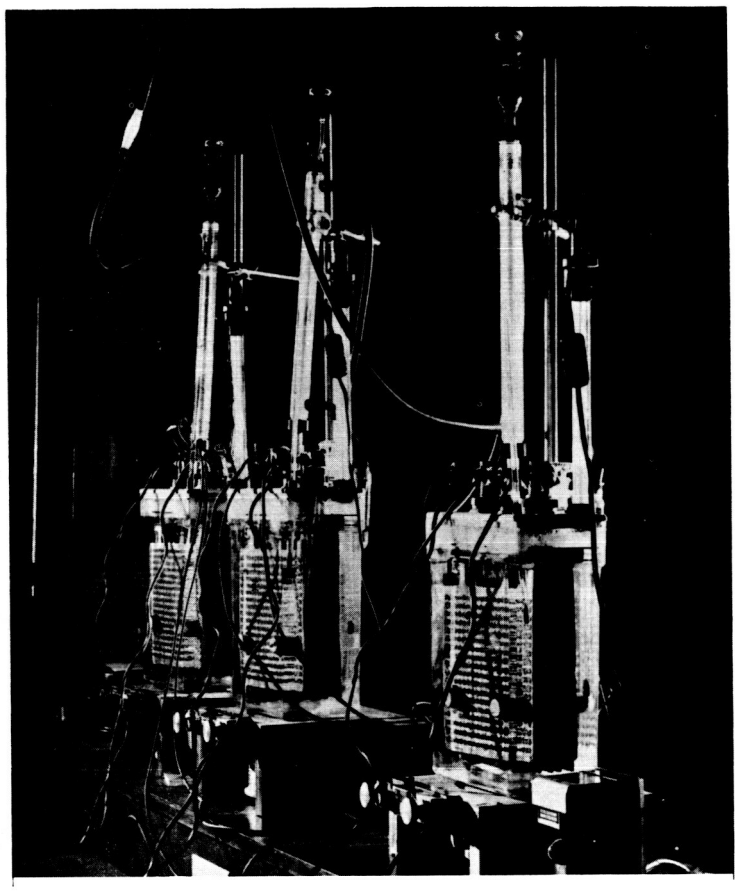

ACCELERATED CORROSION-GROWTH
TESTING OF LEAD-ACID POSITIVES
IN STATIONARY CELLS

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test. We obtained a temperature of 180 degrees by immersing a heating element directly into the electrolyte and with a thermostat we control the temperature within roughly a half degree.

We measured the potential of the positive plate by means of a mercury mercuric-sulphate reference electrode with an acid bridge into the electrolyte. And of course we need a condenser to prevent evaporation of the water from the electrolyte.

We use a magnetic stirrer in the bottom of the cell to minimize temperature gradients within the cell. It is a quite simple test apparatus and it seems to be quite effective.

(Slide.)

The next slide shows the results of three of these tests. These tests were conducted by maintaining slightly different polarizations on the positive plate. The polarization of 75 millivolts was found by Bell Labs to give the minimum growth rate. We chose polarization slightly above and below this for comparison to find the effect on growth rate.

Growth rate was measured directly by observation of the positive plates of each cell by means of a cathotometer. The current was found to increase during the test. Current was adjusted manually to obtain the polarization which we

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180°F. ACCELERATED TEST FOR CORROSION GROWTH OF LEAD-ACID POSITIVE PLATE (50 A.H. DC-5 CELLS)

Polar. of Positive Plate, V.	Float Current, A. 5*	100*	Growth in 30* Δ%	Life,** Days	Mode of Failure
.060	1.0	3.0	.020	114	Break-up of Pos.
.075	1.2	3.6	.014	147	Mossy Short
.090	2.0	5.2	.025	118	Break-up of Pos.

* Days

** To 75% Capacity

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desired.

During the first 30 days the growth amounted to about one and a half percent at the minimum growth rate, and about half again as much at the polarizations above and below this minimum growth rate.

During the second month the growth was about three times as fast. After the second month the growth became erratic and measurements of growth meant very little because the plate didn't growth uniformly.

Periodically after the first six weeks the cells were discharged, roughly once a week, by cooling to room temperature. Then after the discharge was run the cells were heated again.

The life of the cells, as tabulated here, is 75 percent of nominal capacity. That is, after 114 days the cell, the minimum polarization at 60 millivolts, had dropped to 75 percent of its nominal capacity. And the same was roughly true of the cell at the high polarization of 90 millivolts, where the cell at the minimum growth rate lasted not quite half again as long, but did last somewhat longer. The nature of the plates at 147 days was different from those other cells in that the plates had not buckled and grown as much.

You see the failure in this low growth rate cell was by different mode. That is, mossy short form. This was the

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result of our experimental technique in this short form, where we had scraped away some of the protective envelope of the positive plate in order to measure its rate of growth.

I think it would be quite likely that this cell would have lasted roughly half again as long if we had not had this mossy short.

In summary, as a result of this test, we find that 75 millivolts does indeed result in minimum growth rate and maximum life of the cell.

We also find that the initial rate of growth is indicative of the life of the cell which we can expect. Therefore we might have an accelerated cell test which would involve merely measuring the initial growth rate.

We can conclude that a 180 degree F. accelerated test provides a fast method of evaluating experimental grid alloys and experimental designs.

The other test which I will describe involves testing sealed nickel-cadmium cells.

To evaluate the effect of higher currents on cycling we constructed one batch of cells and divided into four lots in our laboratory. These were constructed under carefully controlled conditions, that is, our quality control was strict.

Two lots were cycled at a rate twice per day and two lots were cycled eight times a day. The currents were increased

by four, and time were reduced by a factor of four.

Periodically on these cells also, roughly every 50 cycles, a capacity discharging was run to a cutoff voltage of one volt. The average capacity of the entire lot of cells, each of the four lots, was calculated regardless of whether or not any of the cells in that group had failed by our fail-safe mechanism. That is whether puncture of the seal had occurred because of other pressure. Even though puncture of some cell had occurred, and this began at 250 cycles, the cells were left on test and their capacities were included in the average.

(Slide.)

The next slide gives the results of this test. We have curves here for two different rates of discharging. Two lots were starting at 0.24 amps and two at 2.4 amps. Of these two lots in each group, one was cycled at the fast rate and one at the slow rate. We see from this curve that the capacity of the cells depend on the cycle number rather than on time. Although there was a four fold difference in time there was very little difference in the capacity.

If you plot capacity versus time, there will be a great discrepancy in the results.

Furthermore, the capacity on fast cycling agreed within roughly 2 percent of the capacity on slow cycling.

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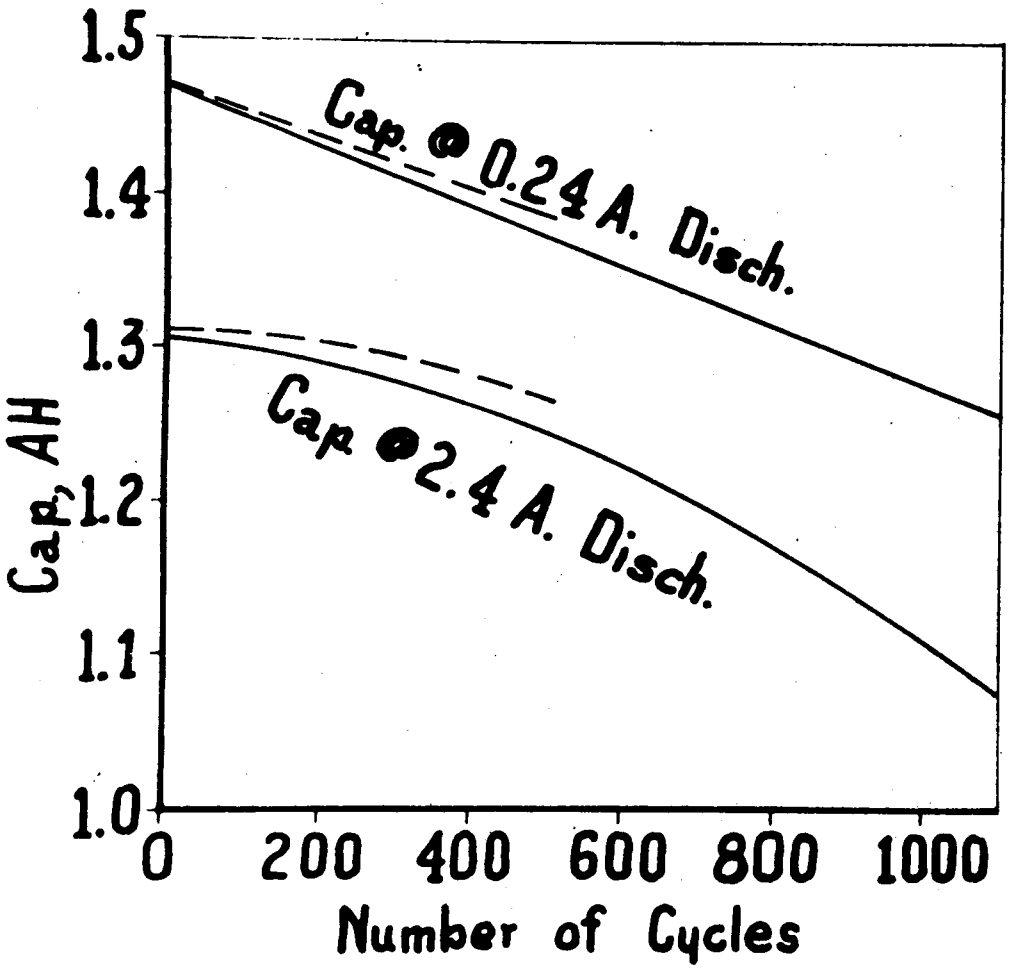
The gradual loss in capacity was the same in both

ACCELERATED TESTING, Ni-Cd SEALED CELLS



2 Cycles per day-----
Input 1.44 AH @ 0.16 A.
Output 1.20 AH @ 0.40 A.

8 Cycles per day———
Input 1.44 AH @ 0.64 A.
Output 1.20 AH @ 1.60 A.

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cases. This was due to degradation of the negative electrode.

Therefore, we can conclude from this test that cycling at 8 cycles per day does give a reliable indication of cycling life and that our development can be increased by a factor of four by using this method.

Thank you.

DR. FLEISCHER: We are right on schedule, so we will go on, unless there is a very quick question.

Dr. Willard Scott, of TRW Systems, will talk on accelerated testing of space batteries, nickel-cadmium and silver cadmium.

STATEMENT OF DR. WILLARD SCOTT, TRW SYSTEMS, SPEAKING ON ACCELERATED TESTING OF SPACE BATTERIES -- NICKEL CADMIUM AND SILVER CADMIUM

DR. SCOTT: The problem that we at TRW Systems are addressing ourselves to these days is one of increasing the reliability of sealed spacecraft cells plus extending life expectancy from something of the order of two years to the three to five year range.

We are concerned with reliabilities, usually far in excess of those that can be tolerated with batteries on the earth's surface. We are talking about shooting for reliabilities in the .99 plus range for three to five years.

In view of the fact that we really don't know at this

point how to design a meaningful accelerated life test to predict one year's life, you can understand that our whole approach here is highly experimental at this time. All I can really give you is some very preliminary results and indications.

Actually we have done relatively little that can really be reported on for nickel-cadmium cells as opposed to -- actually we have done more at this point on failure analysis and accelerated testing for silver cadmium cells, and I would like to give you a little more information on that.

For nickel-cadmium, about all I would like to say now is that we generally confirm the results described to you just a few minutes ago for nickel-cadmium cells in that as a result of increasing the charge and discharging rates, the degradation in performance is proportional to the total number of cycles up to about the C rate of charge and discharge, rather than being proportional to the actual amount of elapsed time during which the cell is cycled.

We are in the process of looking also at the effect of elevated temperature in addition to high rates of charge and discharge. But this work is still very incomplete.

We also have confirmed the observation that the main mode of degradation from the tests so far of high rate cycling has been a decrease in the effective capacity of the negative electrode in a nickel-cadmium sealed cell.

Let me describe now a few more numbers that we have

obtained in the course of looking at failure modes of silver cadmium cells. These were 12 ampere hour nominal sealed silver cadmium cells. We were actually not originally intending to predict life based on the testing that we did. That I will mention to you here. We were concerned with comparing the performance of two different modifications of cells, as internal structure of cells. One modification, for example, had a nylon net layer around the positive plate and polyvinyl alcohol as part of the separator system.

The other cell configuration, which was supposed to be an improvement as far as the life characteristics of the cell was concerned, had non-woven nylon and no polyvinyl as part of the separator system. This general difference was evaluated by accelerated testing. Four different kinds of accelerated testings were performed. One was cycling at normal rates at 140 degrees F. Another was cycling at normal rates with all the free electrolyte removed from the cell.

A third was cycling at a high rate of cycling but still at normal charge and discharge rates. That is, cycling with a very short charge-discharge time, ten minutes to charge, ten minutes to discharge.

The fourth test was at a relatively high charge and discharge rate for silver cadmium cells, namely, at the C rate.

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The results --

VOICE: Were these all at 140?

DR. SCOTT: No. Only one of the four different tests was performed at that, and that was with normal -- when I refer to normal in this case it is for a particular application, which was at the C over two and a half rate of charge and discharge.

The results were rather ragged. Because of this I chickened out on actually putting any of this on slides until I saw what other kind of data might be presented here, and then I may feel better later on and turn it in for publication.

(Laughter.)

I will tell you what it is now and it might show up in the proceedings later.

On the high temperature cycling test the test was run four 40 cycles at C. over two and a half charge and discharge rate. Controls were run at normal room temperature for both types of cells, and in one case the controls increased in capacity by about five percent during the cycling time, in the other decreased by 15 percent at room temperature.

The modification that increased by five percent at room temperature decreased by 45 percent in 40 cycles at 140 degrees F. The other modification which decreased 15 percent at room temperature, decreased 55 percent at elevated

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temperature.

We were hoping to see a much larger differential in performance because of certain structural differences between the cells. We for various reasons had to terminate the test after 40 cycles. We really don't know what might have happened on continued cycling. The rate of degradation was fairly linear with the number of cycles from zero to 40 cycles. If you want to extrapolate, you can, but I would rather not.

At least this form of test in this case did not show a really significant difference in the characterization of these two cell configurations, we feel.

The test with insufficient electrolyte, we charged and discharged the cell a number of times and withdrew all the free electrolyte that we could find in the cell as a test of the ability of the separator system to retain electrolyte. Then we sealed the cell up again and cycled -- actually we cycled only ten cycles in this case at room temperature, again at the C over two and a half charge and discharge rates.

At the end of this time the configuration which contained the nylon net rather than the non-woven nylon decreased in capacity by about 15 percent. The one that had the non-woven nylon did not decrease in capacity measurably during this ten cycle test.

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Ten cycles is not very much, but this is as far as this test has gotten at this point in time.

It does appear, at least so far in this case, that we are able to see in a relatively few cycles a definite difference in the ability of the non-woven nylon type separators in retaining moisture around the plates in this type of cell.

The high cycle rate test appeared to give the most satisfactory results. By that I mean it gave us more of the answers that we thought we were going to get in the first place than any of the rest of the tests. I still can't say at this time how well these results correlate with ultimate life in a specific application. I can only give you right now what happened during the accelerated test period.

VOICE: Was this at C. over two and a half?

DR. SCOTT: This was again at C over two and a half rate, yes.

We discharged for ten minutes, charging for ten minutes, and conducted this for five hundred cycles. The initial capacity to total output capacity, to .9 volts per cell of the configuration with the woven nylon, was 8.6 ampere hours. That of the non-woven nylon was 11.2 ampere hours. After the 500 cycles, the one with the woven nylon was down to four amp hours, the one with non-woven nylon was down to 9.2 nylon hours. The interesting thing about this result was that

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during the test we plotted the cell voltages as a function of time continuously for each charge and discharge cycle. We found that very soon in the test, that is, within the first 50 cycles or so, that the upper discharge plateau of these cells disappeared. It so happens that we have observed this form of degradation on actual lift tests of this type of cell under various other applications. So we are looking into this a little bit further to determine the reason why this has happened and to try to correlate it more with actual use conditions.

We have found, by measuring the individual potentials of the plates in the cells during charge and discharge, that it appears that here again one of the things that happens first is that the ability of the negative plates in these cells to receive charge becomes impaired rather soon under these conditions and this prevents the cells from becoming fully charged, so that the upper discharge plateau can be fully utilized.

The last result is charging and discharging at the C rate. This was conducted for 127 cycles. Here the capacity of both cells at the end of the 120 cycles was greater than it was at the beginning. We apparently got, at least for this number of cycles, no obvious degradation and we are continuing this test to see whether this effect will turn around and will eventually get a decrease. At the last

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reading the capacities had increased and not decreased so we don't know what we are really doing here.

Am I running out of time?

DR. FLEISCHER: Just about.

DR. SCOTT: I will mention one other form of accelerated testing.

VOICE: How many test units did you have under each of these conditions?

DR. SCOTT: A relatively small number.

Most of them had a minimum of three units under each condition up to the order of about six. The sample was rather small and the reproducability was lousy. The other form of accelerated testing that we are conducting is that of accelerating the problem of silver migration.

DR. FLEISCHER: Silver cadmium?

DR. SCOTT: I have to explain that.

In certain types of nickel-cadmium cells presently available, silver brazes are used to make the hermetic seal. I believe we mentioned this problem last time as one which we considered a major failure mode for long-term use of sealed nickel-cadmium cells.

We have been busy since then conducting tests of the seals themselves out of an actual cell configuration by exposing them to various simulated cell atmospheres with a potential difference of flight across the insulator similar to

that it would see across an actual cell. We have been able to duplicate the type of behavior pretty well that we observed in a cell in the lab, without actually having to have the seal in an operating cell.

We have generated silver shorts across insulators at voltages ranging from about 1.2 to 1.75 volts, which is the range of applied voltage we have tested. We have been able to get shorting within the period of about 72 days, which we have been able to show can be pretty well inhibited by coating the silver braze with plating organic coatings and so forth, we have been able to test the effect of different ways of fixing the silver braze migration problem.

We feel this test is meaningful and quite useful discussion.

DR. FLEISCHER: Thank you, Dr. Scott.

For a discussion period we will set up a few ground rules. There are microphones, so please use them so that your discussion is heard throughout the hall, and so that it can be recorded.

Will you please address your questions to the particular speaker you have in mind if you wish him to answer the question. I think with that we will open the meeting. I think we have covered the gamut of problems that you all want to talk about. Let's start right in.

It would be a good idea to state your name and affili-

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ation so that it can be recorded.

MR. LANDER: I'm from the Delco Remy Division of General Motors. This is by way of two comments on Dr. Willihnganz's remarks.

First of all, you would be led to believe, on the basis of his remarks, that we never get negative plate failures in automotive failures any more. It is my impression that this is where we get the most of them. Most failures in automotive service occur in the winter time. It is probably due to a negative plate. If a battery runs for a long time -- for instance, many cells will run out to four to seven years -- then you are apt to run into the kind of degradation of grids as being the major cause that Gene speaks of.

The other comment is this: it appears to me to be true that we are more and more running into failures that can be described by the Arrhenius type. I have seen this, and I think some data was presented in the Schick meeting, that the Schick electrochemical section held last year for the cadmium electrode.

We have seen it in some temperature versus damp tests on silver zinc batteries. Gene mentioned it for his lead acid telephon batteries. I think the sense of it is that the temperature in many cases can be used as a means of accelerating testing, provided that the slope of the temperature curve does intersect failures in ordinary temperatures or in the ordinary

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use to which you are going to put the battery.

DR. FLEISCHER: Do you want to make any comments about that, Gene?

DR. WILLIHNGANZ: Yes. First your chairman cut me off before I was really through.

(Laughter.)

Second, I wouldn't have said anything about it anyhow, because I was trying to talk about aspects of the testing which have a bearing on the testing of Alkaline batteries. In other words not primarily interested in the behavior of lead batteries.

The audience I don't believe is primarily interested in the behavior of the automobile batteries that they are using. They are interested in the behavior of the space batteries that NASA is buying.

(Laughter.)

DR. FLEISCHER: Let's get on.

I think Dr. Hardy had a question.

DR. HARDY: I am Hardy, Battelle Memorial Institute. Dr. Biddick gave some information in the slide. I couldn't see all of it. I was wondering if the acceleration in the failure that you experienced by increasing the number of cycles or the frequency of cycling could be attributed to the increase in the discharge rate, or the charge rate, if you had a means of separating out these two possible effects.

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In other words are we evaluating just one item at a time or several? Are there several possible factors involved in increasing the cycle rate? Possibly I didn't understand what all the conditions were.

DR. BIDDICK: I can only say both, that we can't separate out the effects of charging and discharging. All we did was an overall determination. In general the loss in capacity was due to degradation of the negative. Whether this occurred primarily on charge or primarily on discharge, I can't say. I don't know.

DR. FLEISCHER: I am waiting for some hands to go up. Ernst Cohn.

MR. COHN: Cohn, NASA. In listening to the papers this morning I found the following factors, I believe, that affect the rate of battery failure. One is temperature, another is cycle number, at least up to the C. rate. I don't know that anything definite has been set beyond the C rate. If so I missed it. The voltage, presumably at both charge and discharge.

The current or the rate of charge and discharge.

The electrolyte level was mentioned. But I don't know that anything definite has come out of this so far.

Another point that I think should be mentioned here, particularly in connection with space batteries, is pressure cycling, which doesn't happen on automotive batteries

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of course. And this constant business of getting the pressure up and down, I would think intuitively has something to do with the battery failure.

Just yesterday I noticed in the latest Industrial Engineering News of October 1966 a news item from the proceedings of the British Ceramic Society which notes that "small automating stresses remote from the fracture stress cause ceramic materials to be exhibit high internal friction which results in frequent failure. The physical origins of an elasticity have been studied for metals and some carryover is possible in the realm of ceramics. However the problems in ceramic materials are much more complicated and require separate treatment. Except for some pioneering work in the United States," -- I am not familiar with who did that work or where it was done -- "there appears to be no consistent program of investigation under way."

It seems to me this is one of the factors we have to consider for sealed batteries. I wonder whether in this general scheme of things of trying to figure out how to set up meaningful accelerated test programs, anybody might be able to suggest any other factors that might show effects of accelerated testing.

DR. FLEISCHER: Dr. Willihnganz.

DR. WILLIHNGANZ: I would like to rise to the support of my lead acid batteries.

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In a positive plate, when you discharge it, you are converting lead to oxide to lead sulphate, which has a very substantial higher volume. The life of the battery on cycle test is critically dependent on how deeply you cycle it. In other words how much -- possibly, at least -- how much stress you put on the lead oxide film by building up lead sulphate in the pores and stretching that thing. So it is possible at least that what Mr. Cohn has said is actually happening in our lead acid batteries -- stress.

DR. FLEISCHER: Dr. Dalin?

DR. DALIN: George Dalin, of Yardney Electric. Although this is a little bit premature because the silver zinc battery hasn't been mentioned yet, let me say that my primary interest is in silver zinc and silver cadmium.

These batteries are particularly rich in failure modes.

(Laughter.)

Consequently when you set out to run a test and try to run it by temperature, I think that instead of setting up an Arrhenius plot what you have to figure out is which particular failure mode you are testing. I think it was Dr. Willihnganz pointed out there was a break in the curve at the right hand end. I think actually what this plot should look like, if I may go on here, is something like this (indicating); with each one of these representing a different

failure mode.

To start out, with in testing silver cadmium with PVA, our experience has been that when you get up to 140 degrees Fahrenheit the PVA goes bad and that is all there is to it. There was mention made of a non-woven nylon which possibly was pelon. I hesitate to ask whether those were our cells which were tested, for obvious reasons.

(Laughter.)

Pelon won't take these high temperatures either. Consequently, when you set out to raise the temperature and accelerate the testing, you may be introducing a completely new failure mode which has nothing to do whatsoever with the actual way in which the battery will be cycled and the actual way in which it will fail. I am going to jump the gun on my own paper tomorrow.

We have had silver cadmium cells running on a seventy-five percent depth of discharge for 1800 cycles.

Is Dr. Beck here? At any rate, Ted Beck has run cycles 25 percent depty of discharge for approximately 20,000 cycles. So it is obvious that the change in the temperature isn't going to show up in the various modes. And probably not be meaningful.

DR. FLEISCHER: Dr. Waite?

DR. WAITE: John Waite, Mauchly Systems. In mentioning Ernst Cohn's factors affecting acceleration, I feel that

using the computer to analyze your voltage data to identify failure modes and to identify the changes in the parameters, since any particular accelerated test technique is emphasizing one parameter, you want to see what happens to all of them. I feel that later papers in this program will add to factors of control which you will probably want to have the use of a computer in analyzing their voltage data.

DR. FLEISCHER: Dr. Shair.

DR. SHAIR: Bob Shair, of Gulton Industries.

I think it is very important, when we talk about any kind of accelerated testing, that we also indicate whether we are testing single cells or whether we are testing multiple groups of cells up to as high as possibly 17 to 20 cells in a battery.

In the case of nickel-cadmium cell testing, for instance, we find that even though that cell may be tending toward a failure, its voltage characteristic probably will not get so far out of line that you will get an avalanche effect which will destroy the entire pack.

On the other hand when you are testing silver cadmium cells, as soon as you get to a point where you do have a degradation occurring, the voltage of that cell changes so drastically compared to the others that unless you are controlling individual cells you can actually destroy the whole pack by virtue of just perhaps only ten percent of the cells

actually failing by a degradation of the cell itself.

I think it is important to indicate how we do the testing and how we do the control. Because one thing we want to be sure of is that we are testing the cells, not the method we are using to charge and discharge the cells.

DR. FLEISCHER: Dr. Willihnganz.

DR. WILLIHNGANZ: Bob Shair's remarks emphasize something which I forgot to mention earlier, too, which is that if you are running an accelerated life test I believe it may be good practice to look at the remains before the battery has gone bad. I have seen year after year of testing, in which you look at the final battery, and about the only thing you can say about it is "worn out junk."

Why it failed we haven't the faintest idea. If you however can get in there at the first sign of trouble, you may find out what was wrong.

DR. FLEISCHER: Bob Shair?

DR. SHAIR: I can't help but make a remark. Here we are talking about space, and all the batteries are going in the other direction.

(Laughter.)

DR. WILLIHNGANZ: That is just negative space.

(Laughter.)

DR. FLEISCHER: I don't think we will decide where that place is right now. I think we still have plenty of

time for more comments and more questions. You better get up or I will start calling on you. Here is the first gentleman I didn't recognize this morning.

MR. MAGISTRO: It may be good to remain anonymous. I am Magistro, of Picatinny Arsenal. We have done a lot of factorial type testing where we considered multiple factors. We found in tactical use of Army weapons systems we deal with at least four and five environments at a time. Most of the data that has been presented this morning has been plotted for single environment, for instance temperature versus life -- at least I am making that assumption -- withou also varying currents and attempting to get interactions between temperature cycle and load of the battery.

I wonder if any of this data was checked this way. That is a general comment for all three speakers.

DR. FLEISCHER: Does anybody want to answer that? Or do you want me to say that most of the time the factor that limits the data that you want is the amount of money that is available for carrying out these tests.

(Laughter.)

MR. MAGISTRO: I would also like to add that in our experience with thermal batteries and such as one-shot batteries of reserve type, we find that the factorial type test also reduces the total cost. This has been proven over about ten years. We have fairly good data -- I don't

have it here with me -- which shows the effect of this if you want to make decisions it tells you which direction to move very quickly. It doesn't tell you what the answer is, but tells you which way to move. Maybe this is what we need along with Mr. Cohn's list of factors.

Are there interactions which we can measure? The only way we can measure them is by designed experiment.

MR. LANDER: One comment on the remarks. We may indeed want to test the charging procedure of the charging system that is involved.

I don't know how it works out for silver cadmium or nickel cadmium, but I will show some data later today that will indicate that optimum life may be achieved under a given cycling regime, depending on just how you do cycle a lead battery.

Consequently system design may become an important part of achieving maximum life.

DR. FLEISCHER: Dr. Mauchly.

DR. MAUCHLY: I am very glad that the gentleman from Picatinny Arsenal gave that quick reply about the expense of testing and what factorial design and similar experimental design can do for you.

I felt that perhaps it was so quick that it went right past you without your really giving it the due emphasis it deserves. The whole reason why these various seeming

complicated designs for testing are employed is because they have advantages. It isn't because somebody is trying to be fancy. One of those advantages usually is it reduces the cost. You learn more for less money.

A second advantage which is hard to equate with cost sometimes but is very important in the space program I would say as much as it is in the agricultural experimental field in which Fisher and others first built up the theory of design experiments, is that it saves times, regardless of cost.

There the agriculturalist was faced with the fact he could only grow one or two crops a year and then he would have to wait until next year before he could do another experiment. The more experimental results we can gain in the same time, the faster ahead we can proceed in this field, too.

DR. FLEISCHER: Dr. Cohn.

MR. COHN: There is another advantage that should be added to the experiment approach, and that is that you can get by this means the effects of interactions, which you could not possibly get by other means. In other words, if you want to get, say, the combined effects of pressure and temperature, there is no way you can make the experiment to get the interactions correctly except by some -- or similar design. This has been shown a good 15 years ago or

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so in one of the Chemical Engineering journals where an article indicated that to optimize a product yield, the only way to proceed was by factorial design. That is another bonus you get out of that in addition to saving time and money.

DR. FLEISCHER: Gerry Halpert.

MR. HALPERT: Gerry Halpert, NASA-Goddard. As part of the discussion here this morning, you have heard a lot of the description of various types of cycles. The program at the Martin Company, Baltimore, was an example of a non-statistical type of program. I think we have some results which gave some characteristics of operation versus life relationships.

I brought some slides along this morning. It will be all off-the-cuff except that I have the slides. If we can show the first one I will give you some idea of what the program was and what the results were.

(Slide.)

This is the entire program of battery tests. I have thrown in an extra one just for comparison. We see in one group we look at only the rate of discharge, that is, C over 2, C over 8, and 2C.

In the second group we find various types of charge appearance, two-step type charges, and different rates.

In the third group we see differences in end of charge termination.

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GROUP I	GROUP II	GROUP III	GROUP IV
START PROGRAM WITH CELLS FULLY CHARGED			FULLY DISCHARGED
BATTERY 0 - CONTROL CHARGE-0.6 AMPS FOR 3-1/4 HRS. DISCH.-3.0 AMPS FOR 1/2 HR.	BATTERY 3 - 25% DOD CHARGE- 0.6 AMPS TO E_T DISCH.- 3 AMPS FOR 1/2 HR.	BATTERY 7 - 100% OVERCHG. CHARGE-0.6 AMPS FOR 6-1/2 HRS. DISCH.- 3.0 AMPS FOR 1/2 HR.	BATTERY 10 - 50% HOC CHARGE-1.2 AMPS FOR 2-1/2HR. DISCH.- 3 AMPS TO 1.0V
BATTERY 1 - SLOW DISCH. CHARGE-0.6 AMPS FOR 3-1/4 HRS. DISCH.-0.75 AMPS FOR 2.0 HRS.	BATTERY 4 - 25% DOD CHARGE-1.2 AMPS TO E_T THEN 0.6 AMPS TO E_T DISCH.-3 AMPS FOR 1/2 HR.	BATTERY 8 - CONSTANT V CHARGE-CONSTANT V TO 0.6 AMPS DISCH.-3.0 AMPS FOR 1/2 HR.	BATTERY 11 - 50% HOC CHARGE-3.0 AMPS FOR 1 HR. DISCH.-3 AMPS TO 1.0V
BATTERY 2 - RAPID DISCH. CHARGE-0.6 AMPS FOR 3-1/4 HRS. DISCH.-12.0 AMPS FOR .125 HRS.	BATTERY 12 - 25% DOD CHARGE - 1.2 AMPS TO 1.425 V DISCH.-3.0 AMPS FOR 1/2 HR. (3A)	BATTERY 9 - PRESS TERM. CHARGE-0.6 AMPS TO PRESS. CUTOFF DISCH.-3.0 AMPS FOR 1/2 HR.	
	BATTERY 13 - 25% DOD CHARGE-3 AMPS TO 1.450 DISCH.-3 AMPS FOR 1/2 HR. (5A)		AMF CYCLE-UDC-58% DOD CHARGE-CONSTANT V 65 MIN. DISCH-LOAD - 6 AMP-35 MIN. (Every 4th cycle drain through 0.5 ohm resistor for 1.67 Hours)
	BATTERY 14 - 25% DOD CHARGE-3 AMPS FOR 10 MINS. THEN 0.6 AMPS TO 1.42V DISCH.- 3 AMPS FOR 1/2 HR. (6A)		

BATTERY 5 - 50% DOD	BATTERY 6 - 100% DOD
CHARGE-3.0 AMPS TO E_T THEN 0.6 AMPS TO E_T DISCH.-3 AMPS FOR 1 HR.	CHARGE-3.0 AMPS TO E_T THEN 0.6 AMPS TO E_T DISCH.-3.0 AMPS TO 1.0V

The last group is an interesting cycle in which we charged only from the failure point of 50 percent and then back down again.

May I have the next slide, please.

(Slide.)

Here we see the effect of the first group, the differences in the first group. These are the first three batteries. We see the discharge rate, C over two, C over eight, and 2C. The ampere hour cells are here. The depth of discharge was 25 percent in all cases. The failure is determined by the fifth cell to fail out of a battery of 10 cells. That is, the failure to deliver the 25 percent capacity. As you see, the C over 8 cell was still going at this time. Because computer operation, because of the number of cells left, we terminated the test. May I have the next slide, please.

(Slide.)

Note C/8. This is a compilation of the results of all the batteries in the tests, with a few extras thrown in. Pack 13 and 17 were Crane, and an MF test cycle, upside-down cycles, was Sheer phase.

To look at the numbers, we see the number of days of operation are fairly significant except for batteries five and six which were 50 and a hundred percent depth of discharge and really don't fit into the pattern of the rest

6 AMPERE HOUR CELLS - 25%
DEPTH OF DISCHARGE - 25%

BATTERY	DISCHARGE RATE	CYCLES
0	C/2	3065
1	C/8	3928*
2	2C	2556

*TEST TERMINATED PRIOR TO BATTERY FAILURE

TEST RESULTS

TEST RESULTS	CYCLES	DAYS
BATTERY 0	3065	479
BATTERY 1	3928 *	860*
BATTERY 2	2556	359
BATTERY 3	—	—
BATTERY 4	5599	551
BATTERY 5	537	117
BATTERY 6	322	75
BATTERY 7	2837	830
BATTERY 8	10,105*	803*
BATTERY 9	4266*	760*
BATTERY 10	3835	558
BATTERY 11	5791	480
BATTERY 12	4021 *	419*
BATTERY 13	6768 *	390*
BATTERY 14	3193 *	363*
AMF 25°	6613	513
AMF 10°	5870	557
AMF 40°	2332	268
PACK 13 (CRANE)	4021	250
PACK 17 (CRANE)	2675	331

* TERMINATED PRIOR TO BATTERY FAILURE

of the cells. You see there are quite large numbers there in terms of days and in terms of cycles.

(Slide.)

Here I tried to break out the effect of charging current on the cell. We see in the first three cases, C/10, that we have a fairly short number of cycles. This is C/10 for three and a quarter hours, which is putting in approximately 130 percent of the discharge. As I mentioned, we see the fairly low number of cycles compared with the rest of the test.

As we go down, looking at Crane, C/8 -- that is not C/32, I think it should be C/3 or 3.2. As we go higher we see that we increase the number of cycles. In this particular case we have C/2, C/10, C/5 and C/10. The C/2, I think that C/2 may be an incorrect number. I have to check that number. That doesn't appear to belong there.

At the bottom we see another interesting and very interesting point. These are the two batteries which were only charged 50 percent. We see that C/2 and C/5, better than half, 50 to 75 percent increase in life, by using the higher rate at the lower states of charge over the C/5 rate.

I think we can say in general, about these particular numbers, that the increase in rate during the charge cycle is, at least in the early portion of the charging cycle, is quite effective in increasing life.

EFFECT OF CHARGE CURRENT

6 AMPERE HOUR CELLS - 25% DEPTH OF DISCHARGE - 25°C

BATTERY	TYPE OF CHARGE	CURRENT	CHARGE TERMINATED BY	CYCLES
0	CONST. CURR.	C/10	TIME	3065
1	CONST. CURR.	C/10	TIME	3844
2	CONST. CURR.	C/10	TIME	2556
PACK 17 CRANE	CONST. CURR.	C/8	TIME	2675
12	CONST. CURR.	C/5	VOLTAGE	4021 *
PACK 13 CRANE	CONST. CURR.	C/32	TIME	4021
13	CONST. CURR.	C/2	VOLTAGE	6768 *
4	TWO STEP CONST. CURR.	C/5, C/10	VOLTAGE	5599
14	TWO STEP CONST. CURR.	C/2, C/10	VOLTAGE	3193 *
8	CONST VOLTAGE	VARIABLE	CURRENT = C/10	10,105
10	CONST. CURR.	C/5	CHARGED, ONLY 50% TIME	3835
11	CONST. CURR.	C/2	TIME	5791

* TEST TERMINATED PRIOR TO BATTERY FAILURE

(Slide.)

Here we have the effect of overcharge. Quite a few of you talked about overcharge and its effect on life. We see here, again going down the list, we go from a point at which we purposely overcharged the cell by an extensive amount by a small amount, and then onward until we came to a cycle in which the pressure of the one cell terminated the charge, or the constant potential, when the current reached a lower limit of C/10 rate, in which the current efficiencies are exceptionally high, 90 percent or above, as the percent of recharge is 111 percent.

In this case I have said that the low rate of discharge is bad. We still get 142 cycles. Under the constant potential regime we drop the C rate to C/10 rate and it indicates a substantial increase in the life. Another point about this. Look at this number. This constant potential was at 1.425 volts. This cycling lasted 108 some days or 10,000 some odd cycles. This is quite a low number one would consider for quite a low voltage to charge -- 1.425 average volts per cell.

Something Bob Shair mentioned, just because one cell may be a little low you don't get this avalanche effect. These kept going for quite sometime. As I mentioned, the star points out there was only one failure and that occurred at 3700 some odd cycles during the test.

EFFECT OF OVERCHARGE

6 AMPERE HOUR CELLS - 25% DEPTH OF DISCHARGE - 25°C

BATTERY	RATE	CHARGE TERMINATED BY	% RECHARGE	CURRENT EFFECIENCY	CYCLES
7	C/10	TIME	267%	38%	2837
0**	C/10	TIME	133%	75%	3067
PACK 17 (CRANE)	C/8	TIME	125%	80%	2675
PACK 13 (CRANE)	C/3.2	TIME	125%	80%	4021
9 **	C/10	PRESSURE OF ONE CELL	~111%	~90%	4266*
8	CONSTANT POTENTIAL (1.425V)	I=C/10	~111%	~90%	10105*

*TEST TERMINATED PRIOR TO BATTERY FAILURE

**BATTERY 0 WAS CHARGED ONLY 0.1 AMP HRS (AVG) MORE THAN BATTERY 9

VOICE: At ambient temperature?

DR. SCOTT: These are all 25 degrees C.

(Slide.)

I have listed a couple of things here. Three items, two in addition to the one Ernst had on his list. First of all constant potential or two-step type charge, high current at the beginning of the charge phase. It is rather significant in increasing the life of the cell.

Secondly, the minimum overcharg or maximum current efficiency, that is little or no guessing at the end of charge. The pressure terminated the battery, for one, tended to increase life considerably. In a number of the cycles the voltage cutoffs, on the voltage cutoffs they were all fairly low, below 1.5 volts per cell. In all of those I think we increase our life. As mentioned, of course by the others, in accelerated testing, the low discharge current would increase the life. High discharge current would affect the life, failure being on the cadmium electrode.

That is all I can say about this on this particular program.

DR. FLEISCHER: I think we are about over our discussion period. I want to make one comment, sort of pointing the direction that we might be thinking about in terms of our questions. One of them is that we are trying to direct our attention to how to run an accelerated test

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OPERATING CONDITIONS DESIRABLE FOR LONG LIFE

1. CONSTANT POTENTIAL OR TWO-STEP TYPE CHARGE (HIGH CURRENT AT THE BEGINNING OF THE CHARGE PHASE)
2. MINIMUM OVERCHARGE - MAXIMUM CURRENT EFFICIENCY
3. LOW DISCHARGE CURRENT

for various types of space batteries. In setting up an accelerated testing program we have to keep in mind the object of the accelerated testing. Are we doing it for the purpose of quality control. Are we trying to learn something about separators and other modes of failures.

Finally, we should keep our minds on the fact that we have as yet not been supplied with any kind of an idea of how the batteries have to operate in space.

What kind of charge-discharge cycles do they actually undergo. What temperature ranges do they actually undergo. What kind of rest periods do we have.

There are a large number of items that we ought to know about if we are going to think in terms of are we going to try to reproduce in our accelerated testing some particular application of a battery. This brings me to call to your attention that for many years salt spray tests -- and it is still being used to study the corrosion of metals and for testing whether a metal will stand up -- for about ten years now a lot of people wanted to discharge the salt spray test as not representing what happens in actual applications of metals. But they don't give it up because this is a convenient way of finding out whether you will withstand a certain artificial set of conditions which says that under these conditions we know that in the field we have had success.

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I think we have to look at accelerated testing programs as simply a means of telling us that we have a good chance of success if a battery passes through and yields the number of cycles that we have set up for that particular battery.

We will now adjourn until 10:40.

(Short recess.)

We seem to have lost some of our audience, but we will start in and maybe we can get some questions out of those who didn't hear what was said.

(Laughter.)

The next speaker is Mr. Frederic Bowers, of Naval Ordnance Lab, at White Oak, who will talk on suggested techniques for non-destructive and sample testing of silver zinc batteries.

STATEMENT OF FREDERIC M. BOWERS, NAVAL ORDNANCE LAB, WHITE OAK, SPEAKING ON SUGGESTED TECHNIQUES FOR NON-DESTRUCTIVE AND SAMPLE TESTING OF SILVER ZINC BATTERIES

MR. BOWERS: In silver batteries the silver electrode is normally the limiting electrode. Therefore if we noted the chemical composition of this electrode we can calculate the amount of energy that is available for transformation into electrical energy.

We have been doing some work along the line of

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attempting to correlate the chemical composition of the silver eletrode with the energy that we get out of batteries.

We have been working with automatically activated or remotely activated silver design cells and we have been storing these for periods of time and at various temperatures.

For a particular experiment we remove two cells at one time. One cell is discharged and the other is analyzed.

I would like to show you some of the results that we have.

(Slide.)

Here we have the results that we have obtained with storage at 70 degrees for three, six and 12 months.

We have the composition of the active material. We have here the amount of free silver. You can see that this is small. In almost all the cases it is less than six percent.

Then we have the percentage of the amount available of silver oxide and the amount of the so-called AGO or divalen oxide.

We have taken from these results and calculated the theoretical capacity in ampere hours. These cells that we have used are electrolytically formed and they are normally, they have been rated at 85 ampere hourse.

On the counterpart cells we have discharged these at two different rates and we have taken the data at two dif-

Storage Conditions		Composition of Active Material				Electrical Capacity in Ampere-Hours at the 40 minute rate		Electrical Capacity in Ampere-Hours at the 10 minute rate	
Temperature (°F)	Time in months	% Ag	% Ag_2O	% Ag(I)Ag(III)O_2 (AgO)	Theoretical capacity in ampere-hours	to zero volts/cell	to 1.2 volts	to zero volts/cell	to 1.2 volts
70	3	3.6	46.1	49.8	104.6	102	94	105	95
	6	5.7	33.7	59.8	107.9			113	101
	12	4.7	36.8	57.6	109.3	102	96		

ferent points. To zero volts per cell and to 1.2 volts per cell. We have discharged these at the 40 minute rate and at the ten minute rate.

We can see that storage at three months, at 70 degrees, our analysis shows that we got about 105 ampere hours. To zero volts we got about 102. To 1.2 volts, near the end of the curve, we have 94 ampere hours. These two values are in good agreement. Also it shows that for the chemical composition that our electrode is in the order of 90 to 95 percent efficient.

If we go to the high rate, the 10 minute rate, we get comparable results. Here we have 105 amp hours and 95 amp hours. This shows also that based on this chemical composition that the length of discharge of the silver oxide electrode really doesn't make much difference.

We are only going to pick up a few more ampere hours possibly if we discharge these things at lower rates.

We also see from this data that there has been little change in the chemical composition over a year's time. And similarly there has been little difference in the ampere hour output.

In this particular case it is 113 ampere hours after we had discharged this particular cell. We then went back and measured the amount of active silver that was available in this cell and recalculated it back to this composition.

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We got in the order of 112 ampere hours. This high value is due to an increased amount of silver.

(Slide.)

Here I am talking about different temperatures. We have done essentially the same thing. Everybody tells me this is not a good way to present data because it is so much of it on one slide. You will have to bear with me.

The 70 degree data we have already discussed. Here I am just listing the data at the 40 minute rate because there is so little difference between the 10 minute and 40 minute rate.

If we go to 110 degrees Fahrenheit and we look at our values for 3, 6 and 12 months -- indicentally we haven finished the results, the analysis on this particular cell -- we find that there has been little change in the analysis of the active material over a year's time -- over six months time at 110 degrees.

Similarly there has been little difference in the amount of energy that would be available.

There has likewise been little difference in the capacity that we obtain from these.

If we go to 130 degrees, here we have data at 1, 2, 3, 6 and 12 months. I would like to point out that at 2 and 3 months the data is for cells that were stored in a desiccated condition. We find that we do get some significan

Storage Conditions		Composition of Active Material				Electrical Capacity in Ampere-Hours at the 40 Minute Rate	
Temperature (°F)	Time in months	% Ag	% Ag_2O	% Ag(I)Ag(III)O_2 (AgO)	Theoretical capacity in ampere-hours	to zero volts/cell	to 1.2 volts
70	3	3.6	46.1	49.8	104.6	102	94
	6	5.7	33.7	59.8	107.9		
	12	4.7	36.8	57.6	109.3	102	96
110	3	4.0	44.5	50.1	102.4	105	98
	6	4.8	41.8	51.5	101.9	106	97
	12					106	96
130	1	5.8	49.0	43.1	92.9	91	78
	2*	5.6	41.8	51.3	102.7	98	92
	3*	3.7	43.1	51.5	105.6	93	86
	6	3.5	54.2	40.8	98.3	96	90
	12					89	80
160	1	8.3	61.4	28.2	83.7	86	63
	2	5.3	72.0	21.3	80.1	75	67
	3*	3.5	73.5	21.4	82.7	79	73
	6	2.6	88.5	7.2	72.2	sample lost	

* desiccated storage

changes, that is, after one month at 130 we have dropped in our theoretical ampere hour capacity about 10 ampere hours, roughly. This has been largely due to a drop in the AgO composition or component. This has decomposed. We have according perhaps increase in this area AgO. Similarly we show that in the actual discharge we have also lost capacity. But if we take and store these cells in the desiccated condition we get very little change over three months, at any rate.

So that desiccation in storage may help somewhat as far as the primary silver zinc oxide battery is concerned.

If we go to 6 months we see similarly in an undesiccated condition the amount of AgO has decreased and the amount of Ag_2O has increased. If we go to 160 degrees, we find that here we are in terms that we might be talking about as far as accelerated testing. We find after one month we have had quite an appreciable decrease in the AgO, according increase in the Ag_2O component.

We have had a drop in capacity. At two months this has progressed. Even with three months with desiccated storage this may have slowed down the process some. We still get an appreciable drop in capacity. At 6 months we see real notable differences here, and we have practically no AgO left.

In this particular case we lost our sample on

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discharge. The reason for the loss was that we have another thing that happens on accelerated testing where temperature is involved. In this particular case the plastic case had crazed and would not stand the pressure of activation when the KOH was forced into the cell.

We had tried to force this but the cell was distorted sufficiently that our clamp did not help us in this particular area. This is the information that I have. I think that it suggests a couple of things. One thing, when we are talking in accelerated testing of silver oxides zinc batteries I think we must -- and if we are talking about increasing the temperature, then I think we have to be careful about staying below 130 degrees Fahrenheit at least.

Just where the break is between 110 and 130 we do not know.

DR. FLEISCHER: There is time for a question.

VOICE: Was that silver zinc or silver cadmium?

MR. BOWERS: These were silver zinc. As long as I have time I would like to tell you how we analyzed these batteries.

We used the ERSA method. Perhaps I had better go into detail. We divide the sample into two parts. On one part we treat it with dilute amonium hydroxide. This dissolves the oxide and leave the silver metal on a film. With the philtrate we then determine the amount of silver that is in the

philtrate by the silver chloride method. This gives us the amount of free silver and the amount of silver that is in the oxides.

Then on another aliquote we take and analyze for oxidizing power with the classical ERSA method. Silver metal will react with free iodine to cause an error. But since we have already determined our free silver, we can then correc for the reaction between silver metal and free iodine, and then we calculate to AgO, Ag_2O, and silver metal.

DR. FLEISCHER: Fritz would like to make an announcement about an evening meeting.

MR. BOWERS: The local section of the Electro-Chemical Society is meeting at Georgetown University, 37th and O, in their new Chemistry Building there. Dr. Brenner, from the Bureau of Standards, is going to talk on electroplating. We would love to have any or all of you come. It would be kind of a businessman's holiday for some of you.

VOICE: Did you mention the time of the meeting?

MR. BOWERS: 8:00 o'clock.

DR. FLEISCHER: Thank you very much.

Our next speaker is Dr. Chreitzberg, of Electrict Storage Battery Company, Raleigh, North Carolina, who will talk on accelerated testing methods for the determination of wet-stand life of secondary silver zinc batteries.

STATEMENT OF DR. A. M. CHREITZBERG,

ELECTRIC STORAGE BATTERY COMPANY

DR. CHREITZBERG: The Electric Storage Battery Company in Raleigh has been primarily interested in the low cycle life part of the spectrum. And long charge stand.

As a result of this interest in mission in space, such as Ranger and Mariner and Surveyor, we have conducted two major experiments in charge stand sealed silver zinc batteries.

The first experiment was done with a high rate sealed 25 ampere hour cell. This cell was designed to be dicharged at the 15 minute rate. The first slide will show you the characteristics of this cell on discharge and show you the approximate capacity at each of the rates.

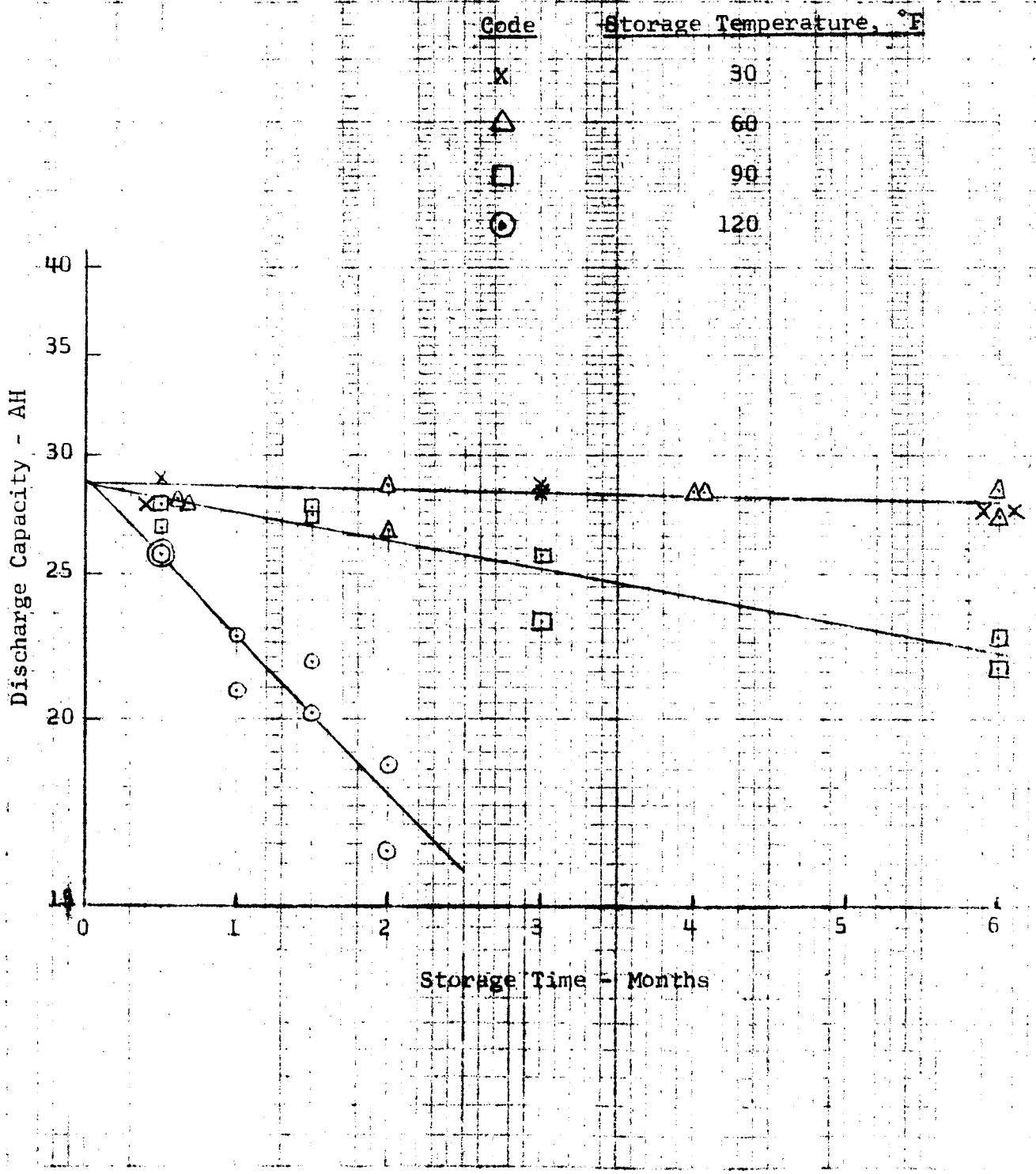
(Slide.)

Also the current density and amperes per square inch on each of these rates.

In the storage program which we have conducted, we took 30 of these cells and we stored them at varying times over the temperature range 30 degrees Fahrenheit to 125 degrees Fahrenheit. The way we conducted the measurement of capacity loss was first to formation cycle each cell through a deep cycle, measuring the discharge capacity on the first cycle at what we would call a normal mission rate for high rate cell.

FIGURE 1

EFFECT OF STORAGE TEMPERATURE AND TIME ON CAPACITY RETENTION OF 25 AH CELLS DURING CHARGED STAND



This rate was somewhere in the range of 191 ampere rate for this cell at about one and a half amperes per square inch. The rate however was three-step. The first step was a medium rate, the second a high rate, the third step was a rate that was about a half ampere per square inch.

Then we would recharge each of the cells, pull it to a constant test-in voltage at constant current, and put the cell on the prescribed test temperature and time. Then we would take the cell out of storage and immediately discharge at the same rate.

Bear in mind that this is a miss-type rate. The discharge is relatively inefficient, 25 ampere hours out out of perhaps 34 ampere hours in on charge.

What we found out when we took the capacity data to the test-in voltage was that we could plot a family of curves that are linear if we plotted the log of the capacity out versus storage time in months at each of the test temperatures. The data was scattered and increasinglyl so at the higher temperatures. At the lower temperatures the data fit very nicely to a linear plot.

We could not distinguish any difference between the storage loss at 30 degrees Fahrenheit from the storage loss at 60 degrees Fahrenheit. Between 60 and 125 the data could be explained by an Arrhenius plot.

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In order to get the Arrhenius plot we measured the

slope of the log capacity versus storage time. There is some theoretical justification that this slope is proportional to the rate constant for whatever reaction is causing the loss on charge stand.

If you will give me the next slide, I will show the Arrhenius. plot.

(Slide.)

This is not the one, but leave it. The next experiment we performed was to take cells that were quite different. These were 170 ampere hour cells and designed for low rate application. These cells were developed for the Surveyor program.

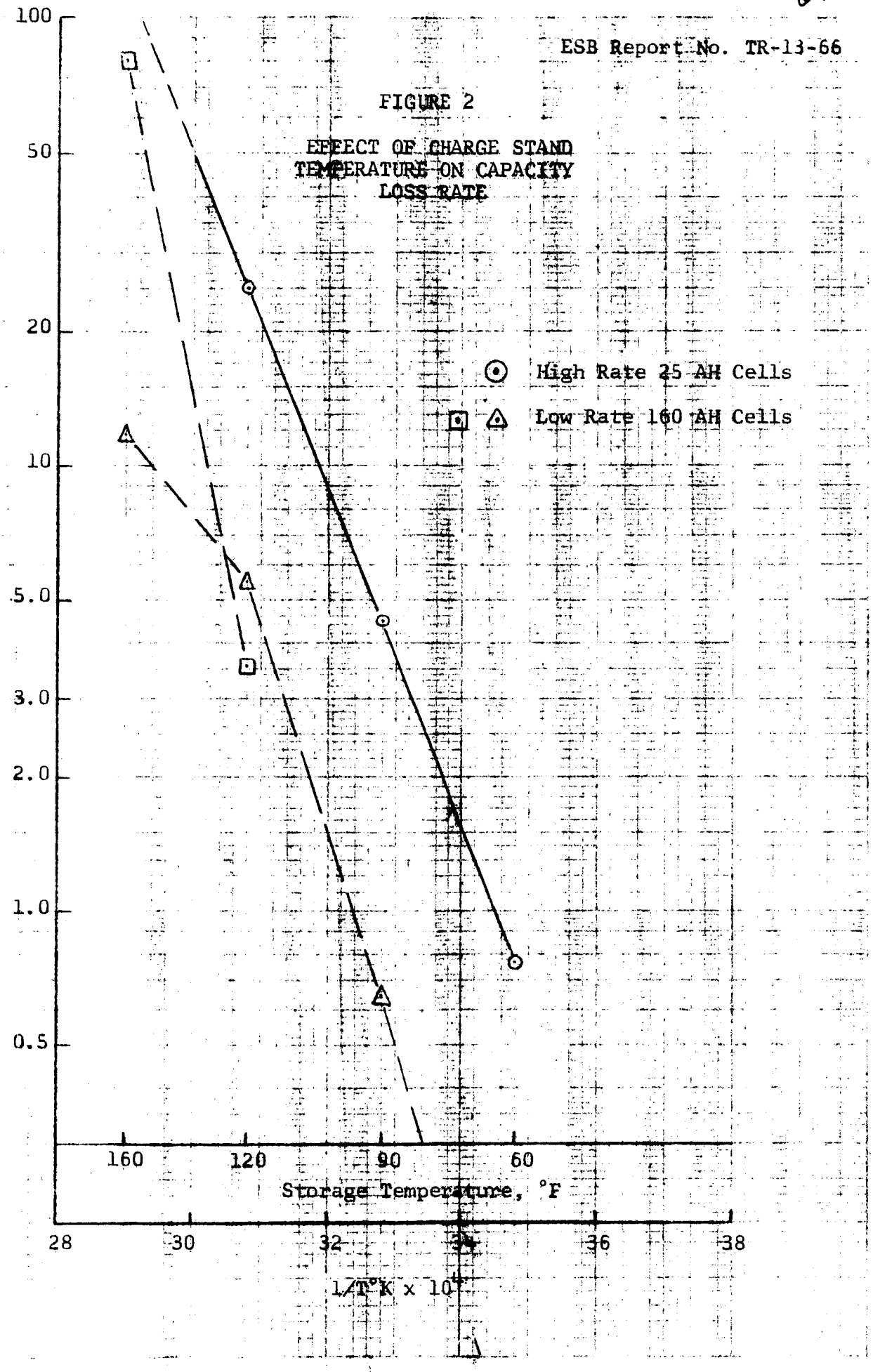
The cell in the normal condition of discharge at about the 23 hour rate would deliver approximately 160 to 170 ampere hours of capacity.

Here we took a number of about 40 cells and stored them over the temperature range zero degrees Fahrenhei to 160 degrees Fahrenheit. Again we found when we measured the capacity loss that there was very little difference betwe the data at zero degrees Fahrenheit, 30 degrees Fahrenheit, and 60 degrees Fahrenheit. There was very little loss. Let me show you how we measured this loss.

We would take these large cells, charge them, discharge them at a low rate, a mission rate, and then recharge them fully to a given test-in voltage, then store them for th

FIGURE 2

EFFECT OF CHARGE STAND TEMPERATURE ON CAPACITY LOSS RATE



prescribed period of time at a given temperature, and take them out of storage. This time in the experimenters science we were dealing with an efficient cell, we recharged immediate after coming out of storage to determine what part of the loss was recoverable. We then discharged and corrected the output for what we had put back in after the storage. And we haveplotted in this curve the ratio of the discharge capacity out after storage to the charge capacity in before storage, corrected for what we recharged after storage.

You will note that the data covers in the case of the low rate cells a period of 12 months storage. The topmost curve in green is data which was taken at 90 degrees Fahrenheit. The blue curve is the same cell stored at 125 degrees Fahrenheit. The bottom curve in a range with the squares is the same cell stored at 160 degrees Fahrenheit. Each of these points represents one cell. There is scatter.

These are not batteries by any means. These would be quite expensive batteries.

You will note about the three curves mentioned, 90, 125 and 160, that they do not extrapolate back to the 100 percent point. In fact they extrapolate back to increasing quantities of capacity loss.

The reason for this, we believe, is the separator system that was in these cells. We had a multi-component system. One of these components was polyvinyl chloride, whose pores are formed by leaching out starch. The starch wa

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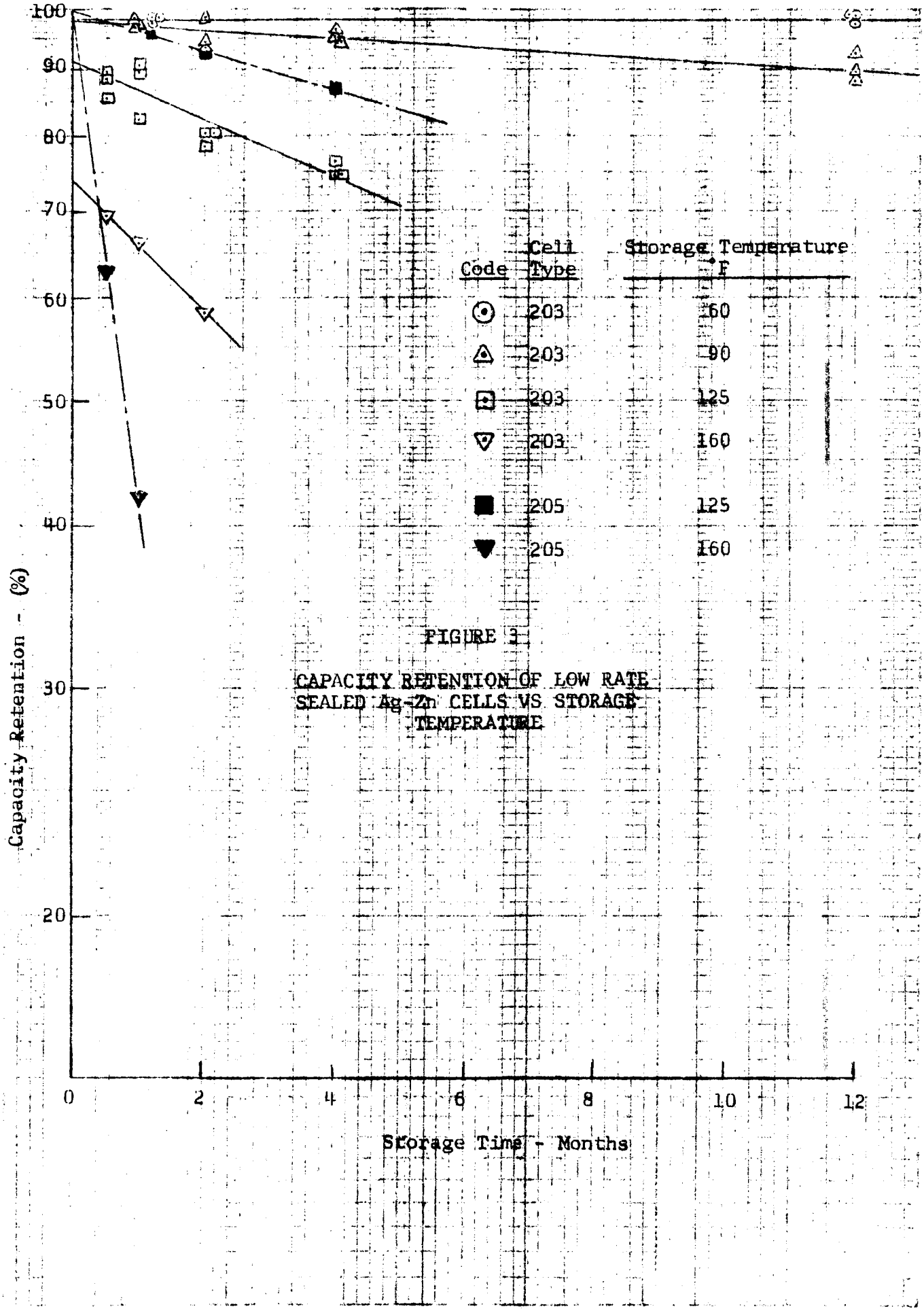

FIGURE 3

CAPACITY RETENTION OF LOW RATE SEALED Ag-Zn CELLS VS STORAGE TEMPERATURE

not leached out fully and we believe the starch reacted within the first two weeks of storage and at that point stopped reacting. Here we got a break in the curve and from that point on the storage loss was governed by some other reaction.

The red line at the top, this is a system, it is th same cell except here the cell has only ceelphane separator constituents. You will notice the pink line for the model 205 extrapolates back almost to the origin at 100 percent capacity retention.

The orange curve at the bottom, representing 160 degrees Fahrenheit storage, also extrapolates back. Both of these were the same fully cellophane cell. This points out the fact that if you do have one type of separator system and one shelf reaction, you should have a plot which would extrapolate back to where you would expect it to. If you do have a separator system, with something in it that causes attack, immediately you will see it.

Again we tried the Arrhenius plot by calculating the slopes of these curves. From the slopes calculating what we would term the rate constant, plotting it against the reciprocal of the absolute temperature. The third slide will show you these points and the curves.

(Slide.)

The Arrhenius plot for the first experiment is the red line, the high rate cells. Good linearity was achieved ir

the temperature rate of 60 degrees Fahrenheit to 120 degrees Fahrenheit. We had one body of data at 30 degrees Fahrenheit. It was superimposed on the 60 degree data. We can't distinguish between the two. This is one break in the curve. It says that you don't have to stow really any lower than 60 to get fairly good results.

We did not carry that experiment over 120.

On the low rate cells however we did go from zero degrees Fahrenheit all the way up to 160. The major body of data is on the blue curve. I have one point which was omitted at the time this slide was made.

That point was at 60 degrees Fahrenheit it would go down off the red. That point is in line.

If you take that point, the 90 degree point and the 120 degree point, you have a slope of Arrhenius plot which is very similar to the slope of the red plot for high rate cells.

The calculated activation Arrhenius activation energies for the red plot, is 20,500 calories per mole. The calculated value for the blue plot, excluding the 160 point, again taking up three points, the 60 degree point not shown on this slide, is 22,500 calories per mole. Fairly good agreement considering the wide design changes that are in these cells. One is a very high rate cell measured, and the capacity loss is measured by inefficient discharge. The large cell is

a very efficient cell, and the capacity loss was measured by an efficient technique, a low rate discharge.

The green curve shows that when you go to an all cellophane system that something different happened. We only have two points here. The bottom point may be on the line. The top point because it is at 160 may be off because some other reaction has taken place. At any rate I would propose that because the activation energies are pretty close to each other in spite of these wide changes in design, we may have a case where we have one activation energy covering silver zinc cells. If so, then a good measurement of it would allow us to perform storages at one high temperat not at 160 by this data. Certainly no higher than 125.

You can perform a storage experiment at 125 degrees Fahrenheit even on low rate cells in a period of four months. On high rate cells you cen perform it in two months.

From the slope of the capacity loss curve, plotting log of capacity out versus storage time at 125 degrees Fahrenheit and from the proposed value of the activation energy of 21.5 kilocalories per mole, one can then use the typical Arrhenius calculation and calculate what the storage loss would be at some lower temperature, provided again you don't go out of the range of the data.

In this way you can probably cut your testing time at least in half, and possibly by one third. We would propos

that if this is true for the silver zinc system, that a similar approach might also pay for the silver cadmium system.

It is true we are dealing only with shelf stand losses. I would point out that in the last comments that were made during the discussion program, many of the conditions of testing, in fact all of the conditions of testing, which led to long life, were those conditions of testing which also led to a load mean cell temperature during the course of that testing.

It may be that temperature is a prime variable. If so, we can measure the life of cells perhaps by storage tests. This is not a statement of fact. This is something to think about.

DR. FLEISCHER: Thank you Dr. Chreitzberg.

Our final paper before discussion is by Martin Sulkes, of the U.S. Army Electronics Command, at Fort Monmouth, who will talk on accelerated testings of silver zinc cells.

STATEMENT OF MARTIN SULKES, U. S. ARMY ELECTRONICS COMMAND

MR. SULKES: Thank you Dr. Fleischer.

Accelerated testing is usually synonymous with testing under conditions of increased severity, as for example; higher temperatures, greater depth of discharge, or loads. This presentation, however, discusses methods rather than testing conditions used to accelerate a

developmental program for sealed Ag-Zn cells. The particular methods referred to are: factorial experiment design and screening test techniques.

Life data, obtained by cycling experimental type sealed Ag-Zn cells at conditions more severe than use dictates, can not be readily extrapolated.

What I mean by experimental type is cells with different separators than are commonly used, different electrolyte concentrations and so on.

Something that you don't have a mass of data backing up previously. The reason you can't extrapolate this data is because the silver zinc system may fail by several different mechanisms, as previously mentioned. These include shorting by silver penetration of separator materials; shorting by zinc penetration; loss of capacity due to negative electrode shape change; and inability to change properly because of positive electrode dryness.

The cause of failure is the rapid uncontrolled venting of gas, known as blowing up the cell. This failure usually occurs in only one cell of a battery and is due primarily to the development of capacity inbalances between cells for which one of the other mechanisms is usually responsible. However, a lowered oxygen recombination rate may be a compounding factor.

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When cycling is done at an elevated temperature in

an attempt to speed testing, the resultant cycle life may be increased if poor change acceptance is the cause of failure or decreased if the failure mechanism is silver attack on the separator. Increasing the number of cycles per day to speed testing may shift the failure mechanism from shorting, to capacity loss caused by negative shape change.

It is clear, therefore, that in most cases the testing of experimental silver zinc cells cannot be accelerated. However, in many applications, it is necessary to complete a research and development program within a minimum period of time.

In a program carried out by Yardney Electric Co. under USAECOM sponsorship development of sealed silver zinc cells was speeded through screening tests and factorial experiment design.

The preliminary phase of the program consisted of screening tests of the various cell components, to eliminate completely unsuitable materials and thereby minimize cell testing. These screening tests included the following:

For separator materials

1. Zinc penetration resistance
2. Oxidation resistance to silver oxides
3. Electrical resistance
4. Electrolyte absorption and wetting speed.

For Negative Electrode Additives

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1. Zinc penetration resistance

2. Hydrogen evaluation

Components that fell within the limits of acceptability were further tested in cells. Cell testing was required because the various cell components can interact with one another to produce either beneficial or harmful effects. An example of an unexpected beneficial effect was the action of highly porous positive interseparators in decreasing negative electrode shape change as well as the expected effect of increasing positive electrode charge acceptance.

In another case, however, positive charge acceptance was unexpectedly lowered when more zinc was added to decrease negative shape charge. Both cases just described were caused by changed in the distribution of electrolyte between the positive and negative compartments, of the cell. Those of you who are familiar with silver zinc realize that the positive electrodes usually are completely wrapped in the form of a "U" and the electrolyte has to diffuse through it. There is no open path that it can slosh around to get from one to the other.

Factorial experiment design was used, to minimize testing time by doing in one experiment what would usually require several sequential experiments, or alternatively the number of cells tested was reduced.

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In a typical multifactor experiment, some of the

construction factors that were evaluated, were the quantities of zinc and silver, the number of layers of separator, electrode area, and electrolyte quantity. Such testing factors as cycling temperature, depth of discharge and storage time among others, could also be evaluated in the same experiment. The various factors were evaluated at 2 or more levels, with four levels usually being sufficient to completely define any qualitative factor. A typical fractional factorial experiment is shown in the slide.

(Slide.)

This particular experiment was a $\frac{1}{4}$ fraction and evaluated three factors at four levels and one factor at two levels.

The results that were obtained from this experiment were extremely useful.

Using factorial designed experiments only 200 cells were required to evaluate approximate 25 different separator materials and systems, four negative electrode binders, 3 surfactants, and 3 single level voltage additives all at several levels of concentration. In addition the same cells also evaluated the zinc to silver ratio, zinc to zinc oxide ratio, positive electrode density, and electrolyte concentration and quantity as well as several other minor factors.

Naturally these 200 cells were not all run at once. They were run in sequence. The total number of factors that

were evaluated were extremely large. The result of this program was a 41 ampere hour metal cased cell using a separator containing 1 turn of 6 mil pellon and 5 turns of C19-300 (Yardney Silver treated cellophane. A negative electrode containing 5 percent Teflon binder and no surfactant was found to be best. A four-cell battery of this construction cycled at 62½ percent depty of discharge yielded 212 cyles to failure. A cell stored charged for 30 days at 125 degrees F yielded 185 cycles, while 90 days charged storage reduced Cycle life to 70.

Anybody who is interested in the details of these cells may find it in the final report of the contract DA 36-039 AMC-02238(E) issued in July 1966.

DR. FLEISCHER: Thank you very much, Martin.

We will now throw the meeting open to discussion.

In the last discussion period I couldn't see on this side. My blinkers were on. I will have a representative of Fort Monmouth talk about statistics for a couple of minutes.

MR. WEINSTEIN: I am Joe Weinstein, Army Materiel Command, Fort Monmouth.

The comment in the early part relating to experiment design of course was reiterated by Mr. Sulkes' paper. I think one of the factors that is important in all of this

testing that we neglected to mention before is the error of a single observation, and the experience that I have had -- mind you I am more interested in statistics and less knowledgeable about the areas in which the statistics are applied -- my experience in the last three or four years has been that the experimental error in this particular field of battery R&D is extremely high.

The real advantage of the planned experiment, statistically designed experiment, as indicated in the slide Mr. Sulkes showed, is that you have the advantage of grouping large numbers of experimental data which essentially balance out all but one factor. The design makes all factors but one orthogonal. In this way you can average out the effects of many errors just as you would attempt to do if you had perfect control over all conditions and wanted to compare averages.

This is relevant to efficiency that was mentioned by the gentleman from Picatinny Arsenal. If I could trouble you for a minute I could show how this could be accomplished very, very readily.

This is a technique which is frequently used in illustrating experimental designs for their value. It is called a weighing experiment.

If you have two objects, A and B, and you put them on a two pan balance and you wanted to find the measurement,

say you got the weight of A but there is inherent in it some error of variation and you wanted to reduce that error to half its size, you might weigh it twice. You would get the true measurement plus the error each time.

If you averaged it, you would get W. A. plus some estimate of your error of variation.

Similarly, two more measurements might be utilized to get the true weight of B confounded with the other error.

But suppose you organized this weighing experiment in a method which chemical engineers would never do, really, and you put both objects on the same pan and found out what was the weight of the combined group. This would have an erro of course. And then the next weighing, assuming that B was heavier than A, and we put B on one pan, A on the other, and enough of a weight that we got the balance, we would in effect be getting the measure of the difference of A and B plus the error.

Here we have made two measurements, here four. And the claim is that you get the same precision with just half as much effort. How?

What is this equal to? This is equal to the weight of A plus the weight of B plus the error.

This is the weight of A minus the weight of B plus the error. If we average these observations we are in fact getting the weight of A plus the error. If we take the differ

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ence of these observations we are in fact getting the weight of B plus the error. QED.

DR. FLEISCHER: I think Dr. Strier has a question.

DR. STRIER: I was interested in the comments and activation energy made by Dr. Chreitzberg before. He gave a figure of 20 to 22.5 kilocalories per mole on the activation energies of charg retention for his silver oxide zinc cells in the wet stand state. I was wondering whether he has made an effort to try to correlate these acivation energies with, say, the energy of activation for gassing related to hydrogen evolution or stability of the silver oxide.

DR. CHREITZBERG: The answer is no, it doesn't look like the diffusion control experiment.

MR. PREUSSE: Preusse from Gulton Industries. I would like to ask a question of Mr. Sulkes.

In their design of their fractional experiment, in order to get comparisons you are going to have to compound some of the higher order interactions with your main effects.

Number one, who makes the decision which high interaction to compound with your main effect?

Number two, how are these decisions made prior to actually running the experiment. This is based on the assumption that the higher order interactions have no effect, or really insignificant effects in your experiment, for this must be known prior to running the experiment. I wonder whether

the statistician or engineer or statistician and engineer sit down and decide this prior to running the tests.

MR. SULKES: Since the engineer is the one who knows the system, there is always some previous knowledge available. On this basis he is able to say that certain things will just not affect it or will affect it in such a small manner that it is much less than the error of being cells which perhaps might run two to five percent.

This is a basic point.

If all of a sudden you should find extremely large error, and you go back and check your manufacturing processes and so on and find that there is no error in manufacturing, you can start hunting down these higher order interactions if they are extremely large. To this date in running many cells we haven't found any above the second order, which were really meaningful.

MR. BORNSTEIN: One comment.

It is a joint effort. In the particular case that Mr. Sulkes mentioned, I recall we visited Dr. Dalin at Yardney, and sat down and asked for the development of a list of the factors and a mutual influence table.

What did this best engineering knowledge indicate would be the possible areas to look for.

Again going back to my comment on errors, the errors exist any way. If you don't plan something to reduce them,

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you are going to get them no matter what happens.

The best engineering knowledge will still not help in this situation.

DR. FLEISCHER: Mr. Bowerman.

MR. BOWERMAN: Ed Bowerman, General Telephone Laboratories. Having worked for very many years with factorial designs in chemical work, I have learned some of the things that we run into that can cause some problems in using this very useful tool.

Ordinarily a factorial design, even a full factorial design, the statistician requires certain basic assumptions to be made that his system of causes will remain constant throughout the experiment.

This is an assumption which is very useful mathematically and which is very improbable engineering wise.

Secondly, and perhaps one of the worst things we run into, is that in the analysis of variance which is made on the factorial design, as soon as you make one Fahrenheit test for significance you run out of independent degrees of freedom. So you make a test which says I am going to test one variable, one factor, for significance, and from then on you can no longer make any statements about the validity of the probability that you have a significance. All of your other tests are correlated with the first one by the common denominator used in the multiple ratios.

There are ways of getting around this. You can break down your error terms into smaller compartments and make independent Fahrenheit tests. I would like to get right to the answer that we have found really works in this.

And we are not alone. And that is that in making analysis of fractional factorial designs, plant experiments in general, we have made the use of statistical quality control charts, small charts for each and every factor.

When probably used we build into the test a verification of the constant error situation. On top of that we yield a lot of bonuses from it. We can now explain it to a wider group of people with a greater degree of confidence that they will understand the explanation.

This technique we did not pioneer particularly. It first came to my attention from some work at Western Electric and it was used very extensively there.

As a matter of fact they have issued an in-plant manual which goes into all of the ordinary designs.

In the absence of that I would not use the ordinary analysis of variance except to set up a multiple regression for a factorial design in order to avoid some of the very troublesome assumptions which the simpler methods that unfortunately are usually taught first, run into.

DR. FLEISCHER: Dr. McCallum.

DR. MC CALLUM: McCallum, from Battelle Memorial

Institute. It is with some uncertainty that I feel compelled to take exception to the general feeling here that there is only one way to do research and that is with statistical analysis.

In fact I think someone has already stood up and said that is the only way.

The trouble with this approach is the very nature of it cannot lead to new laws and axioms. The very things that all of us were trained and brought up in. It concerns me that this whole group seems to think there is only one way to get at failure analysis. I think we ought to think about some new principles, some new laws, some new axioms by which we live.

The fact that I can't do it personally is beside the point, I think.

MR. BORNSTEIN: Or test them by statistics, please.

DR. MC CALLUM: Not necessarily. You can test them like Faradays Law. You don't test a law like that statistically. There is never an exception. There is never an error in Faradays Law. You people can study statistics from now until doomsday and never come up with another Faradays Law. It is against your rules.

MR. MAGISTRO: Magistro, Picatinny Arsenal. If we were dealing with a science, the comments of the previous

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speaker are exactly right. Most of what we deal with is an art. Make a thermal battery or a battery. It is an inexact science at best. Mostly it is an art. You are dealin with subjective judgments of people. How better to analyze somebody's judgment than to organize it in a body of plant experiment since it is an art.

There is no science in picking materials to put in a cell, for instance, ir picking the nominal tolerance or the right weight. This is what we are doing with these designs. We are trying to improve the basic design of the cell which is an art, not a science.

If it is a science, fine. But most of our problems -- and we spend $4 billion a year, according to a report I just read, in this industry -- is related to art, and not science. If we want to get more use of that four billion, this is what we should do. I have no argument about the science part of the discussion.

We are building thermal batteries for 10 or 15 years and it is still an art. We optimize the art. And to get repeatability, this is the only way you can do it if it is an art. I think the statement about science is correct. I have no argument with that. What we are doing here is fool with arts, and not science.

DR. FLEISCHER: I would have to take exception to these remarks.

(Laughter.)

MR. MAGISTRO: I am an engineer.

DR. FLEISCHER: The problem as I see it in the flow of this whole thing is that we are getting to a state of the art when we build a battery or when we test it. But the scientist is the fellow who is thinking about in these tests "we have a negative plate failure," which is probably due in the case of the lead battery to sulfation.

This means a lot of things to the scientist, the chemist, the electrochemist, physical chemist, structural chemist. The point is, he has to go back in his laboratory and find out how to produce these conditions and then to overcome them. So while we are building the batteries and we are not talking about all these things that are going on in the laboratory, we really have them in our mind.

It doesn't mean that it is not a science.

I think there were some other questions.

MR. BELOVE: Lou Belove, Sonotone Corporation. I think we should marry a few of the disciplines here. Amongst them the statistician and Dr. McCallum's suggestion, the art and the statistics here. You need the statistics possibly in setting up the experiment. But behind that there is a certain amount of science and art involved in the failure analysis. I think we expend too much time in setting up these boxes, and analyzing for success. I think that more time

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should be spent in analyzing for failure; the mode of failure If you set up boxes, factorials, to determine these modes, you may have accomplished more than proving how successful you have been.

I would like to add something to this. Mr. Cohn asked, as I recall that we recommend, possibly recommend other means for testing batteries in accelerated modes. Some of our work has indicated that one of the modes of failure, one of the means of testing, is overcharging.

It may very well be that more attention should be paid to testing batteries on the overcharge mode to determine how well the battery can take this type of manipulation.

As you go deeper into the overcharge you will notice that you are playing with temperature and pressure. I should neglect the other thing of course, oxygen. Actually we have found that the temperature factor enters into several of the pieces of data that have been mentioned here this morning, namely when you talk of overcharging, you are talking of temperature and its effect upon organic separator.

When you talk of cycling at a rapid rate, you may look at this as temperature also, since in cycling at this rapid rate you are forced, necessarily forced to charging at a high rate, discharging at a high rate. Both of which factors may lead to higher internal temperatures as well as pressures, as well of course as the formation of oxygen whic

certainly doesn't help the organic materials used as separators.

I would suggest that some further attention be paid to the possibility of using overcharging. Incidentally, as I see it in the satellite, a good deal of the destruction can be wrought by overcharging since as far as I can see you are essentially in an overcharge phase during the entire utilization of the battery. You take out five percent, 10 percent of your capacity, and you go back on charge. So for all intents and purposes you are in the overcharge phase. This is the phase that should be investigated.

DR. FLEISCHER: Tom Hennigan.

MR. HENNIGAN: I would like to add a little bit to Art Fleischer's statement about the art of building batteries and testing them. There is also an art to using them. I would like to base this on the fact that we have flown about seven satellites now, using silver cadmium batteries. None of these batteries have flown according to how they have been predicted. In other words the batteries have not been used as predicted.

We haven't seen any satellite of these seven go up and use something like 10 percent depth of discharge unless we charge it. It is all random cycling; anywhere from 10 to 100 percent depth of discharge. When I say a

hundred I mean down to about nine-tenths of a volt per cell.

It has gotten to be such a problem that we can't really test the battery any more like it is flown. We can only give it some 25 percent depth, recharging it for a while and do that for a couple of weeks. The battery goes through the integration tests with the satellite.

One way, we haven't gotten around it, you might call this a decelerated test, after the battery is flown, after the satellite is flown, then we start the battery test. We get the information from the project office and we run the battery almost exactly like it is run in the satellite

There hasn't been any two of the seven satellites we have flown yet that have any cycle regime that is similar.

DR. FLEISCHER: Dr. Lander.

DR. LANDER: Lander, Delco Remy. I will not continue the trend of thought for a moment. I would like to go back and partially answer one of the gentleman's questions about what is the mechanism of failure of silver zinc batteries on stand.

The activation energy which they have measured as being up around 20 to 22,000 calories is quite far removed from the activation energy for hydrogen evolution of the zinc plate in the system which is around two to three thousand calories. So it is not hydrogen evolution and we wouldn't expect it any way on the basis that you put more than one or

two percent mercuric oxide in the negative plate.

What I would think it is -- and again we need to measure the activation energy in order to demonstrate this -- is the decomposition of the divalent silver oxide plate. I would kind of guess if one measured deactivation energy for this you would find values which are around those which have been measured from the experimental cells.

I don't know, because nobody has stated it. However, this doesn't mean that the silver plate fails necessarily, and this would depend somewhat on construction. The oxygen is produced as a result of the evolution can of course in a sealed system go over and react with the zinc on the zinc plate.

If batteries were built according to the way we would build them, this would then subsequently limit the capacity at the zinc electrode.

MR. COHN: Cohn, NASA. You mentioned the decomposition of the silver oxide plates. What mechanism do you have in mind there?

DR. LANDER: I don't have any particular mechanism in mind. Let's just call it that and worry about it when we get some activation energy values.

DR. FLEISCHER: The next gentleman.

MR. BANES: Banes, Jet Propulsion Laboratory. I think some of the comments that Mr. Hennigan made add to

something here. We talked about art and we talked about science. I think he is talking, and I want to talk further, about which craft --

(Laughter.)

-- that is how you use these batteries. I think one of the problems here that nobody has talked about, is what kind of loads you are using in your tests, what kind of charges you are using, is it anywhere near the load that you are using in the spacecraft.

I have been utterly shocked by some of the things that happened to batteries when we put them in spacecraft as opposed to batteries when we test them on the bench with resistive loads.

At JPL we use mostly a switching type regulator. This type of load on a silver zinc battery is far more damagin to the battery than a resistive load.

I don't know how to accelerate the damage beyond what that does. But I know that all of the testing I have to do, I have to do at least half of it and I would hope all of it, all that I can't get enough equipment really to do all of it, but a lot of the testing has to be done with actual spacecraft equipment or at least very good simulation of this equipment.

Another area that I think we are missing, or that we have missed in the past and we are picking it up very

rapidly, is that in environmental testing of batteries, environmental tests are set up by systems type people who are electronics oriented, who say that the worst case is high temperature on discharge, or something of this nature sometimes.

And when we get into actual spacecraft use we are at such low temperatures we can't meet the voltage regulation systems.

We have to be very careful not only to please these people, which they have to be sometimes placated, even, but to run subsequent testing in areas, as Tom Hennigan says, as close to the more probable flight condition as you can possibly get.

We at JPL actually on our long-term flights, Mariner and some of the other tests, some of the other long-term type flights, run concurrent batteries in all vacuum temperature tests, simulating what is going on in the spacecraft at that time. Mainly because we cannot have enough telemetry to tell what is going on in the spacecraft, and if we know temperature, charge currents, load operations, then we can put a lot more instrumentation on this terrestrial battery.

Unfortunately we can't simulate some of the other environments such as zero-G. But we can simulate some of them. We feel that this is most important in determining the

actual operating characteristics of a battery in space.

DR. FLEISCHER: George?

MR. DALIN: I am no longer in the heat of battle. With respect to what was said as to how the silver electrode decomposes, let me point out that the silver electrode is thermonamically extremely unstable. I think the figures are something like the equilibrium vapor pressure of oxygen over the silver oxide, AgO, about 10 to the 11th power atmospheres, which is not what you would call a stable material.

However, when you put a silver, charged electrode in alkaline and look at it in proper illumination, you will see that there is a very fine particulate material coming off it. Whether this is solid silver oxide or not, I don't know. At any rate, Ag_2O is the solution. I would imagine that the rate of going into the solution, the quantity going into the solution, goes up rapidly with temperature. This goes through the entire separator, always a porous material, and begins to react with the cellophane, which is not stable. Consequently there are at least two or three different mechanisms by which the silver electrode can lose its capacity very rapidly as the temperature goes up. So that it may turn out to be that again these Arrhenius lines are crossing each other and you have to look for the envelope to decide which method is taking place at which temperature. So it is a

complex system. I would like to make a comment about the remark of testing by overcharge.

The gentleman in the back of the room, Mr. Hennigan, worked out a procedure whereby you avoid a substantial overcharge of cells in a battery in space. Consequently this stands a good chance of eliminating the problem of overcharge and leaves us in a position where testing by overcharge is merely testing the effects of overcharge. I hope it will prove to be less useful.

That is a peculiar way of speaking about a test. But I hope that the effects of overcharge will decrease because obviously there are very deleterious to a variety of types of cells, particularly when they are sealed.

DR. FLEISCHER: Dr. Shair.

DR. SHAIR: Bob Shair, of Gulton: I think possibly that with respect to the nickel cadmium system we don't want to get to the point where we seem to be implying that overcharge is a harmful phenomena. We, for instance, have found that a lot of the possible, we can put it, leniencies, that are allowed in electronic circuitry can be picked up by the ability of a battery to cope with an overcharge mechanism. And also fast changes in temperature, which possibly are not compensated fast enough, or for that matter may not be compensated for at all, can be absorbed by a battery that does have the capability to absorb some overcharge.

The nickel cadmium batteries do have this capability.

We are finding, for instance, that if you let a nickel cadmium battery sit, it has a certain self-discharge rate. Once the battery is fully charged, though, if you impose a very, very low rate of overcharge on that battery, even as low as about the C/100 rate, you seem to have imposed a valve effect on the self-discharge process. So that you can stop it, the oxygen pressure inside the cell can remain very low, and the heating effects are very low.

There were a series of tests which were run at the Royal Aircraft establishment in England which indicated that you can maintain a battery which would normally run down in six months on self-discharge, you can maintain it at something like a C/150 rate almost indefinitely.

So I think we shouldn't imply that overcharges are necessarily harmful to batteries. They have some usefulness too, if you can build it into the system.

DR. FLEISCHER: Maybe Dr. Willihnganz would like to say a few words at this point about the overcharge test for lead acid batteries.

DR. WILLIHNGANZ: No, but I would like to say something else with regard to Bob Shair's remarks.

It seems to me the direction we are going is an accelerated life test on some of these batteries, in which you

have, say, 50 different kinds of tests to evaluate 50 different kinds of deteriorations that the battery can undergo. It looks to me as though doing it with a single test at this point doesn't sound very probable.

This question of voltage intrigues me. John Landers is the man who should be making this speech.

If you plot the battery corrosion rate of an alloy, against voltage, and make this the equilibrium voltage of lead dioxide, and on this axis make the log corrosion rate, you get yourself a curve that goes like this. This merely justifies what Bob Shair just said, which is that there is a certain overcharge which is quite important to give you a minimum corrosion rate on a lead acid battery. How this affects nickel oxide and silver oxide batteries, I don't know.

On lead acid, this is down around two ten thousandths of an inch per year at this minimum area here.

DR. FLEISCHER: There is little of the science we forgot about when we talk about building and testing batteries. Mr. Sulkes.

MR. SULKES: This same mechanism you might say holds for silver zinc. When you float these batteries you are actually, you might say, overcharging them at a C/1,000, C/2,000 rate. The constant overcharge actually extends the life by reducing separator degradation and maintains the capa-

city.

In many cases it has been found after a battery has been floated for several years that the capacity is better than it was when it was new. This also applies to silver zinc, although the rates may be a little lower.

DR. FLEISCHER: Nobody has gotten up to make a comment about nickel cadmium batteries so I will say that most of us heard Dr. Turner and his associates tell about the effect of carbonate in the nickel cadmium battery, where carbonate actually accelerates the corrosion of the nickel grid.

This is something that you see in space batteries that come off cycle life tests, the carbonate being derived mainly from the degradation of the separator.

Are there any more comments?

MR. JASINSKI: Jasinski, Tyco Labs. I have a specific question on temperature regarding the high drain rate of silver zinc batteries. At about one and a half amperes per square inch, what is the internal temperature of the system and what sort of decomposition of the silver plate does this bring about?

DR. FLEISCHER: To whom are you directing that?

MR. JASINSKI: To the representative from ESB.

DR. CHREITZBERG: In this type of discharge the temperature will rise almost linearly if you are doing it at

a constant current, from room temperature to about 180 degrees Fahrenheit. This is done in 15 minutes. Temperature maximum will not be reached until after the discharge is complete. This is in the case of a cell. In the case of a battery it would be hotter, I am sure. The question is what sort of decomposition can you expect. I believe Mr. Bowers can best answer that.

MR. BOWERS: Bowers, NOL. Let's take a specific example of a torpedo battery that has 60 cells, and the cells are, say, 75 ampere hour capacity. During a 10 to 12 minute discharge, which is in the order of current density of one ampere per square inch to about one and a quarter, the temperature will rise during the 12 minutes to about 160 degrees, and then it continues to rise -- and I think the reason for this is because of lack of diffusion of the temperature to the thermocouples -- to about 180 degrees.

If we discharge that same battery at say a 40 minute rate, or not the same battery but one as near alike it as we can get, we don't see any difference in capacity.

If we collect the gases that come off of this battery, we find some hydrogen and some small amount of oxygen, but most of the gases are in the form of water.

This indicates also that down in the electrode area that our temperatures are getting up above 180 degrees towards the end of discharge.

DR. FLEISCHER: Are there any further comments or questions?

If not, we will adjourn the morning meeting and return promptly at 1:00 o'clock to start the afternoon session.

I want to thank all the speakers and all those who participated in the discussion.

(Whereupon, at 12:02 o'clock p.m., the meeting was adjourned, to reconvene at 1:00 o'clock p.m., of the same day.)

end jlw

A F T E R N O O N S E S S I O N

MR. SHAIR: Gentlemen, let's get started.

Welcome to the second session this afternoon. Before we do get going, may I please remind all of those here to please sign the sheet indicating that you are in attendance and that you would like to get a copy of the proceedings. Then also will those who do have a contribution for the proceedings please make sure that you get the glossy prints in so that they can be duplicated for the proceedings.

I think we are all set to go.

This afternoon session, failure analysis of silver zinc cells, will cover the subject quite differently than this morning, where instead of doing things rapidly we are doing them in the type of cycle that at one time was considered logical cycles that these batteries were subjected to in space.

Many of these programs do take a considerable period of time to be done, and there is a vast amount of information. So the best statistical techniques and mathematical techniques are being applied to these programs to get useful information for both the user and for the manufacturer.

Just before we start I would like to mention that a couple of weeks ago there was a meeting in Brighton, England, a battery symposium. I notice several of you here did attend it. Karl Preusse and I did attend it also, in

which it became evident that in Europe there is a growing interest in the nickel-cadmium cell. There were a lot of papers on lead acid. There is a growing interest in the nickel-cadmium cell over there.

We ran into a lot of people who are interested in batteries and are very much interested in the volume of work which is coming out of the States on battery technology for space and terrestrial applications.

They asked me do we spend all of our time working on batteries. I said we did not spend all of our time working on batteries. We do other things.

They said while you're over here you ought to take a little bit of time and you ought to go around and see some of the beautiful art works that exist in Europe. And you really ought to enjoy yourself because we have art treasures here that probably you cannot see in the United States.

The stage was set this morning, that this was partly an art as well as a science. So I think that during the course of the afternoon we have about ten speakers, and I want to show you a few examples of art that I did, well, possibly pick up in Europe.

Maybe I didn't. The first one actually is an American portrait which is hanging in the Louvre in Paris. May I see the first one by James Whistler? I think maybe we need the lights. (Slide)

Our first speaker is Dr. John Lander who is very well known to us, from the Delco Remy Division of General Motors, who will talk on failure analysis of silver zinc cells.

Dr. Lander.

FAILURE ANALYSIS OF SILVER ZINC CELLS

DR. LANDER: When you're talking about silver zinc cells you don't have to worry about it.

(Laughter)

As George said this morning, they have a plethora of failure modes. The type of work that we have been doing has been directed at trying to increase the cycle life of silver zinc cells in a two-hour cycle which consists of 35 minutes of discharge and the balance of the time on charge. We have been using constant potential source for charge.

In addition we have been working in 25 and 40 depth of discharge largely during our past programs. In addition to this we had submitted some cells to the Inland Testing Division of Cook Electric for a different Air Force program on which a variety of continuous cycles were involved.

During the course of our work with the Air Force and in failure examination of the cells that were tested at Inland Testing, we have looked at something over, some place between 2500 and 3,000 cells.

And I still wouldn't say that I really know why some of these failed. I mean what are the remote causes of failure. We can tell how they failed pretty easily.

Generally speaking it is a short circuit or it is a loss of zinc plate capacity one way or another.

What I am going to do today is to describe failure analysis procedures and then also make a few comments and show you a little bit of data and some interesting things that we found out.

What do we do in a failure analysis procedure? First of all we stop the cycling at the end of a regular charge. We allow it to stand for a day or so, then measure the open circuit voltage. This is to determine whether the cell failed by a short circuit or not. If it has a short that is bad enough to drop the voltage down appreciably in a day or two, that is a sufficient short circuit to have contributed to a loss of capacity during the cycling.

I think we distinguish between degree of short-circuiting here because you can cycle a battery and these continuous tests for quite a long time in a short-circuited condition if the short is not bad enough.

Also we take a third electrode reading at the end of the last discharge which is given on the automatic cycle if we want to know what plate failed.

This is provided enough short circuits are involved.

We have consistently found out that in our design it is a zinc point which is failing, so we rarely bother with it anymore.

After the day or two stands, if desired, and it has been done on occasion, and it was done as a matter of course on our failure examinations with Inland Testing, on testing cells, the capacity discharge at the same rate which is given originally to the cell to establish cell capacity may be given. This is for the purpose of measuring the capacity of loss against the original capacity -- capacity retention. This is done if it is not short-circuited.

Another thing may also be done at this point, and that is after the capacity discharge, it may be given another charge at the formation rate, followed by a second capacity discharge, and this measures any permanent loss in capacity. What we are saying here is that on an automatic cycle if you have charging inefficiency entering in, then this can result in the cells running downhill simply because you are converting some of the zinc to the oxide and it won't put up with that very long. Giving the formation charge followed by discharge will measure for you the permanent capacity loss.

There is another way to do this and this is I think a preferred technique. It is to put an integrator

in the circuit and have it in there during the full life of the cell or battery of cells which you are measuring. What this will do for you is give you the amount of accumulated overcharge that the cell or battery receives as cycle life progresses. All you have to do is take a reading.

It also requires something else, however, and that is that you have some idea concerning how much overcharge you have to give the cell in order to maintain its capacity as life goes on. It doesn't really require that. It is an aid to failure mechanism which tells you whether you are running downhill because you are not giving overcharge.

If you were designing your tests to keep the charge up, then you need to know how much overcharge has to be put in. This is particularly true if you are talking about a sealed cell which has some peculiarities in this regard and which we discussed in our final report on the Air Force contract which is about to issue.

I prefer the integrator scheme for looking at cells over the progressive cycles that may be given it to get the kind of data I just mentioned because in this case you can leave the battery essentially in the condition it was in at the end of the last (unintelligible) cycle.

Also during the last charge or perhaps following, at some point maybe during the last discharge or after the

last charge, you can give it a high rate pulse.

What you do using this information, you can establish what the resistance of the, the internal resistance of the cell is. I am speaking about resistance in a kind of loose fashion here because all of us electrochemists know that this kind of a measurement will give you the combination of voltage losses which contribute to the voltage that you read out on this pulse.

The next thing we do is to open the cell and drain out the electrolyte and measure it for volume. We call this the excess electrolyte. We do it because on occasion when you are operating with cells and you are trying to operate on a minimum quantity or cycle life, testing the minimum amount of electrolyte, occasionally we run into cells that appear to dry up and you can't get any excess electrolyte out of them.

Also this sample will serve for analyzing for the KOH concentration, carbonate ion concentration, if you want to do it, and any foreign ion concentration that might be in there.

Then we extract the whole element from the cell and examine it for broken lead wires to the terminal, or corrosion of lead wires to the terminal. And we look at the terminal connection. This is a Saturn connection. We look at it to see whether or not any of the wires from

the plates might be coming loose.

At this point, while the element is whole, we examine it visually for zinc drain around the tops and sides and the bottoms of the element stack up. It is an indicator of the separator's ability to retain zinc.

The zinc around the edge of the cell, you're going to have it if you don't wrap your zinc plates of course. But we wrap ours and consequently we make this observation.

Then the plates are carefully separated with their separator wrappings and the separator removed from each plate layer by layer. During this stripping of the separator away from the plate we visually examine the layers for the presence of metallic zinc in the separator or between the layers. And this is for the purpose of seeing how far the metallic zinc might have moved toward the positive plate.

Frequently -- this is very obvious -- you can pull cells apart and see sheets of zinc between separator layers, nice, shiny metallic zinc. And again if separator deterioration has proceeded far enough, the dendrites of zinc that are growing through the positive plates will knit the separator layers together and it is hard to separate them.

We examine the separators for holes, splits, and general deterioration. The samples may be taken

layer by layer and analyzed for silver content and measure the resistance to give you an idea -- the resistance measurement is somewhat a measurement of the degradation of the separator material. If it is cellulosic, anyway.

And the resistance decreases as (unintelligible) goes on, due to the degradation. That is resistance in the KOH electrolyte.

We look at the positive plate and examine it visually for color. This will give you a pretty good idea actually of the state of the charge. And the presence of zinc oxide. Zinc oxide can appear as a pinkish cast over the surface of the plate, or it can appear as a loosely rubbed off white deposit. You can analyze chemically for it if you want to. But as far as we know there is no deleterious effect of the zinc on the silver plate per se.

What it is an indication of is whether or not the diffusion of zinc away from the negative plate has reached the silver electrode.

You can take a sample of the silver plate and x-ray it after you wash it and dry it. This will give you an idea of the distribution of the active material among divalent silver oxide, monovalent silver oxide, and silver. If you want to, you can take the individual platesafter removal and discharge them in a beaker (unintelligible). This will tell you what their capacity

is.

In our experience the positive plate has never failed per se. That is, any ultimate loss in capacity in cells is not due to the positive plate. We know it loses material, and we have a pretty good idea of the rate at which it loses it. But it never loses it fast enough to limit control (unintelligible).

You can weigh the positive plate to establish the actual material loss. This is preferably in the discharge condition.

The negative plate is really the interesting one. This is the one which we look at very carefully, that is after we are done looking at the separator carefully. We examine it visually for what Dr. Dalin calls shape change, and also for the degree of oxidation. Actually after looking at a lot of these you can get a pretty good idea what the state of oxidation of this plate is because the zinc appears as a greyish mass and the oxide is always white. This is true unless you have a very finely divided mixture of the oxides and the zinc.

Usually you can get a pretty good idea of what the distribution of charged zinc is on that plate.

Another treatment that we have accorded these is to charge them up completely in a beaker and low-gravity electrolyte so you don't dissolve out much zinc

oxide. Then wash them and dry them and get weight loss measurements -- make weight loss measurements.

You can do the same thing with the zinc plate in any state of oxidation actually. In any case, some oxidation is bound to proceed on the zinc during this process.

The main thing is to be careful not to wash the zinc oxide out, which will occur very easily.

Then you can take samples of the material for analysis for silver, which would have come over from the positive plate, and any other foreign items. This can be done readily, of course, with the spectrograph, qualitatively, and if you want to look at it, quantitatively. You can go into any other applicable analytical techniques.

We have also checked the grid for mercury contaminant. This is a silver grid, at least the one we use is. One of the things we found out is that as life progresses, the silver accumulates in the grid. It will start with substantially zero mercury content. Then, as life goes on, mercury will build up, especially in the bare area of the grid. And this has an enbrittling effect on it which, so far as I know, has no deleterious action other than one would expect. If a cell were undergoing considerable vibration or something like that, it might tend to break the grid up.

It is highly recommended that during this

examination or at some point in the examination that you take a zinc plate and pot it up in epoxy resin or whatever you want to use and section it for micrographic examination. We like to do this to get an idea of the state of agglomeration of the zinc.

Another thing that we would like to do, and would do if we had a good, reliable measuring technique for doing it, would be to measure the surface area, that is the electrochemically active surface area.

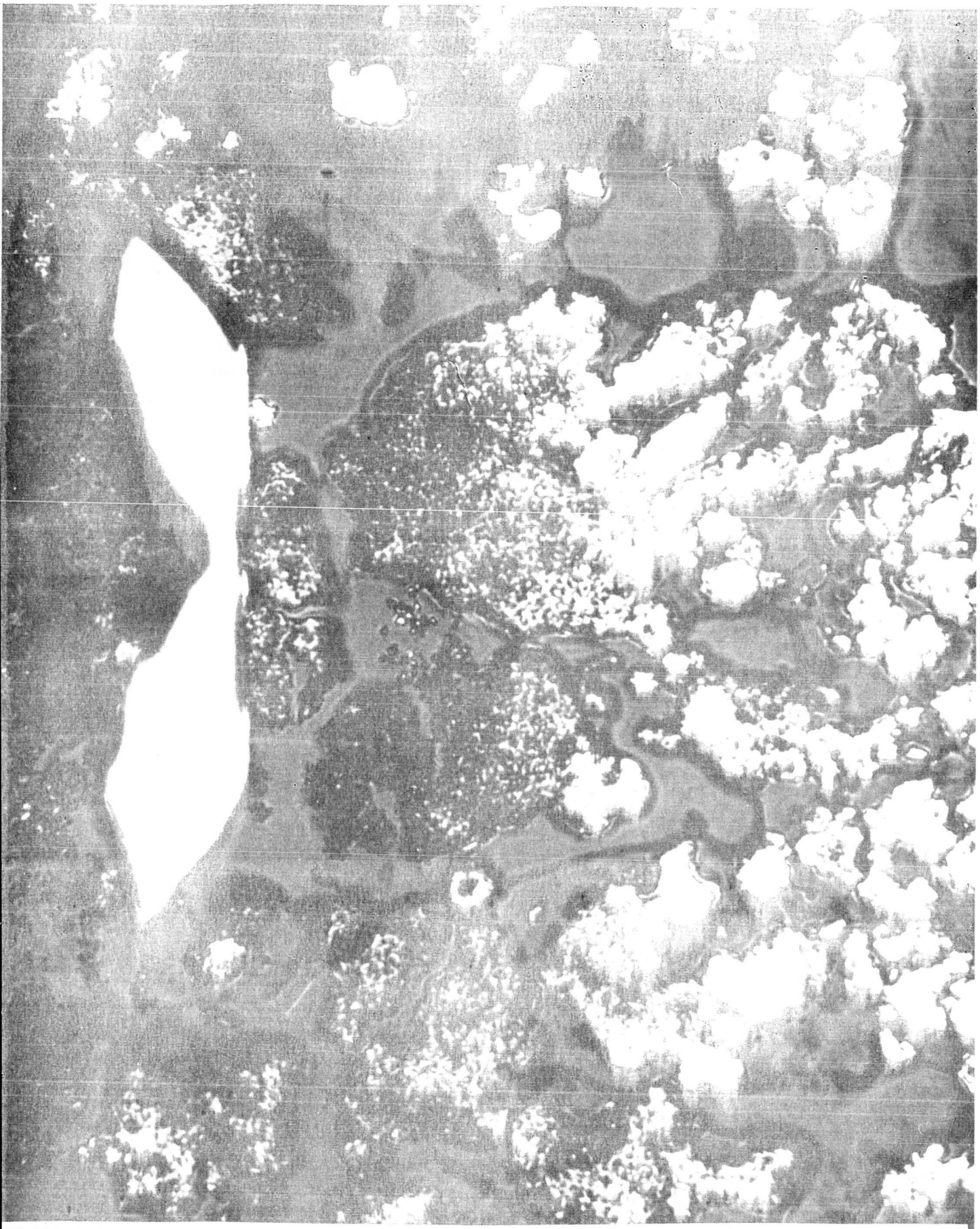
I would make some remarks about gas pressure in sealed cells if I had time, but I don't. If anybody wants to discuss it, we can talk about it later.

I have some photographs I had hoped to be able to project, but the projector won't do it. I will hold them up and the people in the front row can get a look at them. Then if anybody else would like to examine them later I will be pleased to show them to you.

This is a photomicrograph of a zinc plate which is new, that is formed up and new. This plate contains 2 per cent polyvynil alcohol.

This is the silver grid. You can see that the active material is in good contact with the grid wire.

Here is a plate which contains polyvynil alcohol which has undergone 231 40 per cent depth of discharge cycles. This 40 per cent depth of discharge does not



Photomicrograph of a Formed, Uncycled Plate (2% PVA)

Photomicrograph of a Plate Containing 2% PVA (231 Cycles)

refer to the capacity of the zinc element in there. It refers to the capacity of the cell. You can see that there is a good deal -- these are to the same magnification -- there has been a good deal of reduction in thickness of the active material there, either because of loss of active material or because of state of agglomeration. And it is quite evident that there is a good deal of agglomeration of that metallic zinc.

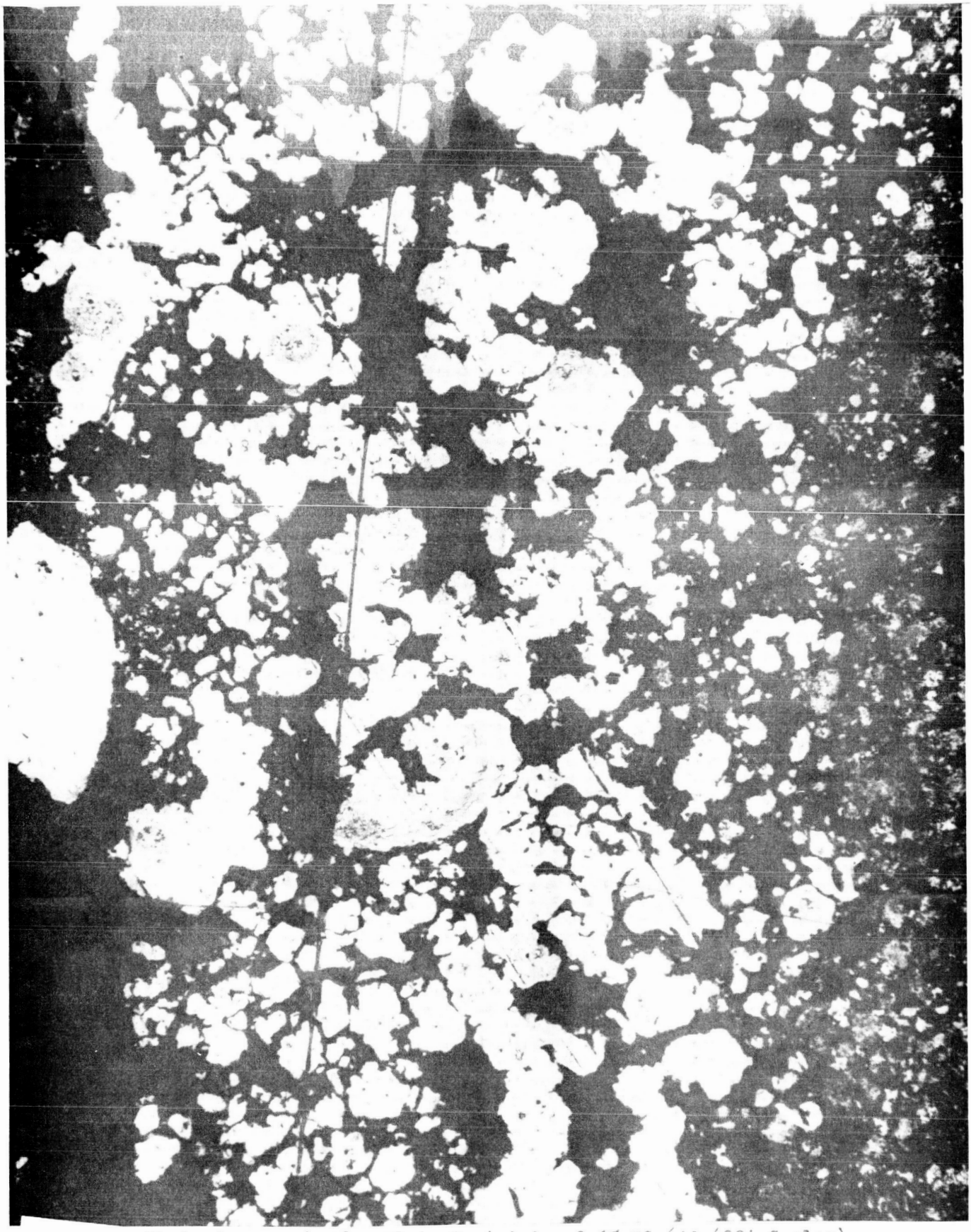
This is a picture of a plate which contains or contained at the start anyway, .01 per cent of amalfagene(?), a surfactant, BC 610. We can compare that with the plate containing the 2 per cent PVA. To my mind there is a difference in the degree of subdivision of the agglomerated zinc.

This is a picture of another plate containing amalfagene which has undergone 324 cycles and this contains 1/10th of a per cent. There is a clear difference in the degree of agglomeration.

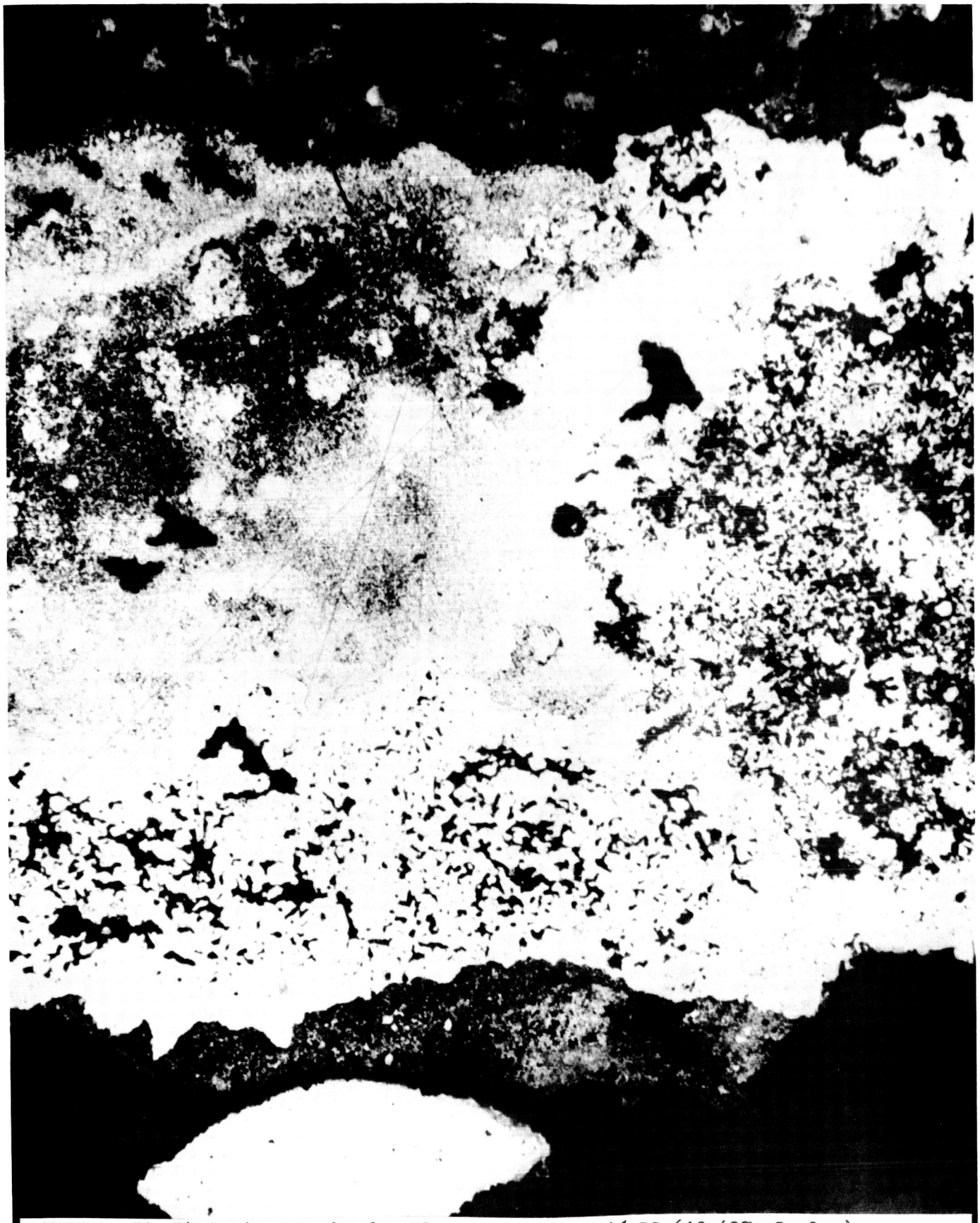
This is a picture of a plate which has gone 372 cycles, with 1 per cent BC 610. This is, I believe, characteristic of what a healthy zinc plate really looks like.

The zinc in here is very finely divided. It looks more nearly like a new plate than a new plate itself, if you want to put it that way.

Photomicrograph of a Plate Containing 0.01% BC-610 (240 Cycles)



Photomicrograph of a Plate Containing 0.1% BC-610 (324 Cycles)



Photomicrograph of a Plate Containing 1% BC-610 (372 Cycles)

I have another photograph. This shows the plate which was made originally with 122 zinc dust. I forget what screen it passes. There has been a reduction in thickness of about that much -- from that much to what you see (indicating).

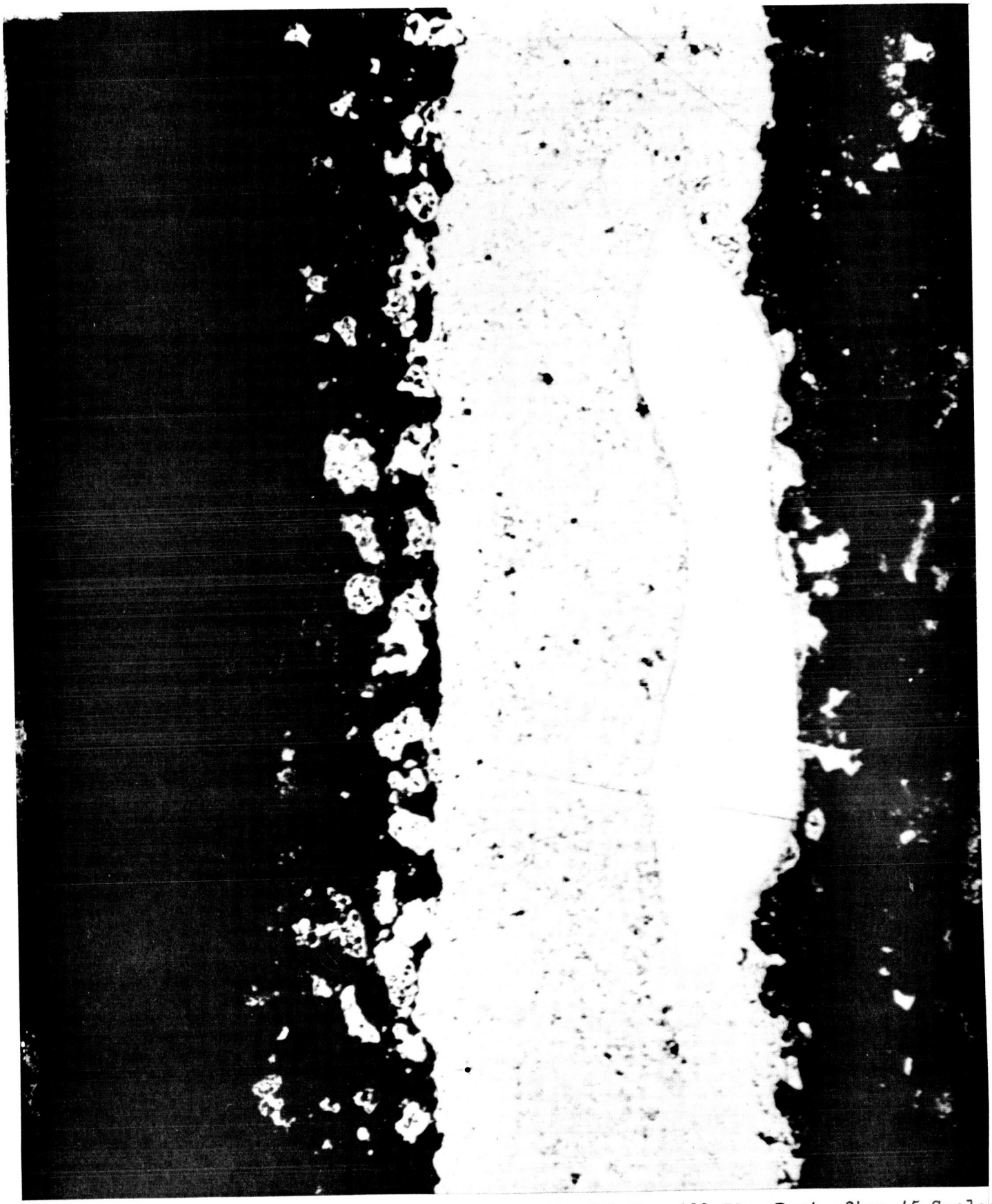
This stuff, while I don't know whether any agglomeration has gone on, it was a dense plate to start with and it did not give very good capacity.

That is the sort of information that you can find out by looking at the potted zinc plate after life testing, with a metalograph or with a microscope. It gives you some idea of the available surface area -- active surface area.

As a matter of interest I would like to show you another piece of information. Again I am sorry I can't project it on the screen. Again you may look at them later if you so desire.

This is a result of a quality assurance test that we ran on our last Air Force contract. What it shows is a family of curves of 28 to 30 cells which have been tested at the same 40 per cent of discharge. They are supposed to be made the same way.

We introduced one variation into this test. We had an auxiliary electrode in there which was supposed to use up hydrogen. On that account we varied the end of



Photomicrograph of a Zinc Plate Made with Nr. 122 Zinc Dust after 45 Cycles

Figure 1 - Quality Assurance Test: Cycle Life of Cells with Auxiliary Electrodes

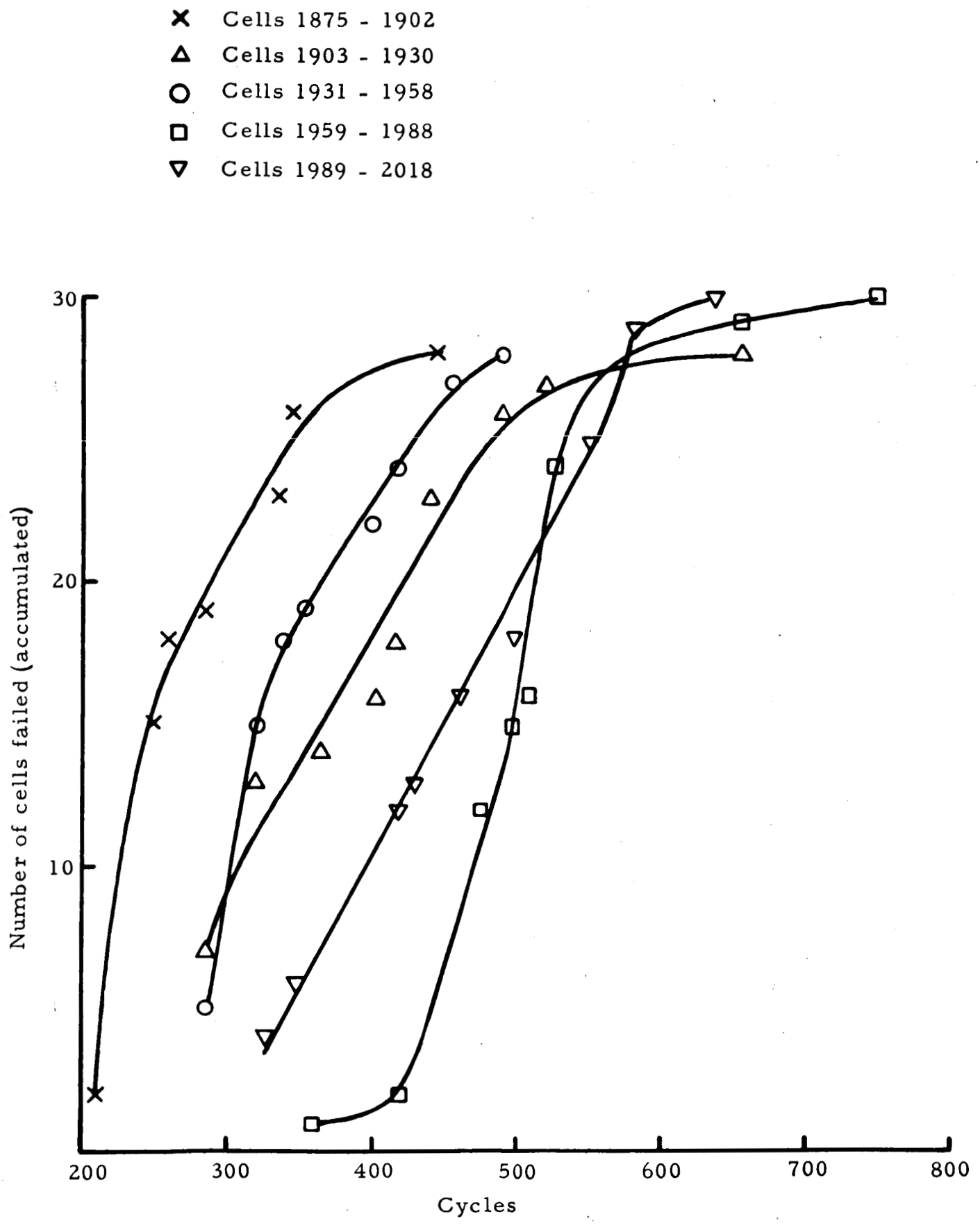
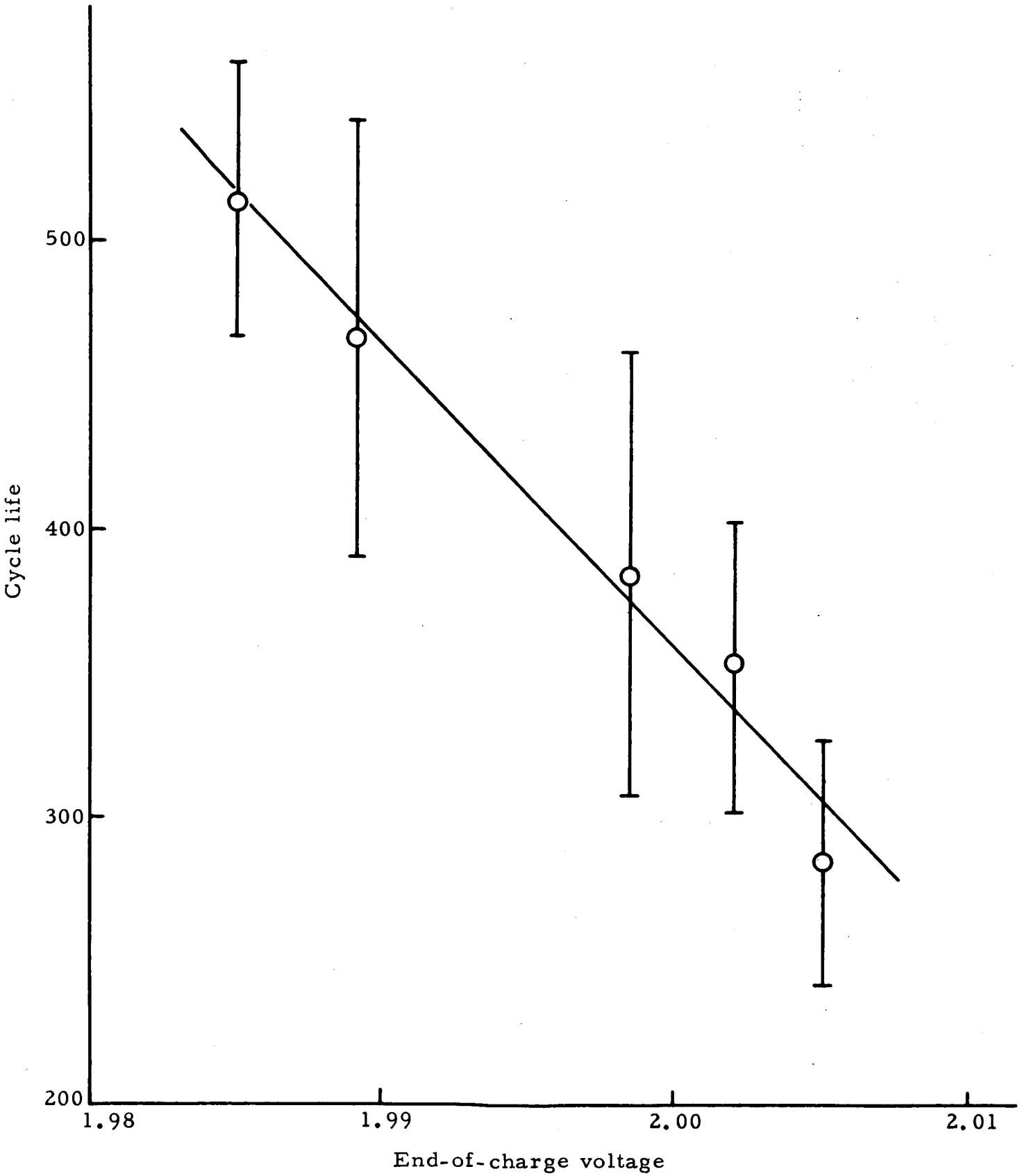


Figure 2 - Cycle Life as a Function of End-of-Charge Voltage



charge, and this was a constant -- modified constant type current charge -- we varied the end of charge voltage to see how good that auxiliary electrode would be for taking up gas in the system, and we get that family of curves describing the life.

This is a cumulative failure plotted against cycles.

If you take the average for each of those groups, the average cycle life, and plot it against tons of charge voltage, this is the kind of voltage you get.

It goes from about 515 down to about 280.

There is some more discussion we could have concerning this, but we don't have time.

MR. SHAIR: Thank you very much, John. We are just a little bit behind on time, so we will save the discussion until the discussion period.

The next speaker is Don Mains, from the Naval Ammunition Depot in Crane, Indiana, who has given papers at previous meetings describing the test programs going on out there. The topic of his paper today is "Visual Failure Analysis of Nickel-Cadmium Cells."

VISUAL FAILURE ANALYSIS OF NICKEL-CADMIUM CELLS

MR. MAINS: There is very useful information which can be obtained from cell failure. In our program a cell is considered to be a failure after the terminal voltage drops below .5 volts any time during the

discharge-charge cycle. When a cell appears to be failing, a recorded cycle is made so that it can be put into the permanent pack record. After the recording, the cycling is stopped at the end of the discharge, the cell is removed, and the pack is returned to cycling.

The manufacturer is notified when several cell failures have occurred so that a representative may come in if he so desires to witness the cell failure analysis.

The analysis consists of the following tests and observations: A short test, weight, external appearance, and internal appearance.

The short test consists of a C/5 charge rate for one minute, and 24 hours open circuit stand.

At the end of the 24-hour period the open circuit voltage will indicate whether the cell is shorted or there is just a partial short. If there is no decrease in the voltage, then the cell failure was probably due to some other cause.

A visual inspection is also made of the exterior of the cell case, noting any leakage or deposits such as those shown in Slide 1.

(Slide)

MR. SHAIR: What does the first one show?

MR. MAINS: The first slide shows a cell deposit around the seal. This is a ceramic-to-metal seal.

(Slide)

The next slide shows the leakage around the weld between the top of the cell and the sides. This again is a cylindrical cell.

This is due to a poor weld of this particular cell.

Also the external appearance is noted for any deformations of the case, especially due to concave sided or high-pressure voltages which are shown in the next slide.

(Slide)

This is sideways, but you can see what the bulge looks like here.

(Slide)

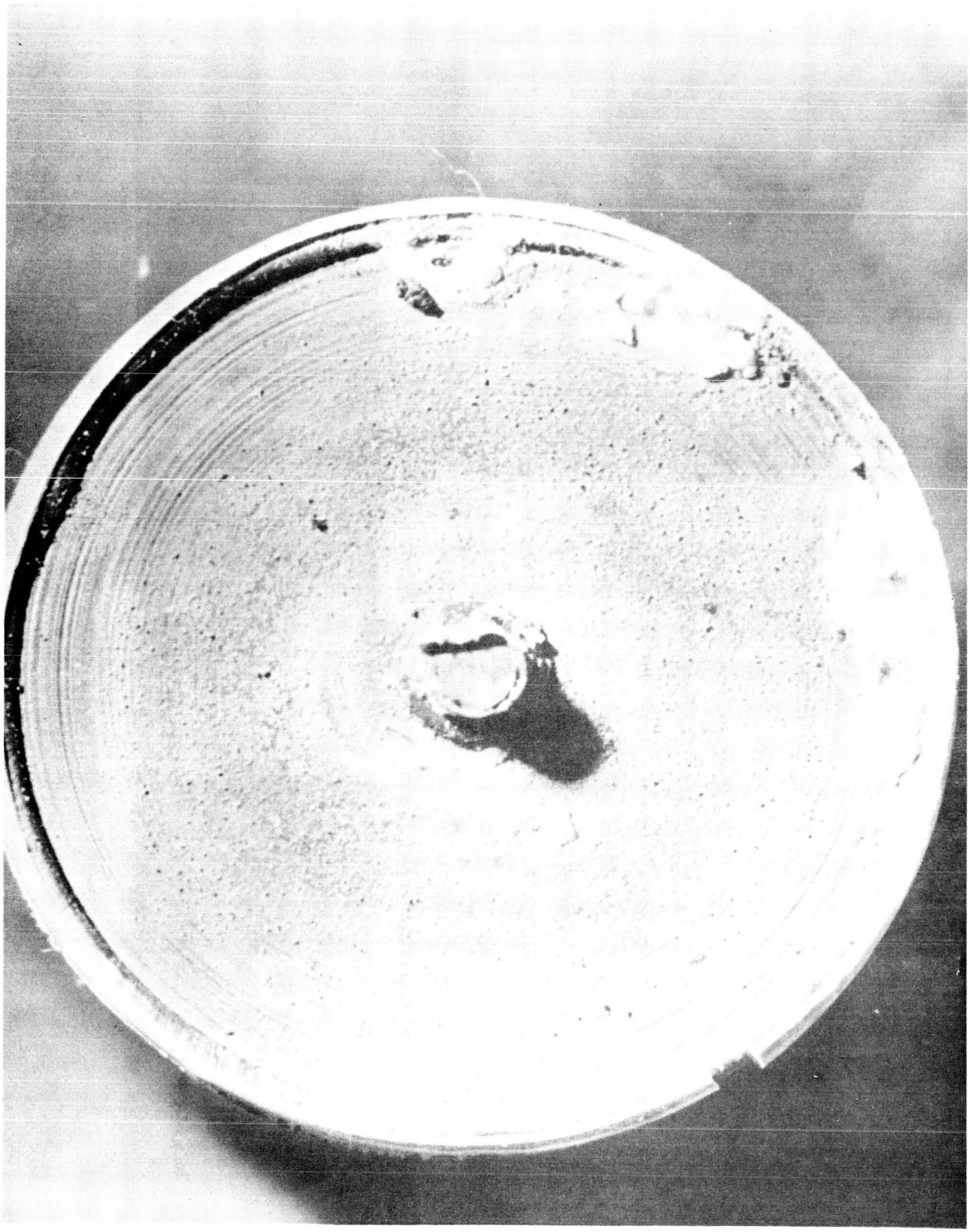
Next, the cell is opened and a visual inspection is made of the tabs, plates and separators. A weak tab -- weak tab weld -- is very easily discovered. Normally the tab area is very weak and can be separated with a very small amount of pressure.

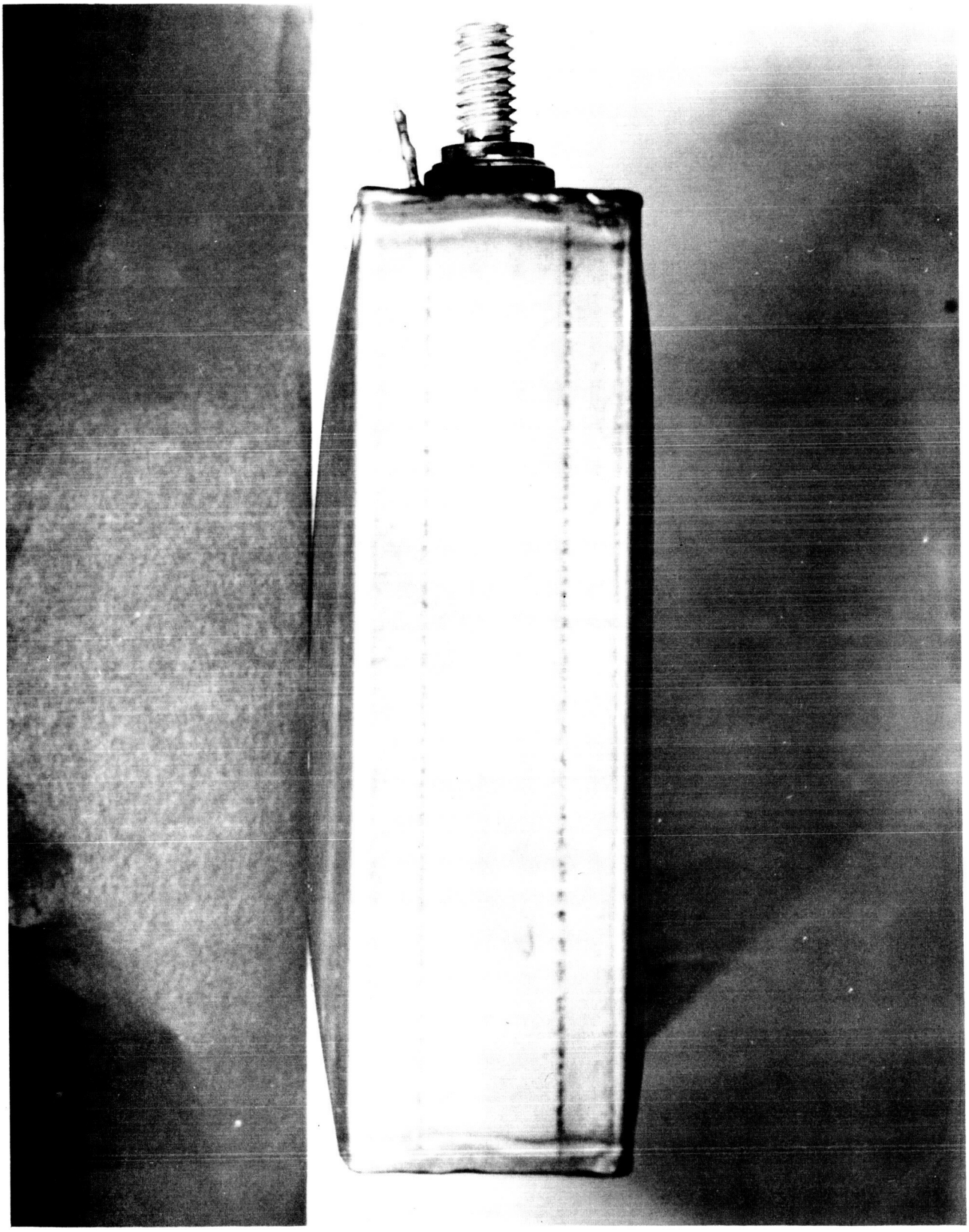
The next slide shows a tab weld to terminal area, Slide No. 4.

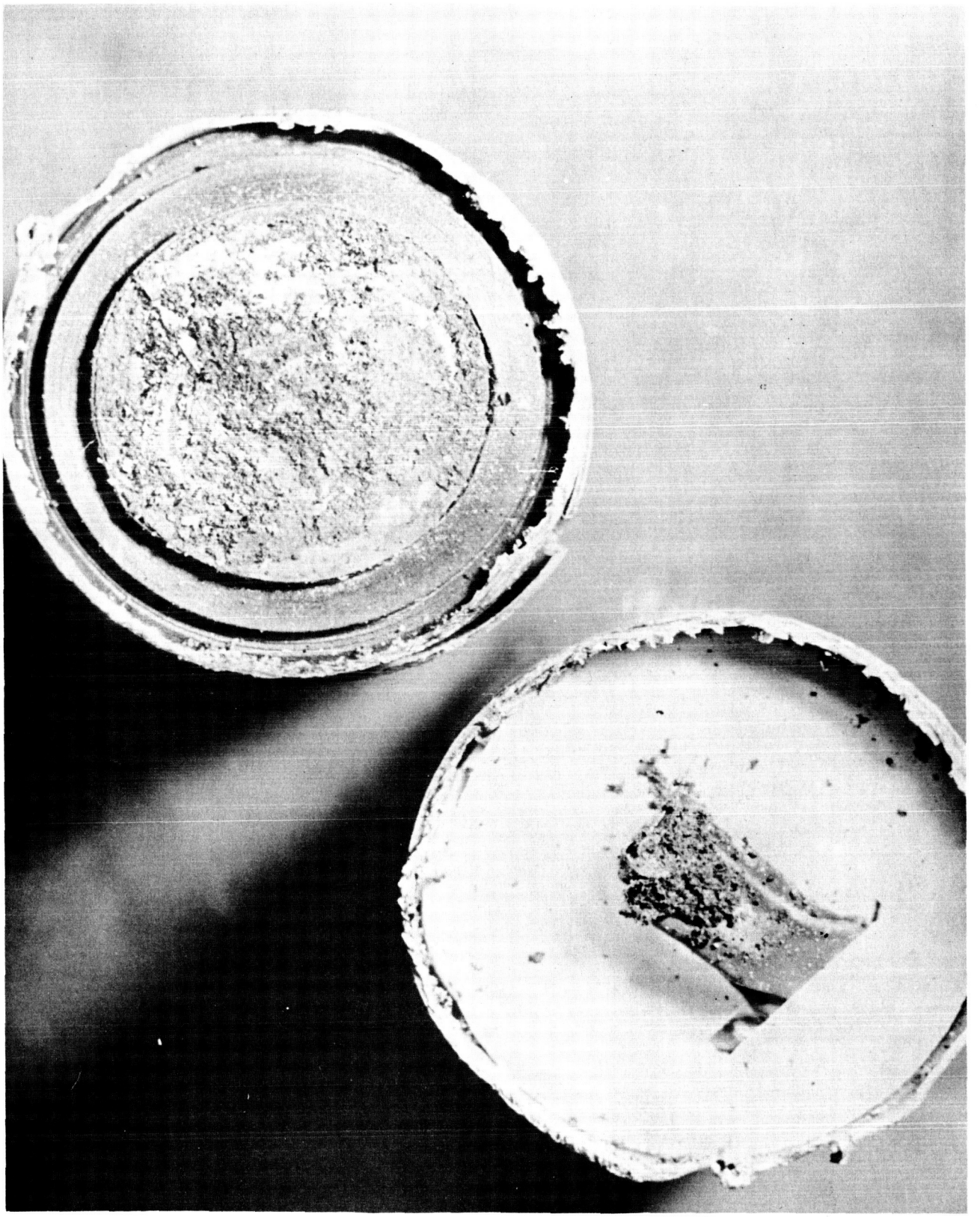
(Slide)

In this one the tabs were to be welded between the two parallel bars. The tabs are pulled out without leaving any welded material whatsoever, the tab was so weak.

Also there is deterioration which takes place in







the tab material itself. The next slide shows deterioration which looks like a burning or some kind of deterioration of the nickel itself.

(Slide)

In the next slide we see where this deterioration or corrosion has started to take place. You can see it on the tab-to-terminal weld area.

(Slide)

The next slide is a side view of this. And the following slide shows a cross-section of this same tab.

(Slide)

This deterioration starts on one side, it appears, and progresses across the total tab area.

This shows the cross-section. The positive tab is on your right.

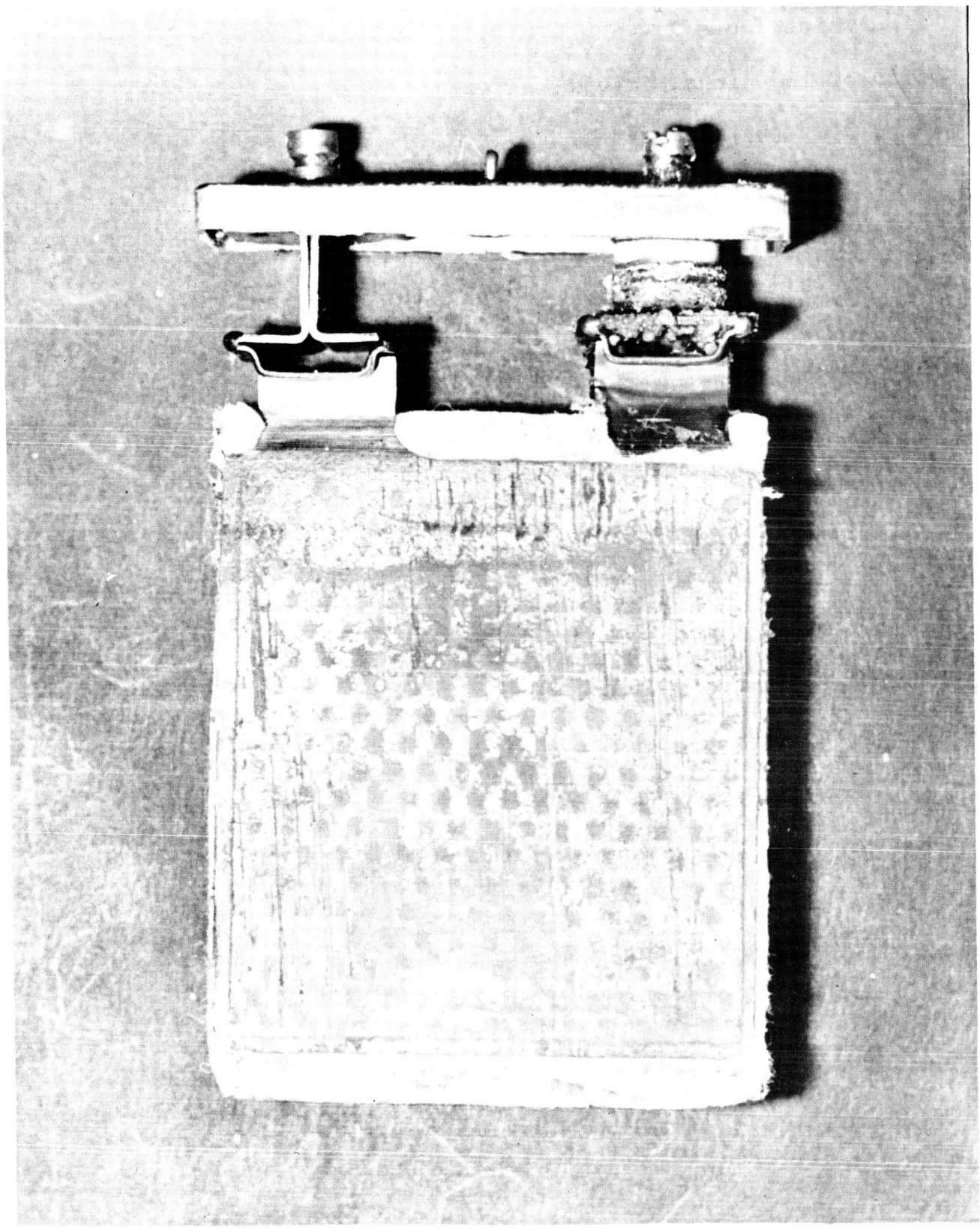
The next slide also shows a burning of the positive tab where the insulation was burned off due to the high currents in the tab itself.

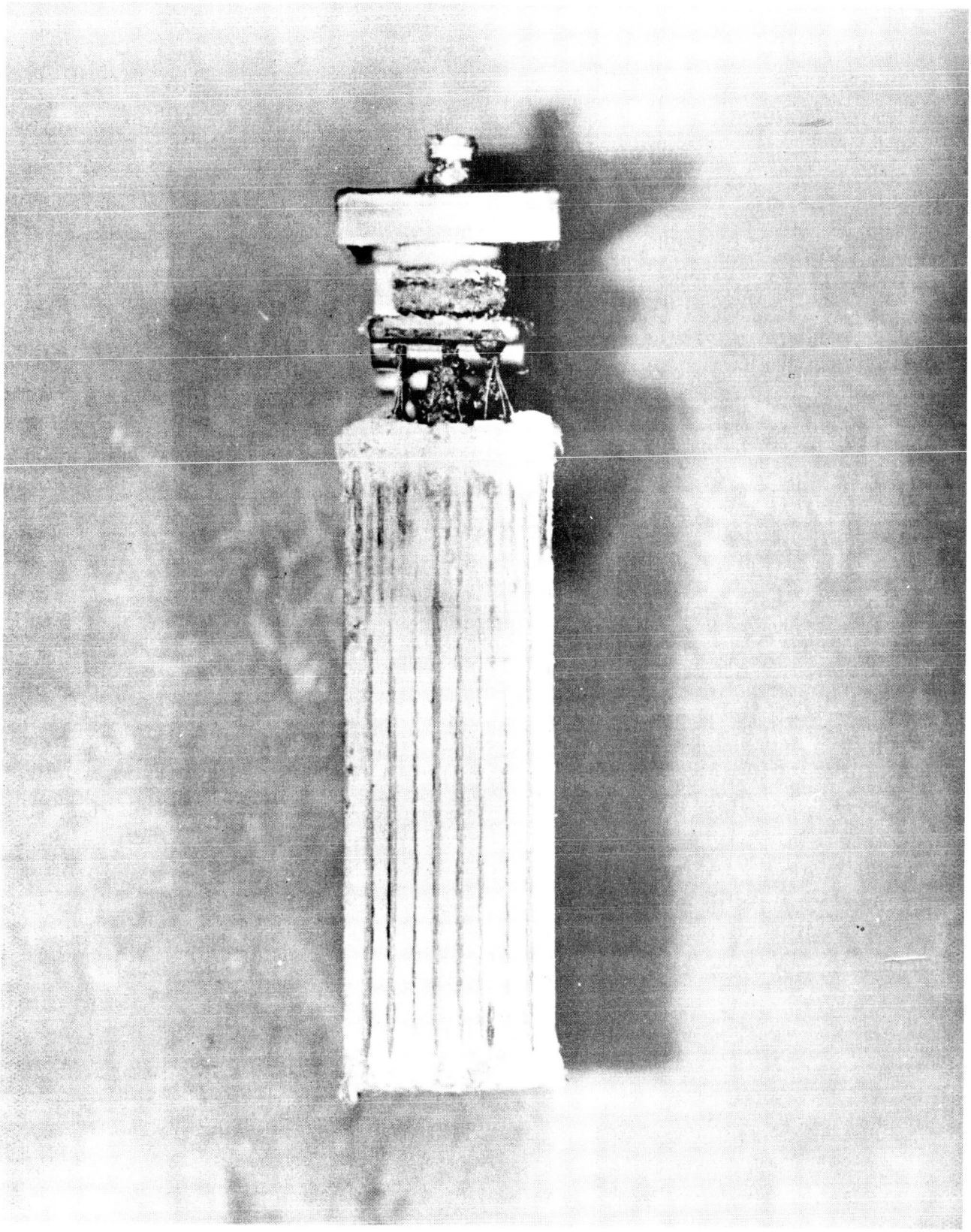
(Slide)

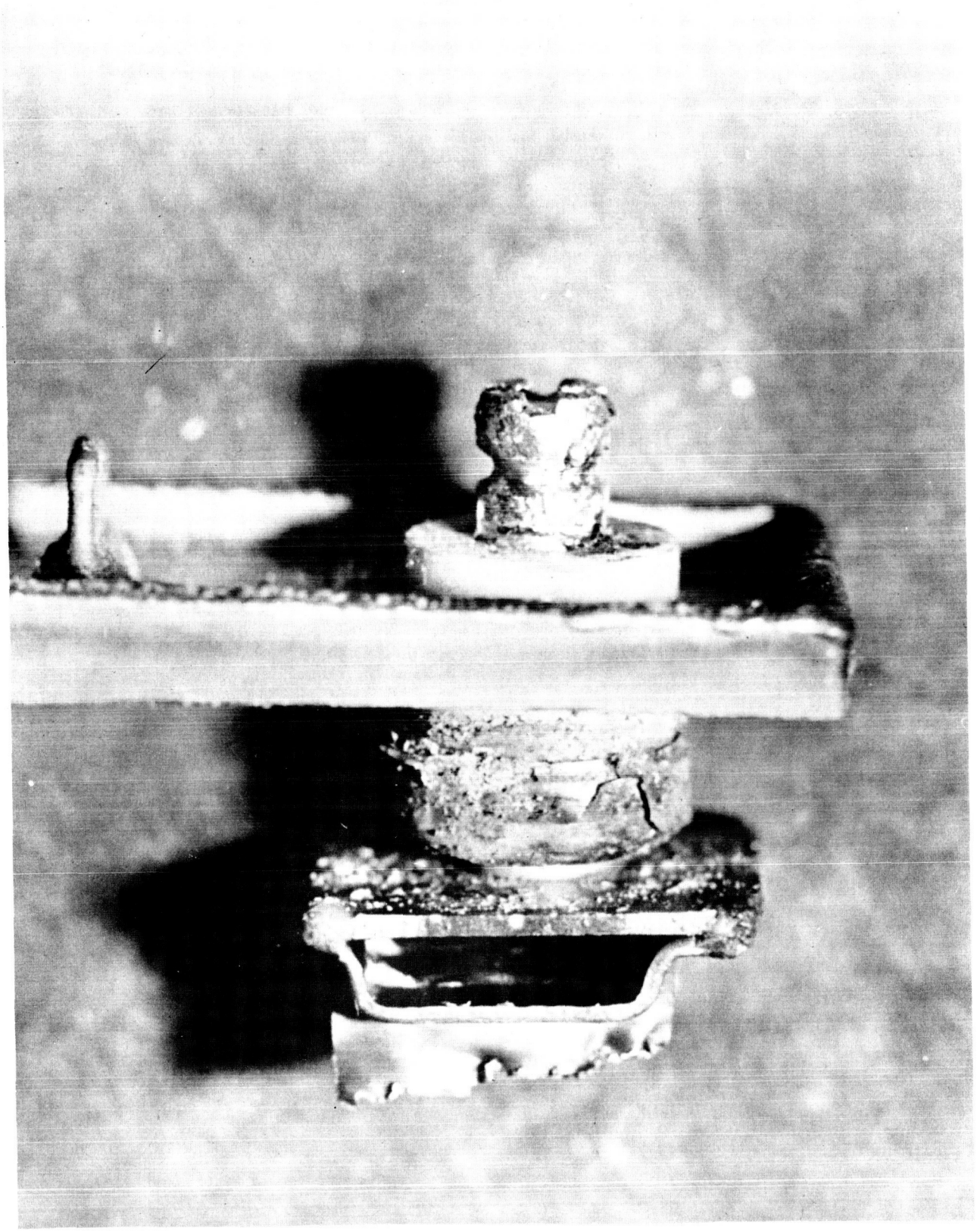
Another major cause of cell failures is the ceramic short which is caused by a bridging of the ceramic insulator with some of the brazing material, especially silver.

(Slide)

Some attempts have been made to eliminate this







by plating the area. This plating has not always proved to be completely satisfactory. As this slide shows, the plating has flaked loose and the ceramic short has taken place.

The plates of the cell are generally in excellent condition when the cell is opened, even after several thousand cycles. A few exceptions are blistering, loosened active material, and extraneous active material.

Blisters like the one shown on the next slide range in size from pinpoint up to a half-inch across.

The next slide shows, not too well, blistering that has taken place over the entire surface of the cell, or a loosening up of the material itself.

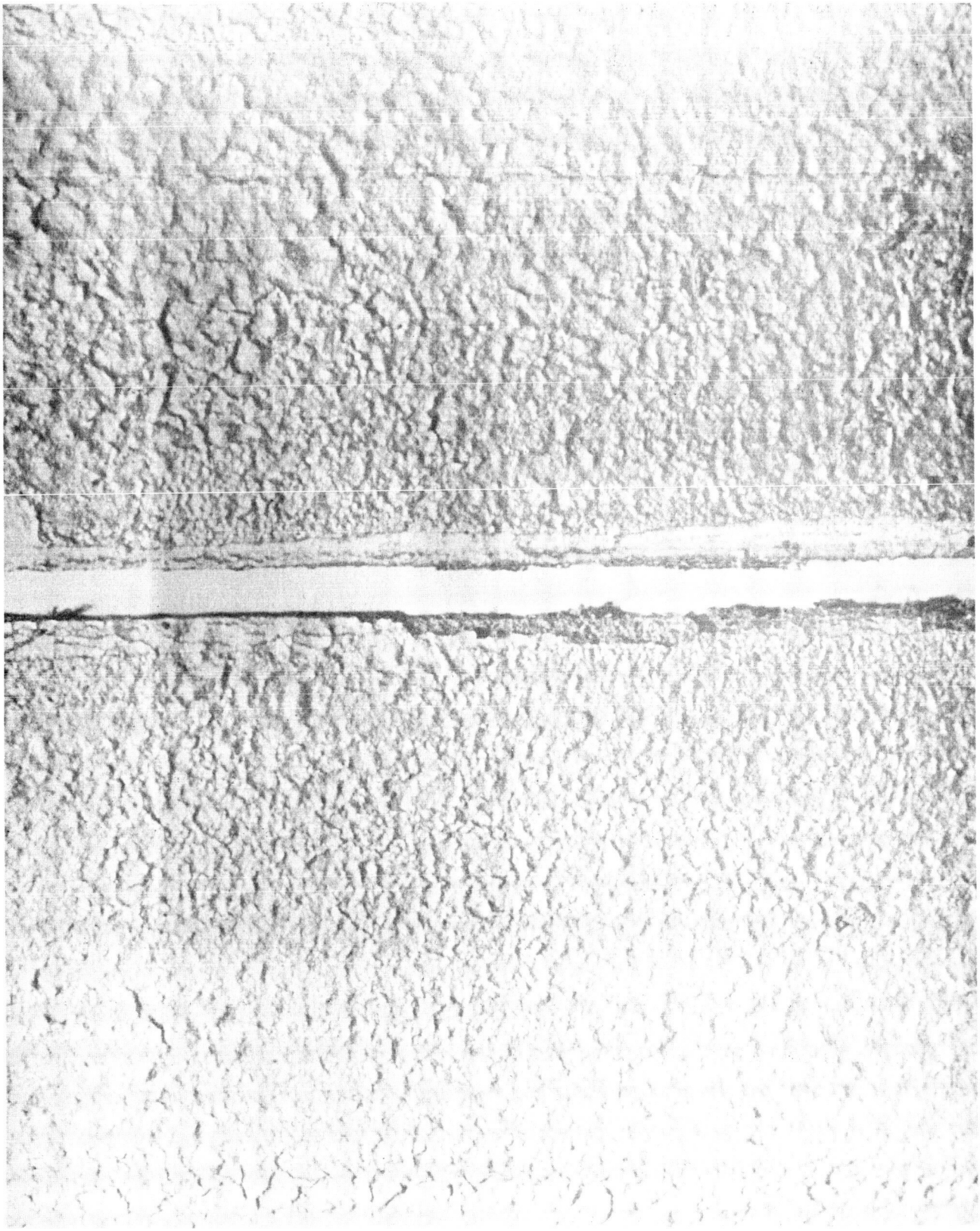
(Slide)

The next slide shows the plate material actually coming loose from the grid.

(Slide)

This is especially common incircular cells. This material is loose before the cell is actually unwound. It is just laying against the material.

Also in certain cases the pieces of plate material are found that came either during construction or in the process of putting the cell in the case that did not exist in that particular plate or in that area and caused additional pressure points on the separator.



Usually the separator will contain plate material that has migrated into it or all the way through. The migration usually comes from the negative plate.

(Slide)

The next slide shows the difference between the positive and negative plate, and that that is not.

(Slide)

The next slide shows the opposite side of the same separator, to give you an idea of how much of the active material is actually starting through the separator.

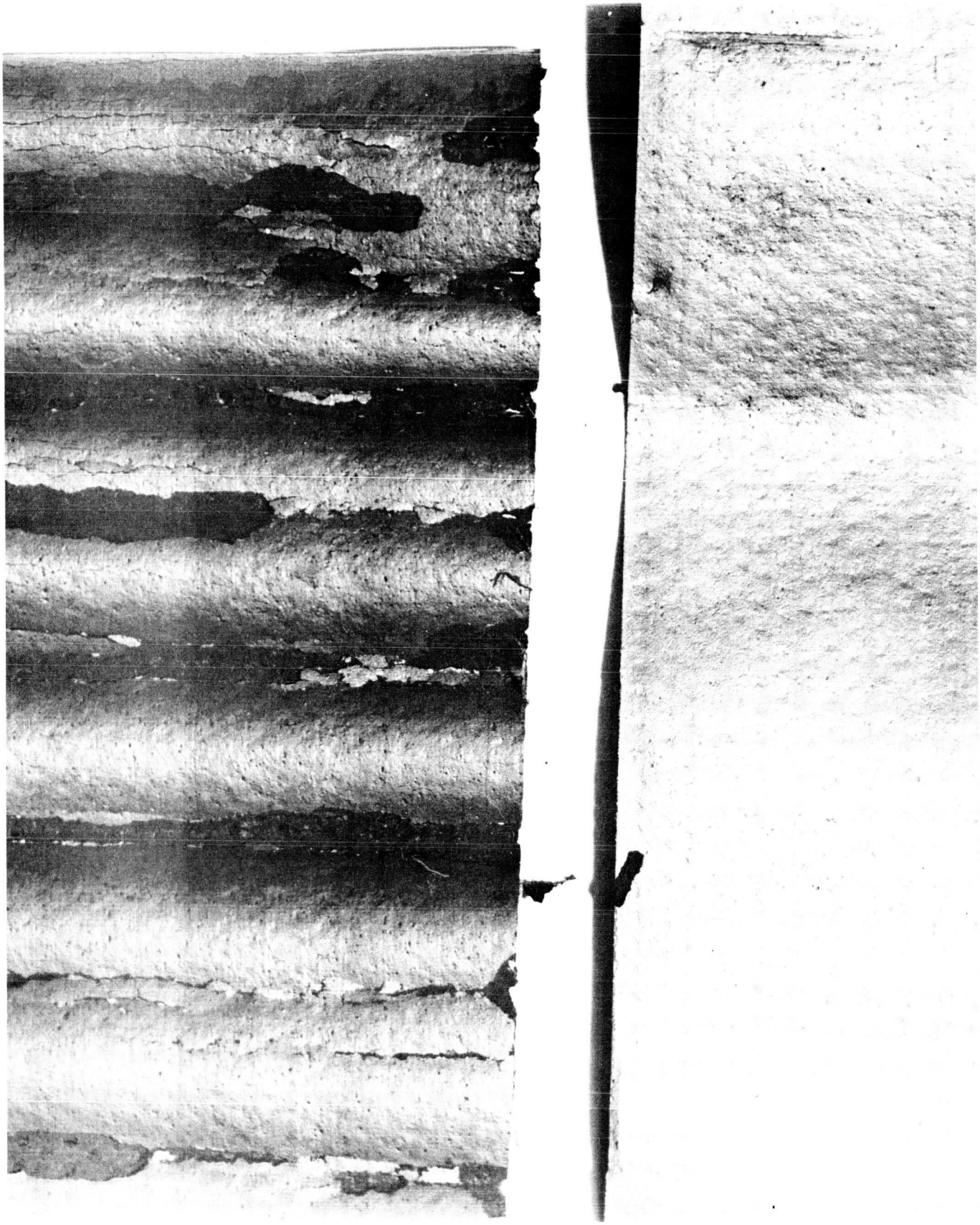
(Slide)

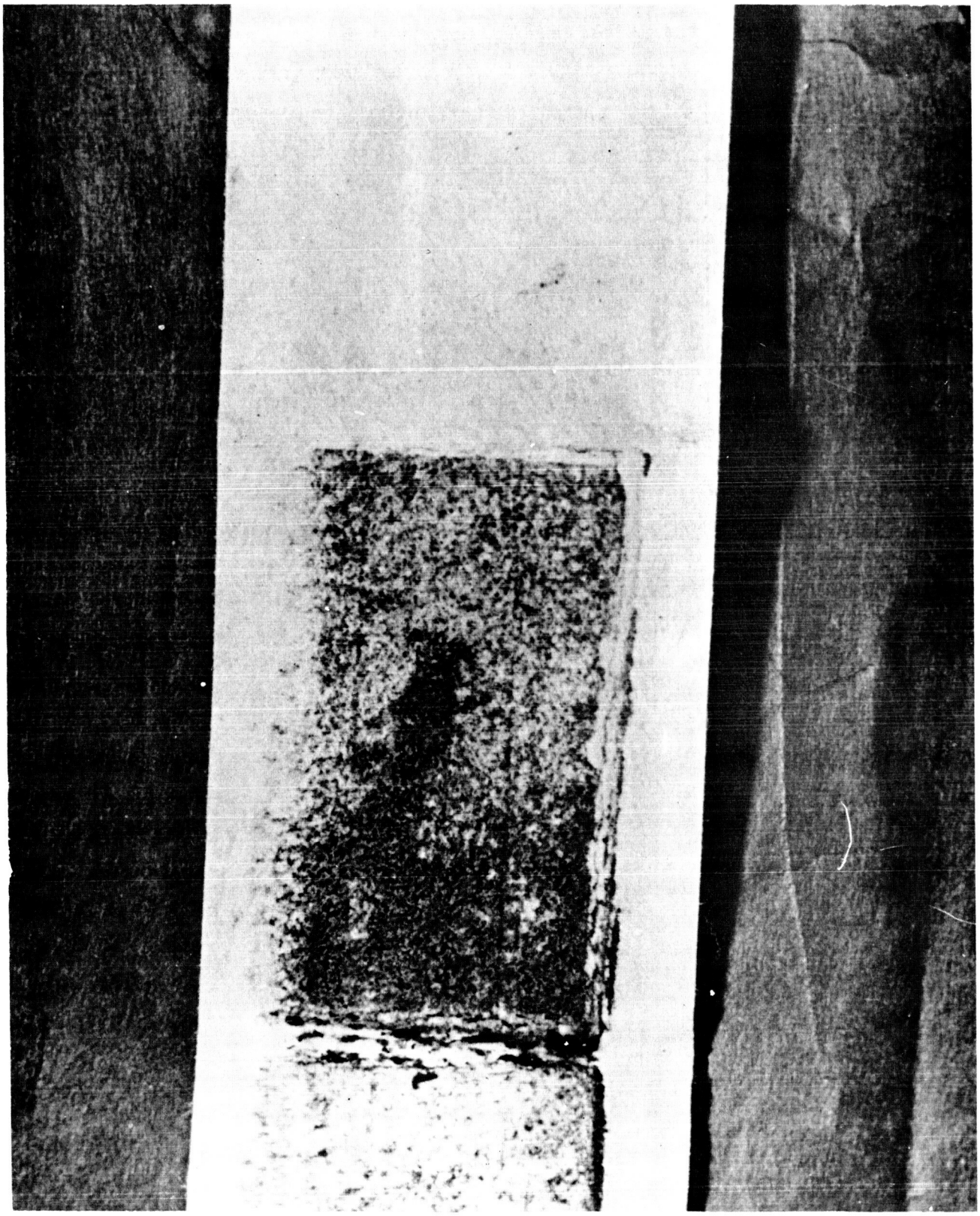
The next slide shows a positive and negative plate from a cell that has excess scoring. This excess scoring was an attempt to hold the cell in place for vibration. But this condition causes localized wear and tear on the separator and plates, sometimes to the extent of wearing the separator completely through or breaking down the plate materials themselves.

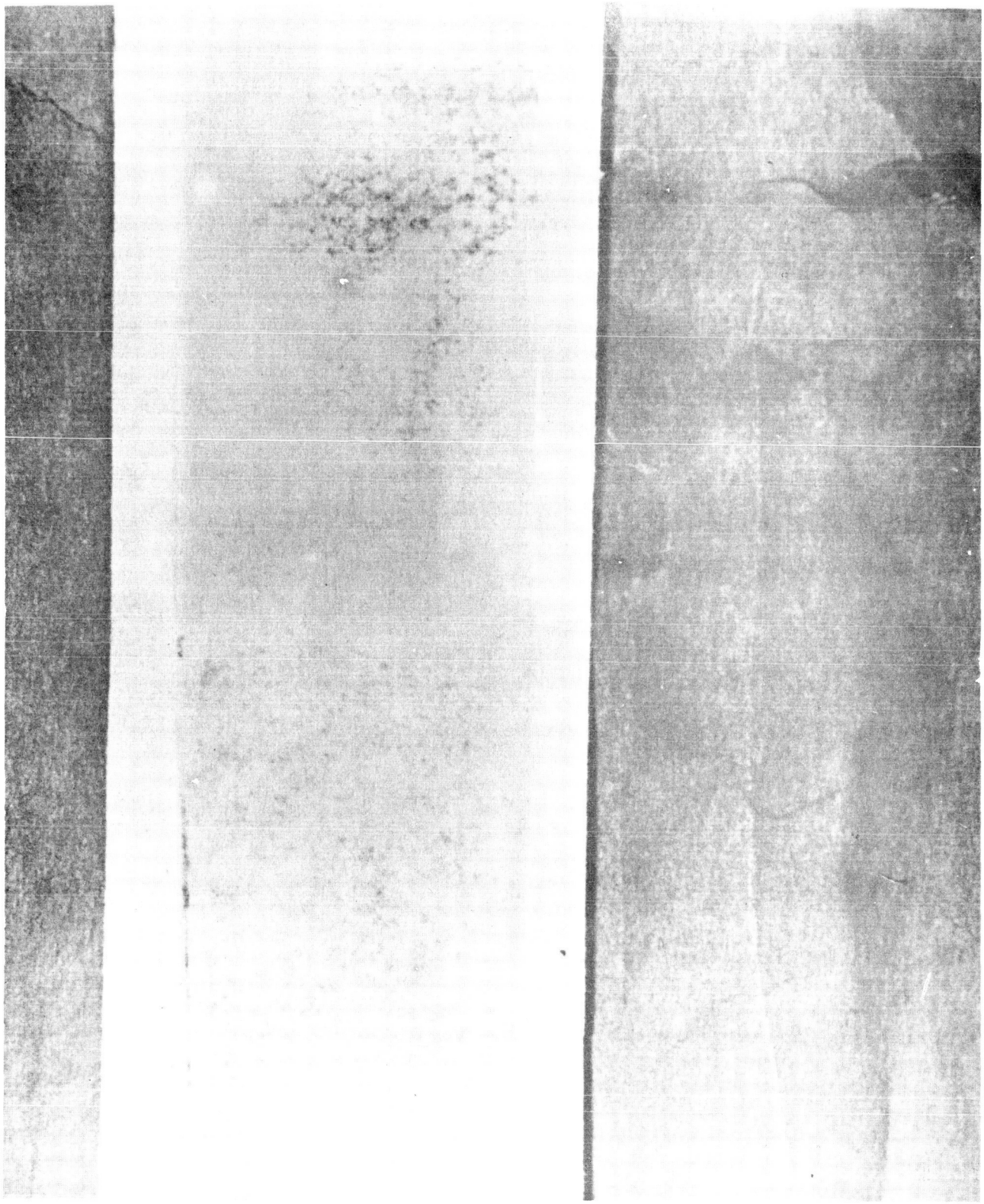
With the exception of cells operating at zero degrees, most cells show signs of separation or deterioration after several thousand cycles.

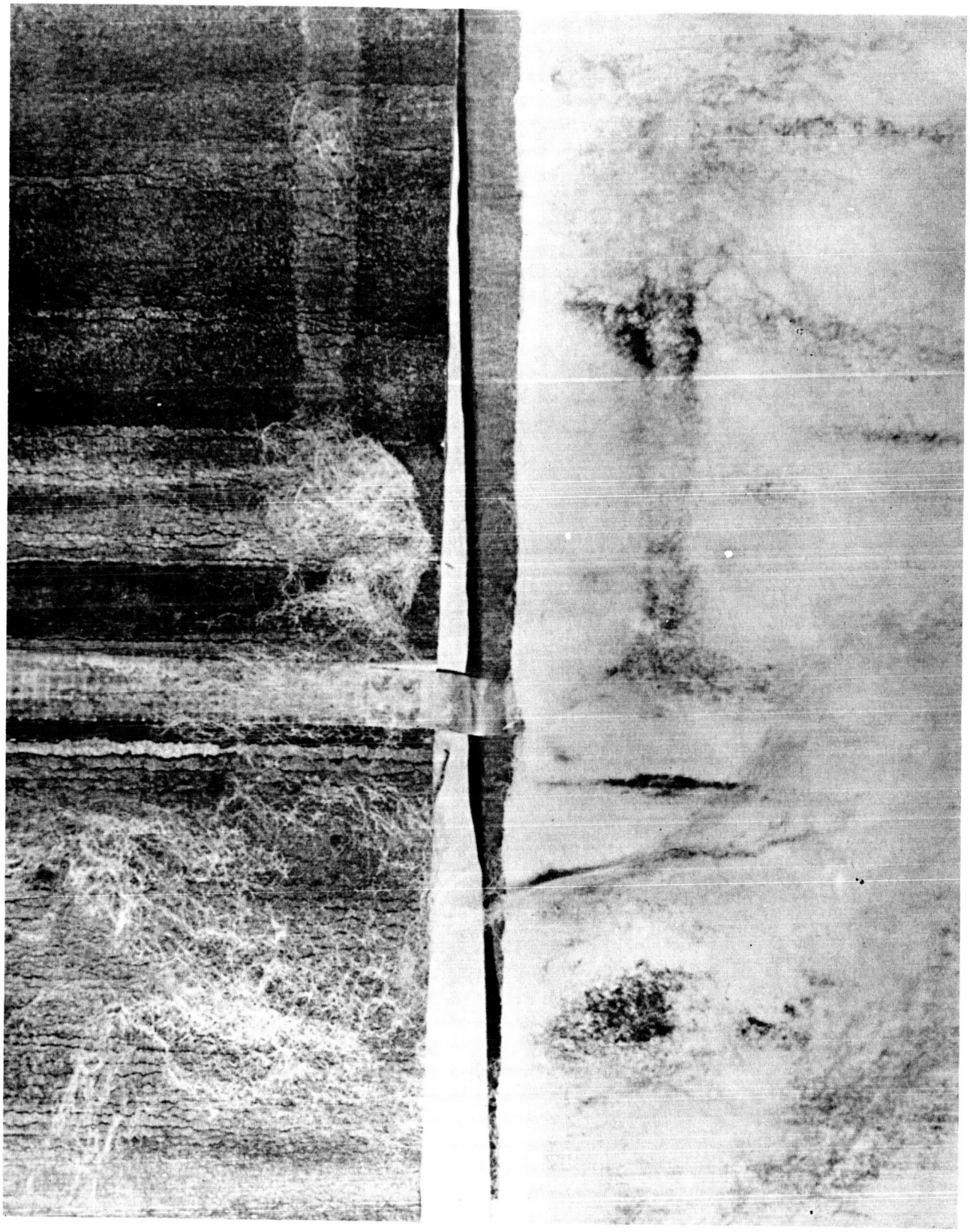
(Slide)

The next slide shows a separator that was operated at 40°. On this one the separator is just about equally divided over both the positive and negative plate. It was just a smear at the time the cell was opened.









It was just a smear at the time the cell was opened. Sometimes the separator deteriorates to the point where the cells actually short together, as shown in the next slide.

(Slide)

And a closeup of the following slide.

(Slide)

Most of the cell failures shown thus far are in the conventional cells.

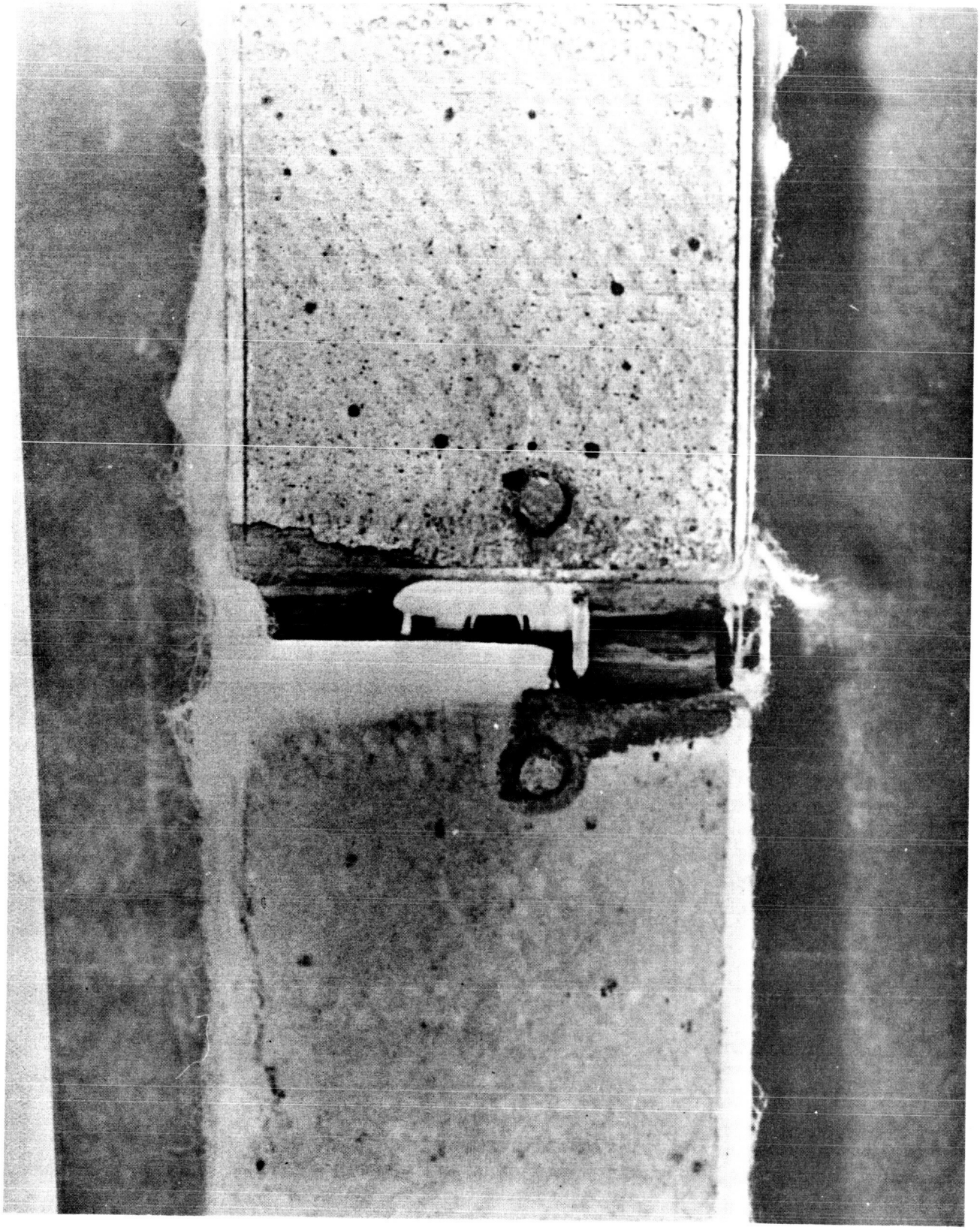
(Slide)

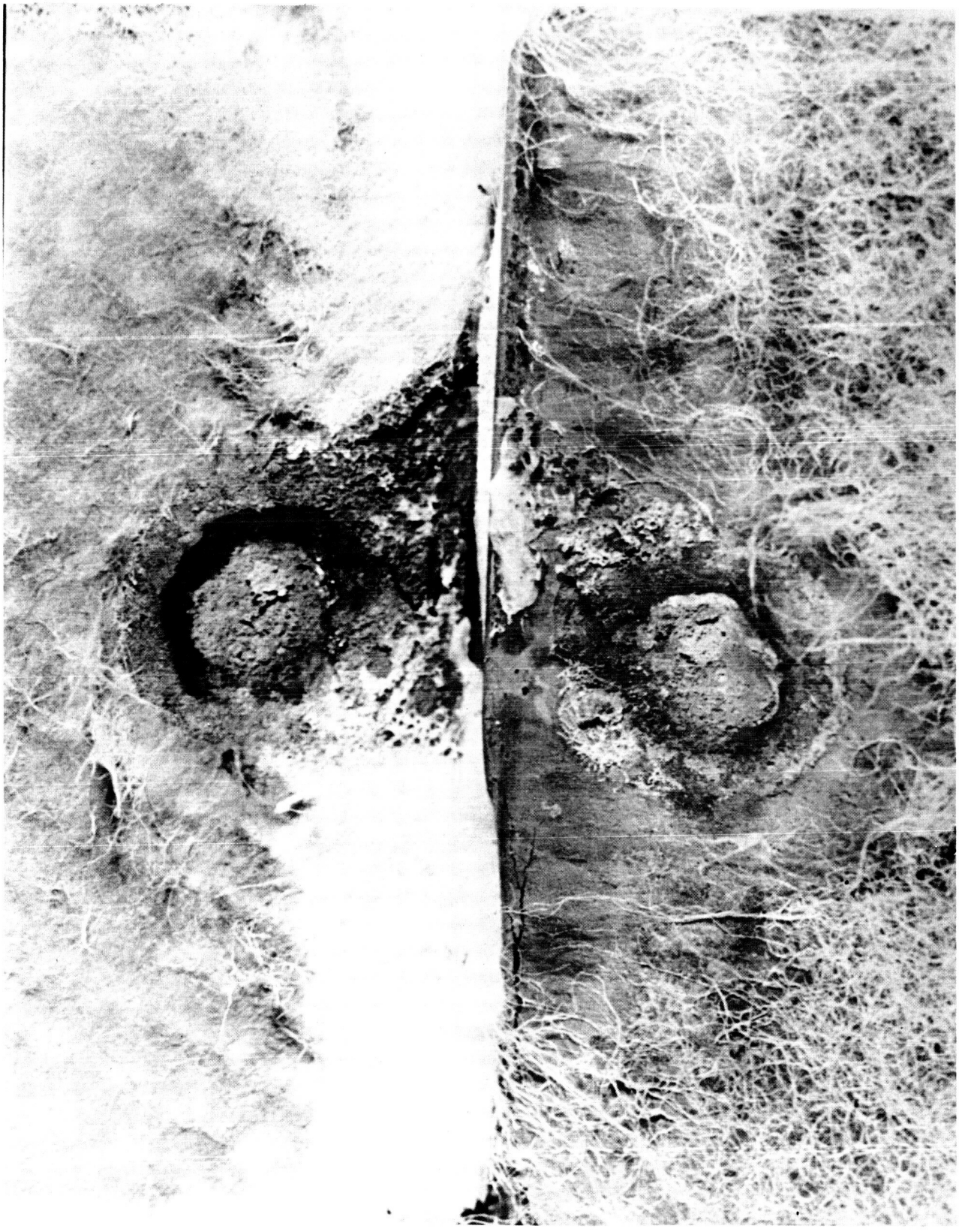
The next slide shows a failure in an auxiliary electrode cell. Failures to date in this type cell have not been directly caused by the auxiliary electrode.

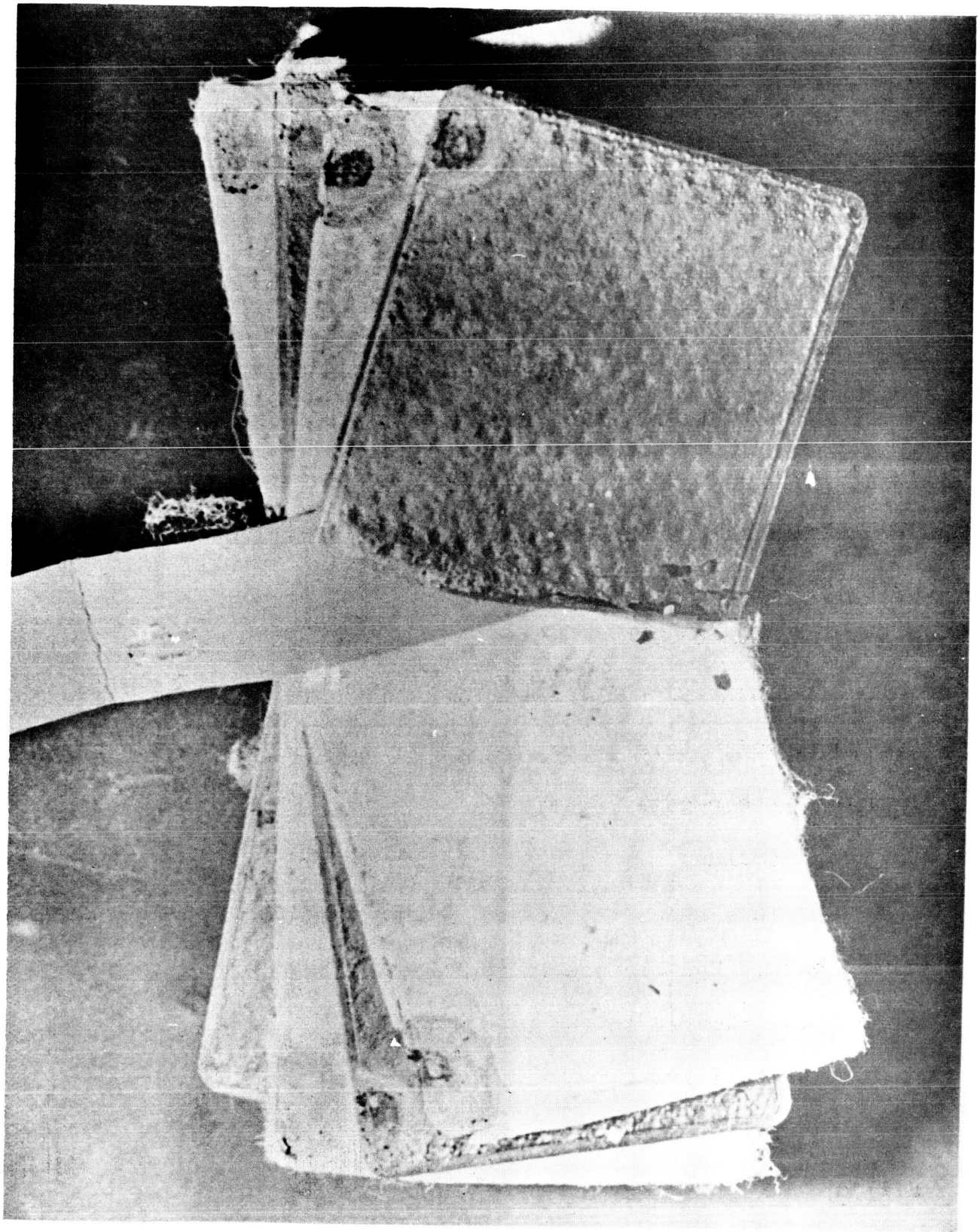
Even in this one, you can see that the short took place back from the edge where the auxiliary electrode was. This is for the interest of those who are wondering whether the auxiliary electrode is a major cause for failures in this type cell. Not all the cells that have failed have been caused by long-term cycling. Some of them are the result of the way the cell is designed, that is, in the next slide.

(Slide)

This slide shows that there was not enough insulating material around the positive tab, thus resulting in the short which you can see in the center. Other failures







result from the way the cell is constructed.

(Slide)

The next slide shows the inside of a cell that was caused by severe burns. The cell was opened up and this is the way the plates looked on the inside.

(Slide)

There was shorting between the positive tabs and the top of the negative plates, all along here and around both tab areas.

(Slide)

The next slide shows the same type cell, except in this one we can see how the positive tab was pushed down inside the insulator that was to prevent this type shorting.

(Slide)

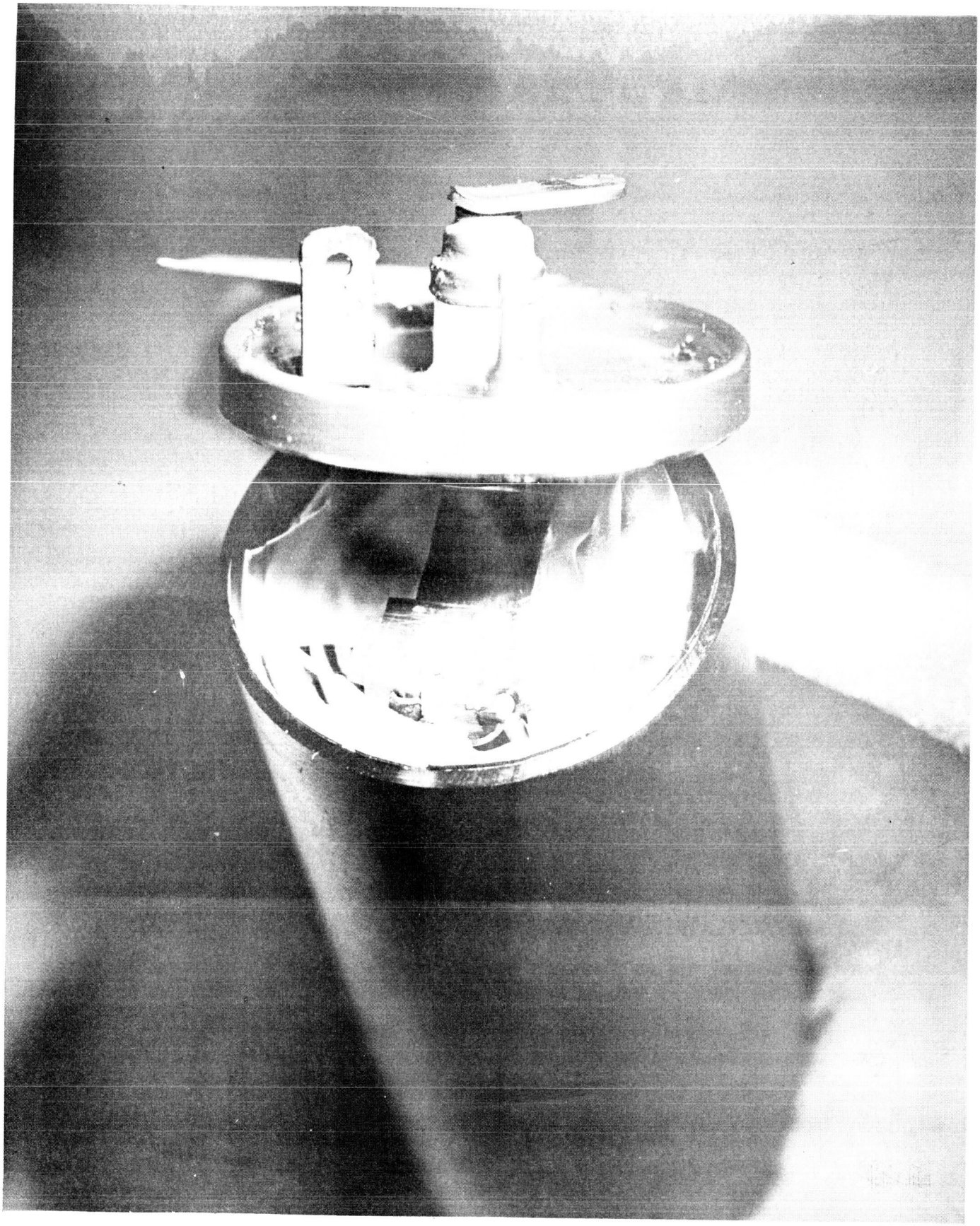
The next slide shows the same cell with the insulator removed. Here we can see again this tab is pressed down over the negative plate.

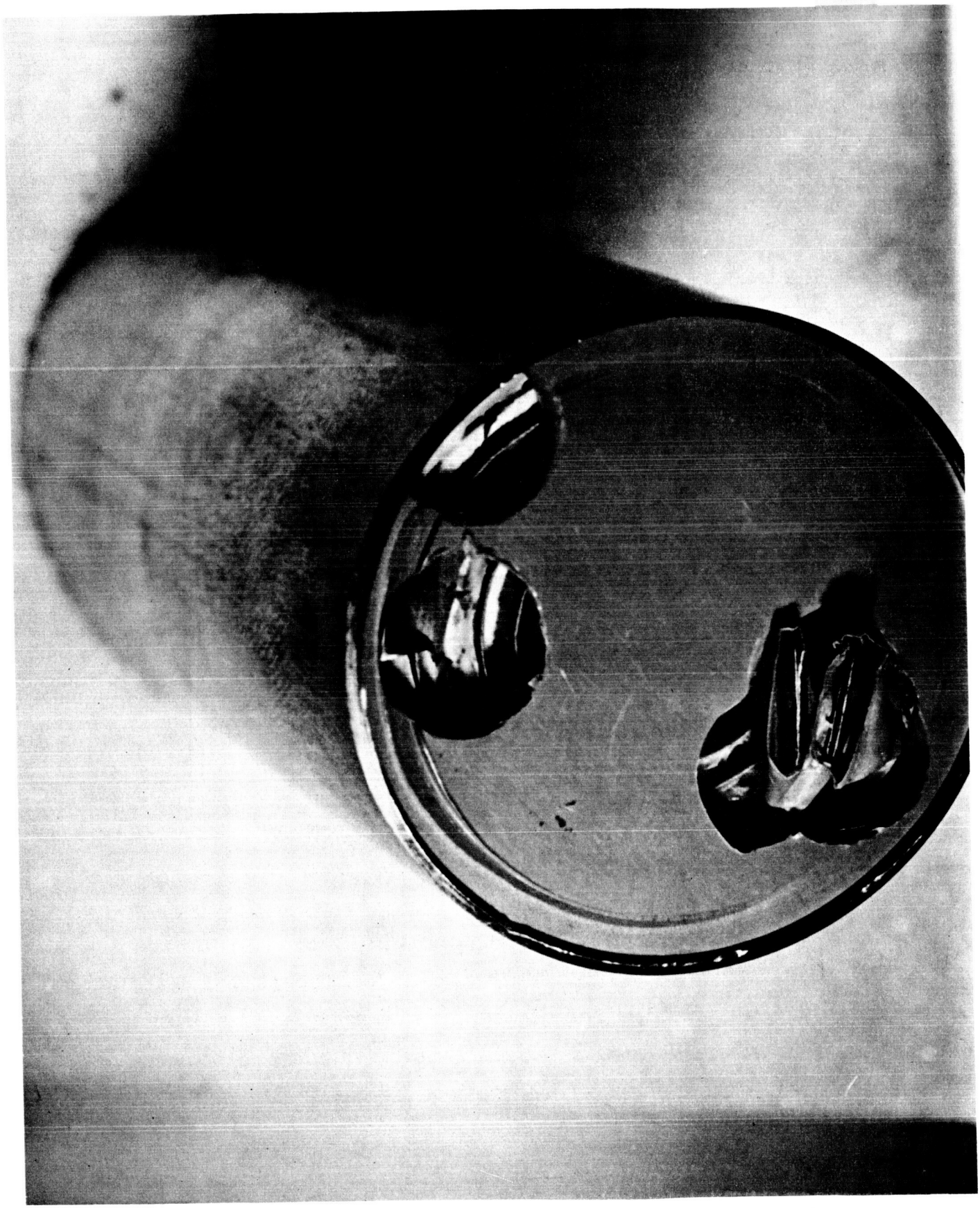
(Slide)

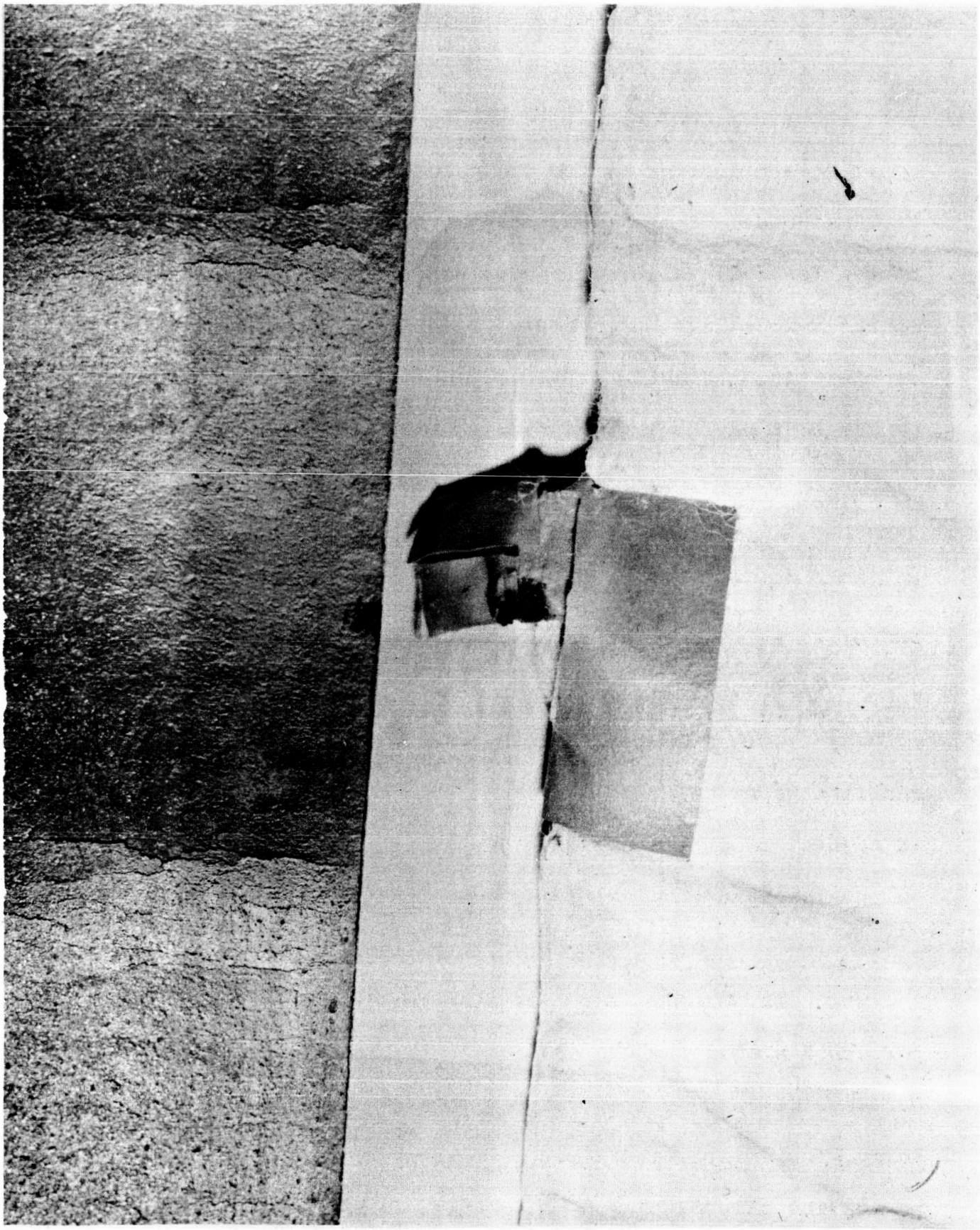
This shows the actual short. This has the tab turned back. You can see where the positive instulator was cut and shorted to the negative plate right here.

(Slide)

This is the plate, both plates from the same cell opened up. This is where the short took place.







That is all for the slides.

These are some of the mechanical cell failures that show that cell cycling could be improving by quality control, and another method would be to improve the separator material. These two processes seem to be the main causes for cell failures in most of the cells that we have operated to date. So either by finding a better separator or operating the cells at lower temperatures would probably be the best way to improve this.

Thank you.

MR. SHAIR: Thank you very much, Don. The pictures were quite interesting and colorful. Not a single one of us -- manufacturers -- came through unscathed.

(Laughter)

The next speaker is Lee Waltz, also from the Ammunition Depot of Crane, Indiana. His talk is definitely an adjunct to the one we have just hear. He will be talking on physical and chemical failure analysis.

PHYSICAL AND CHEMICAL FAILURE ANALYSIS

MR. WALTZ: I represent a services organization -- perhaps I should say the services organization, at NAD/Crane. Our services are in the field of physics, chemistry, metallurgy, photography and x-ray. In these things at Crane, we are the only place you can get it.

The photography came from our outfit that you

just saw. Some of the slides, all the slides that you will be seeing, came from there.

My original intention for this presentation was to run through a cell, a battery that we have taken apart and looked at. This was pretty well covered in the last two presentations. I don't think you want to go through it again.

Our intentions in doing this, in looking at these batteries, is to find out what a new battery looks like when it is new, so that we can, after it breaks down, find out why or where it broke down.

We are right now in the act of tearing down good batteries to find out what they look like when they are new. From this we hope to find out just where they fall apart.

I have a couple of slides on a silver-cadmium battery that we tore down.

(Slide)

We went through essentially the same procedure that was outlined in the first talk this afternoon in tearing all these things apart, step by step, and recording photographically and by visual observation defects and defects that we see as it comes apart. We do photograph it so that in years to come, if things should last this long, we can go back and see what a good battery used

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to look like. Unfortunately this was a good battery, but it was brand-new. It hadn't even been filled with electrolyte.

The material you see at the bottom of the cadmium plate came out of the separator.

(Slide)

Our next slide was taken from a different battery. There again you can get an impression of what a new battery looks like.

(Laughter)

We will save these for posterity in hopes that perhaps in the future when we get a bad battery we can tell where it went bad.

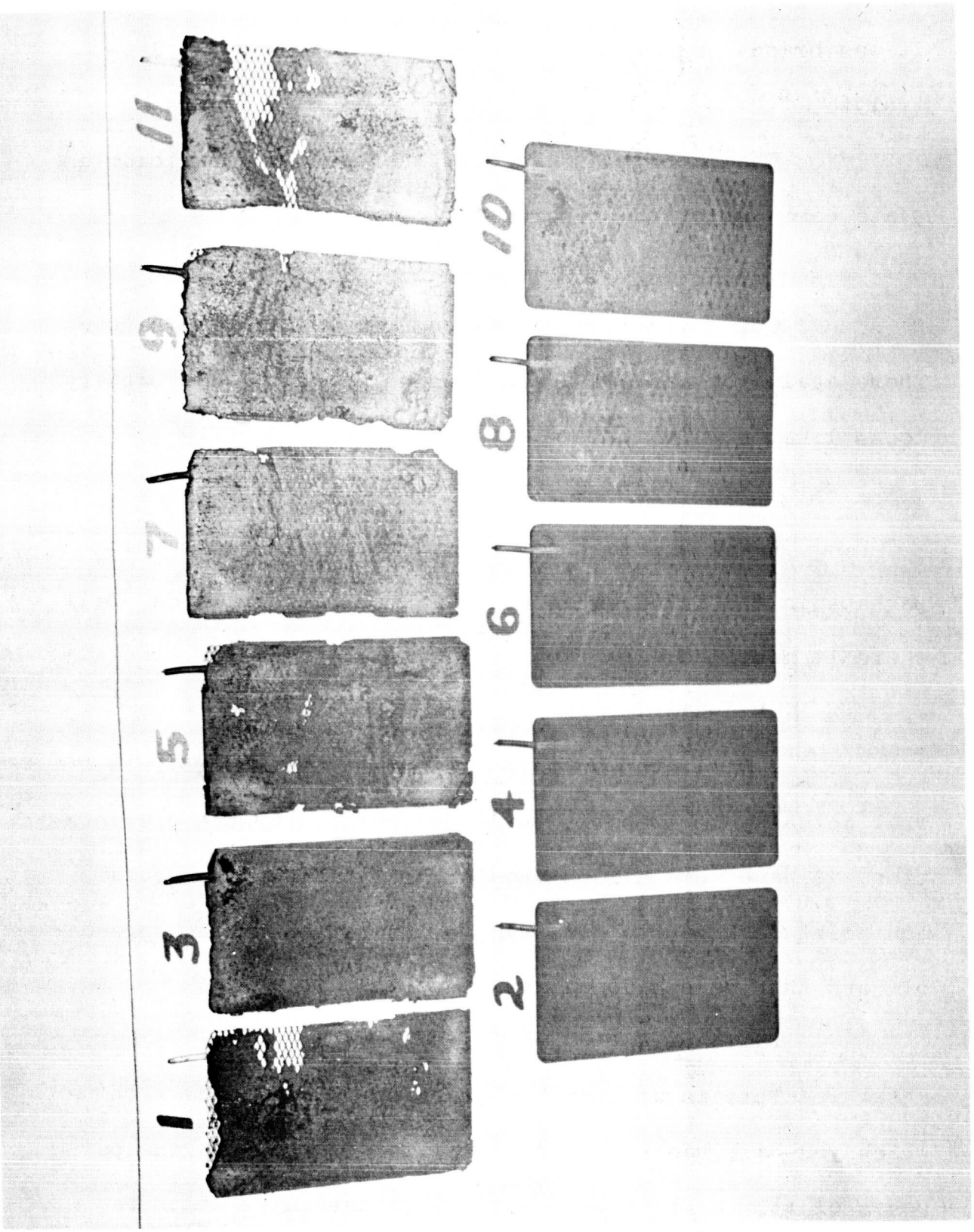
(Laughter)

I will stop on that part of it now and go into what actually is probably the minor portion of the presentation. I have some slides showing essentially some of the equipment we have, to give you an indication of the type of work that we can do on a battery.

(Slide)

This is an x-ray diffraction fluorescence machine which you have had eloquently explained to you and the purposes of it, in the use of battery failure analysis. We also like it and use it to a large degree in our analysis.

However, in our case we are trying to find out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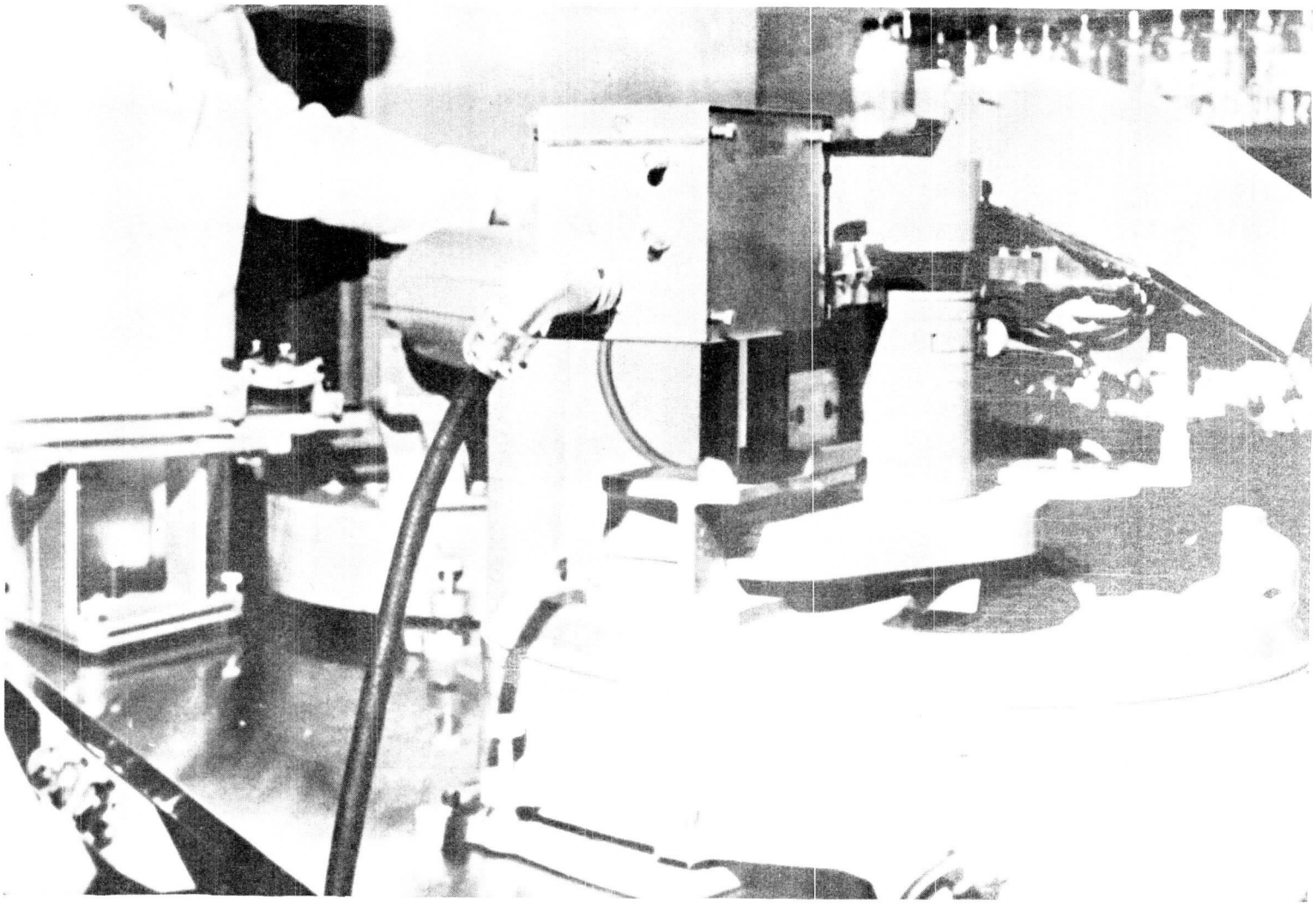


what is there when the battery is new so that later, when we come back with the used one, or failed battery, we can find out what the difference is.

(Slide)

This is an FNM gas chromatograph used to detect gas in a sealed battery. It is quite useful sometimes in failure analysis. We like it for that. Of course it is used for many other things also.

(Slide)

This is a differential thermal analysis apparatus which we use to obtain chemical information, I should say, about the plates. It is extremely small sample-size and it is very accurate.

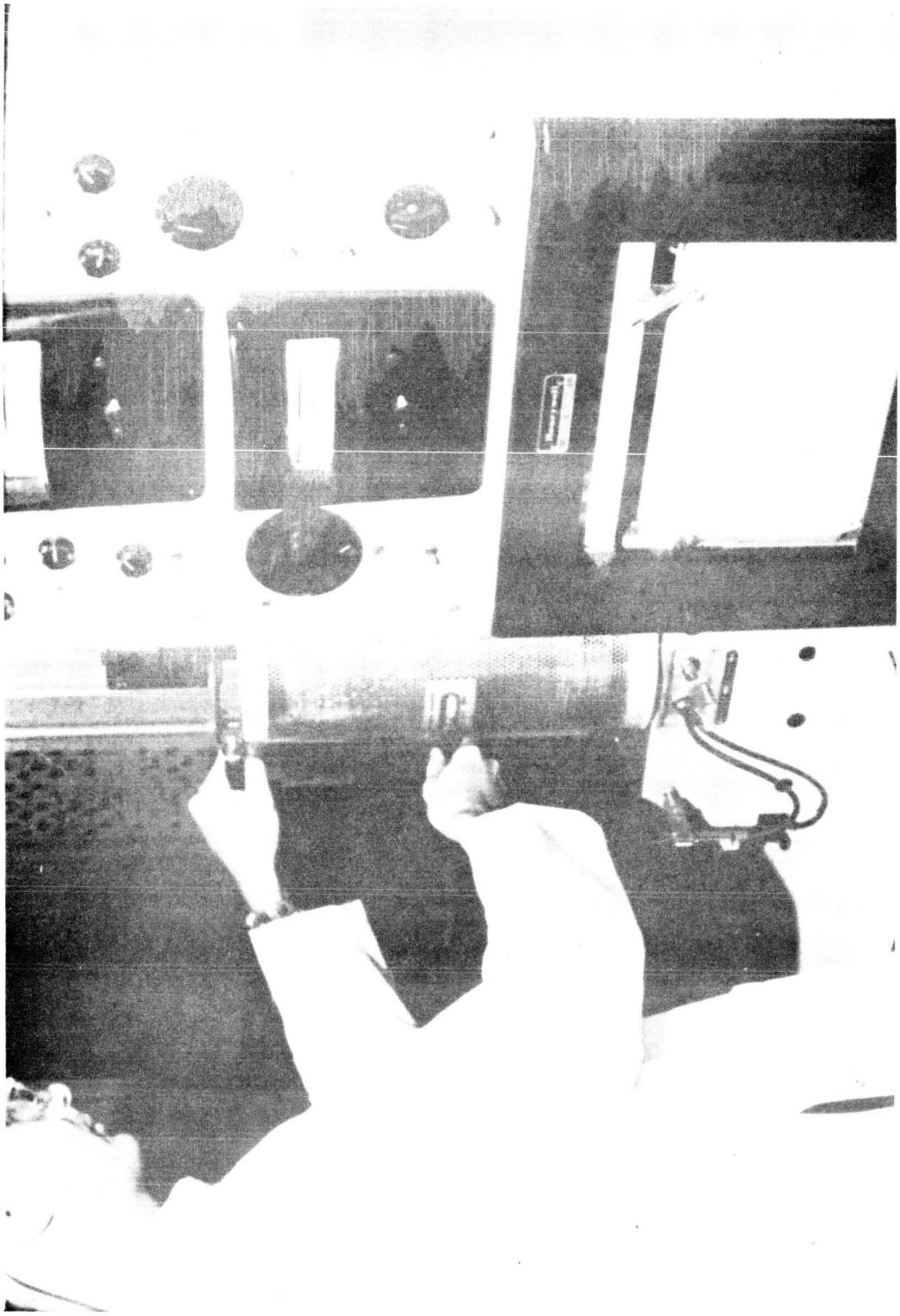
(Slide)

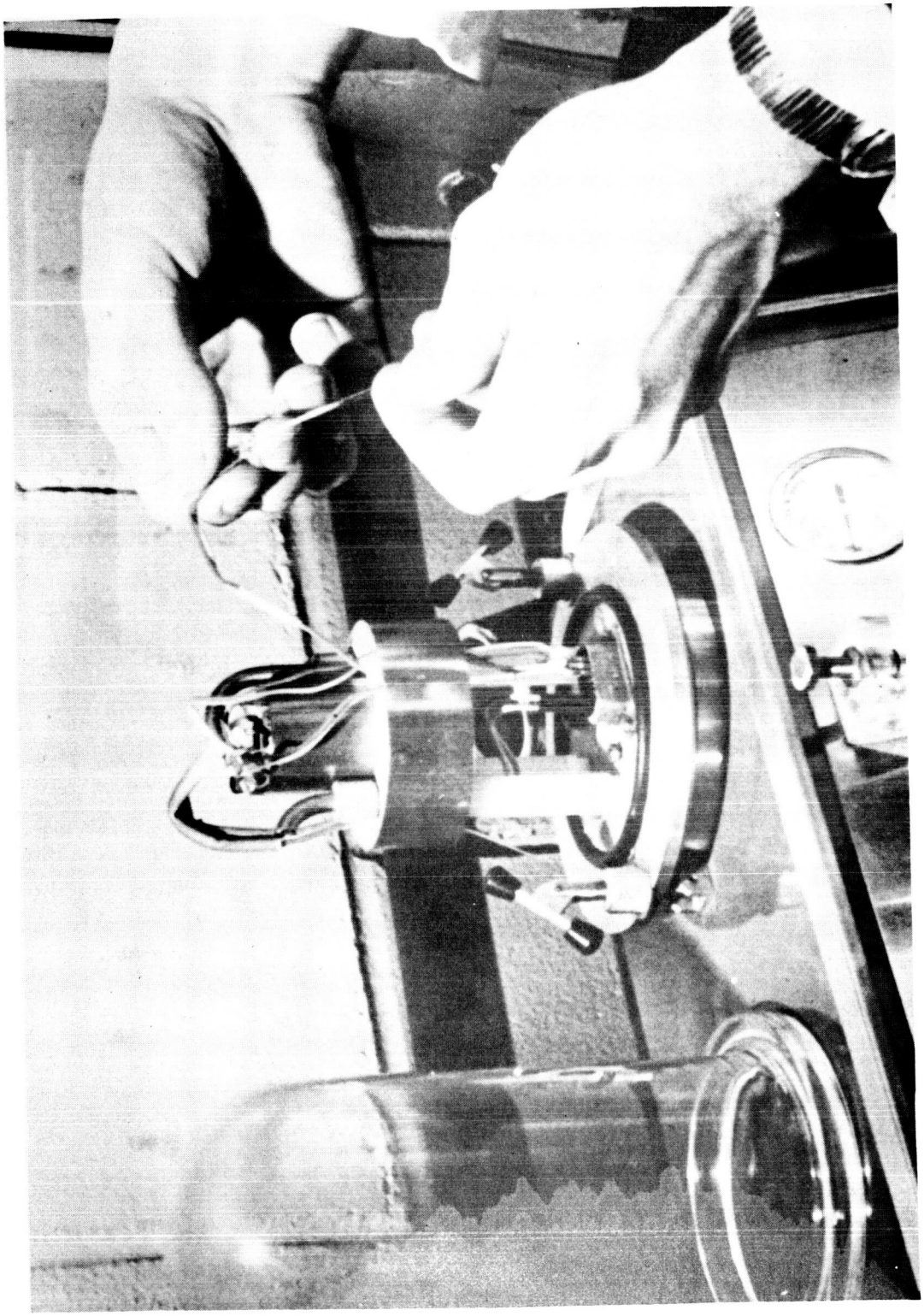
This is a metalograph. You have already seen some examples of its work. It is used for examining sections of plates.

In this area I would like to show you a photograph of our micron probe. Unfortunately it was only shipped from the company Monday, so we don't have it yet. Perhaps by next year we can show you some examples of scanning a plate edgewise, with a micron probe.

(Slide)

This is their tensile tester and it is used for tensile test of the plates, the separators, the case, the





INSTRON

terminals, whatever we should happen to need. We also use it for compression.

(Slide)

This is our arc spark stand for the spectrograph.

Our next slide is an interior view of the same thing. I'm sure all of you are familiar with that. We use it in our phase of the studies.

We spectrograph virtually every item that comes out of the battery for file purposes, so that in the future we can see where the elements are migrating to and from.

(Slide)

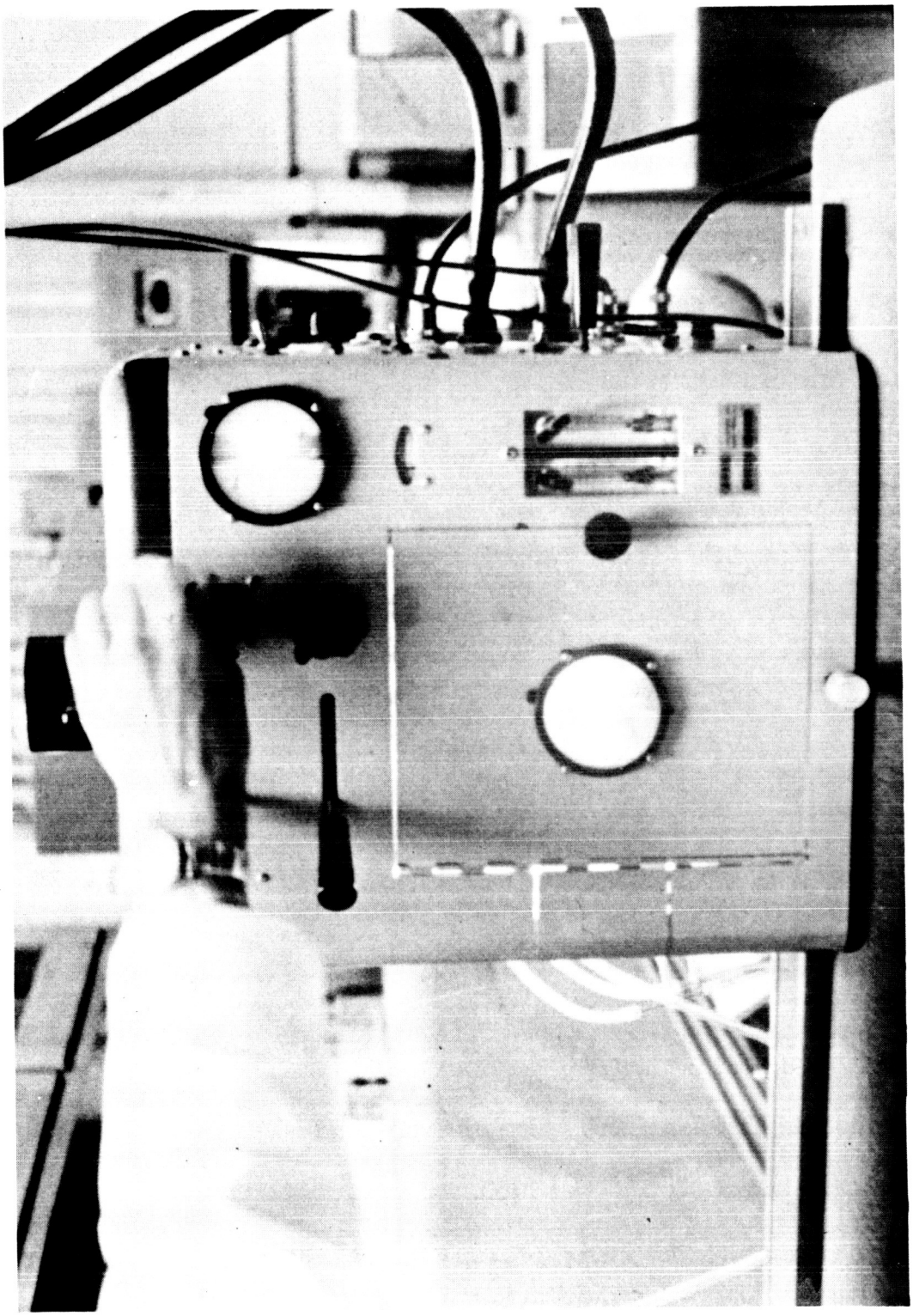
This is the infracord(?) spectrometer used mainly in the identification of organic or plastic materials in the battery. We use it for identification of the separators. We tried it on cellophane. We found out we couldn't identify it. It was unidentified cellulose product. It is also used perhaps in the electrolyte, picking up some of the organics in it.

(Slide)

This is our last slide. This is an example of the one section that we have not previously discussed, and this is microbiology. The boss of the branch has his doctorate in microbiology. I did not feel I would leave him out of this rightly. So there he is.

(Laughter)

I presume that will go into the record.



MR. SHAIR: That is very interesting. I think we can see that we are tending back toward the scientific end of things in batteries, and there certainly is an art involved in it. But there is a lot of science called into play to explain what is going on and how we can improve it.

The next speaker was scheduled to be Carl Berger, from Douglas. Instead of Carl Berger, Dr. Murray Strier is here today and will talk on micro fuel cell gas detection as a criterion for battery failure analysis.

MICRO FUEL CELL GAS DETECTION AS A CRITERION FOR BATTERY FAILURE ANALYSIS

MR. STRIER: (Douglas Astropower): Mr. Chairman and gentlemen: Unfortunately Dr. Berger had some unexpected urgent company business and I was selected to come here in his place.

The work on micro fuel cells that we have been doing for the past year at Astropower Laboratory Division of Douglas was presented as far as its early beginnings during the previous battery workshop symposium held here last April by Mr. John Unger, of NASA-Goddard. At that time he described the capability of the micro fuel cell to relieve the pressure built up in silver zinc batteries,

and he did describe two types: a micro fuel cell that consumed hydrogen and used oxygen delivered from the outside. He was also able to describe at that time what was our earliest development of a metal gas type of micro fuel cell which had the capability of eventually allowing complete sealing of a battery, rather a silver-oxide-zinc cell, which could be extremely useful particularly at high rates as well as higher temperature operations.

What the micro fuel cell does, uniquely, is to consume hydrogen or oxygen. You can take two (unintelligible) cells and each can consume hydrogen and oxygen and return product water as necessary so that there is no drawing out of the electrolyte and no pressure buildup.

We feel that there is still another application of the micro fuel cell. In addition to merely consuming the gases, it also has an analytical aspect, that of actually registering a current, and here we can apply Faraday's law which would be related, coulomically, to the amount of gas that is (unintelligible) by the battery. This current can be integrated as the battery or cells cycle and give a relationship between gas evolved in cycle life. A program that we have recently initiated, which involves a statistical interpretation, would entail first studying a large array, say at least 30, silver-oxide-zinc cells of a particular class, cycles according to a specific regime.

From this we could calculate statistically with error analysis what we call the main failure current, the current that is registered by the micro fuel cell, which is an integrated current, at the time of failure. And then analysis of the cycling -- of the relationship between cycles and integrated current, could give a semblance or family of curves, the coefficients of which could be used in a statistical analysis to predict what would happen if an unknown battery, or an additional battery of this array, were to be cycled according to the same regime.

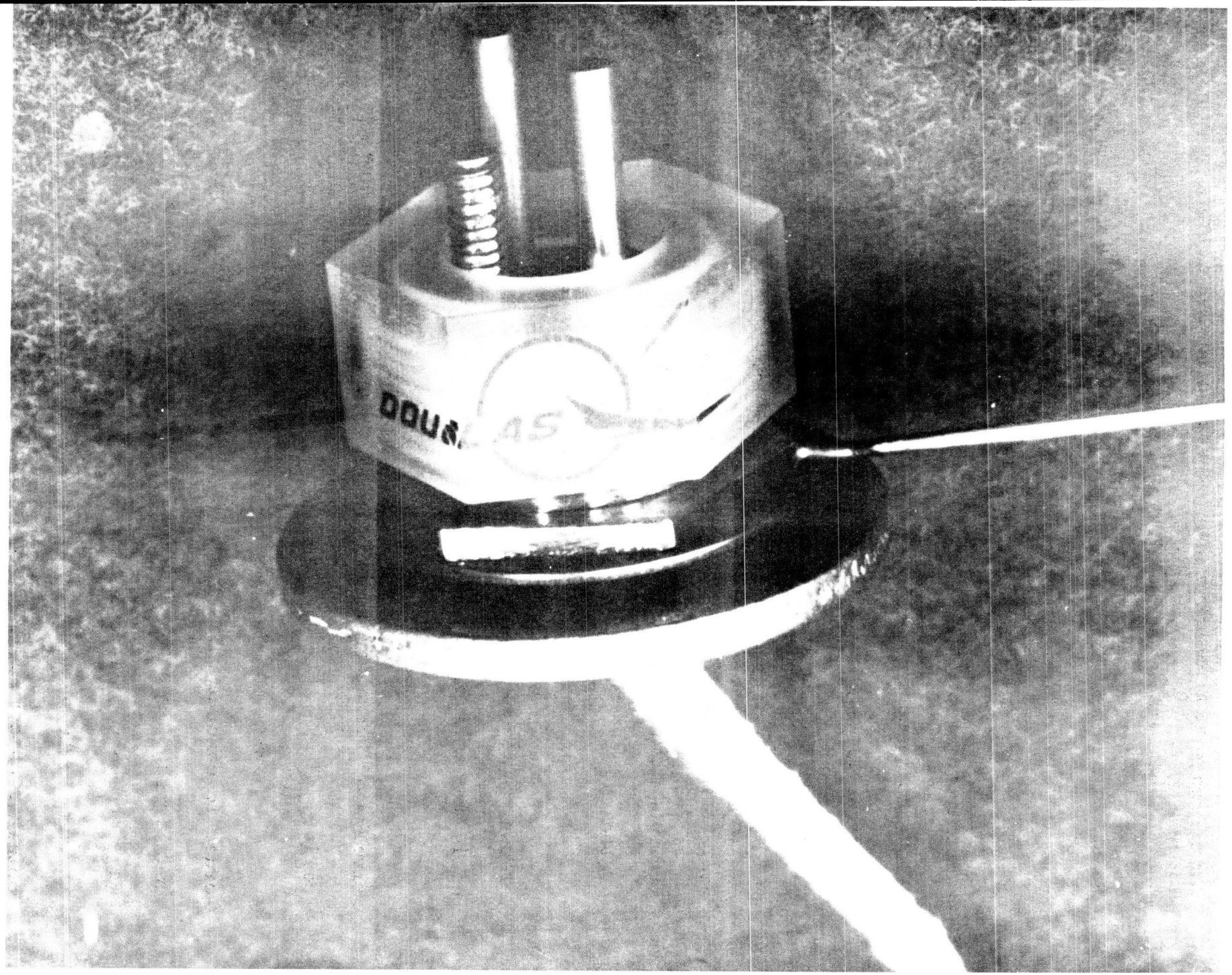
Knowing what the mean failure current would be after a full cycle, and knowing what the essential format of the curve is, we could eventually predict what the failure time would be for this battery.

(Slide)

The first slide I would like to present is really nothing more than just one of our several micro fuel cell designs. This actually has an electrode through the section area of one square centimeter.

Although it is not clearly shown at the bottom, threads are present which allow the micro fuel cell to be screwed into the battery or cell case. This is an open-ended type. It can receive either hydrogen or oxygen gas from the outside, as shown by the inserts at the top.

The white stuff sticking out at the bottom is



wicking material, which can be connected to the electrolyte so that the product water is returned as it is produced.

(Slide)

The next slide shows a laboratory setup. Unfortunately the background is not too clear. This involves a 100 ampere-hour silver-oxide-zinc cell, a commercial cell, containing two micro fuel cells, each of which is installed into the sides of the case.

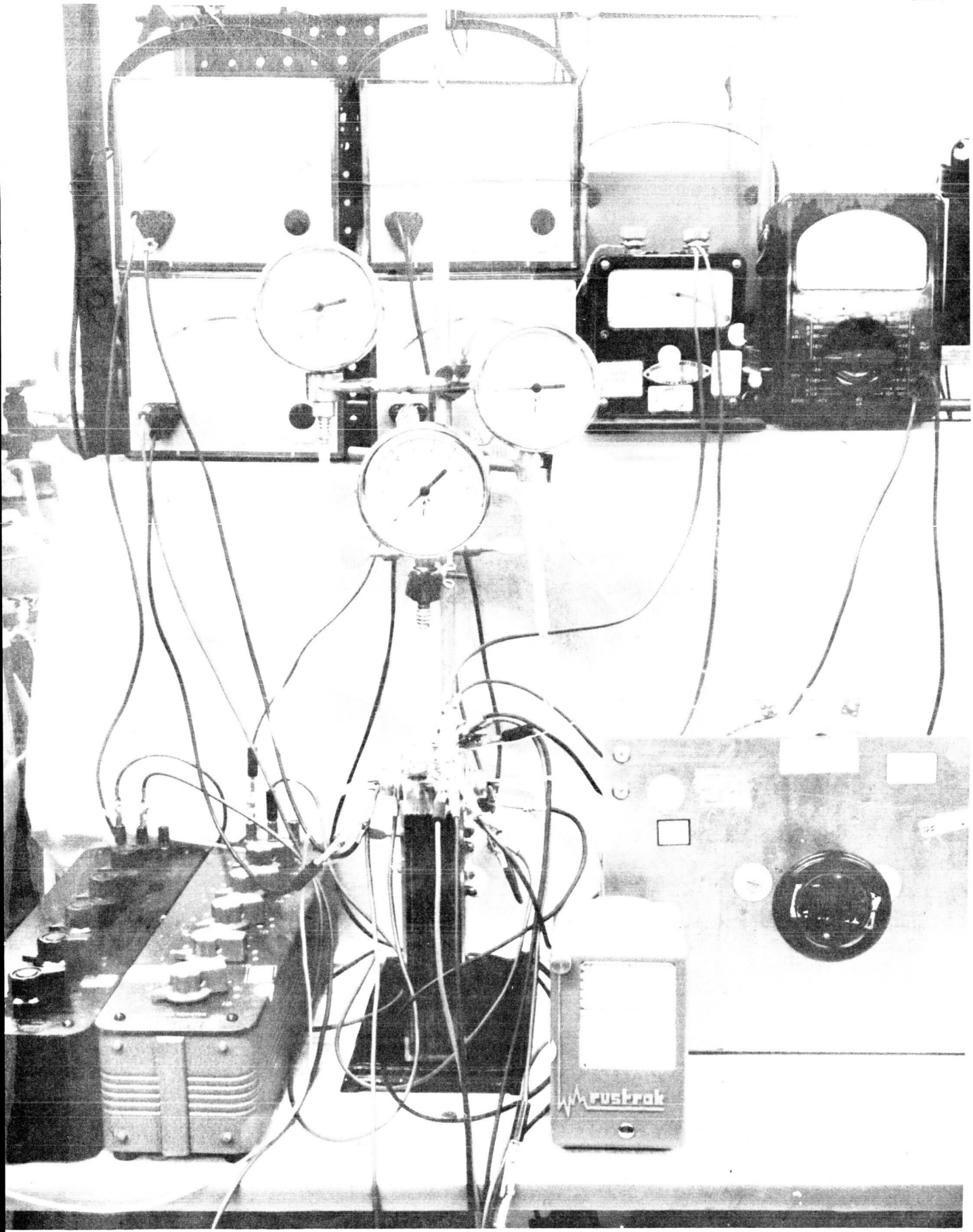
These slides did not come out as clearly as we would have hoped. The background is not quite right. There are two micro fuel cells actually installed into the sides of the case.

Pressure gauges tell us actually what kind of pressure was developed and how efficiently the micro fuel cells are acting. That is the middle pressure gauge.

The pressure gauge on the left and right respectively for hydrogen and oxygen, which enter the micro fuel cells.

As I indicated before, it is very important in order to conduct this type of analysis to know what the relationship is between a cycle life and mean, what we call the mean fuel cell current.

The next slide shows some data that we have obtained on commercial silver-oxide-zinc cells into which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had been installed a micro fuel cell for detecting or actually consuming hydrogen, and what we have plotted as the abscissa is the accumulative or integrated fuel cell current.

(Slide)

This is for actually two commercial 15 ampere-hour silver-oxide-zinc cells operated at half-hour discharge at 10 amps and one-hour charge at 5 amps. Of course there is a difference in the relationship from the standpoint of the displacement of the curves.

In a general sort of a way they are somewhat related.

The next slide shows the same pattern.

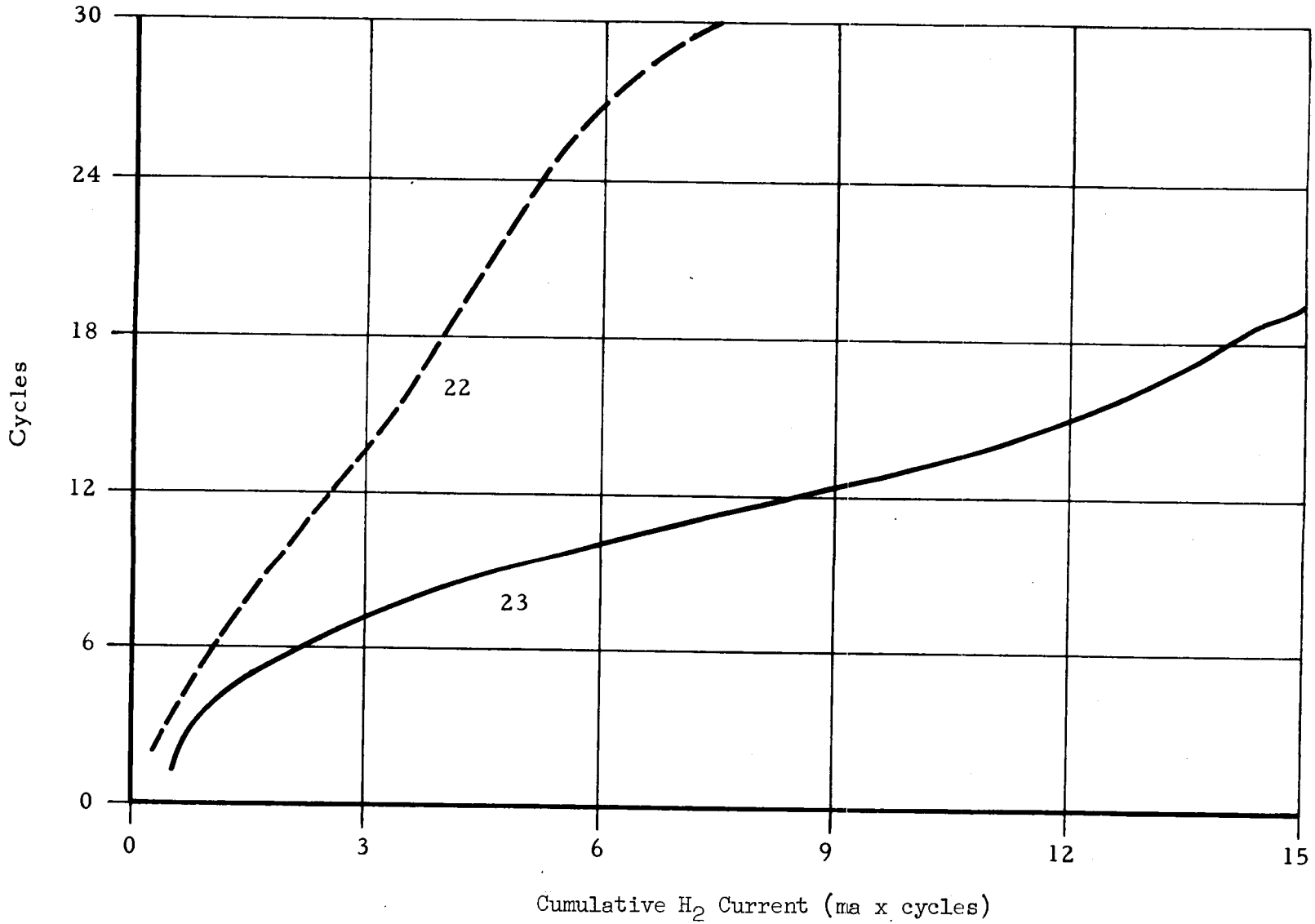
MR. COHN: Is your abscissa then essentially timed?

MR. STRIER: The Y axis is cycle life or timed. The abscissa is actually the accumulator or integrated hydrogen current, current due to the consumption of hydrogen gas by the micro fuel cell.

VOICE: Which curve is which?

MR. STRIER: Each curve here purveys the cycle life, with cycles versus cumulative or integrated hydrogen current for one cell, and current D is the same for another cell.

In other words, let's say up to 4 cycles or any cycles as shown, for a particular time T, we have that many cycles and that total amount of current as shown



Cycle Life Plotted versus Cumulative H_2 Current for 100 Ah Silver Oxide-Zinc Cells Operated at 2-Hour Discharge at 20 Amps and 22-Hour Charge at 2 Amps

by the micro fuel cell.

VOICE: That is not clear. Do you mean current times time, or do you mean just the average current?

MR. STRIER: This is the actual integrated current times time.

VOICE: Do you mean that is milliampere minutes?

MR. STRIER: Right. We will call that a cumulative current. Coulombs. That will be the coulomb equivalents.

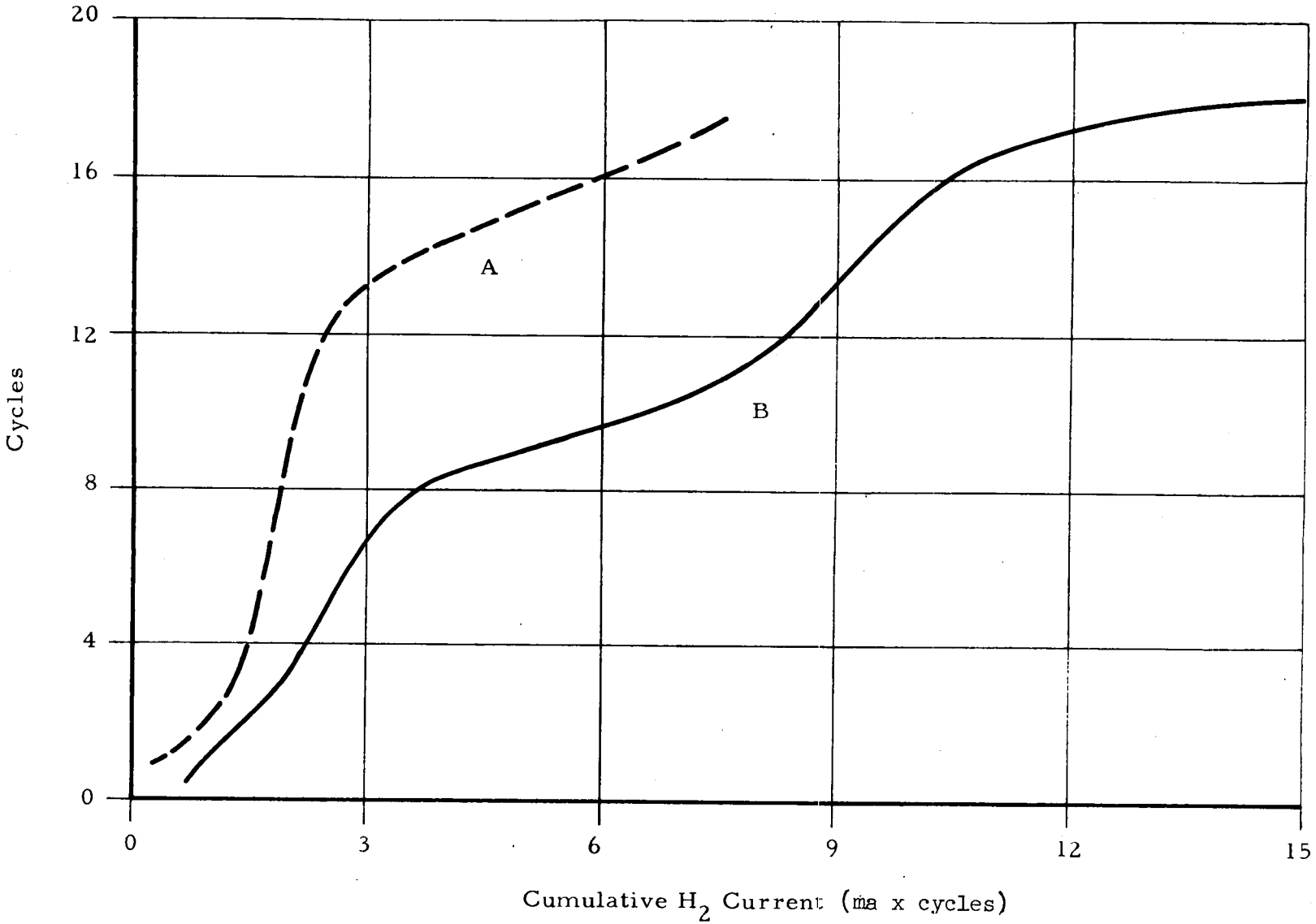
The next slide.

(Slide)

This represents a similar pattern that was obtained -- this demonstrates the relationships obtained for a 100 ampere-hour oxide-zinc cell operated at 2 hours' discharge at 20 amps and 22 hours' charge at 2 amps. There is an indication that the two curves are not really unrelated.

What we consider most important here is to be able to calculate the failure current time value based on a statistical analysis of, as I said, at least 30 cells, and then being able to fit a curve, a generalized curve, for the points that are obtained, from which we can deduce eventually the cycle life for a cell of that type based on its early gassing data.

So that let's say if you get about 10 cycles or so, and have a reasonable enough number of points, you



Cycle Life Plotted versus Cumulative H_2 Current for 15 Ah Silver Oxide-Zinc Cell Operated at 1/2-Hour Discharge at 10 Amps and 1-Hour Charge at 5 Amps

can, by using the statistical method which I'm going to go into right now, predict cycle life when the points are extrapolated to the mean failure current time product.

(Slide)

The next slide represents how this sort of thing can be put into a computer program. And actually we have written the FORTRAN program on this particular basis.

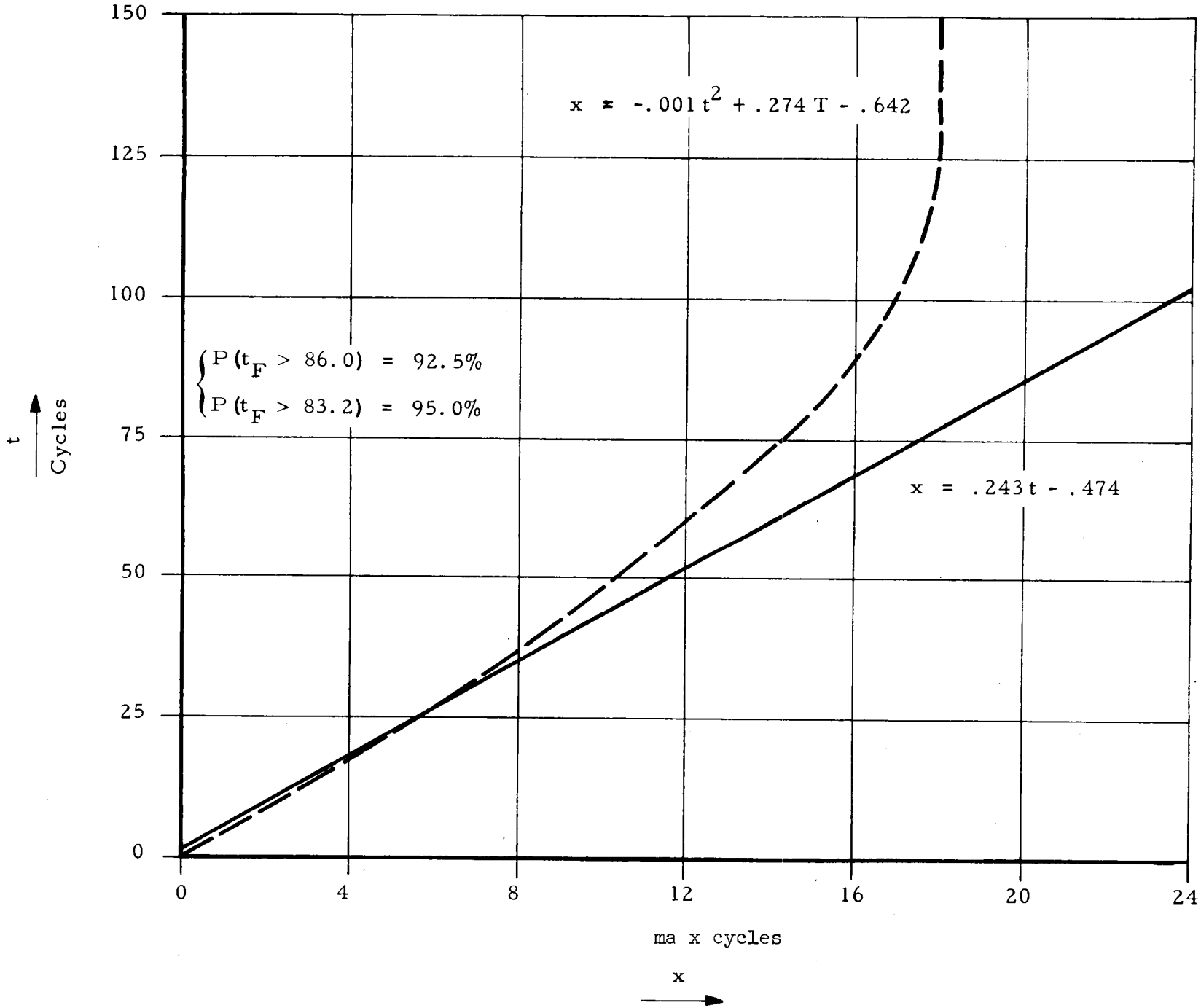
First the observations of current, I_i, and cycle, are put into the input. The data are transformed into linearity. Let's say you might have a straight line so you have no problem. However, you might have a parabolic function which is what the data seem to be at this point. Then you would differentiate that.

The regression coefficients are obtained from the best line fit. Then the line is extrapolated to the mean failure current to yield an estimate of the failure time or cycle life, Y_f.

All of this is based on, as I said before, knowing the mean failure current and some early gassing data.

Then we can calculate the errors involved, how good the probability is based on the amount of data that we have.

Naturally the more gassing data we have and the further along we are in the progress of the cycling regime with the battery, the closer we are to being able



Cumulative H_2 Current for 100 Ah Silver Oxide-Zinc Cell Based on Assumptions of Parabolic and Linear Relationships

to estimate the eventual true failure time of the battery. And calculating the error alpha leads us to a failure time to 92½ per cent, or .925 probability. Beta gives us .95 probability.

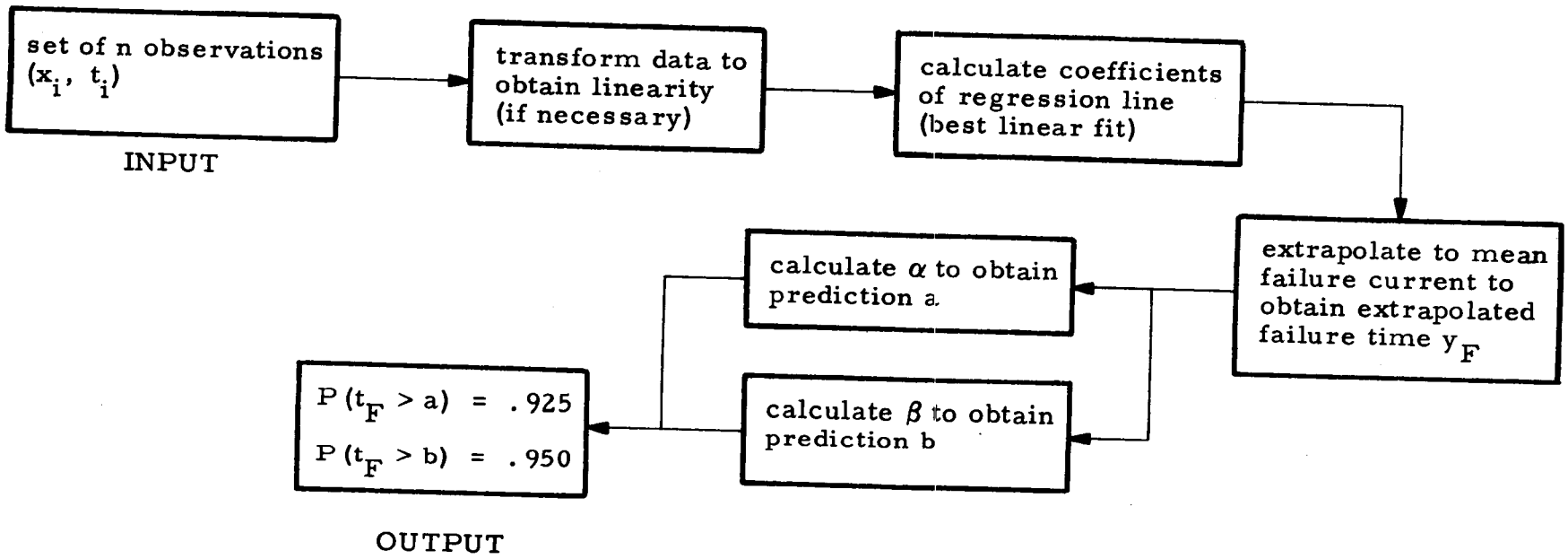
(Slide)

The next slide is really straightforward fundamental statistics which allow us to calculate from, let's say, studying the cycling pattern for N cells to failure, we can get an M_f value, estimated value of main failure current based on a random sample of N batteries -- it should really be cells.

Mu is the actual value of the mean failure current for the entire population of batteries or cells. X_f would be our corrected value for M_f based on the determination of the integral estimate of the mean failure current sigma, which is 1.96 times the sample standard deviation. And this gives us a value of X_f, the corrected mean failure current, which is less than the true actual value of the mean failure current to .975 probability.

(Slide)

The next slide merely is a least square relationship. You have a line, essentially describing the plot of cycle life versus fuel cell current time. We can calculate the regression coefficient A and B. This is on linear relationship.



Flow Diagram of Computer Program for Prediction of Cycle Life

Let μ = actual value of mean failure current for entire population of batteries

m_F = estimated value of mean failure current based on a random sample of N batteries ($N \geq 30$)

$x_F = m_F - \sigma$

where

$$\sigma = \frac{1.96\ s}{\sqrt{N}}$$

s = sample standard deviation

Then

$$P(\mu_F > x_F) = 0.975$$

Calculation of Interval Estimate of Mean Failure Current

Using the same least square relationships, we can get A and B. For example, here we suppose that a lotarithmic line, curve, expresses this relationship. We have this brought to a straight line in this way.

(Slide)

The next slide allows us to calculate the errors involved to both .925 and .95 probability. Alpha -- mind you, it is necessary to reduce our data to a straight-line relationship even though it initially did not seem to be that way. But we must use the various statistical approaches to get to that point -- alpha would be based on the use of the T tables, T distribution coefficient tables, .05, knowing the standard deviation, and beta would be the tables for T .05. That would give us .9 probability that the final extrapolated failure time is less than the true failure time to .95 probability.

(Slide)

The next slide, and I believe this is the last slide, actually refers to earlier data that I gave for actually test 22 for a 100 ampere-hour cell that was run for 30 cycles.

We found that it was possible to either fit a straight line or parabolic function through those early points. We felt more that a parabolic function would be apropos in view of the fact that we would expect

$$P(t_F > y_F - \alpha) = 0.925$$

$$P(t_F > y_F - \beta) = 0.95$$

where

$$\alpha = t_{.050}\, s_{yx} \sqrt{\frac{n+1}{n} + \frac{(x_F - \bar{x})^2}{\Sigma x_i^2 - n\bar{x}^2}}$$

$$\beta = t_{.025}\, s_{yx} \sqrt{\frac{n+1}{n} + \frac{(x_F - \bar{x})^2}{\Sigma x_i^2 - n\bar{x}^2}}$$

and

n = number of observations (x_i, t_i) of micro-fuel cell current vs. time

$t_{.050}$, $t_{.025}$ = t-distribution coefficient for n-2 degrees of freedom (obtained from tables)

$\bar{x}$ = mean value of the observed x_i's

$$s_{yx} = \sqrt{\frac{\Sigma(t_i - y_i)^2}{n-2}}$$

$y_i = a + bx_i$ (from least-squares regression line)

Calculation of Probability of Failure After N Cycles

(a) Linear Relationship

Let n = number of observations (x_i, t_i) of micro-fuel cell current vs. time of operation cycles)

$y_i = a + bx_i$ = least-squares regression line (best linear fit to observed data)

Then

$$b = \frac{n \Sigma x_i t_i - \Sigma x_i \Sigma t_i}{n \Sigma x_i^2 - (\Sigma x_i)^2}$$

$$a = \frac{\Sigma t_i - b \Sigma x_i}{n} \qquad (1)$$

(b) Nonlinear Relationship

$$y_i = A + B \log x_i$$

where

$$B = \frac{n \Sigma (t_i)(\log x_i) - \Sigma t_i \Sigma \log x_i}{n \Sigma (\log x_i)^2 - (\Sigma \log x_i)^2}$$

$$A = \frac{\Sigma t_i - B \Sigma \log x_i}{n} \qquad (2)$$

Calculation of Least-Squares Regression Line

the rate of gassing increase to actually go down with time owing to the fact that more and more active electrode materials are lost, and assuming, that here we are detecting hydrogen, that this is due to zinc, there is less active zinc around, and therefore the rate of increase in hydrogen partial pressure with time should go down.

We were able to fit two equations for these early points, one for the linear relationship, and the other for the parabolic function.

Differentiating TXBT, where X is the mean failure -- where X is actually the current and T is the cycles, differentiating the parabolic function with respect to T, we get DXDT which, plotted versus T, gives us a line, and from the least square relationship we get the alpha and beta error estimates based on .925 and .95 probability.

We initially assumed -- and here once again we have not carried out enough experiments to failure, and I want to say that I am basing all of this on a very, very limited amount of data at this point, and I am merely proposing several different approaches to analysis of this data -- here we assumed a mean failure current time of 17, which gives us, according to the upper curve, 100 cycles.

By differentiating and extrapolating and integrating we get a probability of 92½ -- a 92½ per cent

probability of 86 cycles, and actually the true failure time is greater than the 86 cycles to 92½ per cent probability.

The true failure time or cycle life is greater than 83.2, based on 95 per cent probability by this means.

We feel, in summary, in conclusion, that the type of gassing relationship that you get of this nature, as indicated by this type of plot, using the micro fuel cell, is susceptible to some theoretical analysis. This could help decide on just what the shape of these curves should be with some additional information about the nature of the constituents in the particular cell that is involved.

Thank you.

MR. SHAIR: Thank you very much.

Our last paper before the break is a contribution from TRW Systems Labs, by Dick Sparks. He is going to talk about the application of the space hardware program failure data to actual space battery design.

APPLICATION OF SPACE HARDWARE PROGRAM FAILURE DATA TO BATTERY DESIGN

MR. SPARKS (TRW Systems Labs): Good afternoon, gentlemen. The discussions on accelerated testing and failure analysis which were participated in so far have concentrated mostly on laboratory data and R&D background. The input which I wanted to add in the discussion extends

this effort further to include a very large source of data for analysis not adequately considered so far in my estimation, that of the operational experience on the hardware programs themselves.

Could I have the first slide, please.

(Slide)

Some of you will recognize part of this. This slide will help me emphasize the "Why we should look more carefully at the hardware data program."

In Carson's recent report, NASA CR 62029, he reflects the first two battery design problems. This represents his consensus, his summary of the consensus of the thinking in the battery industry. One is how to match the battery characteristics to the power system. The second is how to control the operation of the battery itself to optimize energy storage and delivery capability.

I would like to add one more design problem to his list: How to meet power system reliability and life requirements.

I will try to explain this more fully as I go along. Let me place a note on this particular design criteria. It is especially applicable to the new spacecraft hardware designs which require lifetimes of more than one year, and up to five and more years.

I have a couple of other items which I can't

THREE BASIC BATTERY DESIGN PROBLEMS

- How to Match Battery Characteristics to the Power System.
- How to Control Operation of Battery to Optimize Energy Storage and Delivery Capability.
- How to Meet Power System Reliability and Life Requirements.

project. They will be entered in the record.

What I have done, is put together a partial listing of those programs presently using nickel-cadmium batteries that I know about. There are approximately 22. This represents an awful lot of cells, since most of the programs usually run somewhere between 500 and a thousand cells.

On OGO and (unintelligible) spacecraft alone the analyst has access to more than 1500 cell-hours of operation with approximately 20 years of in-orbit battery operation. There is no doubt in my mind that this is by far the largest data resource for analysis. And it lies in the documentation of the hardware programs.

It is suggested -- I am suggesting to the reliability people, and I am glad a lot of the statistical people are here today, who require fairly accurate records on hardware program operational data be kept, and who have access to this data -- might look beyond a fixed-time data (unintelligible) into deriving more realistic cell failure rate models.

This could greatly help us in the design areas.

Could I have the next slide?

(Slide)

This particular slide shows a typical way that the battery failure modes are documented in our hardware

SPACE MISSIONS USING NICKEL-CADMIUM BATTERIES

Alouette
Anna
Ariel
Courier
Discover Series
Explorer Series
Injun
Lunar Orbiter
Midas
Minitrack
Nimbus
OAO
OGO
OSO
Pegasus
Pioneer Series
Relay
Syncom
Telstar
Tiros
Transit
Vela

BASIC FAILURE MODES AND CAUSES FOR NICKEL-CADMIUM BATTERIES

Battery Failure Mode	Cause
Open-circuit	Loss of electrolyte
	Leaks from defective seals
	Cell rupture from repeated cell reversal
	Cell rupture from excessive overcharging
	Mechanical failure of plate tabs or cell interconnections.
Low capacity	Internal cell shorts
	Plate-to-plate shorts
	Terminal insulator shorts
	Improper cell balance and control
	Repetitive cycling resulting in low voltage potentials at high discharge rates.

programs. I think this holds for not just our company; this holds pretty much all through NASA. Particularly the two main battery failure modes, open circuit and low capacity. Not short circuit, you will note.

The cause in the way it is documented, one cause of course is loss of electrolyte. Another is leaks from defective seals, mentioned previously, cell rupture from repeated cell reversal, and cell rupture from excessive overcharging.

The other area in which you saw some evidence in the Crane slides, mechanical failure of plate tabs or cell interconnections.

In the low-capacity cells, typically they are able to gain access to the data to say whether it is internal cell shorts or plate-to-plate variety, or terminal insulator shorts; improper cell balance and control; repetitive cycling resulting in low-voltage potentials at high discharge rates.

I might go further to say that much of this type of data is available in the contractor agencies, NASA and the Air Force, QC reliability organizations.

That is the last of the slides. I have one other slide which I particularly like. I presented a paper yesterday to the IEEE, and guess where it is? In the other projector.

TYPICAL FAILURE RATES FOR NICKEL-CADMIUM BATTERIES

	Failure rate x 10^{-9} per hour					
Years of Life	1	2	3	4	5	6
Failure Mode						
Plate-to-plate short	50	50	50	100	200	400
Ceramic-to-metal terminal insulator seal alloy migration—single-seal design	10	10	20	50	100	500
Ceramic-to-metal terminal insulator seal alloy migration—two-seal design	3	4	6	8	12	17
Cell case seal closure	10	20	35	55	75	100
Cell divergence (unbalance)	10	20	50	100	500	1,000

So I will try to duplicate that on the board.

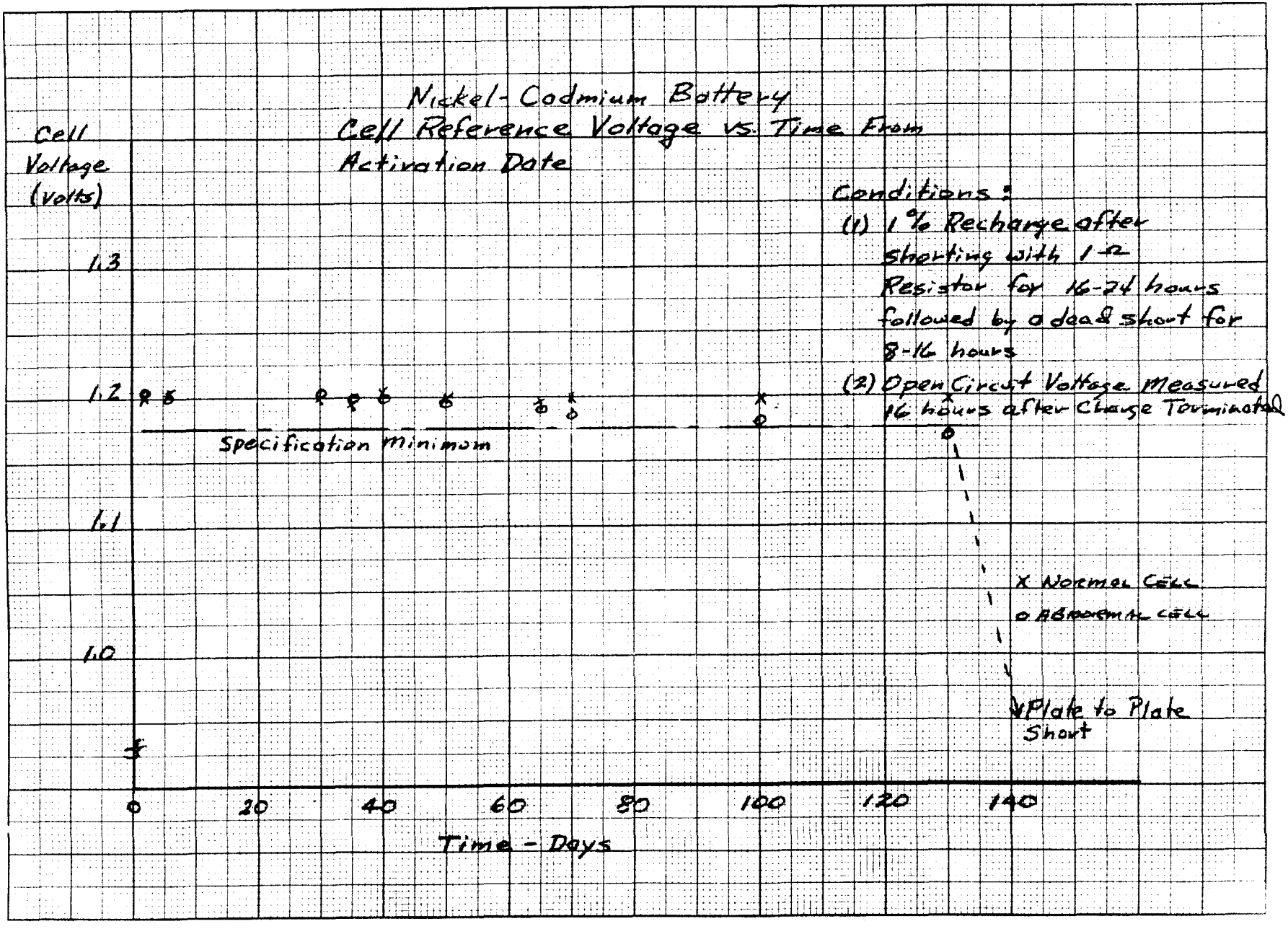
What I am going to put on the blackboard represents a slide which I had on the sample failure rate based on limited data random engineering judgment which we have been using recently at TRW Systems to study the best approaches to long cell life designs.

You will note that as I get it up there, that this approach helps one to realize that for long-life missions the present method of battery and control design is totally inadequate.

I will do some abbreviations and turn the photograph over for documentation later.

Let me say that the modes of failure that I have data on here are components of the slide that you saw previously. The plate-to-plate short; the ceramic-to-metal short -- in other words a terminal short; and I have two cases of single-terminal and the multiple-terminal design which have quite an influence on this; and cell case seal closure, which of course is your open failure mode; and I have another category which I call cell divergence, which is primarily a function of the way you use the cell, and how long you use it that way.

This particular category is more applicable to cells used improperly in the overcharge ranges for long times or on short orbits where you are forced to charge


Nickel-Cadmium Battery
Cell Reference Voltage vs. Time From Activation Date
Cell Voltage (Volts)
1.3
1.2
1.1
1.0
Specification Minimum
Conditions:
(1) 1 % Recharge after Shorting with 1 Ω Resistor for 16-24 hours followed by a dead short for 8-16 hours
(2) Open Circuit Voltage Measured 16 hours after Charge Termination
X Normal Cells
o Abnormal cells
Plate to Plate Short
0
20
40
60
80
100
120
140
Time - Days

at real high rates.

These failure rates that our reliability group have been able to gather so far are based on two programs really. These are years 1 through 6, and they are failure rates 10^{-9}.

The plate-to-plate shorts look like 50, and they take off when they start getting older.

The mechanical ceramic seal rates typically run low bit rates. For multiple seals they run lower, because of reduced voltage stress on the particular interfaces. However, as we get farther along, these particular designs start to show up as design limitations.

The cell case seal closure, for the one-year type mission is pretty good. And I think most of our space data indicates that.

As we go beyond this, we start seeing an increase in the failure rate that is going to get us into problems. Beyond about the fifth year we really start to see some problems.

The cell divergence is the last one. Again let me premise this as based on method of use.

This is an estimate based primarily on using constant voltage charging of a fixed level in the over-charge range. As you can see, these really go up in the latter part of the life.

The question thatarises naturally is how do we use this. This is the kind of data we are looking for from the reliability people to tell us how to design our charge controls for one, to take care of this mode.

The second thing, one of the previous speakers mentioned low plate-to-plate shorts you can cycle any way. It turns out in a spacecraft, where you are cycling over and over and over with random cycles and varying amounts of overcharge, that does not hold; that the cell actually decays and will become a premature low-capacity cell. The question arises: How do you get around this? There are ways of designing electronic circuits to shunt the cells or improve the cell designs.

The ceramic-to-metal seals, about a year and a half ago this failure rate in here was like out of this world. It was like a thousand compared with the Year 1.

A lot of design emphasis has gone into this particular area. You can see it is greatly helping the problem.

On the cell case seal closures, this is based on one particular cell design. It varies all over the map. Some seals can't last -- as a matter of fact, the majority of the cells don't seem to be able to last much beyond here (indicating second year). However some do fairly well up to about three years.

The cell divergence is strictly a use-duty

cycle type of design where we can use charge controls such as Hennigan developed with the silver-cadmium to keep down the stress in the overcharge range.

To give you a feeling for what this little story tell you, and I might tell you, especially the battery cell designers, is that for the five-year missions such as the COMSAT missions or the Communications Satellite missions, it looks like if you use a battery, a 20-cell battery, you need a cell failure rate of about 10 to make the power system reliability requirement.

As you can see, these are only part of the overall failure mode. And you don't approach it. We don't either, the way we use the cells.

It is obviously not achievable within the cell alone. So this says that part of the requirement for the long-life missions is going to stretch beyond what we have been talking about here on straight cell failure analysis, and cell accelerated testing, and we will have to go to the combined system approach where you look at both controls and methods and the cell.

To sum up this part of my discussion, let me repeat: I feel a different approach to the problem of data analysis and its application to battery design is required. If we can use the hardware program data to come up with models of what the cell really looks like in its applications,

then we can help the battery industry quite a bit by telling them where they have to concentrate much of their efforts, and where the cell tests should be designed to find out what the cells look like.

The second contribution which I would like to make, just as a kind of side point at this meeting -- side point to this discussion, but getting back to the use of accelerated methods of detecting problems in cells -- is a kind of controversial test, but it has been used quite successfully at the TRW for about the last three years. Again I cannot project it. I have a graph of it, which will go into the record. Let me briefly plot one.

I am sure you have all heard of the so-called cell short test, or the tests, a method of detecting whether you have plate-to-plate shorts in the cell, premature loss of capacity, whatever you want to call it.

As a user, you have access to the cells for quite a period of time in the hardware programs. Typically from the time the cell is activated until the time it is launched. And based on this we run a short-circuit test which amounts to roughly the short-circuit tests that (unintelligible) is running, where we put back in about five minutes of charge after the battery has been shorted for 16 to 24 hours, and watch for decay of the voltage, or for any cell which falls out of the group by more than 20 millivolts.

Typically we see cell voltages of about 1.2, depending on the design, 1.6 on some designs, as a typical cell. And say a cell in this lot that runs 1.8 or below, we really look very closely at it. The real thing we are looking at here, if you take a typical good cell and plot it, from the date the cell is activated, and you run this test, you will get a bunch of points that vary within the 10 millivolt range over time, if you can get the cell back to the same initial reference condition that you had before.

If you take a look at another cell you will find -- and we have had on the OGO program two occasions to verify this -- what we have seen happening is a drift, and this might be in this minimum specification level, with some 20 millivolt range here, where it allows an acceptable 20 millivolt deviation, the battery may still be within the specification, so our inspection people are passing the battery.

But what has happened twice on one program is that where this trend did exist, out here at about just before we got ready to launch, ready to put -- one was already in the spacecraft and one was about to go in -- these particular cells both developed plate-to-plate shorts, one from an impurity particle and another from a piece of plate material which had flaked off.

We have been using this and we cull out cells showing a kind of a trend like this.

To give you an idea of the places that we get a good enough look, we can run this test, this short-circuit test, at the supplier post-assembly when he completes the activation. When we receive the new cells, after we have done our selection in matching and before we assemble the batteries, after we assembly the battery packs, every 30 days on storage, pre-vehicle installation, shipping, and post-vehicle installation and shipping. This gives us quite a few data points and essentially makes use of the results we have had from the previous failure analysis which showed that indeed we do have a pretty good check on the short-circuit situation.

Thank you.

MR. SHAIR: Thank you very much, Dick.

We do have a good 15 or 20 minutes for discussion. We have this afternoon seen some detailed information of a silver-cadmium examination program, some visual failure analysis of cells in the test program, some indication of the analytical tools, a rather interesting method from Dr. Strier, at Douglas Aircraft, and now the application of failure analysis to battery design. So let's jump into some discussion.

Mr. Gandel of Lockheed.

MR. GANDEL: The idea of obtaining this data from the flight hardware over this period of years is really good. How do we pinpoint the mode of failure though?

By our application we have bus voltage. We can see if this starts to fall of. Again we have more than one battery in parallel.

If we have a shorting between inter-cell connectors due to perhaps leakage of electrolyte, or if the plate-to-plate short is developing, this is kind of buried among so much other data, or let's say the complexity of the system is such that we can't adequately diagnose it.

The other question I would offer is, on your flight batteries do you have individual cell voltages monitored? Is this data transmitted back?

What I am saying is, it is a good idea, but how?

MR. SHAIR: I presume that question was directed at Dick Sparks.

MR. SPARKS: I will try to answer that.

In the first place much of the data available on flight programs is available mostly on batteries that are either not launched, that is spare batteries, the qualification batteries, the test batteries, and on the flight batteries up to the time that they are launched.

You are perfectly right on the batteries in orbit. It is difficult to determine what the failure modes

were. However, on several of those modes that were up there, you can determine from your hardware data.

Load sharing gives you one indication of the type of failure. Also, your telemetry data on battery voltages gives you different information.

We have been successful in determining some of the failures we have seen, even in orbit.

MR. SHAIR: Very good. Another question?

Karl Preusse, from Gulton.

MR. PREUSSE: A question for Dick. I have two points to bring up. One is on your failure rate data.

I would like to know, was this generated using 100-minute orbit type application?

Also, was a generator using various depths of discharge?

Was it generated over a spectrum of temperatures?

And indeed, if you did generate this information with this type of testing, how do you intend to extrapolate this failure rate data to the five-year synchronous rate orbit mode of operation where there may only be 80 cycles a year and a fixed temperature range of operation?

MR. SPARKS: The data that I showed there was, as you notice, broken down into parts of the overall failure mode. It was combined data as best we could estimate it from what we had. It included variations in

temperature, it included different cycle depth of discharge.

As you know, we don't run cycle tests. So it includes variation. On that basis we try to extrapolate it to the 24-hour requirement since the data on the OGO gives us data at the 100-minute orbit condition and at the 60-hour orbit condition, and the (unintelligible) information is on the 40-hour condition.

What we are trying to do is bring it all together and see what we can best make out of it.

MR. PREUSSE: My question is, the reliability people, when they extrapolate the failure rates which you have published with regard to the synchronized orbit, how do they look? I am sure they are not using the same numbers for the synchronous orbit.

MR. SPARKS: Frankly, if you just take the bare battery for the synchronous orbit for five years, it doesn't look so good. We have gone to electronics to get around this problem and take care of two of the failure modes that are there, that allow us to barely meet our 24-hour requirement.

MR. PREUSSE: My second point is the open circuit voltage test, and the questioning of the validity of it. Not really the validity of it but the question of what is the voltage which we should really select to.

I am sure some users may be using 1.15 volt for their selection criteria of cells, some users may be using voltages of 1.10 volts. Other people may be using 1.18. Apparently these manufacturers all must be having the same degree of success with the spacecraft that they are utilizing.

What is the validity of this open-circuit voltage test, and what does the voltage actually tell you when you're in this neighborhood?

MR. SPARKS: These particular voltage levels that we use are based strictly on the specific cell design we are using and they are only established after we run experimental data on that design. We have not been able to find a universal voltage which we can use.

MR. PREUSSE: I think this is one area where there could be possible investigation just in general.

What does the open-circuit voltage test and what does it tell you? As a result you may be rejecting cells which may be good cells, and as a result this is a reflection in the cost of the cell.

MR. SPARKS: I might comment further. I know NASA-Goddard has been working on this problem. They have a different type of test for this short-circuit detection. That is why it is said the test is quite controversial, because we haven't been able to get a good, repeatable test

of any real validity. We are merely using this one to find trend information, wherever it is possible.

MR. SHAIR: Thank you, Dick. I notice Tom Hennigan.

MR. HENNIGAN: Somebody asked if we could get much data from the satellites on the batteries. Batteries are not an experiment and they are not going to give you many measurements. You are lucky you get the total voltage.

We have asked many times to have the cells measured out. We just can't get it.

Even some of the larger satellites, the more expensive ones, they will give something like three cells in 22. That is not much data you can get from a flight program.

MR. SHAIR: Dr. Fleischer.

DR. FLEISCHER: I would like to make a comment about the short-circuit test. It is apparent that we haven't done any experiments in which we find out what is going on. We should start and assemble cells with positive and negative plates in which we have no separator. That is, we keep the plates apart with polystyrene or some means so we don't have an interaction of a decomposing separator on the positive or negative plates.

We measure what happens when we charge this in the same manner, using the same plate areas, then we have

established something to start with. Is the shorting effect fundamental when you do this? Is there a change of voltage over a period of a month with a cell in which you know you should have no problems whatever?

Then the next thing to do, you pull the plates closer together and then you start adding separators.

It seems to me that with the requirements you put on it, a five-minute charge after a 24-hour short circuit, there shouldn't be any problem in doing this in the laboratory whatsoever.

MR. SHAIR: Thank you, Art.

The gentleman over here.

MR. SHAFFER (American Machine and Foundry Co.): I just want to comment on the question that I think Mr. Sparks already answered during his talk, but didn't reiterate when somebody asked him what do you make of this data on the flight programs.

It is not important what the open-circuit voltage means except in a kind of philosophical sense, which some electrochemists might be interested in. But the trend of the data is terribly important.

I think this is well known in all kinds of preventive maintenance programs that have been set up and used for many years, in other application than batteries in space.

It is my impression that even when you have very incomplete data, if you have trends and go at this with a statistical approach, you can often deduce things that you would not have suspected in terms of any planned experiment.

MR. SHAIR: Lou Belove.

MR. BELOVE (Sonotone): How does he intend to make a sealed place with plates, with no separator?

MR. SHAIR: The question was directed from Lou Belove to Dr. Fleischer: How do you intend to make a sealed space cell with just space between the plates and no separator?

DR. FLEISCHER: You start in with fully submerged electrodes, obviously, because you want to know the discharge of the cell. The change in voltage on stand is a fundamental thing. You first want to note it is not something that happens under ideal conditions.

Once you have established this then you can start deducing that whatever happens, your change of voltage is something that you did in the construction of the cell, or something which you put in there which is causing the thing to discharge. The problem is that a simple test like this cannot have no reliability. You can approach as to what it means by doing the experimental work. If you don't do it, you are guessing as to whether this is a reliable test

or not.

It won't take much to go over to the next point because you fellows make polypropylene separators and various other materials, Teflon separators, in which you don't have to worry about current densities, how high you are going. All you are worrying about is to now maintain the conditions and approach the conditions that you get in the sealed cell.

MR. BELOVE: I want to caution you there. The open-circuit voltage between sealed and vented, because that is what you are comparing, is quite different. The charge retention, or decay of voltage, is not the same the moment you flood the system.

DR. FLEISCHER: We are going to seal this cell, aren't we, if you want to? Now you have the sealed cell, and you are going to charge for five minutes. You are at an end where you have no problems with oxygen evolution. If your cadmium plates are properly formed, you won't have any hydrogen evolution at the start. So you are working at a place where you can find out what is going on.

The suggestion that I made is simply that by experiment we can find out whether this test is reliable. And I think that the satellite designers who deal with batteries want to know if this is a reliable test.

I interpreted that Mr. Sparks would like to know

if any deductions he makes from that curve are reliable. So you do it by experiment, not by guessing.

MR. SHAIR: Did you say "guessing" or "gassing"?

(Laughter)

DR. FLEISCHER: The same thing.

(Laughter)

Do we have any more questions.

The gentleman from Picatinny Arsenal.

MR. MAGISTRO (Picatinny Arsenal): On this trend analysis, has there been an attempt to compute the tolerance limits say from average voltages to the specification requirement along this cycle? Instead of watching what we have done in a similar manner, almost plot a control chart, standard three-sigma quality control chart here, or any other limit you want to specify for probability of falling below, and then we say okay, we don't have to wait as long, we can make our estimate a lot sooner because we compute the probability based on the distribution at any point in time on this curve.

Has that been attempted?

MR. SPARKS: I think we have looked at that, but the variation in the data has been quite random. And we haven't been able to draw any correlations based on the three-sigma type of specification limit.

DR. FLEISCHER: Very good. One more question.

MR. WEINSTEIN: This is addressed to Mr. Waltz on the Crane data. He showed some photographs of new cells which had been taken apart. The question I have is how new were these cells? Does he have any records of how long they have been in storage, and under what conditions?

MR. WALTZ: All I have is that they have not been filled with electrolyte. I have no indication of its age. Sorry.

MR. SHAIR: Mr. Martin Gandel, once again.

MR. GANDEL: With respect to age in the dry condition, I have just a little bit of limited data to add.

We ran some tests on over-age batteries, batteries that we wouldn't fly because they exceeded a one-year shelf life limitation. On the battery which had been sitting on the shelf for five years, we found after activation that virtually all the cells shorted very soon after being activated.

These cells, by the way, had one layer of Visking and one layer of Viskong.

Going down the scale of time we found that we had shortings occurring in batteries that had been on the dry shelf for 26 months in one case, and another case 22 months. The time factor is important.

MR. BOWERS (NOL/White Oak): What type of batteries are you talking about?

MR. SPARKS: Silver-zinc.

MR. JASINSKI (Tyco Lab., Inc.): On the batteries shorting, the way the shortings occurred, at the plates, terminals or seals?

MR. SPARKS: Separators.

MR. SHAIR: The discussion has been lively. It is an interesting subject. I guess we have time to take a break for about ten minutes.

Don't run away, Gene Stroup; I have a couple of slides to show also just before the break.

(Whereupon a short recess was taken.)

MR. SHAIR: This afternoon we jump right into some analysis of the large amount of data which has been collected.

The first paper which was originally Jerry Halpert's as No. 2; but the first paper will be given by Peter Fowler of the Martin Company, in which he will talk about the control of battery quality for high reliability vehicles -- approach and case histories.

CONTROL OF BATTERY QUALITY FOR HIGH RELIABILITY VEHICLES -- APPROACH AND CASE HISTORIES

MR. FOWLER:(Martin Company): Thank you. I was asked to talk here today. I assume it can't be as an expert on batteries because I know practically nothing

about batteries. But I want to take the opportunity to express a customer's point of view.

My company, Martin in Baltimore, is in the business of building very high reliability vehicles. The Gemini launch vehicle is the most notable. We are in a number of other similar businesses.

In the course of these programs we have learned quite a lot about reliability of piece parts. With all due respect, batteries are a piece part.

Lack of reliability, which is my problem, implies failure. And there are three reasons for failure, and only three.

The first reason, and it is the one which accounts for probably most of the major space catastrophies, is that some component is inherently incapable of performing the mission that was required of it, while working in the environment which was required of it. We have attempted to eliminate this tight requirement from our program by subjecting the qualification samples to very exhaustive functional testing at the limits of what we expect them to withstand, by subjecting them to environmental testing at approximately the 99 per cent level. That is, we apply environmental tests of a severity which less than one vehicle in a hundred would ever see in real life.

We usually use test times which exceed the flight

time by enough margin to insure a part capable of withstanding the pre-flight testing as well as the whole flight afterwards.

Having got a qualified part, and in some cases I would say if we get a qualified part we then attempt to permit no change whatever in the design of the equipment that is actually supplied for flight. Unfortunately, piece parts manufacturers are prone to put "improvements" in their process.

(Laughter)

Our experience is that an improvement in a qualified piece part is virtually never an improvement.

I would like to take this opportunity to put in this request, and I am sure I speak for other customers: Please, if you must change your process, whether you think it is an improvement or not, tell us first. We hate surprises.

(Laughter)

Particularly we hate surprises when on your battery rides a couple of astronauts' lives, a hundred million-dollar program, a considerable investment far outweighing anything you could ever do in cost reduction on batteries. What is much more, it is doing it on television.

(Laughter)

I had some pictures of typical qualification test

failures, and I'll explain later why I'm not going to use them. Some typical failures in qualification tests on batteries are detachment of the connections from the plate to the terminal on the high shock.

A wear-through of the separator due to bumps of various sorts on the plates which under high prolonged vibration eventually work their way through the separator and short-circuit the battery.

Leakage and spilling of electrolyte is a very serious problem in qualification. We take a ten-cent battery and we ruin a $10,000 unit because it spills.

The second reason for failure, and in our experience this is by far the commonest, outweighing all others by an enormous margin, is that inherently qualified equipment has been degraded by either faulty manufacture or mishandling. So that after a little while in test or application in stress in flight, it fails prematurely and frequently catastrophically. We have several methods we apply to eliminate this type of failure.

We go in fairly heavily, for instance, for personnel motivation programs as ED programs, the principal one.

We go in a great deal, as I think many of you know, for vendor audit and process control.

We put our people in to insure that the part

we qualified is eventually the part we get.

We also go in very heavily, and I think most other people do, too, for very exhaustive pre-flight functional testing and for a great deal of pre-flight environmental testing. What we try to do at this level, we apply to the piece parts the critical environments which are usually vibration, sometimes thermo-vacuum, at a 95 per cent level. We apply the test which 5 per cent of the flights could exceed.

We get some quite interesting failures in this phase, in the acceptance testing. We had a battery the other day which suddenly expanded to several times its original size. On failure analysis it turned out this was a vented battery, it turned out that when we inspected the vent hole somebody in the process had cleaned out the vent hole with a piece of silver wire. We know it was a piece of silver wire because an eighth of an inch of it was still in the vent hole. We now have an inspection specifically that there is a hole through the vent hole.

(Laughter)

We have had batteries on acceptance tests again, vibration failures due to wear-through of the separator. Vibration failures due to crossing of the components inside the cell. Particularly on plates molded onto wire. If the wire is crossed, then that will wear through the

separator under vibration and short-circuit the cell.

What we are told extraordinarily frequently on things like that, after we buy ten cells, and one of them has a crossed wire, the manufacturer informs us that "That couldn't happen again once in a million times." I want to know how it is that on every program, out of ten samples, I get something that could only happen once in a million times. Again we put in an inspection station with the manufacturer just to see if he has crossed the wires on the plates.

I have three slides -- only three slides -- on battery failure.

(Slide)

This is a rather subtle one. I am not sure how the slides show it.

This is a battery. I don't know whose battery it is. I am sure somebody here does.

(Laughter)

Just to show the outside appearance.

(Slide)

Now I will show you the fault. I think you can just see where the arrow is, a little lump on the plate. Hardly perceptible. It is really there.

(Slide)

You can almost see that from that little lump

on the plate a dendrite of metal grew through the separator and short-circuited the battery.

You can hardly see it.

A little hair is really there. It is not something wrong with the photograph. It is something wrong with the plate.

Again what we did about that, we now have a 200 per cent inspection of the plates. That is, they get inspected twice. We don't accept into our cells plates that have little lumps on them.

The third reason for failure, and the third reason is very rare for us. I gather for other programs it has not been so rare, that a good part that is qualified and is properly applied wears out. There are two reasons for something to wear out. One is thermodynamic equilibrium will eventually take over. The other is that there may be cumulative effects of the environment.

For instance radiation damage which you can't stop, accumulates over the years and eventually kills the part.

To my mind, and I don't know that I have changed it from what I have heard today by experts, a tremendous proportion of what we call wear-out is in fact defective manufacture in the first place. Certainly among other components than the battery this is the case.

Further, for genuine wear-out, there is a growing feeling among specialists in piece parts reliability that a general model for wear-out is the EYRING relationship. Whether it is because it is physically true this is a general model or whether it can be that you can fit any set of data into an EYRING relationship, it doesn't matter for our purposes.

We have done a little preliminary work on looking at some battery data on an EYRING basis. I havessome slides about it in a moment.

The trick, the problem that we found with applying EYRING relationships to predicting life is that you have first to find what parameter it is of the piece part which is actually directly affected by the wear-out.

On the cells we looked at, storage batteries, and these are nickel-cadmium, it turned out that the efficiency was not in any way related to the stage of life you were at. A battery had a 90 per cent efficiency when you started, and it is liable to be 92 when it no longer works, when it can hardly hold a charge.

The voltages on the cell seem to be irrelevant. There was no particular relationship between the voltage of particular parts of the cycle and how old the cell was. It is a very small effect.

However, my next slide, if I could have it,

shows the capacity of a certain battery and it is one of the batteries on the Goddard test, discharged through a fixed resistor.

(Slide)

We measure capacity by the number of hours it takes to discharge to one volt. This has a very characteristic appearance. This has not been smoothed. This is the real data. It has the characteristic of a broadly drawn exponential.

(Slide)

This is the same plot, same data with no smoothing. We had plotted log of capacity against the number of the cycle.

You see this shows the highly characteristic intersecting straight lines. What is significant to me about this type of plot, and we have seen several of them, is that while I hear everybody telling me how complicated the modes of batteries are, for the plots I have seen they have reduced to one or two straight lines this way. Maybe, I am sure it is, we haven't taken them over a nearly wide enough temperature range or a nearly wide enough set of conditions. We see rather simple mechanisms. In fact we have some guesses about what they might be.

It seems to me that batteries, like most other piece parts, if you want to do life predictions,

particularly if you want to do screening for life, plotting EYRING relationships, is a pretty good way to go about it.

That is the end of my slides.

Just to end up, I will tell you why I don't have any slides of battery failure and qualification testing. The reason is, I asked the manufacturer first for his permission to use the pictures here. He decided that he didn't want to let me use the pictures. He had two reasons, and I think they are illuminating. The particular failure I wanted to show was broken connections of the battery terminal. And his two reasons were these:

First, it is a very unusual failure for a battery -- broken external connections he has not seen before. That was a little surprising to me because wire breakage amounted to over half the qualification failures on that program. Not the batteries but for all components. This is generally true. If that is the first time he has seen a broken wire, I am very surprised.

His second reason was that the picture I was going to use was unfair to the battery as the connections had not failed in their electrical operation, and the material of which they were made was electrochemically entirely compatible with the battery. In fact it was a part of the plate itself. And they had not failed to work

as part of the battery collector. The battery, in other words, was perfectly good as a battery. It just didn't work in our environment.

That is the essence of what I wanted to say this afternoon, gentlemen. I accept that you know much more than we do about batteries as batteries. The problem is: Will they work in our environment?

Thank you.

MR. SHAIR: We are right on schedule.

Following, we have a series of two papers on computer programs, and Jerry Halpert, from the Goddard Space Flight Center, will give the first one on computer program for the analysis of battery data.

COMPUTER PROGRAM FOR ANALYSIS OF BATTERY DATA

MR. HALPERT (Goddard Space Flight Center): A series of computer programs for analysis of battery data has been completed and is now available. The programs were a necessary outgrowth of the nickel-cadmium battery project at the Martin Company (NAS-5-3027), in order to analyze the large amount of data generated. This project was initiated by Joe Sherfey in order to set up factors relating to operation and life.

These computer programs as a whole have been given the name of the Battery Analysis system and were

written with a great deal of flexibility so that they could be used by others in government and industry to perform analysis of battery data.

This report contains an outline and brief description of the Battery Analysis system, its use and what can be expected from it. I might say that computers are a little out of my line. I will try to give you the over-run down to the program as best I can.

This particular subject of computer program is partly of a set of six reports on the nickel-cadmium battery test project. The first two on the acceptance testing and computer-operated facility are complete and reports are available. Part 4, which contains the results of the battery test, it says here, will be available soon. I will try to wrap that up in a little better report later on at some other time.

Part 5 on the physical chemical analysis of the cells and their components is also being prepared.

Part 6, the computer analysis of data, is progressing now that the battery analysis is complete.

Before getting into the analysis, it is important to consider the data generated during a test. In taking data from batteries, one immediately sees that there are two distinct types of data. One type is the data recorded during charge and discharge, such as

voltage, pressure and current. The other type is data compiled at the end of a cycle such as amp hours, watt hours, and current efficiency.

In the Martin battery test, data was automatically recorded on punch cards which were designated "outcards" for the data generated during the cycle, and "endcards" for the data compiled and recorded at the end of the cycle.

(Slide)

This is a recoup of what I have just said. We have the two types of output from the computer-operated battery test, the outcards recorded during the charge and discharge, and endcards at the end.

(Slide)

This is a format of the type of card that comes out from the program, including all the data. As you see, we have the data groups, namely fields, called fields in computer terminology, of all of the various functions: battery, cycle, and so forth. At the bottom, the number of digits allowed for each. At the top, examples of the actual data.

The first five or so columns that you see here are identifying columns and would not be used in analysis except for the cycle number which comes out directly as part of the program.

OUTPUT FROM THE COMPUTER-OPERATED BATTERY TEST IS IN THE FORM OF PUNCHED CARDS.

1. OUTCARDS

DATA RECORDED AT A SPECIFIC TIME DURING THE CHARGE AND DISCHARGE ARE RECORDED ON OUTCARDS

2. ENDCARDS

DATA RECORDED AT THE END OF THE CHARGE AND DISCHARGE WHICH HAS BEEN COMPILED OR INTEGRATED DURING THE CYCLE ARE RECORDED ON ENDCARDS

OUTCARD DATA - DATA TAKEN DURING THE CHARGE & DISCHARGE

02	BATTERY NO		2	662
662	CYCLE NO		4	4
4	YEAR		1	78
78	DAY		3	18.723
18.723	REAL TIME		6	.1226
.1226	ELAPSED TIME		5	14051
14051	AVG INSTANTANEOUS POWER	*	5	1
1	PHASE	*	1	12.656
12.656	CURRENT	*	5	19.73
19.73	PRESSURE	*	4	1.110
1.110	VOLTAGE CELL 1	*	4	1.096
1.096	VOLTAGE CELL 2	*	4	1.105
1.105	VOLTAGE CELL 3	*	4	1.118
1.118	VOLTAGE CELL 4	*	4	1.113
1.113	VOLTAGE CELL 5	*	4	1.112
1.112	VOLTAGE CELL 6	*	4	1.113
1.113	VOLTAGE CELL 7	*	4	1.103
1.103	VOLTAGE CELL 8	*	4	1.099
1.099	VOLTAGE CELL 9	*	4	1.130
1.130	VOLTAGE CELL 10	*	4	6022
6022	SEQUENCE NO		4	

The items or fields labeled with the asterisk are used for the -- can be exchanged for any other piece of data that an analyst might want to use, somebody setting up a battery test might want to use. Instead of voltage, for example, he might want to use temperature or pressure or current or any other thing that he has in mind. As long as they would fit in the number of digits, that piece of data could be put into those points.

On the second, next slide, we have a format of the endcard data.

(Slide)

A similar type of card, punchcard, with the data shown here as being the type that is compiled during the battery -- compiled throughout the actual cycle and then punched out at the end. As you see, we have one great advantage of using the computer and operating the battery test, that a number of calculations are automatically made and punched out directly at the end of the test rather than somebody sitting at a calculator or integrator and trying to work them out later. I won't go into too much detail about different fields. I think they encompass a wide area.

Another point about the computer-operated facility. It allows you data reduction automatically in that one would normally expect a number of outcards for every

FORMAT OF ENDCARD DATA

ENDCARD DATA - DATA TAKEN AT END OF CHARGE & DISCHARGE

BATTERY NO	CYCLE NO	YEAR	DAY	TIME DURATION	AMP MINS	WATT MINS	ENERGY EFFICIENCY	AMPERE HOURS	WATT HOURS	AVERAGE CURRENT	MINIMUM CURRENT	MAXIMUM CURRENT	AVERAGE POWER	MINIMUM POWER	MAXIMUM POWER	CURRENT EFFECIENCY	ENDCARD NUMBER	PHASE	SEQUENCE NO
02	1090	4	150	3.2333	122.82	167.58	67.4	2.047	2.793	0.633	0.631	0.634	0.864	0.779	0.906	77.1	1	1	6162
				*	*	*	*	*	*	*	*	*	*	*	*	*			
2	4	1	3	6	6	6	3	5	5	5	5	5	5	5	5	3	1	1	4

B/91

one endcard. In our case it actually was 20. We had 20 data points during the cycle for each of the charge and discharge.

The computer itself, in operating the program, can set its own limits, or you can set limits into the computer. When the limit is exceeded, the data is automatically punched out. In our case we used two per cent change in watt hours. Whenever this was exceeded, the computer punched out the data.

As it turned out we had more endcards during the battery test than outcards over the whole complete test.

In order to use the Battery Analysis system, the data on the cards must be transferred to magnetic storage tape by a simple set of computer programs, which sort, check, and arrange the data in sequence. At this point the data is now ready for analysis. It is on tape and is duplicates of these cards.

(Slide)

The Battery Analysis system consists of a series of five programs which are listed on this slide. The five programs are the retrieve formatter, which does what it says, it abstracts the data that one is interested in from the data tape and puts it in a format that can be used by the rest of the programs. With 500,000 cards or so of data, one would not want to take every piece of data

5 ROUTINES

1. RETRIEVE -FORMATTER
2. PSEUDO FIELD GENERATOR-(COMPUTES)
3. LIST
4. PRINTER PLOT
5. STATISTICAL ANALYSIS

   (MEAN, VARIANCE, STANDARD DEVIATION, CORRELATION AND REGRESSION)

off every time. He gives the opportunity for the analyst to take only what he desires. The pseudo field generator actually computes any data that is required that is not available from the actual computer test. The last program obviously lists the data, whatever data you have abstracted.

The printer plot allows one to plot the data.

The statistical analysis program allows one to find the mean, variants, standard deviation, correlation, and regression of the items that one has abstracted.

It is obvious that the last three are the output of the program and the first two really set it up.and choose which data you would like.

In order to use these routines the analyst must first decide what he is going to choose in the way of data and then punch into a control card in a coded manner the items that he is interested in. Each of these programs except the last one has a control card in the pack.

(Slide)

This will give you some idea of what the analyst has control of. In the retrieve formatter routine he can choose any or all batteries or combinations thereof. He can choose any groups of cycles, increments of cycles, any or all cycles in a given increment.

RETRIEVE - FORMATTER ROUTINE

THE ANALYST HAS THE CHOICE OF:

1. ANY OR ALL BATTERIES OR COMBINATION THEREOF
2. ANY GROUP OF CYCLES, INCREMENTS OF CYCLES, ANY OR ALL CYCLES IN A GIVEN INCREMENT.
3. CHARGE DATA, DISCHARGE DATA OR BOTH
4. DATA FROM A % OF ANY CHARGE OR DISCHARGE (BEGINNING OR END)
5. UP TO 26 DATA FIELDS IN ANY COMBINATION
6. CHOICE OF EITHER ACTUAL DATA OR LEAST SQUARES POLYNOMIAL FIT OF DATA
7. STATISTICAL RETRIEVE (STOPS AT FIRST ZERO) OR NON- STATISTICAL (ALL DATA REQUESTED).

He can choose between charge data, discharge data, or both. Data from a percentage of any charge or discharge, if he wants the first 10 per cent of the charge and last 10 per cent of the discharge, he can do that.

He has up to 26 data fields. Choice of either actual or least squares polynomial fit of data. This is helpful in picking up certain points not available from actual data. And obviously, I should say in the last case, he can choose a statistical or non-statistical retrieve. In the statistical it is obvious you don't want anything that includes batteries. If the battery goes off, you want the program to stop retrieving. In other cases where you want to plot the data, it is helpful to have the non-statistical.

(Slide)

Here we see the choices that the analyst has in the pseudo generator routine. He has all of the possibilities that are allowed by FORTRAN 2 programming language. I have listed a few of them.

The one on the end is absolute value, not dne times one.

He can in this program write a little computer program of his own. In the case of Mr. Waite's method for analysis, if he would like to subtract one card from another, he can set up a little program of a few

PSEUDO GENERATOR ROUTINE

THE ANALYST HAS THE CHOICE OF:

1. COMPUTATION USING ANY MATHEMATICAL OPERATION ALLOWED BY FORTRAN II PROGRAMMING LANGUAGE

   $+, -, \times, \div, \sqrt{\ }$, log, ln, e^x, x^n, 1×1, etc.

2. UTILIZING FORTRAN II PROGRAMMING LANGUAGE TO PERFORM SPECIFIC OPERATIONS WHICH THE RETRIEVE PROGRAM DOES NOT HAVE AVAILABLE.

cards and put it into this area and have it continue along as part of the regular program.

If he wants to run an EYRING relation or something that would involve an inverse logs, he can automatically do this.

These are the two preparation routines. Now we have the last three, the output and the next slide.

(Slide)

The analyst has the choice of any or all of the following output routines: He can run them all or only one, or any of the others. Here in these he has the choice of his routine, obviously to get what he asks for.

In the statistical he can get the mean, variance, standard deviation, correlation, regression of any or all of the variables versus any or all, up to 26.

He can obtain a printed plot of the data on which he can choose his own plot, essentially X and Y scales, grid lines (unintelligible) X and Y variables, and choice of ranges.

I have put these all together. On the next slide we see the flow of the entire program and how it works out.

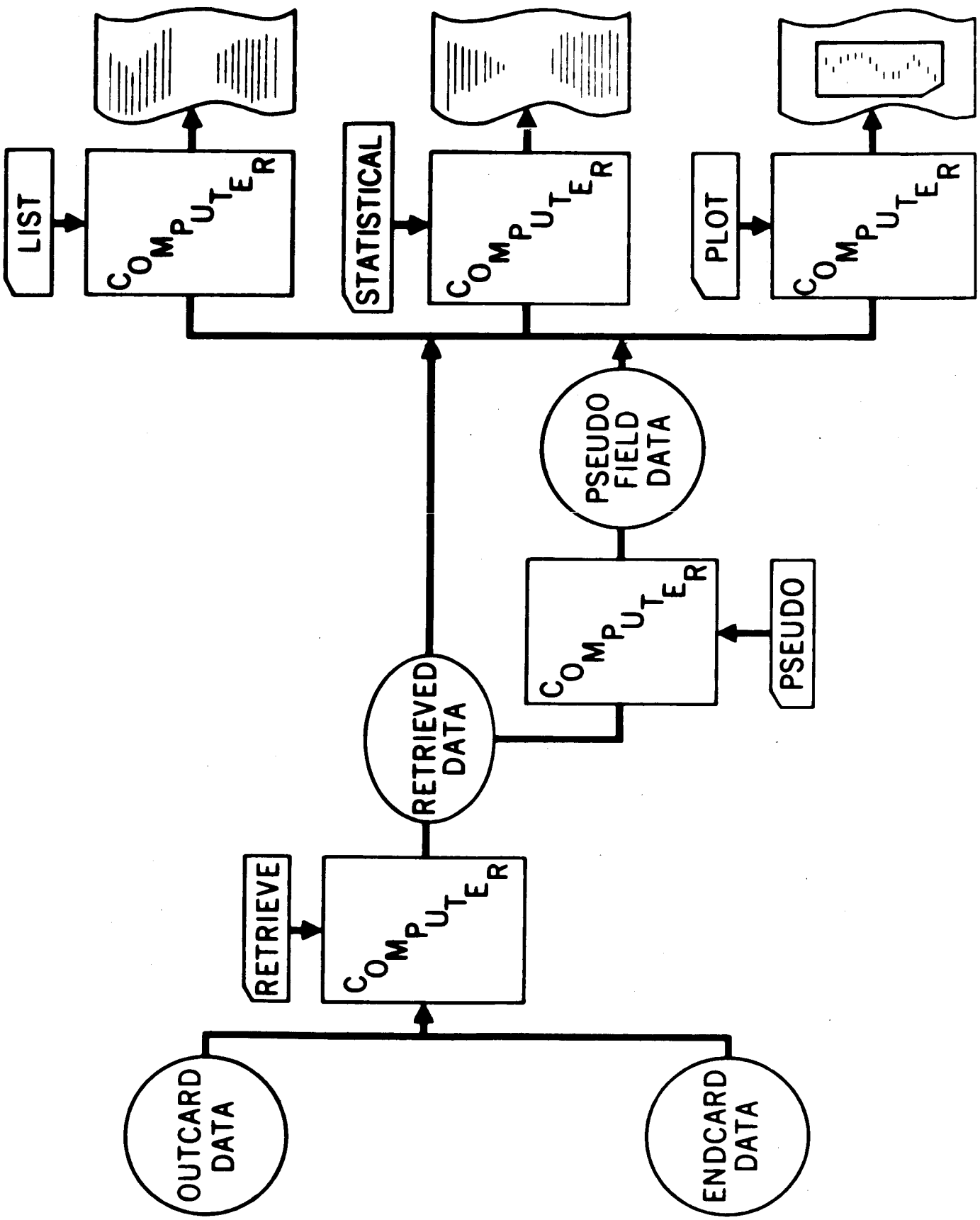
(Slide)

It is one step, although it appears differently here, it is a one-step operation. You supply only the cards of the computer program that you are interested in.

OUTPUT

THE ANALYST HAS THE CHOICE OF ANY OR ALL OF THE FOLLOWING ROUTINES:

- LIST ROUTINE – AUTOMATIC PRINTOUT OF DATA.
- STATISTICAL – MEAN, VARIANCE, STANDARD DEVIATION, CORRELATION AND REGRESSION OF ANY OR ALL VARIABLES VS ANY ONE VARIABLE.
- PRINTED PLOT – CHOICE OF X AND Y SCALES.
  CHOICE OF GRID LINES AND SPACES
  CHOICE OF X AND Y VARIABLES
  CHOICE OF RANGES


OUTCARD DATA
ENDCARD DATA
RETRIEVE
COMPUTER
RETRIEVED DATA
PSEUDO
COMPUTER
PSEUDO FIELD DATA
LIST
COMPUTER
STATISTICAL
COMPUTER
PLOT
COMPUTER

And you supply one time, along with the data. Here we see the data for the outcard data during the cycle, the endcard data at the end of the cycle. They can be used separately or together, as desired.

And different card inputs to the computer, that is the card program inputs, including the control card.

After it comes through the computer you get another tape which has been sat on by someone, retrieved data. If he desires to go through the pseudo field program, he can do that or go directly to the other three and take any one of the three. So we can have a minimum of two steps, a minimum of two program runs at the same time, or a maximum of five if he desires all.

I might mention the fact that -- I think I did -- this program is written in FORTRAN 2 programming language. We have used it for ourselves on the IBM 7094 computer. It is available and can be used with a number of systems having reasonable or like capacity to the 7094, and most of them will take FORTRAN, too.

I might also mention the fact that this program can be used by other time-dependent -- other operations requiring time dependency, any components, transistor testing or anything which involves the time-dependent operation, and also, the data can also be used for analysis in this program.

A Goddard X document describing the analysis of the battery system, its use, instructions to the operator as well as all programming operation, will be available before November 1. The number of the document, for those interested, is X-735-66-385.

It might be well to mention that that document was written for those who have little or no knowledge of computer program or operation, so that they might be able to use it with ease.

Thank you.

MR. SHAIR: Thank you very much, Jerry.

I think Jerry would welcome from anybody any suggestions regarding what kind of information you would like to get out of the large volume of data that has been collected, using some of his program.

MR. WEINSTEIN: With regard to the data, the endcard and outcard both had a four-digit sequence at the end called "sequence number." Can you tell me something about that field? Is that a reference field of some kind?

The only reason I ask is that I totaled up all of your card columns, and you have used up 80 cards. I am afraid that you may not be able to distinguish one deck of cards from another unless that sequence number does this for you.

MR. HALPERT: Let me say that the end channels

are for sequential operation, that is, they know what sequence the cards were taken. For outcards it is easy. You would want to use that because it would allow you to arrange the cards on the tape in the sequence number. For the endcard there may be a problem with separating because they would come at different intervals.

I am sorry that you caught that, count those numbers at the bottom. I did so yesterday myself and they did not come out right. So there may be an error in the actual number of digits.

MR. WEINSTEIN: It does total 80 in each case.

MR. HALPERT: It did?

MR. WEINSTEIN: Yes. This is what disturbed me. You have no way of distinguishing a computer run on battery type X from the computer run on battery type Y. You wouldn't know which is which.

MR. HALPERT: I am sorry about that. Yes. In the actual computer run and in the actual program output, the data, the request by the analyst is automatically printed out so that you know exactly which batteries you are abstracting, which cycles, and the complete request.

In addition, throughout the actual printout of all the data, everything is repeated again so you know which battery it is, which field it is, and so forth.

MR. SHAIR: One more question, and then an allied paper and more discussion afterwards.

MR. MAGISTRO: You have all the descriptive statistics shown on the cards. Has any statistical inference been drawn or is that done later after you have reviewed the initial data?

In other words, you compare the mean of one lot with the mean of another lot. Is this done manually?

From what you have on the runs there, all you have is the descriptive information. I wondered how this was done.

MR. HALPERT: Do you mean the mean for certain values on endcards?

MR. MAGISTRO: Let's say you are comparing different lots of batteries and you have a mean life of several thousand cycles and you compare it with the mean life of the next lot of batteries. How is this done? On this program or in a separate program?

MR. HALPERT: The ones that are in this program can be compared within the program. There is the ability to compare within the program.

For other kinds of data I think there would be -- for data from other tests we would have to find a way of putting it into this or actually matching the two. Anybody who has the program can do so on their own basis.

MR. SHERFEY: Jerry, perhaps you understood the question and I did not. I don't think you answered

the question. You didn't stress the fact that the data you have worked with has all been on the same type of cells. These cells were made in the batteries and each battery was run in a different way. Does this clarify it?

They are all Gulton VO sixes. We had something like 13 batteries consisting of 10 cells each. What he is doing with the program he described here today is to compare the performance of these 13 batteries, to intercompare these performances, in the light of the fact that each battery has a (unintelligible) in a different way. We are not comparying, say, GE and Gulton, or something like this.

MR. MAGISTRO: You buy your material in very small lots for each program. You buy material for this flight, and buy material later on at a point later on for another flight. You want to compare improvement in quality if there is one with time. You want to compare, in the Army when you buy material tactically, you procure it yearly, so you want to compare this year's material with next year's or subsequent years. That is what I had in mind, whether or not this program was set up to compare different lots of the same material.

MR. HALPERT: The programs, the few short programs which convert the cards to the tape are fitted

with a built-in updating system so that any new data put on goes right in back of the old data, alongside of it, or wherever it is required.

MR. SHAIR: Thank you, Jerry.

The next paper is by John Waite, of Mauchly Systems, on the use of the computer in monitoring large field battery tests.

USE OF THE COMPUTER IN MONITORING LARGE SCALE BATTERY TESTS

MR. WAITE: I would like to make a comment on the paper just described. That was a description of the computer system and software backup to do the Martin work.

I am not going to describe the computer system too much in this paper. I am rather going to describe the problems that you are faced with in trying to take a lot of data and predict a failure of cells and also predict the fact that cells will not fail.

I do think this whole approach is rather new. I believe, too, that it is here to stay and that we will have maybe as much contention stirred up in the future with methods of doing this that you have presently in your battery work itself.

The work, the paper itself is based on the NASA contract NAS-10203, the purpose of which was to identify techniques to reduce, analyze, and correlate

data obtained from the Crane test program pertinent to early prediction of the cell failure.

Equally important was the reliable early prediction of cells which would not fail for any given number of cycles. Although the cells used in the Crane program are now considered outdated, the methodology developed here on the Crane data is believed to be useful in a new test program.

Since this is a workshop session, I feel the best way to organize this paper is to discuss the major divisions of work as we face them in doing this job, and to associate problems, solutions and results achieved on this work.

The work areas actually involve data reduction, analysis, prediction, programming, and conclusions.

One of the surprising features was the data reduction aspect. The first decision that resulted in the data reducation for the Crane work was made in the design of the experiment. The decision was to take every thirtieth cycle to be monitored. As a result, the total amount of data which accumulated throughout the whole Crane program will approach something like 1,080,000 column punched cards. For cell life statistics and program control this sampling rate is probably more than sufficient, but for analysis and prediction purposes there are several desirable changes to this procedure.

One, the temperature measurements taken every two-day intervals lose all meaning of continuity.

Two, any data reduction techniques involving more than one cycle of information requires too many elapsed cycle times to provide enough statistics for early prediction. In other words, you are stuck with the elapsed time plus the actual data you get. There are better ways to reducing data than just dropping out data in the very beginning.

The next decision affecting the reduction of data was the selection, was our decision, and this was the selection of the use of first differences between voltage levels as measured by consecutive monitored points. Here again the test design predetermined for us five-minute intervals for monitoring discharge voltages, and ten-minute intervals for monitoring charge voltages.

The orbiting regime was an hour and a half. This meant 12 readings.

As mentioned above, an on-line computer test system could accept much smaller time intervals and reduce the data to any desired interval with an additional gain in reliability in information. I think this is a point I want to emphasize.

If you can put a cheap computer in your data acquisition and data reduction cycle, you can afford to

monitor every cycle coming in and for storage reasons, keeping either your reduced data patterns for analysis, or as many cycles as you want for your history.

The use of the first differences in the Crane test data resulted in a 3 to 1 reduction in data. The reason for this was the voltage data was three digits long. The differences usually involve one digit.

This reduction, however, cost some loss of information which loss was felt to be acceptable. And this is something else.

In your data-reduction area you need a whole system approach to your reduction, and you should have this in mind before you design your first experiment if you are going to use this data to analyze. You will find as we go on in the analysis that we did have a system approach to this.

The loss of every single decision you make to reduce the data is going to lose you something. What you want to lose is what you plan to lose. So that what you are left with is worthwhile information for evaluation.

The loss that we accepted by taking first differences was the longitudinal displacement of the charge -- discharge curve. You can say that with this did go some things.

Another decision which resulted in a further

2 to 1 reduction in the data was the consolidation of all first-difference values obtained in the charge or discharge portion of the cycle into a single table or distribution histogram, listing only the numbers of occurrences of each different level for that charge or discharge cycle.

This meant that if you had a voltage difference of 7 at one monitoring point and another one of 7 at the next, you would just have a figure 2 to record opposite the seventh ordinate -- point in the graph. Actually, if you look at all the levels of differences you may tolerate, you will find you will average out to a reduction of about 2 to 1.

Also, a loss here was associated with this decision: This loss was the sequential relationship of each voltage difference associated with each consecutive pair of values monitored. Since these are words, I think I would rather show you on the board, because this seems very strange if you are not used to it, and you begin to wonder what sense the evaluation later will mean.

In effect your differences are measured here. If this difference happens to be two, and this two, and this two, here you have time, here you have voltage, delta voltage, you will find in other words if this were a straight line instead of a curve -- I think that

is probably a better way to show it -- you will find that you will just have the number 3 here.

If you try and reconstruct this by taking this and going backwards, you find you cannot, because you have lost the sequential information.

This makes you wonder what you have. I think this will be answered a little later in the paper.

In effect, the data sets that you have thus obtained did not provide any way of examining particular portions of the charge-discharge cycle directly.

The final decision resulting in a reduction of a further 5 to 1 decrease in the data volume was the consolidation of five cycles of data into one histogram.

The loss associated with this decision was the capability to identify a variation within one cycle of data out of five. However, the gain that you got was enough of a distribution in your table to begin to give you a fingerprint of what is going on. And I think in light of this one can understand why it would be better to have more than every thirtieth cycle of data, since the fingerprint could take every cycle of data, consolidate 15 or 20, and still have more reliable information than five 30-cycle ones, and in a much sooner time.

As the result of all these reduction techniques, the total numbers of cards at Crane, which was 600,000-plus,

resulted in less than 20,000 cards of reduced data on which we based our analysis. And that is the data reduction system we have used to look at the Crane data.

The next problem in the course of the program was analysis. I would like to show you this exhibit. The red border on the top of the page represents the reduced data that we worked with. The rest of the page is the acquisition data that we received from Crane. It just gives you an idea of the reduction that is possible with these rules.

It was mentioned several times during the program, why don't we use a high-speed very fast computer. We are using a low-speed very slow computer, the IBM 1620. I feel still that there is really no need to use a high-speed computer because in the development of a system to analyze large data like this, most of your work is brain work and a relatively small amount of your time is the computer work. And you find that the computer is keeping pace with you much faster than you can keep pace with it. It is just efficient costing, it is good at this time of development to use a small machine. As your indicators get developed and you want to play games with them over all the raw data, you may wish to go back to a big machine and save time.

I do think it is important to realize that

the speed and the cost of the equipment that you are using is also part of the total package.

The analysis problems follow to a certain extent in the same order that the reduction steps have set and can be described in association with them, once the data reduction system has been defined.

The initial reduction imposed on the data bring the test design -- that is, the five- and ten-minute orbit periods, also the use of every thirtieth cycle of data -- places a serious restriction on the ability to predict failure as early as would be desired. The reason is simple enough. Any predictive technique requires a look at performance for a certain length of time. If any of this time is discarded, more elapsed time and elapsed cycles are required to obtain sufficient data for the prediction.

Two solutions could help the situation. The first would be to monitor every cycle and reduce the data on-line to a computer. The reduced datawould be used to predict cell behavior.

The second concept, if feasible, would be to accelerate the test. A side comment is found appropriate here, and that is if a computer could be used on-line to reduce data and monitor parameter behavior, an accelerator test might be made more meaningful, and comparisons with the field behavior could be studied better.

In the first computer reduction operation, that is the conversion to first differences, the most important problem is the elimination of errors. This is done in your first computer reduction phase.

I can give you a few examples of where these errors come in.

There actually are two types of errors. There are errors of order, and there are errors of data. In the Crane data, they have a time figure which actually spells out the exact point in time of monitoring. In our discharge it should be every five minutes. If we look at our discharge curve, this should happen at intervals of five minutes.

It often happens, however, something goes wrong and this is not five minutes, but one minute. What happens then to our monitor point? It is moved out this way. Now our differences can't possibly be what we thought they were.

Furthermore, for some funny reason, to compensate for this, the next reading is probably 20 minutes. So here it is 1, and there a 9. The associated differences error that you get from this time error is going to give you a bad indicator when you go into analysis. And so the time to reduce the errors in your system is when you do your first reduction.

Our reduction program was written and I feel very happy to explain that it actually got all ordering errors defined and printed out and data errors too. The total number of errors in the over 600,000 cards were 17,000, which were perhaps one-digit errors, and the card has 80 digits. So if you calculate that out it looks like Crane has been able to accomplish a .00025 error rate, which I think is a credit to the Navy. I don't think the Army could have done as well.

(Laughter)

I am an Army man, by the way.

(Laughter)

The next problem in the analysis of data: The data error listings are listed out and corrected in your first error reduction.

The next area of analysis is studying the reduced data sets for change patterns. The assumption is that -- I am going to have to hurry, so I will read through these -- the assumption is that the voltage behavior in a good cell, and the voltage behavior in a bad cell, are going to vary very early in the game. The purpose of our project is to prove that there is information which is not available by inspection in the study of this voltage behavior.

Therefore we expect to look at these histograms

for good cells and for bad and see if we want to define patterns and associate these patterns with failure modes.

We have looked at all the failure modes and analyzed them. But the trouble is that by the time a cell has failed, it looks like black glue and it is very hard -- it ends up as having all the failure modes possible, and this, of course, makes it very hard to identify this had a particular failure mode.

I am afraid we are going to have to tell the chemical analyst what his failure mode is, rather than he tell us.

Another analysis of factors affecting the sensitivity of the patterns, you need thresholds. At different depths of discharge it looks like you will change your thresholds. Analysis of performance efficiency for failure indicators. We have identified about 16 indicators which we want to pass all of the Crane information to, that is all of the reduced data, and predict the failure of cells.

Also the analysis of modes of failures. And analysis of failure reports.

Having completed the analysis -- and all of these are sort of trading off back and forth with each other as you develop your suspect, you come to prediction itself. We have three types of predictors.

One is a predictor that involves only one histogram for five cycles. We have looked at histograms for 10 cycles and 15 cycles in order to evaluate the period and the sensitivity of the indicator.

We found that you can do very well with five, which lets us predict sooner. I think if you monitor every cycle you can really do very well with early predictions.

With these five-cycle histograms we find we need about a thousand to two thousand cycles to make our first prediction. I will tell you the results of that later.

The next prediction element will be pairs of histograms. That is a histogram for charge and histogram for charge and histogram for discharge. You compare the differences between them.

The last indicator, the prediction indicator, is sets of either pairs or single. In other words, you take them for ten five-second periods at a time, and map what is going on, and you will find that the cells that will not fail are sort of staying in a channel by themselves and the other cells will start falling above or below the channel, and you can begin to associate this with failure modes.

I think that is about all I want to say there. I would like to say that the conclusions to date I feel are very important.

I have plenty of computer runoffs to show you if any of you would like to see them. But the conclusions to date are these:

The voltage data does contain information on a single orbit -- it does contain valuable information not easily visible on a single orbit at a time observation.

The data reduction system should be considered before the design of an experiment.

The establishment of an acceptable prediction criteria and thresholds will require the joint efforts of battery experts, computer analysts, and statisticians.

The to-date prediction appears feasible for improved test processing program within a thousand cycles. And this prediction can vary all the way from 9,000 cycles before failure to very few hundred cycles before failure.

The modes you get, some of these indicators will show up for a time and then they will disappear, and then they will show up again, and then they will disappear.

Other indicators will stay for the whole time consistently. The study of these things I think is a new field that I haven't seen anywhere else.

Thank you.

MR. SHAIR: Thank you very much. Since this is such an interesting tool, maybe we ought to take a few

moments to discuss these two papers right now.

Since there aren't any questions right now, thank you very much. We will probably get back to it.

Still staying in the same vein of the previous papers, we have a paper from the Naval Ammunition Depot, Crane, Indiana, by John Lannan, on mathematical and statistical approach to failure analysis.

MATHEMATICAL AND STATISTICAL APPROACH TO FAILURE ANALYSIS

MR. LANAN (NAD/Crane): It is pretty rough to drag up here at four o'clock.

Many of the things which I am concerned with in our analysis at Crane in the approaches we are taking, we are concerned with the same problems which John Waite is concerned with. Mainly because we are working with the same data, basically.

In our approach we are choosing primarily nickel-cadmium batteries. Here we have more data to work with, more samples, that is, and some other similar advantages.

For those of you who are not aware of the nature of the test measurements taken, I will give you a brief description of the thing. John has been through part of this. Some of this may be a bit repetitious.

The battery packs we are working with consist of five- or ten-cell packs. Each of these is subjected

to continued charge-discharge cycling until failure. Every five- or ten-cell pack of a particular manufacturer undergoes this charge-discharge cycling with a slightly different set of environmental conditions. That is, we vary the factors such as the depth of discharge, orbit, or cycling time, the temperature, the per cent recharge, et cetera. All these factors will vary pack to pack.

For selected cycling points, as John pointed out, every 30 or 40 cycles the cell voltage and cell temperatures, or cell temperature measurements, are taken as the cell discharges and recharges.

The number of cycles to failure is eventually determined for each cell of a pack. This is, I guess, only partially true since a pack failure is called six failures. After six failures sometimes they cut off the cycling.

It has happened that all ten went out basically at the same time, so we had six failures. Our initial approach to the analysis of the data has been based on the use of statistical tools to determine failure distributions which govern the way the individual cells and packs act. And the relationship of the various environments to the reliability of the packs and cells.

Most of our work in this area has been based on, as I said before, the ten-cell packs. This is where we get ten samples per pack per a particular environment.

Our attempts to explain the overall behavior of the batteries by a single probability distribution, as you might of course guess, have not been satisfactory. The tendency of the test is to fail to follow a particular pattern, and seems to depend heavily on the manufacture or failure mode or cause of the failure.

The problem here is the difficulty in accuracy encountered in determining an initial cause of the failure. As someone pointed out earlier today, these packs of batteries are rich in failure modes, failure causes.

Most of the failures observed seem to be due to flaw in design. I should say nearly all of them seem to me are due to flaw in design, or to manufacturers' workmanship. Of course, the good ones are still going.

Few of these failures could be considered to be wear-out types. The failure seems to be exponential more than any other we have examined. I say this with tongue in cheek. There are many ways of examining such data.

Although we are certainly not advocating this distribution for general use in describing behavior in batteries, we do feel that its use in determining the estimates of mean lives of battery packs is interesting and useful.

(Slide)

TABLES OF MEAN LIVES OF BATTERIES IN CYCLES TO FAILURE

TABLE I (All Environments Considered)

MANUFACTURER	ORBIT TIME											
	1.5 HOURS						3.0 HOURS					
	TEMPERATURE (DEGREES) & PERCENT RECHARGE						TEMPERATURE (DEGREES) & PERCENT RECHARGE					
	0°C 115%		25°C 125%		40°C 160%		0°C 115%		25°C 125%		40°/50°C 160%	
	DEPTH-DISCH. 15%	25%	25%	40%	15%	25%	15%	25%	25%	40%	15%	25%
[redacted]	119,780	119,560	16,241	8,016	10,209	3,413	58,140	58,710	28,195	8,320	3,784	6,692
[redacted]	34,910	117,090	23,658	9,240	14,348	5,474	58,780	57,500	17,867	5,802	9,692	5,920
[redacted]	119,950	17,496	6,057	4,558	6,433	1,258	58,640	58,370	6,351	3,090	3,167	1,343
[redacted]	6,970	17,552	5,094	2,356	7,137	1,464	25,060	4,844	3,730	1,859	2,267	4,277

TABLE II (Only Temperatures Considered)

MANUFACTURER	0°C 115%	25°C 125%	40/50°C 160%
[redacted]	89,047	15,193	6,024
[redacted]	66,570	14,142	8,858
[redacted]	63,614	5,014	3,050
[redacted]	13,606	3,260	3,786

The first slide contains estimates of the mean number of cycles to failure. This table should give you a better idea of the experiment itself and the type data we use.

The black marks on the left are places where I have blocked out the manufacturer's name. It seemed that we shy away from this type of thing. It is probably good because these batteries do have some age on them and manufacturers have improved and "deproved" possibly since that point.

(Laughter)

Some of these monstrous numbers you see, these mean times to cycle failures, I call them here, again with tongue in cheek, are not typing errors. They are based on the calculations.

The purpose in mind, I am trying to get some numbers in this box, as we called it before today. From this run some different types of analyses.

We have computed the numbers for these cells in other manners also.

You can see the different requirements, the two different orbit times that we considered, the 1½-hour orbit time which consists of one half-hour discharge and one hour of recharge, and the three hours also has one hour of discharge.

You can also see the different depth of discharge levels, 15, 25, and 40 per cent. And you can see our design is a bit lopsided because we don't really have all the different possible combinations. But then it seems that you never have these.

An estimate such as the 119,780 cycles, is based on a pack where all the ten cells were still operating successfully after 11,978 cycles.

We transformed the data shown here to equalize variances even though we are hurting as far as samples and of course our assumption of the distribution.

Analysis shows that the variation is primarily due to the manufacturers -- we will call them A, B, C, and D for the moment -- and the differences in the temperatures. This is the primary. Most of the variation falls back on this.

By the way, notice the per cent recharge which is completely confounded with the temperature. I believe in actuality these per cent recharges came out to be a bit less than what they are, as marked here: 115, 125, and 160 per cent.

That should be 40/50 degrees centigrade in each case.

The reason for this, the batteries in the cells were initially cycled at 50 degrees centigrade. After

the first few hundred cycles it was found that these conditions were not compatible with the successful behavior of the batteries. So the temperature was cut back to 40 degrees after that point.

We really have something here between 40 or 50. Who knows really what we have. At least it is a higher temperature than a 25-degree centigrade.

I give these as estimates; I don't have much confidence in these mean TTS, or what I should call them here. If you were to pin me down, I would back off quite readily. I believe they do give you some idea.

I can say some of the slots or boxes or environments of a particular pack do seem to follow in the (unintelligible) distribution. Several do. Later data may not bear this out. At least I get a comparison of the different magnitudes and numbers. And it very vividly shows that temperature is playing a role in the life of these things. I think you will agree after seeing a later slide.

This would indicate that if one would construct an accelerated test, temperature should be one of your considerations. Previous data has shown this to date also.

No overall differences were found in orbit times, although the table revealed some variations between

the packs -- rather, of similar environments. This overall conclusion implies that the life of the cell is a function of the number of charge-discharge cycles of some particular environment, and that the time per cycle or the orbit time is not such an important factor as one might first conjecture.

Although only slight overall differences were found among the various depths of discharges represented here, there are indications that the 40 per cent depth of discharge is stressing the batteries considerably more than the 15 per cent and the 25 per cent.

The potential of depth of discharge, as an accelerating factor, certainly has not been demonstrated or established in this particular design.

(Slide)

Slide 2, I have regarded only the temperature and manufacturers. If you lump these things together, you get averages something like this. You can see the magnitudes. Only in the case of manufacturer D, the last one, you can see for 25 degrees and 40/50 centigrade temperatures, it starts to go back just a bit.

(Slide)

In the next slide here is simply raw data. You can see, thinking back to the two previous slides, you can get an idea of why the numbers were such as they are.

TABLE LII GIVING NUMBER OF CELL FAILURES FROM 10-CELL PACKS AND NUMBER OF CYCLES ENDURED AT TIME OF SUMMARIZATION (1/31/66)

MANUFACTURER	ORBIT TIME												TOTAL
	1.5 HOURS						3.0 HOURS						
	TEMPERATURE(DEGREES) & PERCENT RECHARGE						TEMPERATURE(DEGREES) & PERCENT RECHARGE						
	0°C 115%		25°C 125%		40°C 160%		0°C 115%		25°C 125%		40°C 160%		
	DEPTH-DISCH.		DEPTH-DISCH.		DEPTH-DISCH.		DEPTH-DISCH.		DEPTH-DISCH.		DEPTH-DISCH.		
	15%	25%	25%	40%	15%	25%	15%	25%	25%	40%	15%	25%	
[redacted]	0 11,978	0 11,956	6 10,382	6 5,013	6 8,109	7 2,509	0 5,814	0 5,871	1 5,846	5 5,410	6 2,656	6 4,487	43
[redacted]	2 11,581	0 11,709	3 11,361	6 6,671	6 9,328	6 3,625	0 5,878	0 5,750	2 5,573	5 4,608	4 5,487	6 4,141	40
[redacted]	0 11,995	5 11,665	7 4,751	6 3,163	6 4,485	10 1,811	0 5,864	0 5,837	6 4,173	7 2,494	7 2,517	6 974	60
[redacted]	8 10,146	4 11,278	6 4,021	6 2,086	6 6,064	6 1,377	1 5,012	6 4,414	6 2,885	6 1,550	6 1,689	6 4,133	67

Note: For packs with six or more failures, cycling was stopped at the number of cycles indicated; the remaining non-failing cells were not cycled to failure. The non-failing cells of packs with five or less failures were still cycling at the point indicated.

It is a little obvious and it is something which you would expect, I think.

We ran an analysis trying to consider just failure, success, or no-go data, whatever you choose to call it. Here again we have to make some assumptions.

These assumptions were again weak, but they were not based on exponential. They are based on normal approximation, binomial, this type of thing. We also used the (unintelligible) transformation to try to see what happens. We got consistent results with the other means that you saw on the previous slides.

Again I want to reiterate the reason for the six. These quite possibly, had the cycle been continued, would have been complete pack failures. For example, for 40 degree centigrade, 25 per cent depth of discharge, the sixth failure occurred at 1,377 cycle point.

We have examined this data from several other viewpoints. Most of these have been from the standpoint that we need to predict failures, as Mr. Waite pointed out. We have attempted to relate the battery deterioration by using the Arrhenius model or equation that was mentioned earlier today. We found many inconsistencies.

We found for some packs we would get, based on just the three temperatures, the Arrhenius relationship, and for other packs we would get no relationship at all.

Our three points are scattered all over the place.

That is all for the slides.

To evaluate this, as pointed out before, we need many more points than three. That is not so good.

If one plots the end of discharge voltages of successful cycles, you get a result something like this. We will make our abscissa, number of cycles; we will make our vertical axis, voltages; and plot this thing out.

For about the first 500 to 700 cycles, roughly, we get a fairly consistent pattern and a fairly consistent slope by using best fit regression analysis.

Going ahead, however, we get points which give us some degradation which is very linear. We get a regression R^2 of roughly 9 per cent or better, which is not bad. This goes out somewhere to some failure point out here, which could be one of the values we had before for a particular cell.

We took particular packs based on the failure modes and we picked out those where we thought we could classify the failures as wear-out type. The thing we had in mind was to look at the different cells of this pack, find the linear relationship, the slope of this line by regression analysis or least squares, and then compare the different slopes.

In two or three cases we looked at, where we thought we had wear-out type failures, we would get something, a scatter like this. The variation of the data out here seemed to be less than it was up here for the first few hundred cycles.

It would not be quite so bad at this point; out here it would get worse and finally drop off down towards zero.

.5 volts again is called a failure.

So let's call this Cell 1, and for Cell 2 we had a different situation. These things have been slopes.

In one case, using six cells of a pack which had failed -- I think they went somewhere around anywhere from 8,000 to 13,000, something like this, cycles to failure -- we got a correlation coefficient of .96, or 96 per cent. You recall one indicates a perfect relationship here. This is based only on six samples, which is not so good. It is significant.

What it seems to show is that in some cases there is a definite relationship between the degradation of these voltages and the time to failure which we find here. If someone could find an accelerator test which would induce wear-out type failures early, something like this could be used in an accelerator test to advantage.

In other situations where we thought the type of failure was simply a manufacturer's flaw, maybe the

thing failed after two or three thousand cycles, or even less, we could not establish even such relationship. The correlation is more nearly zero than anything else. It could be anything. This is one approach we had taken.

Another, very quickly, was taking the number of cycles -- let's make a plot. This would be the discharge part of the curve and this part the charge part of the curve. Many of these cells (indicating) look typically like this. This again being voltage. The plateau appears a bit higher. This is a general shape. The discharge point keeps dropping down with time, with age and cycles.

We have written a computer program and worked with the area under the curve of this. We considered slopes here, we considered an area in here, areas in here, and this type of thing really may be somewhat similar to what John has done with his data. The end result may be basically the same.

At any rate, the end discharge point dips down with time, with the successive number of cycles.

Preliminary plots and some computer analysis on this has indicated that there is definitely a relationship here. But the problem seems to be that it takes so many cycles of testing before we can predict.

In other words, it may be four or five thousand cycles you can predict a failure somewhere. But our

initial idea and hope was to predict with just a few hundred cycles of testing. We are pessimistic about this type of prediction.

We have looked at data from other viewpoints. I think these are some of the major aspects of the investigation.

Thank you.

MR. SHAIR: Thank you very much, John. There is a question over here.

MR. WAITE: I don't want to leave it quite that way. We have quite associated work here.

I left out the most important part of my paper, which was the results. This result is a prediction computer run where it has taken pack 52 and predicted correctly all the cells that failed.

Furthermore, it has more surprisingly shown no predictions or very, very low predictions for cells that did not fail. This prediction did require a couple of thousand cycles before you could start it. But I blame this on the one-every-30-cycle data monitored.

I am not as pessimistic, I would like to make that point, and I have runoffs that I think will make this clear.

MR. LANNAN: We have not made final conclusions on this. We have taken basically just 15 or 20 packs.

I would hesitate to agree or disagree really at this point, John.

MR. SHAIR: Let's get in the last paper and then we can open the floor for some discussion, and possibly some art work.

The next paper is by Ralph Brodd, from Union Carbide Consumers Products, and the subject is, "Computer Controlled Battery Test Facility."

COMPUTER CONTROLLED BATTERY TEST FACILITY

MR. BRODD (Union Carbide Consumers Products): I will try to make it as brief as possible consistent with the amount of material that I want to get across to you.

We all know that the applications of rechargeable batteries are forcing a greater reliability, higher energy density, as well as increased cycle life upon the battery systems. So that any program that requires the development of superior rechargeable batteries must have some means to test and evaluate the particular energy storage system that you are dealing with.

Today with the availability of reliable computer systems, it is a logical step to use the computer to combine the test control functions with the data accumulation and data reduction functions. Such concepts are not new, as evidenced by the many papers that we have been

hearing this afternoon.

I would like to describe for you a particular approach that we have taken in our laboratory to develop the equipment as a computer controlled battery test facility. Since this equipment must be used both for research as well as to develop new test methods, we tried to make the facility as versatile as possible consistent with the actual costs.

So that the computer then must be a reasonable-priced facility; it must be capable of doing routine work on experimental systems, both the types of cells which might be included in satellites as well as the materials that you might find in a beaker construction in some research laboratory.

The system that we decided upon is, as I mentioned, a particular solution to this particular problem.

The computer that we have has a real-time clock to keep track of time, and it will automatically initiate the charge and the discharge or the open-circuit parts of the program schedule. That is, we have 12 different cycles that we can use for our testing. We have available on each of these 12, 16 test positions. We have a total of 192 test positions.

The items that we use for process control are charge and discharge current, the charge and discharge

time, and we have included a cutoff voltage which I don't believe the other people have mentioned.

It is possible to change our process information as the test goes on, because of the nature of the computer.

We use constant current power supplies for charge and discharge, and in any one of these 12 tests it is possible to select by computer control, program control, any of four different charge or discharge voltages, so that we may select a high current to start with and then lower it to that lower current as the time of the test goes on.

We measured the voltage on each of these test positions every 36 seconds. This is part of our routine of trying to get down to a hundredth of an hour as a test unit.

The voltage is measured to a millivolt with a 10-meg input impedance device. We also have reference positions so that most cells will be expected to include our reference electrode to monitor the performance of the various components of the system.

I mentioned that every cell has an upper and lower limit. So that during the charge or discharge when it reaches that limit, whether one volt, a tenth of a volt or in flow reverse, the computer will remove that particular cell position from the test routine

without disturbing the other cells on that particular test.

We store in the computer ten readings on charge and ten readings on discharge. And these readings are determined by the computer at the particular time they start a significant change in the voltage.

The computer also monitors the current to maintain that it is within our set limits. It is also periodically measures the voltage of an established cell to be certain that we are indeed measuring proper voltages.

The parameters which we record and accumulate for each cell, besides throwing the charge and discharge voltage readings, are ampere-hour capacity, watt-hour capacity, error voltage -- one we think is very important, time to cut off as well as the various efficiencies.

At the end of a complete charge and discharge cycle the decision of whether to output the data that we have now stored in our computer is based on these six parameters which I have just mentioned.

If a significant change has occurred in the parameter, we output the information to magnetic tape. If not, this information is wiped out. But we do have a choice.

We could say we could program to every cycle if we desire.

(Slide)

Here we see a schematic of the system that we have been telling you about. We have a DSI computer with a 4K Elastiline memory and 32K drum. The computer operates the relay operators. They put the cells into the circuit for the testing.

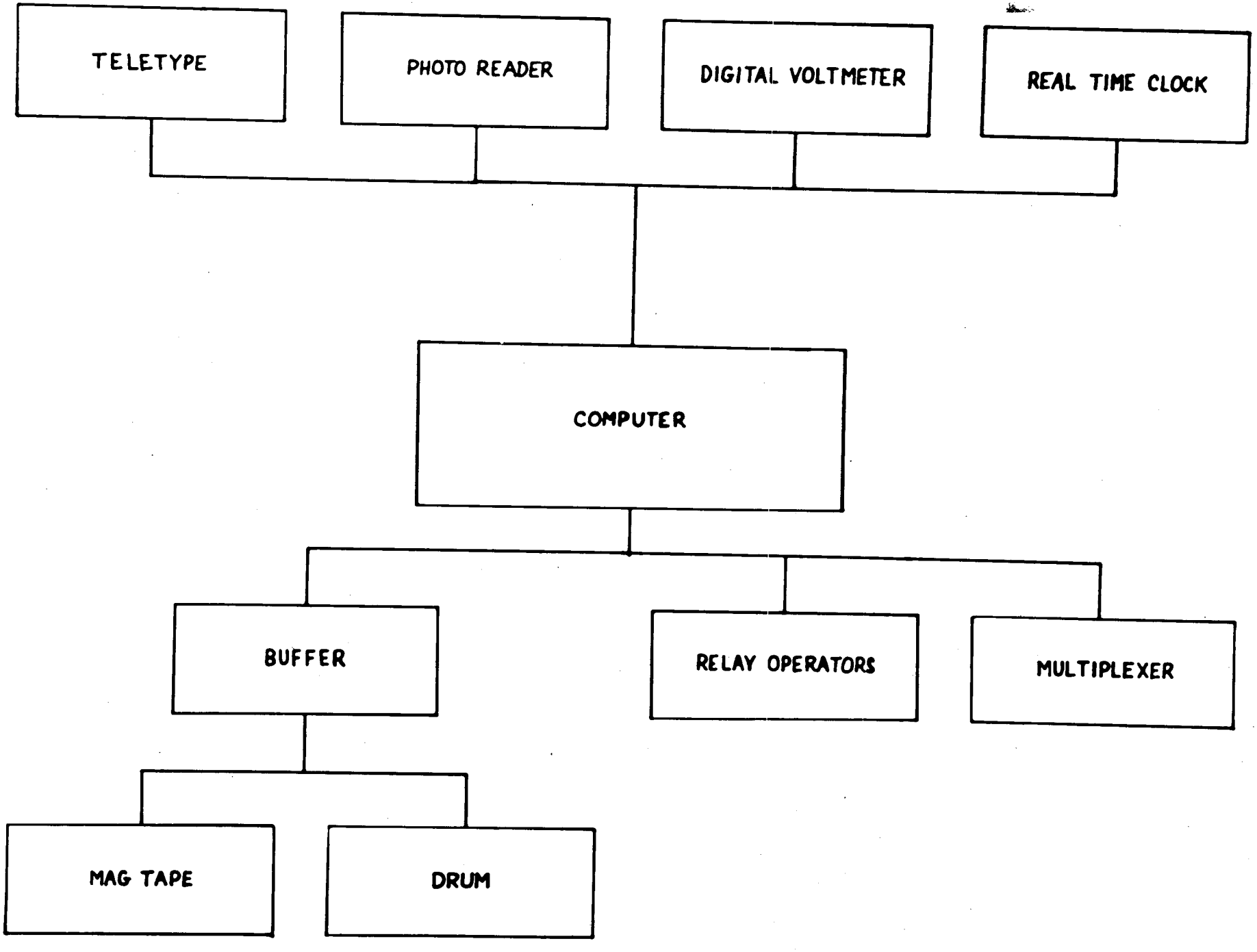
The teletype and photo-reader are for input of the program and program changes. The magnetic tape is the output portion of our computer. We take the magnetic tapes to another facility nearby for the actual output of hard copy to the investigator.

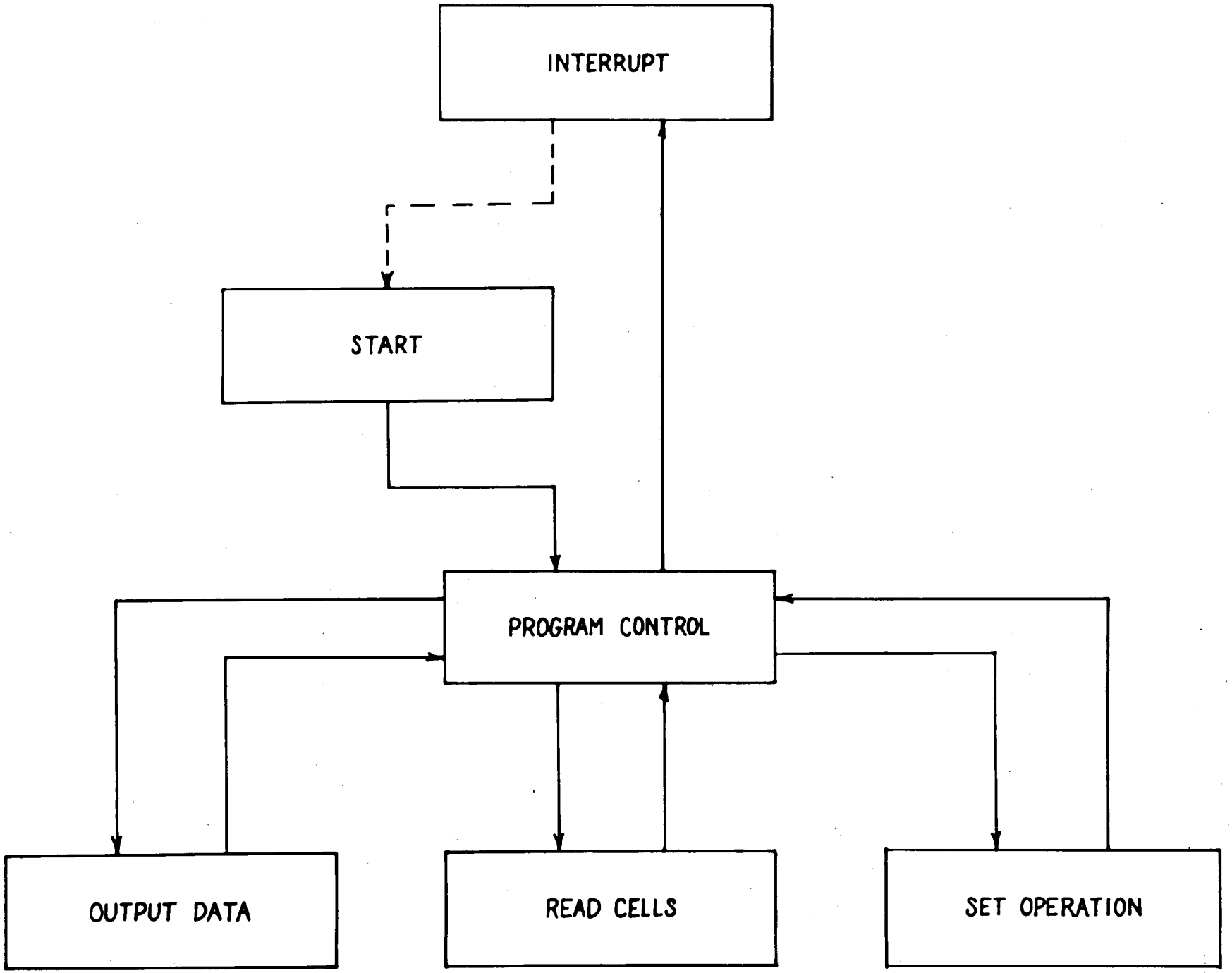
(Slide)

The next slide shows very sketchily the program control as it cuts through. Every 36 seconds it reads 8 cells. Every 36 seconds it decides to start or stop the particular operation of a charge or discharge or open circuit, or perhaps even on current change from one value to another.

The interrupt features that we have, have to do with the problem of maintaining power to the system. We have an emergency power supply in the laboratory which comes in about two cycles, about a tenth of a second. So that we have to be able to withstand power interruptions of this nature by having the computer on a fail-safe power.

The other interrupts that we might wish to include


TELETYPE
PHOTO READER
DIGITAL VOLTMETER
REAL TIME CLOCK
COMPUTER
BUFFER
RELAY OPERATORS
MULTIPLEXER
MAG TAPE
DRUM


INTERRUPT
START
PROGRAM CONTROL
OUTPUT DATA
READ CELLS
SET OPERATION

are things such as complete power -- I mean not complete power failure but improper operation of the various devices, so as to prevent the cells from being destroyed. And the output of the data from the drum occurs on program control during the open-circuit portion of the charge-discharge curve.

I have a sample charge-discharge curve on the next slide.

(Slide)

This used to be green, but on the blackboard it comes out not too clear.

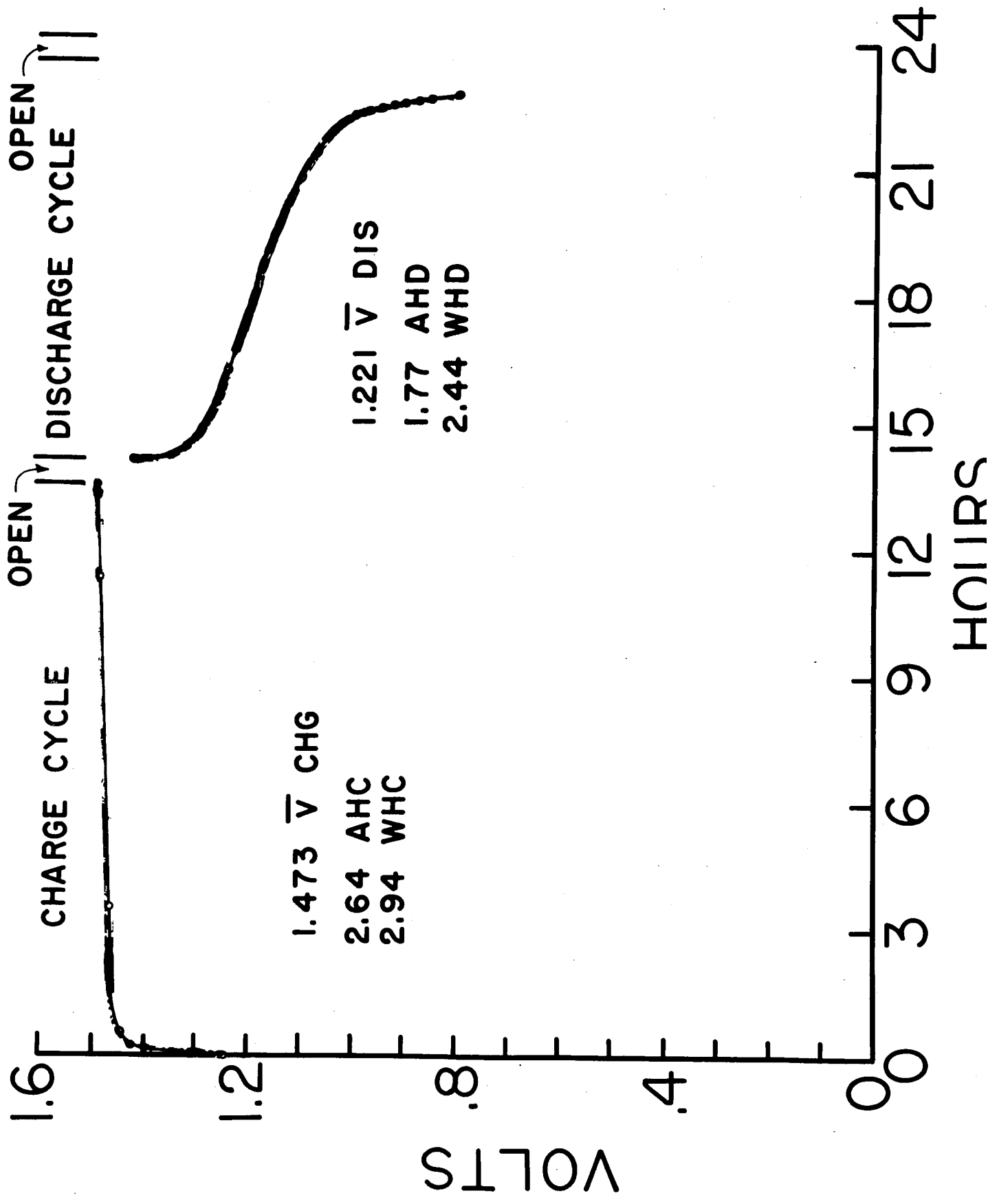
There are points submerged in this green line for charge and discharge. We see that as we accumulate the voltage readings, we also accumulate ampere-hours. We also accumulate watt-hours. From that we can get the average voltage for both the charge and discharge cycle.

To give you some idea of the type of room that is required for this facility, the next slide will show us the actual computer itself. It is a DSI 1000.

(Slide)

The multiplexer and the digital volt meter, power supplies, and the ballast resistors are teletyped, and the photo-reader and magnetic tape units are shown here.

(Slide)


OPEN
DISCHARGE CYCLE
OPEN
CHARGE CYCLE
1.221 V̄ DIS
1.77 AHD
2.44 WHD
1.473 V̄ CHG
2.64 AHC
2.94 WHC
1.6
1.2
.8
.4
0
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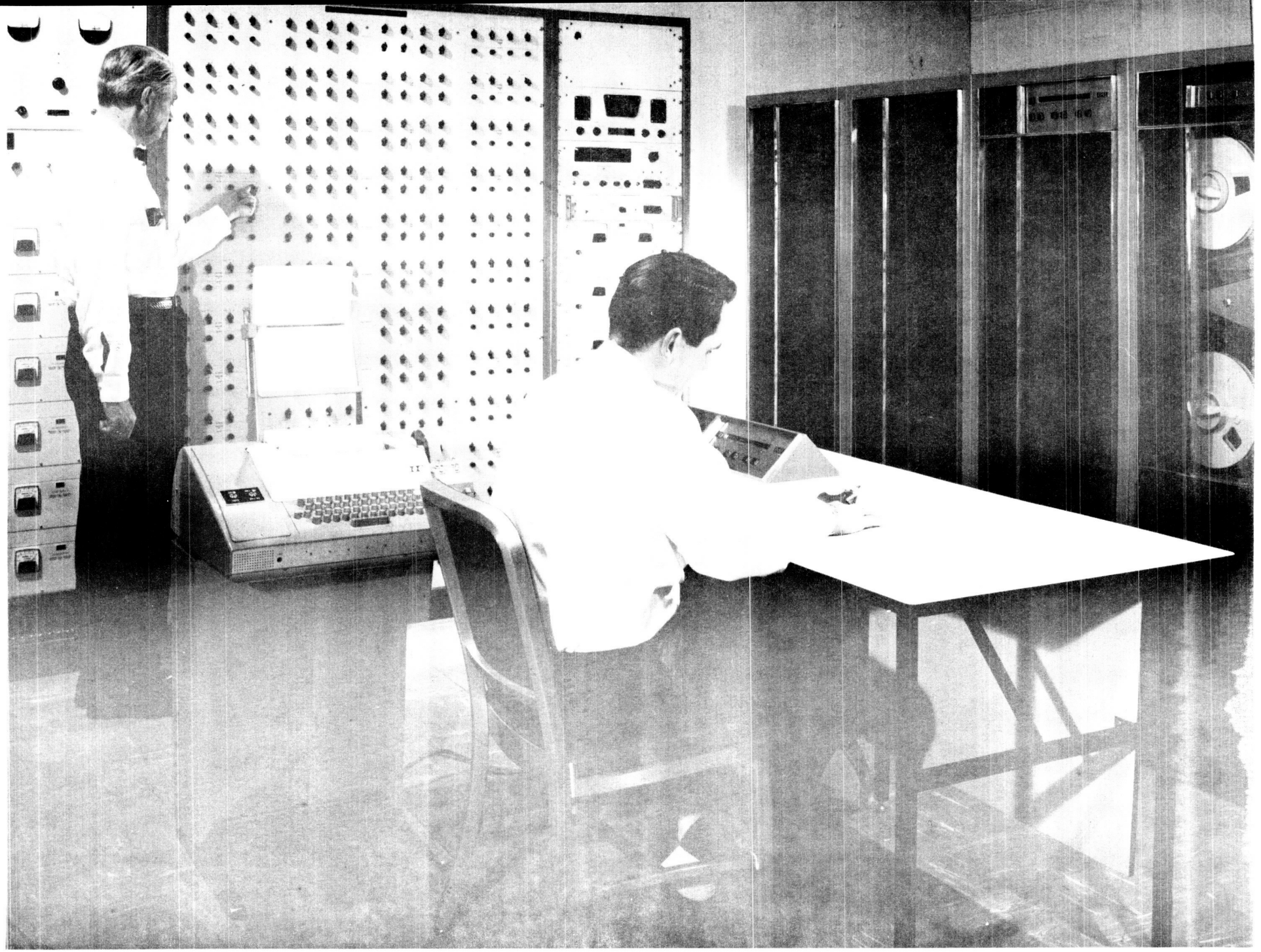

The next slide shows us a portion of the test facility. The pictures were taken before the cells were completely in operation, and these are not connected. So don't be disturbed. This picture was taken before the operation began.

You can see if you like you can set a beaker here, or if you like, you can use a cell. Or if you have a bigger facility, bigger device, you can set it here.

We also have temperature cabinets for controlling the temperature from -40 to +200 degrees Fahrenheit. We have provisions in our multiplexer for inclusion of information of pressure and temperature. These are not as yet installed in our facility.

Perhaps I might say that we feel, in closing, this is a very useful tool for us to study rechargeable battery systems. We feel, along with the people that have been discussing the work previously this afternoon, that this will indeed be a very powerful tool in helping us to develop new and better battery systems.

Thank you.

MR. SHAIR: Thank you very much, Ralph.

The floor is now open for discussion on this and all the preceding papers.

I don't see an awful lot of questions.

Ernst?

MR. COHN: I would like to make a little remark here. I have to translate these things into simple concepts for myself. And I am foolish enough to believe somebody else does, too.

There were two presentations here today, as far as I can distinguish them at least -- one was by Dr. Strier and the other by Dr. Waite -- that gave us something other from the usual statistical approach.

When you toss a coin statistically, the chances are 50-50 it will come up one way or the other. What you would like to know beforehand is how will this particular coin come up. It appears that there may be ways of predicting this by trying to match profiles.

This is what these people have been trying to tell us. The first time this was done, as far as I know was on relays around the time of World War II, or so I was told by a mathematician from Princeton, where they tried to find out the incipient failure by looking at the initial data and, indeed, found that they could distinguish this, and indications came apparently from faulty spring material in the relay. So they improved the springs and that was the end of that.

They didn't bother to go deeper into it because the relays were now satisfactory.

The point I am trying to make here is that I

think the approach of predicting failure on a deterministic rather than on a probabalistic basis, is extremely important to us. As far as I am concerned I am willing to throw away all the traditional statististical approaches if I can find a good deterministic approach.

The first indication that all is not well came today when two people, Mr. Waite and Mr. Lannan told us it may take several thousand cycles before we can tell whether something is going to fail or not. That just isn't good enough. However, this doesn't mean that we have to give up yet, because we don't know enough about it.

I think the emphasis that we have to place on such work is to try to find indicators, and there is nothing that tells me that the 16 indicators or whatever number it is that has been picked so far, is the right number, or that they are the right indicators. I think the emphasis on the work has to be on finding the right kind of indicators and getting the right kind of data in the first place, to see whether we can get predictions in the first few dozen cycles at most. That may still be possible, and it is certainly worthwhile trying to shoot for.

MR. SHAIR: Thank you. A question from Mr. Max Sherfey.

MR. SHERFEY: I would like to comment on Ernst's remarks just now. It seems to me to be pretty

obvious if you think about it that any indicator that you find will be dependent on the failure mechanism of the battery that you find it in. And this implies that these two will go together and only together.

For instance, you might see a decreasing end of discharge voltage or something like this. But that wouldn't work, we will say, on a battery if operated in a different way, because it is failing, say, to increasing pressure at the end of the charge.

I think we ought to all realize that there is not going to be one index but perhaps many. And each one related to its own particular failure mechanism.

The other thing I want to bring up is this: There seems to be general agreement among the statisticians here that we need more data. I am not going to argue that point. I would like to make this point though: Those of us who are designing battery tests are up against a very real problem here. With present-day computers, if you want to you can take a complete scan -- I suppose every millisecond. But the volume of data generated is just fantastic.

You have got to draw the line someplace. This is especially true if you are putting your data on cards. It is not quite so true if you are putting it on tape. But there are good reasons for putting it on cards.

I would like to hear comments from anyone who wants to comment on it, and in particular from John Waite, as to just -- I would like him to comment on two things: First of all, how often within the cycle and where in the cycle should we take the data if we are going to look at that cycle.

And second, how often should we look at cycles. Should we make this an arbitrary thing like once every 30 cycles, or once every five cycles, or should we do the type of thing that was done at Martin, you store in the computer what the previous reading was during a given time in the cycle and look for a change, what hopefully will be a significant change in the data.

MR. WAITE: Thank you for the question. It is just the one I want.

I think, No. 1, one of the things that a computer is able to do for you is accept this data acquisition on-line and reduce it so that you do not keep all the cards. As a matter of fact, you feed the signals in because they are monitored, but you don't keep the record of the cards. In fact, I see only keeping reduced patterns, that we have to decide altogether what these patterns are, what these fingerprints are.

I think to date I like the histograms. I would rather have my 20,000 cards of histogram than

Crane 600,000 cards of voltages. And this could have been gotten without ever making one card.

However, I think for a record you might want to printout every thirtieth cycle or whatever you want. But the data reduction problem is possible on-line, and that is an answer to that question.

What portion of the cycle do you want, and how many monitoring points do you want? I think the computer gives you a capability to take as many as you want, because it reduces it and makes for you the resultant reduced data that you are going to keep.

I would say the more the merrier. I would like to take as much -- I think the limitation is going to be on the acquisition equipment. They are not going to be able to take more than so much. The computer will be able to absorb it all and reduce it to what you want.

I think that just like in code work, in comes the computer and all of a sudden the whole techniques change because you can gobble up the thing and digest it at speeds that are unbelievable, and you can get out the criteria or decision that you want. This is where the problem is.

Does the voltage data, or any other data you are collecting, have the criteria for decision? If it doesn't, then back we are to the labs. But if it does,

and I feel it has some of it -- I don't want to say it has all of it -- we ought to use it. Especially if a computer system as described in the last paper is able to cope with it.

MR. SHAIR: I would like to make a comment here myself.

Today I have gotten a very good review on what you can do with data, but I haven't seen any of the data analyzed. I would like to welcome a session coming up where somebody having done analysis of data throws a curve or a phenomenon on the board or on a slide projection and says, "Look, we conclude that cells do this, this, and don't do that and that." And the manufacturers and users can get up and try to figure out what is going on.

Is there something fundamentally wrong with the cell? Is there something fundamentally wrong with the use?

I see now all the techniques for collecting and analyzing this data. I am looking forward to the next session when we will show the data on the screen and try to take it apart.

MR. WILLIHNGANZ (C&D Battery Corp.): Did anybody here read a book called "Alice in Wonderland"? I feel I have gone through one of the last scenes in the book in which Alice -- Let's skip the details. We

have seen cells of various kinds which are failing because somebody left a screw inside it, because somebody didn't seal the edge properly, there is a defective weld, a terminal burned off inside, a hole developed through the separator because there was a pinhole short by the metal thing there. And what are you doing trying to run statistical analyses on these things?

You had better take a look at your battery and find out what is wrong and fix it, and don't try to run a million cards through a statistical analysis to find out.

(Applause)

MR. MAGISTRO (Picatinny Arsenal): I would like a comment on the technique.

(Laughter)

In the field of explosives, in one-shot devices, we only have one opportunity to check whether the explosive or the one-shot device will work or not work. The man from Martin, Mr. Fowler, I believe, referenced what he called the 99 per cent point, I believe he said. He had estimated that there is a range of use conditions which will have a distribution from here to here. And he said okay, this will be the one chance in a hundred that this stress will occur. And then he considered testing at that point.

In explosives, and sensitivity tests, there

is a primer. It will react to a certain energy that strikes the primer. You have to find this energy. We have called this the stress, as Mr. Fowler has, and we have defined another curve as the strength.

There is a slight subtle difference between picking a point here or a point on this curve. In other words, we say this is the expected use condition. Let's continue going up an increment at a time until we get a failure.

In talking about efficiencies -- a lot of this data was generated with respect to thermal batteries, by the way -- we could with 15 items determine margin of safety between the one per cent point, and in a hundred, and the average strength to failure. A lot of this work was done by Lesser at Redstone about ten years ago. He started this technique.

The question I have is, can something like this, where you improve the efficiency of your test with very small samples, and demonstrate a margin of safety far above this one in a hundred techniques, be utilized? The thermal battery impedance is very high, so you can say, okay, I will pulse the battery and measure voltage drop and use that as my criteria.

In a very few cycles, by measuring this decrease in voltage, they can tell whether the battery will

fail or not in less than 30 items.

I am throwing this out as a possibility. This pulse drop of five times normal current practice may not apply to the other systems. But this stress versus strength technique has proved very efficient for artillery shells and one-shot items. I wonder if anybody would care to comment on that. It is used for multi-cycle battery. What you might impose as a load, for instance.

MR. SHAIR: I might mention that there doesn't happen to be a simple diagnostic test such as that. Most users who are applying these aerospace cells in the satellite programs have set up a group of criteria which they use in order to select cells which, according to their best intuition and best experience, indicates that the cells will be successful in a battery. But there is no nice, quick diagnostic test. That is what was hoped would emanate from some of these programs and statistical analyses.

One thing that the statistical analysis does do, is it does tend to indicate what some of the mechanisms of failure are. These mechanisms would be of interest to the battery manufacturer so that he can remove these really, what they appear to be, kind of random faults, poor workmanship, and things of

that nature. And from this information we can take out of the cells these faults which are leading to these kinds of defects.

I think it was significant today to hear several people say that, no wear-out mode has yet been found for the nickel-cadmium cell, which indicates that the five- and ten-year battery can be achieved, provided QC is achieved. Peter Fowler brought that out.

The human aspects of building a battery are quite as important as the statistical end of it. And QC has become a real important aspect in aerospace battery manufacture.

MR. MAUCHLY: I don't know anything about batteries. I have taken them apart and looked at them. But I don't know what goes on inside them, and I'm not going to try to tell anybody.

On the other hand, I thought there was one point raised a while ago which wasn't answered by Mr. Waite's answer, which dealt with one aspect but left this one out, and that was the question of how many different indicators are you going to have to have. Are you going to have a different kind of battery, or are you going to need different kinds of indicators?

But of course. Does anybody suspect otherwise?

What was Peter Fowler talking about when he said, "Don't 'deprove' your product without at least telling us first"? We don't like to be surprised.

If you are going to have any kind of a non-destructive test which is going to tell you anything about whether a battery is going to fail or going to hold up in service, you certainly have got to have experience on testing such batteries before you can construct that test.

I, for one, don't believe that a test made on some outmoded old things which had junk in them is going to be good for everything else in the world hereafter, whether you use a computer to do it or not. That is quite immaterial and irrelevant, beside the point, and the computer, as usual, is just an aid for doing these things better, and to reducing the data such that you don't get overpowered with the data.

I would like to drop one more thought, since this seems to be the thought-dropping point of the session. It does seem to me as if the possibilities of finding out more about what goes on in batteries have not been exhausted. I think Dr. Fleischer pointed that up from one side.

There is also the possibility of constructing different kinds of tests which in themselves may not tell you what is going on in the battery, but which may

be found to be well correlated with some kind of behavior in the field, and that correlation itself may be useful.

In particular, I note that, it has already been dropped several times, the idea of pulsing. But I haven't heard anybody say that they found anything useful or they have tried pulsing. Maybe they have.

This is obviously a good way of getting -- to me it seems -- I don't know anything about batteries, you understand; I happened to start out as an electrical engineer -- pulsing in the electronic components sometimes is a good way to quickly find out something about electrical characteristics without generating heat problems. Here we are apparently living in a world where we are talking about thousands of cycles and orbits which go from 90 minutes on up, and we haven't yet found out that not only can we make measurements in milliseconds, we can make pulses in microseconds.

Given the proper regard for the capacities of the circuits -- the electrical capacity I am talking about now, not the battery capacity -- given proper regard for the electrical capacity and conductions and other things, you ought to be able to find out an awful lot about electrical characteristics and perhaps electrochemical characteristics of some of these things by

techniques which do not damage the battery because they have created heat in it.

I will finally end this by a little thing that I don't know much about, but I have heard about, that the people doing electroplating, for instance, do this of course with DC. What else? If you put AC in an electroplating bath, you will take off as much material as you put on. But somebody found out someplace that if you superimpose AC on DC, you could do some nice things in electroplating, I believe, whether it is called electropolishing or what.

I wonder what would happen if we added to some of these tests a superimposed AC ripple, not necessarily all the time, every time and all that. But what extra information do we collect, and what more diagnostic tests could you construct on these bases?

These are just ideas. I don't know whether they will work. Maybe somebody tried them all and exhausted them, and we are at the end of the road.

I don't think we are at the end of the road until we have taken all the material out of the batteries and know what is going on.

MR. SHAFFER (American Machine & Foundry): This idea of pulsing has been around I think for about ten years. All the battery people are probably aware of it.

The electrical capicitance of a standard battery is enormous. There are pulse devices described in the literature that have been slightly useful in fuel cells and battery-like applications.

One I think of is the Core-Marcobridge described in the Journal of the Electrochemical Society.

I think it is great to think about this. Don't misunderstand me. But typically you could get hundreds of microfarads per square centimeter when a metal surface is in contact with an electrolyte, and in a battery we go to a lot of trouble to get a finely divided service.

We are up against it when it comes to pulsing, although basically you keep hoping that you can work something out.

Has anybody more recent work on pulsing? It is a fascinating subject.

MR. SHAIR: I see three questions. Willard Scott, Peter Fowler, and then the last speaker.

MR. SCOTT: (TRW Systems): First a small word on pulsing. We have done a little bit of this and the results are far from conclusive. I was surprised to find out by analysis of the frequency characteristics AC voltage versus current frequency characteristics of cells that they behave as if this large capacity is in series with a cell impedance and not in parallel.

So that this large capacity doesn't actually really interfere as much with pulsing as does the internal inductance of these cells. Especially, say, the nickel-cadmium cell which has a lot of magnetically susceptible materials in it.

So that, in terms of using these rapid pulses we find that the internal inductance gets in your way more than this capacity effect. I can't really give you much more of a dissertation on this. This is my impression from some brief experiments we have done.

I want to put another question to you, Bob. You mentioned that it didn't like there was a wear-out mode for a nickel-cadmium cell. I have heard a lot about the loss of capacity over a long period of time of the negative plate, due to things like carbonate formation, migration of cadmium into the separator, and so forth. How do you classify these phenomena in terms of wear-out modes?

MR. SHAIR: I would say these are potential wear-out modes. I think much of the cycling which has come to an end possibly has not come to a wear-out mode because of the cell isolated from the routine in which it was being cycled.

We talk about separator degradation and buildup of carbonates. I am a little surprised at that, because we don't put cellulosic separators into cells anymore

today. This is something that happened years ago. So the buildup of carbonate in the cell should be relatively small.

I would say that the migration of cadmium, yes, that is a wear-out mode. But as yet I don't know of any tests that have conclusively shown that that wear-out mode caused the cell in a particular routine to fail. This is as contrasted possibly to some cells such as the silver type cells which do have a wear-out mode which is somewhat associated with time.

Did you have another question, another part to the question?

MR. SCOTT: Only a small counter to one of your remarks just made, and that is that we have done some analysis for carbonate in the electrolyte of nickel-cadmium cells recently which are made with polypropylene separators, I believe, and found a very high carbonate level. We don't know where it is coming from.

MR. SHAFFER: This is very pertinent to what he said. It seems to me -- I am not an electrical engineer, so you straighten me out if I am wrong -- it seems to me that once we have a black box and we apply a frequency to it and say we are going to analyze this in terms of a reactance and resistance, we can put the reactance and resistance in series or in parallel.

We will get different numbers.

We can put them in series or parallel, and it makes no difference. The key to the thing is to study a dispersion curve. Get the behavior over a great range of frequencies from something that might be near DC to something that might be indeed a very very high frequency.

MR. SHAIR: I have to hold back a couple of people, like Dr. Fleischer and Dr. Brodd, who worked a lot on this subject and has expounded on it at great length in many Electrochemical Society meetings. I am not going to let you fellows get talking.

(Laughter)

MR. FOWLER: I would like, while talking pulses, to draw to your attention something you may not all be aware of.

Pulse test has been used extremely successfully on resistors and transistors. And this commercial equipment, I can't remember the name of it, what they are doing -- and this might be worth trying on batteries -- is this: They take a resistor and put a very large current pulse in it so the resistor heats isothermally. It heats with no heat loss. What they look at then is the exact shape of the --

VOICE: Adiabatically.

MR. FOWLER: I beg your pardon. You are right.

They look at the shape of the voltage pulse across the resistor, and on a perfect resistor it would look like that.

What they found is that the actual shape you get, which has all sorts of ripples and wiggles in it, is extremely characteristic of certain failure modes of the resistor.

This turned out to be a very, very efficient screening test for resistors. Somebody might try it on batteries.

DR. FLEISCHER: The answer to that is that it has been tried.

VOICE: Let him have a few words.

(Laughter)

DR. FLEISCHER: Most of the questions that have been brought up have already been written about in two articles about eight years ago by Von Dehmelt. They went to the limit of what you can do in this type of work by using the (unintelligible) plot. If you really want to have an opinion about this, we will have Dr. Brodd work on it.

MR. MAGISTRO: The overstress by pulsing is not really what I wanted to get at. In fact it probably was a wrong analogy for me to use.

To give you the steel beam analogy, civil

engineers take a steel beam at 30,000 psi elastic modulus and design for 5,000 stress level. The beam will never fail because it is used way below its strength.

You have a battery that is inherently very good, several thousand cycles, and you are applying very low, so to speak, use conditions to this battery. It is almost inherent that you will never see a failure until you get way out there in many thousands of cycles.

What we should look for, and I used the pulse analogy maybe improperly and misled somebody -- is some discriminatory stress, whether it be a pulse or a combination of pulse and temperature, which gives us a noticeable effect in the early series of tests. This is what I really meant.

I guess the word I should be using is a test of increased severity to detect each one of these many failure modes. There must be one combination of several stresses that can do this for us.

I used the pulse because it does work in a thermal battery, because its impedance is high. That is what I really meant.

MR. SHAIR: Ralph Brodd.

MR. BRODD: I might give you a quick indication of some of the troubles you get into by drawing the diagram of the impedance equation of, say, a

decised nickel-cadmium battery.

Let's call this X reactance versus resistance. The units of resistance are about a hundredth of an ohm, on this axis. And you find that you get something like this, with this about 50 cycles and this about 50 kps. So that you have, first of all, a very large capacitive effect that you have to work with.

You have a very small value of the resistance. And this places a great deal of severity on the measurement techniques that you can use in order to make a significant measurement. You can show that there are some changes that occur during charge and discharge. That is to say, this curve will change.

If this is a charge, this would be the discharge.

So that there are changes such as this that occur with frequency on charge and discharge. Whether these can be used to predict battery failure is hard to tell. It is primarily to do with the electrochemical aspects of the system.

The frequency effects are due to the electrode reactions that go on. You can get some judgment about how fast reactions go on, in other words, how reversible the system is by its frequency dependence.

The resistive part that is due to the separator,

electrolyte and the terminals, is to be found there.

To make failure analysis by this technique you are going to have a very precision measurement of this resistance to pick up your changes in terminal connections, problems of spot-welding, problems of carbonation of the electrolyte. These will show up. But I am very much afraid with current pulse techniques that you are going to be hard-pressed to measure ten-thousandths of an ohm when you are going to have to use a good, healthy pulse to do it.

It is a big inductance. You'll get a strange-looking pulse sometimes.

MR. SHAIR: Thank you very much. I guess we have about come to the end of the day. I would not like to see this session end with an aura of doom, because in reality these batteries are pretty good.

Today's sessions were aimed at finding out how we can overcome of those improvements that are still needed. However, how we can arrive at the improvements is still needed.

There are many cells that are working successfully, and in reality I think batteries have powered many pieces of equipment in many vehicles very successfully.

Let's not end it on an aura of doom.

My appreciation to all of the speakers who did

a really fine job, and to all of the people here in the audience for a very fine participation and discussion.

Tomorrow morning we reconvene at the same spot at 9:00 a.m.

(Whereupon, at 5:15 p.m. the meeting was recessed, to reconvene Friday, October 7, 1966 at 9:00 a.m.)

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P R O C E E D I N G S

MR. HENNIGAN: We would like to bring this mornin session of the Battery Workshop together now.

Just as a reminder to everyone who gave presentations yesterday and today, would you please turn in your glo prints, pictures, graphs and so forth to Ernst Cohn, Code RN NASA Headquarters, Washington, D. C.

MR. COHN: Code 20546.

MR. HENNIGAN: I think yesterday many times in th discussion there came up problems which appeared to be with quality control of the batteries when they are first made. the looks of it, this seems to be one of the major problems that we are running into. We spend a lot of money in testi batteries, running computers day and night. If we are gett batteries with shorted tabs, leaks, and sombody leaving out the separator, or part of it, these computers aren't going tell us anything.

But this morning we have a few papers on quality control techniques, and a couple of papers on component tes

Just to get the thing going this morning, our firs speaker is Peter Voyentzie of the General Electric Company, who will speak on "Quality Control Techniques to Produce Hi Reliability Secondary Cells for Space Applications."

Mr. Voyentzie.

QUALITY CONTROL TECHNIQUES TO PRODUCE HIGH RELIABILITY SECONDARY CELLS FOR SPACE APPLICATIONS

MR. VOYENTZIE: Gentlemen, yesterday there were several statements that manufacturing defects were the cause of many cells and/or battery failures. It is my purpose today to describe our efforts to eliminate these faults.

The very complexity of cell components which are utilized in the production of aerospace nickel-cadmium cells are subject to strict quality assurance, including many individual in-process component tests. The various components utilized are conveniently categorized into three main groups: One, the raw materials or the chemical type, such as the nickel-cadmium nitrate impregnation solutions, the electrolyte, the nickel power; two, the procured components and subassemblies, such as stainless steel cases surrounding metal seals and the separator; and three, in-factory produced components, the main and most critical being the positive and negative plates.

Once the plates are produced, the plant is primarily an assembly and testing facility. In order to produce aerospace quality cells, we use a system which is comprised of four coordinated elements. These elements are chemical and physical property evaluations and audits of same; incoming planning and receiving inspections; in-process control for quality assurance; and fourth, engineering development for quality improvement.

All chemicals such as the nitrate impregnation cells

are procured through strict requirements, including the establishment period levels. Materials from prior approved vendors are supplied by lot number, along with certificates of test analysis. These certifications are periodically audited in-plant. The separator material is also procured through our specific conditions. The material is checked for thickness and weight per cubic centimeter on an established schedule, with periodic audits of other variables such as the weatherability, physical strength and electrolyte retention.

The certificates of test and periodic audits of same are also conducted on other materials such as the hardware item The plan in covering inspection has been specifically develope for aerospace cells. The plan includes the complete first chie inspection and the fact the inspection is based on a classification of characteristics.

In general, the critical nature of the end usage dictates 100 percent inspection. There are problems. In order to eliminate the factors which are detrimental to this mode of inspection, we maintain small lots of less than 200 pieces and utilize multi-parameter equipment such as optical gauges for ou physical measurements.

We maintain restricted incoming and stock areas in order to prevent usage of unauthorized materials; that is, since the receiving inspection and main stockroom are one fenced area, the use of unauthorized material is prevented.

Shelf-life schedules have been developed at age control, as imposed on all components subject to this mode of deterioration. Epoxy seal materials in the electrolyte are prime examples.

Instruments and gauges are maintained in calibration on regular schedules. Extensive training programs have been developed and are implemented for personnel who produce, control or insure quality. Such programs include training of special process operators and the subsequent certification testing of them.

Ceramic and metal hermetic seal is one of the most important incoming subassemblies. All such seals are procured from the approved vendor and are subject to 100 percent inspection. This includes both physical measurements and the helium leak rate, the maximum allowable for that being $1x10^{-7}$ cubic centimeters per second.

In process assurance, this element of quality assurance, process control and test programs most importantly are applied to the heart of the nickel-cadmium cell; that is, the positive and negative plates. The plate preparation process is the most critical factor in the determination of final cell performance, and is the most fertile area for further research. These plates are received by our aerospace group with defined dimensions and high-grade levels. The plate manufacturing facility checks the high-grade levels and determines,

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in the case of the negatives the weight gain, and the hydrogen reduction in the case of the positives.

In the aerospace area the plates are inspected to establish visual standards in the matter of incoming materials. All plates are then made into temporary cells and are subjected to 100 percent electrical EC testing -- consisting of several charge/discharge cycles in a flooded condition -- in order to first of all confirm the high-grade loadings in terms of electrolyte, electrical capacity; two, to determine the positive-to-negative ratios in the lot; and three, to precondition the plates and determine visually their suitability for cells.

In effect, we have built and tested a cell and have assured ourselves that plates are of suitable quality and characteristics for aerospace use at this point.

The plates are then washed in 500,000-ohm resistivity water, dried and re-examined 100 percent visually for any evidence of degradation, such as blistering, loose materials, cracks and sharp edges.

Slide one is one lot of cells on this EC test.

(Slide on.)

This depicts one group of cells which are on test, and they are here in the flooded condition (indicating). They go through several charge and discharge cycles.

The recombination electrode, which we are not working on, is a special case of plate assurance testing. One-hundred

percent of such electrodes are pre-tested before incorporation into the final cells in a manner which is parallel to EC tests conducted on positive and negative electrodes.

The recombination electrode is completely characterized as to its oxygen reactivity versus current density and pressures over the use-temperature range. These tests, however, do differ from the normal electrical tests, in that the test assembly more nearly approximates the conditions experienced on a final cell.

The tests are basically accomplished in a semi-solid sealed assembly -- and I have a slide showing the breakdown.

(Slide on.)

This shows the breakdown of the assembly rig. I think it is upside down.

From left to right we have the separated material, a porous membrane-type material, a counter electrode, a reference -- this is a recombination electrode -- and we have a reference electrode which is a partially-charged nickel plate. The pack is then assembled and placed in a lucite fixture which is then compressed to a preset specification, and the separated material does extend below and acts as a wick for the reservoir in the final fuel cell assembly.

(Slide off.)

I have some typical response terms, but I am afraid

that that instrument is not working. If anyone wants to see it, they can see me later.

VOICE: It's working.

MR. VOYENTZIE: It is?

VOICE: It's working, but you have to pull it around to here.

(Overlay.)

MR. VOYENTZIE: On the vertical axis we have the voltage which is versus the half-charged positive plate, and the linear axis down below is the current density. These thre curves here (indicating) represent the performance at 25° Centigrade as three different oxygen pressures in the cell.

The first curve up here represents where we ran into a slight problem at minus 20°. We have straightened out the curves somewhat later on here by changing the electrode. Thes two curves are minus 20° characteristics at two different pressures.

(Overlay off.)

Elements 1, 2 and 3 of our quality system follow standard techniques, such as covered in the military specifications. Our design is to insure as uniform a product as possible and to eliminate gross manufacturing defects such as those described yesterday.

The fourth element of this program is concerned with the development effort designed to improve the quality and lif

expectancy of the cells. The engineering development test for components represents what is intended to be a long-range view toward the greater-than-five-year cell, and it is upon these tests that I wish to concentrate.

The major cell failure modes of properly-made cells are related to changes in the plate structure -- failure of ceramic seal and separated degradation. We have chosen at the present time to concentrate on the ceramic seal in the plate structure. The ceramic to metal hermetic seal is one of the most important determinants of cell reliability. Before any new cell is accepted for use on the aerospace cells, samples are subjected to excessive test programs. One of these tests that we have is what might be called the Group IV test.

These tests include total emergent in 1.3 specific gravity KOH of 110° Centigrade. A voltage of 1.70 is impressed across the seal, and this voltage is alternately finite, and then cuts out equivalent periods of time across the seal. It is not AC.

At predetermined intervals of exposure the seals are removed and inspected for migration of seal braze material across the ceramic interface, erosion and pitting, weight loss or gain, sludge formation and helium leak rate. The results of this test are used to determine the acceptability of seal type. Test cells are then constructed with the seal type under investigation and are placed on a life test. Upon satisfactory

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demonstration of improved life, prototype cells are submitted to the customer for approval or design change.

I might add at the present time we are testing a new proprietary hermetic seal, and the preliminary tests are indicating a potential of better than five years for the seals.

In addition, I might add we would welcome any suggestions for additional tests which might be performed on this cell to better prove it out.

We, as well as the rest of the industry, have for a long time made measurements of the various plate parameters, both with 4-cell assembly, for process control purposes, and at the life test, to understand failure mechanisms. Both plates have been found to increase in thickness with cycle life. The positives have increased in capacity due to corrosion of the substricts. The negatives have shown the redistribution of acts of negative material cycling, and we have semi-quantitat results regarding this redistribution by using the electron beam x-ray microprobe.

There are problems, that the probe point is so smal and the surface of the plate is so rough, that these things have been semi-quantitative in nature.

Since these changes appear to occur at different rates in cells under identical test conditions, we are workin to correlate life test results in initial plate measurements. We are reasonably sure that these changes are closely associa

with the particular cycle in being, such as depth of discharge and temperatures.

In the area of elevated temperatures, we may be introducing additional complexities rather than accelerating normal failure modes or introducing new ones.

Before I leave, I would like to draw a curve of a plot of some cycle life tests. (Drawing on blackboard.) These are 90 minute orbits on nickel-cadmium cells at three different depths of discharge.

This axis will be in a semi-logarithmic axis. I am not going to attempt to show you the exact figures. I know all of you know them.

Let's assume this dotted line here (indicating) represents 25 percent depth, and here we have 50, and here we have 75 percent depth; that is, depth of discharge. Here we have a logarithmic curve. In this area we will call it 3,000 to 6,000 cycles, and up here we may have 18,000 to 20,000 cycles on a semi-logarithmic basis.

So we plot the various temperatures, the mean time to failure at the different temperatures. This is somewhat ideal, but nevertheless, these things do seem to represent almost a straight line on this curve in a lot of instances -- for instance, minus 10° Centigrade.

If I extend this thing to a lower depth of discharge, we see things happening like this. There are still some cells

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on which there are under 20,000 cycles. Then we might take 25° Centigrade. We get down here to 50° Centigrade, and we see this thing going like that (indicating).

I think something else is happening here. You migh say it is a separator failure, that is true. But this is a case of the "chicken or the egg". If you open up a cell, you find some separated degradation and you find plate thickness increasing and various other things happening. It is a quest ion of which comes first. If you had a good separator, would it last.

That's all. Thank you.

MR. HENNIGAN: We have time for a short question or two, if anybody wants to ask them at this time.

(No response.)

One thing that seems to be coming out, which is nothing new -- it is getting kind of old, saying the same thing all the time -- but it looks like we have to run these batteries cold if we are going to run into a life problem. W have got batteries running both at Crane and Inland of 15,000 or 20,000 cycles, and no failures. That is at zero an minus 10° Centigrade.

Our next speaker will be Dr. George Dalin of the Yardney Electric Company, who will speak on the "Preparation of Uniform Plates as a Basis for Increased Battery Reliabilit

Dr. Dalin?

PREPARATION OF UNIFORM PLATES AS A BASIS FOR INCREASED BATTERY RELIABILITY

DR. DALIN: Before I start this paper, let me remark that when I was "requested" to give this, I made a comment somewhat similar to the one I did yesterday, that I thought we couldn't contribute much in the way of accelerated testing. So I was asked to comment on work that had been done by Otto Wagner and Robert Enters, so I am reporting on someone else's work which I have tried to digest.

This is entitled "The Control of Cell Components as a Method of Matching Cells."

The problem of cycling sealed cells is too well known to require any extensive discussion here. Of the sealed systems, nickel-cadmium on partial discharge has been the most successful because the recombination of oxygen with the negatives proceeds rapidly in the absence of an interfering membrane.

On the other hand, the fact that coulombic efficiency on the positive is lower than 100 percent results in production of oxygen before the positives reach full charge, so evolution of oxygen is a fact of life in the operation of sealed nickel-cadmium.

Another fact of life is that nickel-cadmium batteries occasionally rupture, particularly on high-rate charging. This type of failure is attributed to cell imbalance. An individual

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cell can be gassing vigorously without producing a rise in battery voltage great enough to either cut the batter off cha or, alternatively, to decrease the charging rate appreciably

So far as silver-cadmium is concerned, the problem of oxygen evolution before reaching full charge on the positi is absent, but the rate of recombination with the cadmium is much lower due to the fact that the separator system includes membrane which prevents oxygen from reaching the negative eas and to the presence of free electrolyte. Moreover, it is customary to use a sponge negative which does not catalyze th recombination as strongly as the nickel in the plaque of the impregnated negative. The overall problem, consequently, is similar since cell imbalance also can cause the battery to rupture.

We undertook to study the problem of cell imbalance on a contract with Wright Air Development Center. Examinatio of data from our own production lines showed that silver-cad- mium cells varied in capacity by as much as ± five percent. Cells cycled as a battery tended to stay within closer limits than this, but nevertheless, the differences were great enou to cause concern. An analysis of our production line operati showed that variations among the components were substantial and were particularly great with respect to the cadmium negat It was decided, therefore, that we would try to match cells the basis of component characteristics.

For silver-cadmium cells we started out with the following steps:

One, control of silver powder particle size and surface area as determined by BET.

Two, control of silver and cadmium oxide powder by batch utilization values. This is with respect to the number of ampere hours per gram.

Three, control of silver plate dimensions, density and weight.

Four, control of negative weight.

And five, constant input-output formation cycling of cells.

The C-19 separator, which is a silver cellulose, proved to be sufficiently uniform so that no selection was necessary. Electrolyte content was measured to 0.1 cc. The nominal cell size was 15 ampere hours.

For the positives, we found that the rolling and sintering process gave better control of plate capacity than did the process of manufacturing by pasting silver oxide powder. The rolled positives consisted of 90 percent high capacity silver plus 10 percent of cadmium oxide. The design weight of the positives was 5.17 grams. The mean proved to be 5.15 with a standard deviation of 0.084. Forty-six percent of the batch would, therefore, fall within $\pm$ one percent.

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Figure 1 shows what a distribution curve looks like.

FIGURE 4

POWDER WEIGHT DISTRIBUTION OF SILVER POSITIVES FABRICATED

BY THE ROLLING MILL PROCESS

Active Mix: 90HC Ag + 10 CdO

Grid: Exmet 5Ag8-1/0

Dimensions of Electrode: .014" x 1.93" x 2.75"

Design Weight of Powder: 5.17 gms

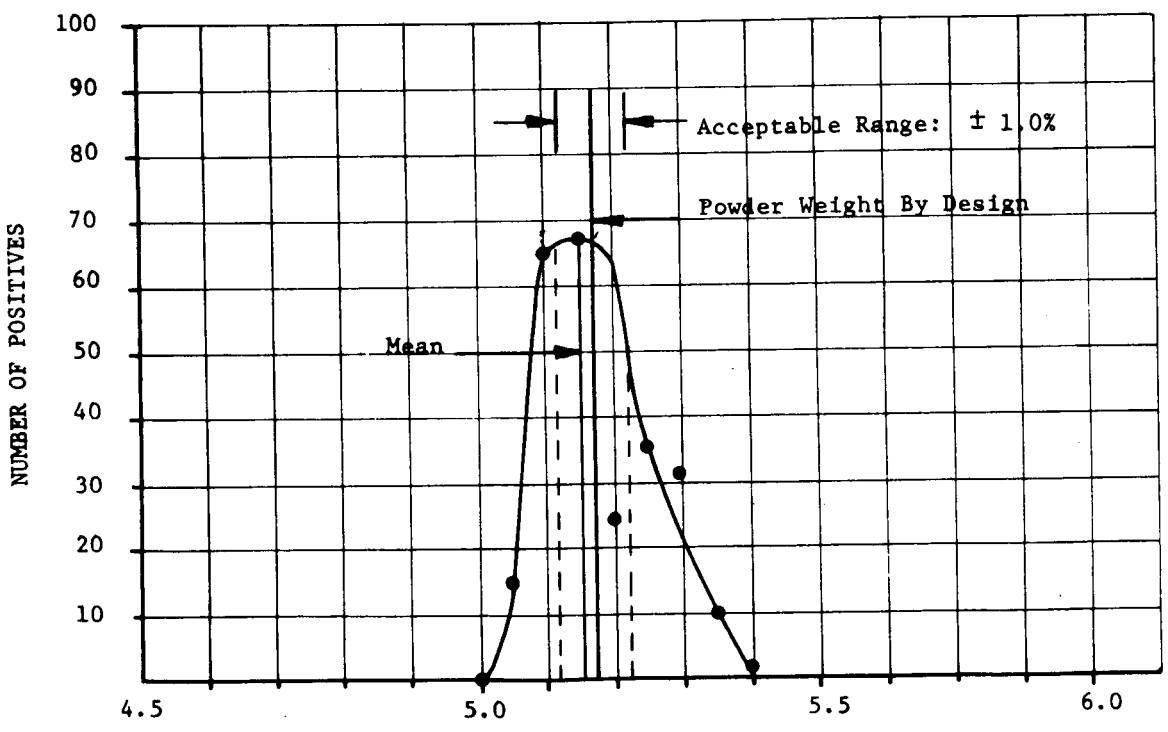
Mean: 5.15 gms

Percent Acceptable: 46.13% To ± 1.0% of Design Weight

S. Dev.: .084

Number of Samples: 250

Three Sigma (99.73%): Min. 4.90, max. 5.40



(Slide on.)

I guess that's about as well as you can do.

Lights, please.

As to the cadmium plates, we found that sponge negatives gave better results than the impregnated negatives. This we attribute principally to the fact that the silver-cadmium cell operates in 44 percent KOH, whereas the impregnated negative for nickel-cadmium operates in 31 percent KOH. The design weight of the negatives was 7.80 grams; the composition was 94.5 percent cadmium oxide, 5 percent high capacity silver, and 0.5 percent binder. When we speak of high capacity silver, this is primarily a matter of particle size. The mean plate weight was 9.29 grams; the powder weight was 7.74 grams, with a standard deviation of 0.192 grams. On this basis, 65.2 percent of the batch was acceptable within ± one percent.

As the next stage individual plates were characterized. Individual plates were cycled against counter-electrodes under controlled conditions, to establish the capacities of the plates. However, this proved to be unnecessary for silver and sponge cadmium negatives, provided the other variables, such as plate weight, et cetera, were properly controlled.

Consequently, individual characterization was stopped for silver and cadmium. After measuring the individual silver and cadmium plate weights, these were assembled into cells so that the sums of the weights in each cell matched within ± one

percent.

The plates themselves were allowed to vary to the extent of ± two percent. Plates which varied by more than tw percent from the mean were rejected. Cells were charged to a constant input of 27.6 ampere hours at a rate of 1.2 amps for 23 hours. This constitutes an overcharge of about 50 percent for the positives. The objective was to provide for the low efficiency of the negatives with respect to the first dischar The cells were then individually discharged at 6.0 amps to 0. volts. At this point, cells were assembled into 5-cell batte ies, matching the cells within each battery, so that they var by no more than ± one percent. The batteries were then charg until the first cell of each battery reached 1.65 volts, and then were discharged until all cells had reached 0.9 volts or lower. The capacities to 0.9 volts were recorded and are sho in the next figure.

(Overlay.)

This shows the procedure. They are all given 27.6 ampere hours on the first charge, then discharged down to 0.9 volts, and then discharged as a battery. But the output is recorded on every one of them.

Notice there are three batteries, and each one has five cells. They are then charged again at 1.2 amps, until t first cell of the battery reaches 1.65 volts, and then is dis charged again. At this point they are sealed.

Appendix V - FORMATION AND PROVE-OUT CYCLES OF SEALED Ag/Cd BATTERIES FOR THE AIR FORCE

	Battery No. 1 Ampere-Hour Capacity					Battery No. 2 Ampere-Hour Capacity					Battery No. 3 Ampere-Hour Capacity					REMARKS
Cell No.	5	8	9	18	20	2	3	6	14	16	1	4	7	10	17	Constant input-output
Cycle 1 Charge	27.6	27.6	27.6	27.6	27.6	27.6	27.6	27.6	27.6	27.6	27.6	27.6	27.6	27.6	27.6	Charge 1.2A for 23 hrs.
Cycle 1 Discharge	16.6	16.8	16.8	16.2	16.6	16.0	16.3	16.4	16.2	16.2	15.9	15.8	15.8	15.7	15.7	Discharge 6.0A to 0.9V.
Cycle 2 Charge	19.7	19.7	19.7	19.7	19.7	19.9	19.9	19.9	19.9	19.9	19.8	19.8	19.8	19.8	19.8	Charge 1.2A. until first cell of battery reaches 1.65V.
Cycle 2 Discharge	17.80	17.95	17.95	17.75	17.90	17.75	17.85	17.80	17.95	17.90	17.55	17.95	17.80	17.65	17.80	Discharge 6.0A until each cell reaches 0.9V.
Cycle 3 Charge	19.05	19.05	19.05	19.05	19.05	19.0	19.0	19.0	19.0	19.0	18.9	18.9	18.9	18.9	18.9	Sealed charge 1.2A. until first cell of battery reaches 1.65V.
Cycle 3 Discharge	18.80	18.80	18.60	18.90	18.55	18.90	18.70	18.60	18.80	18.60	18.70	18.50	18.50	18.50	18.60	Sealed discharge 6.0A. until each cell reaches 0.9V.
Mean Spread Ave. Dev. Std. Dev.	18.73 AH 1.8 % ± .66% 0.122					18.72 AH 1.60% ± .54% 0.173					18.56 AH 1.08% ± .45% 0.245					Discharge 3

Incidentally, I should point out that these are not arbitrarily put into these batteries as you see in cells numbe 5, 8, 9, 18 and 20, at that stage. That is actually a recapit ulation, because after these cells have been run off on the fi charge and discharge, and the second, then at that point they a matched within one percent and reassembled into the 5-cell batteries. So that this is really an anticipation of what has been done down below.

(Overlay off.)

Capacities were close enough so that no cell reverse Excess electrolyte was then removed and the cells were sealed and cycled on an orbital regime.

These batteries are now up to 1800 cycles and are still holding within ± one percent on almost all capacity cycl Where the difference has exceeded one percent, it has been ver small. Uniformity is slightly better for cells with PVA binde than with Teflon treated negatives.

Rupturing of cells has not occurred and the batterie are still yielding the required capacity.

Parenthetically, I want to point out that control of components proved to be necessary in manufacturing silver-cadm cells for Mr. Hennigan, who first really put the arm on us in this case. Here again we found that it was particularly neces sary to control the density, thickness and weight of the spon cadmium negative. Much of the input to this plate on the firs

cycle is unavailable for discharge. Unless the physical characteristics are closely controlled, the capacity of the plate will then vary too widely.

The situation for nickel-cadmium cells is similar to that for silver-cadmium, although somewhat more complex. Plaques must be controlled as to weight, linear dimensions and porosity, as well as surface area. BET was used for this last.

Of the various impregnation procedures tested, the use of the nitrate followed by precipitation with alkali proved to be the best. The process is slow, but it is possible to adjust the content of active material within close limits. Impregnant content was held within ± two percent of the impregnant.

An attempt was made to control the nickel positives by characterizing them in groups of seven. This proved to be unsuccessful in that cells made with these groups varied too widely. Subsequently, individual plates were characterized.

We owe this conception of characterization to Dr. Dennis Turner and his group at Bell Telephone Laboratories -- although I suspect that this is not unique, from what I have heard here -- and we wish to thank them for their help in setting up the methods of making nickel-cadmium cells.

The characterization process consists of a series of cycles in which the individual test plates are run against excess counter-electrodes at specified rates and temperatures.

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The capacities are measured on successive cycles until they stabilize. It was found, in some cases, to be necessary to r as many as 11 cycles before the plates became steady with respect to capacity.

To prepare the 14 ampere hour nickel-cadmium batter ies, electrodes with a spread of ± two percent were placed in cells in such a way as to make the totals agree within ± one percent. The cells were then charged at 4 amps for four hour putting 16.0 ampere hours into all of them. They were then discharged until all of the cells had dropped to 1.0 volts an all free electrolyte was removed.

After this point, the cells were grouped according to capacity at 1.0 volts, so that the cells within each group would match within ± one percent. They were then sealed, giv a charge of 4.0 amps for 3.5 hours, or until the first cell o the battery reached 1.48 amps and started cycling.

The next figure shows the results.

(Slide.)

Again, this is too much of a job to try to digest just looking at it. A copy of this figure will be given with the paper. The procedure is essentially the same as on silve cadmium.

Although the silver-cadmium cells have remained in balance for over 1800 cycles, with depths of discharge rangir from 25 percent to 75 percent, results were not so satisfacto

Appendix IV - FORMATION AND PROVE-OUT CYCLES OF SEALED Ni/Cd BATTERIES FOR THE AIR FORCE

	Battery No. 4 Ampere-Hour Capacity					Battery No. 5 Ampere-Hour Capacity					Battery No. 6 Ampere-Hour Capacity					REMARKS
Cell No.	1	3	10	11	16	2	5	8	18	19	4	7	12	13	15	Constant input-output
Cycle 1 Charge	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	Charge 4.0A for 4.0 hrs.
Cycle 1 Discharge	13.1	13.2	13.1	13.1	13.1	13.2	13.4	13.5	13.4	13.2	12.7	12.8	12.9	12.8	12.7	Discharge 6.0A to 1.0V
Cycle 2 Charge	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	Sealed charge 4.0A for 3.5 hrs. or until first cell of battery reaches 1.48 volts.
Cycle 2 Discharge	13.0	13.0	13.0	13.0	12.93	13.10	13.21	13.22	13.22	12.90	12.85	12.80	12.82	12.90	12.80	Sealed discharge 6.0A. until each cell reaches 1.0 volt.
Mean	12.99 AH					13.15 AH					12.83 AH					
Spread	0.5%					2.42%					0.78%					Discharge -3
Ave. Dev.	±0.9%					±0.8%					±0.3%					
Std. Dev.	0.05					.09					.07					

with the nickel-cadmium. These stayed in balance at 25 percent depth, but were only fair at 50 percent and were poor at 75 percent. This raises the question as to why the performance of the nickel-cadmium cells is so much less uniform.

Dr. Turner's group has shown that part of the nickel plaque is converted to active nickel oxide. We suspect that the plaques which we have used may have been oxidized non-uniformly. These plaques were obtained from a variety of sources, but even plaques from any one source were found to vary substantially in density, weight, thickness and surface area. Consequently, it seems likely that, especially with 75 percent depth of discharge, the plaques may have been substantially and non-uniformly oxidized.

To sum up, silver-cadmium cells with components made under close control, can be assembled into batteries which stay in balance for many cycles, even when cycled rapidly at 75 percent depth of discharge. The situation with nickel-cadmium is not so advanced, but there is a substantial possibility that better performance can be obtained if plaque quality is more closely controlled.

Thank you.

MR. HENNIGAN: We would like to show some data later on during the discussion period of what we get out of all this 100 percent inspection. I think we will go on to the speakers and wait for that.

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Are there any questions here? We might have time f
one or two.

(No response.)

If not, the next speaker was supposed to be Tom
Wetherell of RAI Research Labs, but he was called away on an
emergency last night. So Mr. D'Aftostino of RAI is going to
read his notes.

DETERMINATION OF PROPERTIES OF GRAFTED
MEMBRANES FOR USE AS BATTERY SEPARATORS

MR. D'AFTOSTINO: Rather than only read notes, whi
would lead to chaos, I have tried to prepare something in th
same vein speaking for myself.

Before I describe the techniques in determining th
properties of separator materials per se, I would like to br
describe how a grafted membrane is made. Incidentally, the
membranes that will be referred to here are for use in silve
zinc systems.

As you are well aware, the chemical environment wh
a membrane material would see in a silver-zinc battery is qu
severe. The caustic concentrations would run anywhere up to
40-45 percent.

The membrane is subjected to strong oxidizing envi
ments. The temperature extremes can vary from sterilizable
conditions to sub-zero temperatures. And if the battery is s
jected to shock tests, the membrane actually must sustain th

tests.

In the selection of a membrane, one can use a material such as cellulosics which have the prerequisite low electrical resistance and prevent the diffusion of metal ions. The inherent properties of this material, however, are such that it is not totally resistant to caustic environments over long periods of time, and it has a relatively poor oxidation resistance.

Numerous other polymeric materials have, in fact, excellent oxidation resistance and resistance to caustics. However, they do not have prerequisite low electrical resistance.

As an example, I would like to cite polyethylene. In order to alter the properties of this polymer, we have to add to it certain chemical units. We do this by a process which is called graft polymerization. This is as follows. I will give you a very brief description.

If we take a polyethylene film and place it in a solution of acrylic acid and benzene, and we initiate on the surface of the polyethylene films three radicals, which can be initiated by either a chemical means or by radiation means -- the radiation being beta, gamma, UV, or a large number of initiating methods -- we can effect a grafting of the acrylic acid onto the polyethylene. There is no change.

The uniformity of the graft is dependent upon a number of factors other than the initiating source. Once the

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acrylic acid is grafted, it is washed in a caustic solution t
remove certain side products -- primarily what we call homo-
polymerization. In other words, grafting which takes place i
this solution as opposed to in the film.

The film is then washed with caustic to change it to the salt form. In this state the grafted polyethylene material is a membrane with relatively low resistance and sti retains its excellent resistance to caustics. It has a relat ively good oxidation resistance.

Improvements, more recently in membrane materials, have been made by radiation processes and have been shown to take place by pre-crosslinking of polyethylenes.

I would like to draw on the board for you.

(Drawing on blackboard.)

We assume that the polyethylene is a linear change. When we talk of crosslinking, using radiation processing, wha we are talking about is tying the linear change together in a fashion which gives us a 3-dimensional network. We go back a say that the pre-crosslinking of the polyethylene changes the polyethylene polymer from a linear polymer to a 3-dimensional network. This can be done by subjecting the film to either gamma or beta radiation, and it can also be done by chemical means. Each has its own inherent advantage.

The second way of improving the membrane materials is by changing the type of monomer which is used in the graf

process.

I have spoken to you of acrylic acid. When one takes a polyethylene material and initiates a site on it and reacts with this acrylic acid, a structure is formed (drawing) such as indicated here, and it is repeated.

On this change there is a site which contains _____ air hydrogen. This site is more susceptible to oxidation than certain other sites.

If one uses a meta-acrylic material, this is what occurs. When one takes off the hydrogen and puts on the CH_3 group here, it causes two things to happen. You increase the blocking effects which take place due to the diffusion of metal ions , and you also make this site from a relative susceptible site to an oxidation-resistant site.

The third method of improving our membrane material is by variations in the conditions which are used in the grafting process.

I would like to get into the test procedures, some of which are currently being used and some of which are being proposed for checking out membrane materials. I will run through them briefly and then describe them in a little more detail.

The first one is what we call the Gel fraction of the crosslink polyethylene. Since we have shown that we can improve membrane materials by crosslinking the polyethylene prior to grafting, it now becomes necessary for us to determine

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what is the extent of crosslinking at various processes.

Incidentally, I would like to point out here that if one plots a percent Gel formation, which is in effect the amount of 3-dimensional character of a radiation grafted polyethylene against the dose, you find -- if this is a log, you get a linear plot. (Drawing.) At about a level of 90 percent Gel formation it is apparent at a dose level of about 60 megarads.

Further, it is shown that depending on the type of polyethylene which is used for a comparable dose, you get a different Gel factor.

For instance, if this is low density polyethylene, a medium density polyethylene will give you a lower Gel fraction, and the high density prolyethylene will give you less yet.

In order to determine the Gel fractions, what we do is very simple. We take the polyethylene itself as very soluble in zylene. So what we do is take the radiated material and heat it up in a solution of xylene, which contains an antioxidant. On this basis you end up with some material which is solublized and some which is not. That which is not solublized is derived and the weight is determined and from this you get a Gel fraction.

Another important factor in crosslinked polyethylene is not only the amount of Gel that is formed, but what you want to know is the distance between the crosslinks in the polyethylen

The distance between crosslinks we assume should have some bearing on diffusion of certain materials to the polyethylene, and should to some extent be related to the pore size. I will back away from this if anyone pins me down, but it is a logical assumption to come to, although we have no data to back it up.

What we are talking about here now is a method of determining this M_c value, where "M" means the molecular weight between the crosslinked sites. This can be determined very readily from known techniques and _____chemistry, where all one has to do is determine the young modulus, and from the young modulus in relationship to the density. From the molecular weights of materials you can determine the molecular weight between crosslinked sites. This should be an indication of the pore sizes, although this pore size means nothing when you get into caustic. It only would mean the pore size of the polyethylene per se.

An additional method which is useful in characterizing polymer materials is by special photometric methods. Here we can use both IR and UV. The infrared curve of regular polyethylene can tell us what the percent of crystallinity in polyethylene film is.

We can also use this in grafted film, since we are grafting onto our membrane materials, materials such as acrylic acid, which have a boxile (?) function, which gives characteristic IRPs and UVPs. We can use the IR and UV checked at

various spots along the membrane to determine what the percentage graft is at various spots along the membrane.

As I mentioned before, we checked the tensile strength of the crosslinked polyethylene also.

Another place where the IR is very useful is in checking out the amount of carbonyl which is formed in a crosslinked polyethylene prior to the grafting process. What this has done for us is as follows:

If you take a sample of polyethylene and you irradiate it in the air, you get reaction with oxygen in the air, and the formation of carbonyl subsequently degrades, and degrades very rapidly. If you do this in a nitrogen environment, you do not get this carbonyl formation.

The IR here is a handly tool to make sure that during the radiation -- this is the beta radiation for crosslinking of the polymer -- none of the polymer is in the form of carbonyl. Rather, what you have gotten is a true crosslinking of the polymer and not the formation of carbonyl.

In addition to this, there are a number of other things which are checked: thickness of grafted films are checked, both wet and dry; the exchange capacities are run on the grafted film; electrical resistance is run on the grafted film; and cycle tests are run in a three-plate silver-zinc cell.

This is an area where Mr. Wetherell would have been able to give you more data.

I think my time is about up, so I will let it go at that.

MR. HENNIGAN: I think we will go on to the next paper here, and any questions to be asked can be asked after this paper.

Our next speaker is Dr. James Oxley, of Atomics International, who will cover the area of component testing, particularly under zinc electrodes, the methods that can be used in this area.

CHARGING CHARACTERISTICS OF ZINC ELECTRODES

DR. OXLEY: What I am going to talk about today represents an attempt to develop an increased understanding of the charging process of zinc electrodes in electro-chemical cells which have been employed as metals.

The work is therefore equally relevant to silver-zinc and nickel-zinc, as well as to the more sophisticated, or shall we say the more recent developments of zinc-iron and zinc-oxygen batteries.

This work was performed while I was at Lockheed Missiles Laboratories, under contract to our Space Flight Center, and at the start I would like to acknowledge the people with whom I worked with there: Mr. Johnson, Mr. Fleischman, and Dr. Oswin.

The principal course for the progressive change in shape of the zinc electrode during successive cycling is uniquely a result of the fact that zinc oxide, the discharge product, is readily soluble in the alkaline electrolyte in the form of the zincate iron.

During the subsequent charge process, therefore, the reduction of zincate is subject to the usual customary difficulties generally associated with electro-deposition processes or plating processes.

Two damaging effects can result during the charging process, depending upon a combination of current density and

the quantity of available zincate.

Firstly, dendrite growth, or "tree" as it is often termed, and secondly, the formation of non-adherent deposits. The importance of the total quantitative zincate which is available during the charging reaction is of critical importance. During the discharge of dendrite, during the relatively slow discharge over several hours, it can be assumed that the whole battery will become saturated with respect to the zincate iron. This, of course, includes the silver electrode which is not -- I don't know much about silver electrodes; I don't think it is best as to density -- but it must then be regarded as presenting a reservoir of available zincate for the charging reaction.

This is not so critical, of course, when one uses zinc-oxygen electrodes or zinc-air electrodes, because here the quantity of zincate or quantity of electrolyte which can be associated with the structure is almost negligible.

Since the total quantity of non-adherent or dendritic deposit which can be deformed is strictly a function of the amount of zinc available, one might therefore suspect that the problems of non-adherency dendrite growth would relax with zinc-oxygen electrodes; that is, unless you select carbon, which would again have high capacities for electrodes.

Depending upon the charging current density, we have two types of deposits. Mossy and crystalline can be formed.

First slide, please.

(FIGURE 1)

Here we have plotted a graph, if you can call it that, showing the types of deposit which are obtained at different current densities as a function of temperature. The transition between the so-called mossy and crystalline variety is associated with the onset of diffusion control. We measured the diffusion coefficient of zincate iron in this electrolyte, with a value of 1.8 times 10^{-6} centimeters squared per second.

We studied, therefore, the diffusion of zincate in a separate series of studies which are reported in papers given in Buffalo and Atlantic City. I won't dwell on them here.

However, at yesterday's meeting Dr. Dalin did draw attention to the possible role of temperature as a means of performing accelerated testing.

If we suppose that the most dangerous variety of zinc deposits is the crystalline or dendritic variety, we see that raising the temperature causes this form to be deposited to a lesser extent, whereas raising the temperature has damaging effects on other parts of the cell -- for example, the rate of silver oxide dissolution is enhanced, and the rate of cellophane degradation can be increased also.

Next slide, please.

(FIGURE 2)

This slide illustrates the mechanism of dendrite

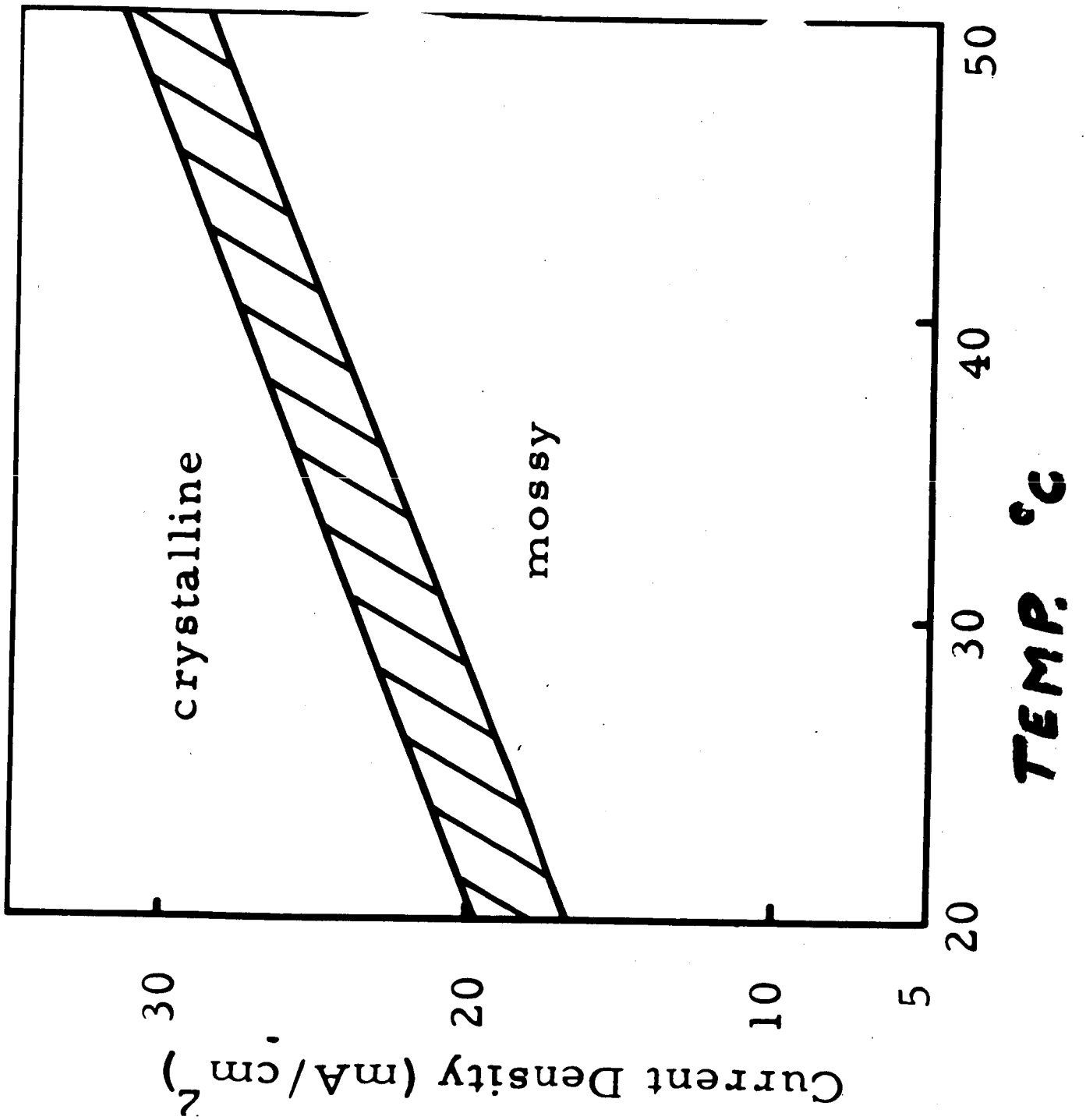
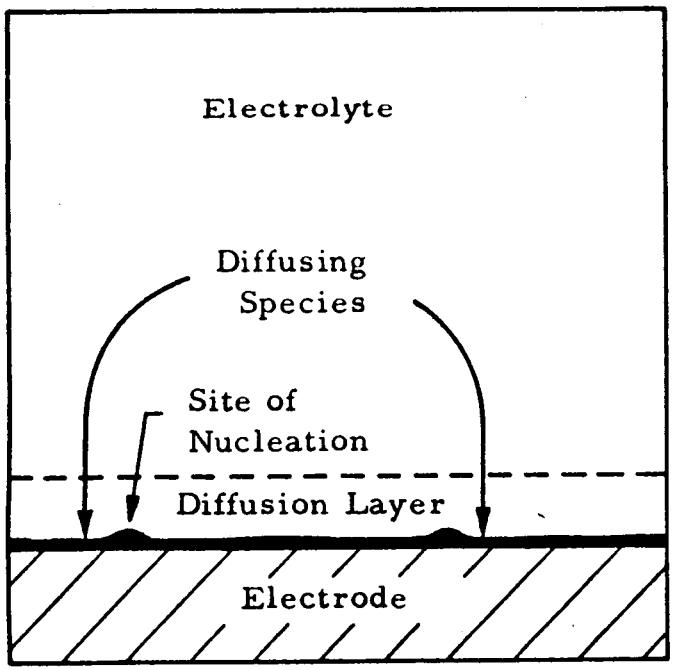
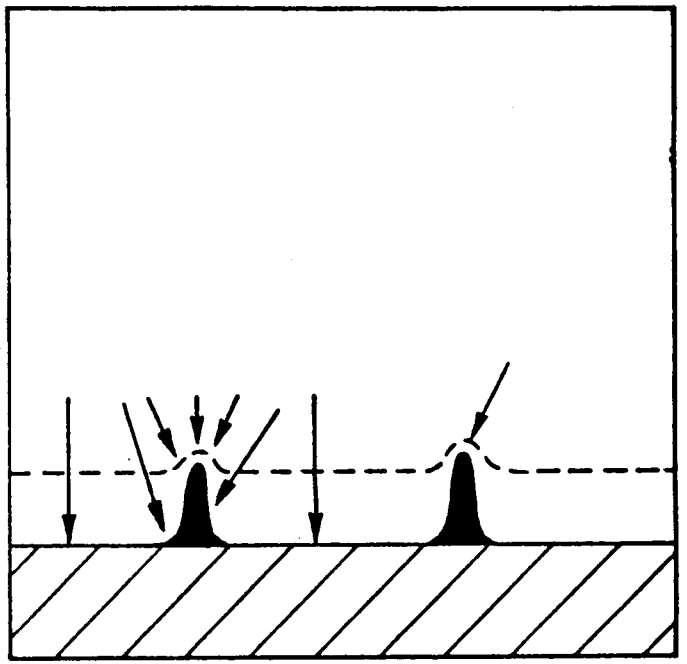

crystalline
mossy
Current Density (mA/cm²)
30
20
10
5
20
30
40
50
TEMP. °C

Figure 1



Linear Diffusion onto Flat Surface



Spherical Diffusion onto Dendrite Tips

Comparison of Linear and Spherical Diffusion Processes

propagation. Unfortunately, the nucleation and initiation stages would be on the scope of the work we carried out at Leesona Moos.

Let's assume now that following nucleation and initiation protrusions form on the electrode surface. These protrusions can then grow by the normal processes of spherical, or more exactly parabolic diffusion, to these ends.

Since the flux of the depositing zinc iron, the reducing zincate iron is great at these points, and therefore these "spikes" as it were, or dendrites, tend to grow preferentially, seeking out the source of the zincate.

Such considerations of diffusion have led us to suggest the possible use of pulse charging. This hasn't actually been put into practice. The theory is more or less as follows:

One maintains the on-charging cycle until such a point as the diffusion layer becomes of the same order of magnitude as the surface irregularities. At this point one turns off the charging current and lets the diffusion lab concentration gradually build up decay. One therefore can have a series of on/off pulses, depending on the frequency, depending on the current density.

This is also a very similar method to what Mr. Hennigan referred to yesterday in the discussion, which is limiting the voltage to which the zinc electrodes can arise. This is tantamount to saying minimizing the possibility of concen-

tration polarization taking its effect. Because gradually the concentration of zincate dissolved in the electrolyte decreases and the effective polarization decreases with it.

(Slide off.)

Adherency is always a critical parameter in electrodeposition. We made a short attempt to study this and study the deposition of zinc from zincate electrolyte at different current densities of 15 and 30 milliamps per centimeter squared, where the reactions are activation and _____control respectively.

Next slide, please.

(FIGURE 3)

This slide shows the percentage of the deposit that is non-adherent on different metal substrates in the activation on the left, and on the right the diffusion control region. On the left the type of growth is mossy, and on the right it is dendritic. But both have this non-adherent characteristic.

In the activation control region it would seem that the most apparent deposits were found on lead, with amalgamated zinc following a close second. In the diffusion control region, the most inherent deposit was found on tin, with lead following a close second.

We felt that if the tactical effects could be excluded and therefore the difference in behavior, I think this could relatively be attributed to either a combination of the

EFFECT OF SUBSTRATE MATERIAL ON ADHERENCY OF ZINC DEPOSIT

(a) 15 mA/cm^2 (b) 30 mA/cm^2

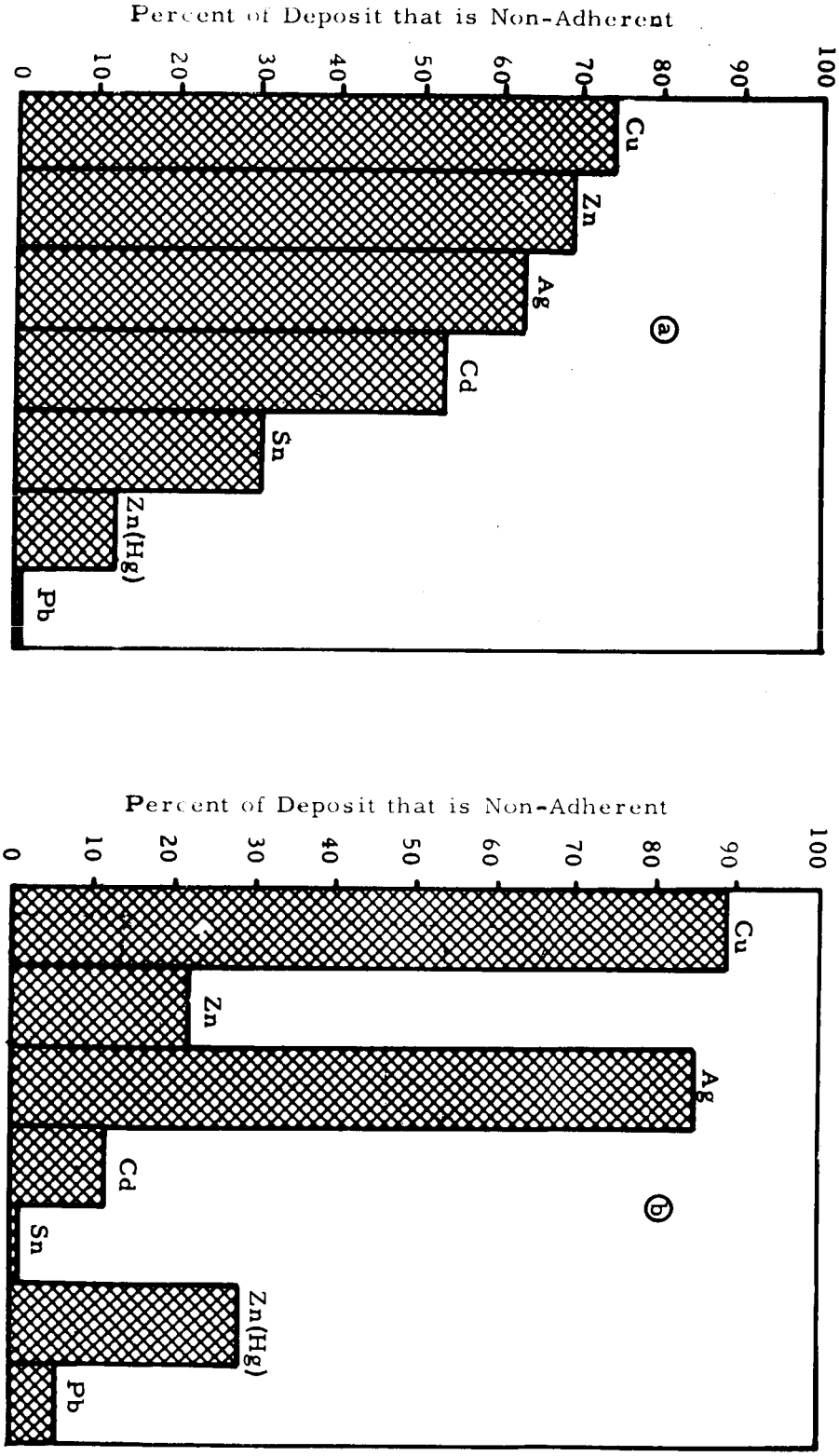


Figure 3

effect of these metals which may deposit simultaneously with the zinc on the hydrogen voltage, or conceivably in the nucleation and initiation processes through this mechanism small enough quantities of lead, for example, whatever it is, tin, might cause a uniform structure to be obtained.

Next slide, please.

(FIGURE 4)

Since lead was found to be the best, we tried the effect of adding different small concentrations of lead ions -- actually, in this case in the form of lead acetate to the electrolyte, again in both the activation "A" and diffusion control regions.

Interestingly, about the same concentration of dissolved lead ions was found to be appropriate -- or rather, to give the maximum adherence to the deposit. This was in the case of deactivation control processes, about 0.4 grams per liter, and diffusion control process about 1 gram per liter.

Next slide, please.

(FIGURE 5)

This slide shows a cross section of a zinc deposit obtained at 50 milliamps per centimeter squared from saturated zincate solution containing 0.4 grams lPb(11). The total thickness here is 0.01 inch, and a deposit of about half that. So we have got here quite a nice thick deposit of zinc for the electrolyte.

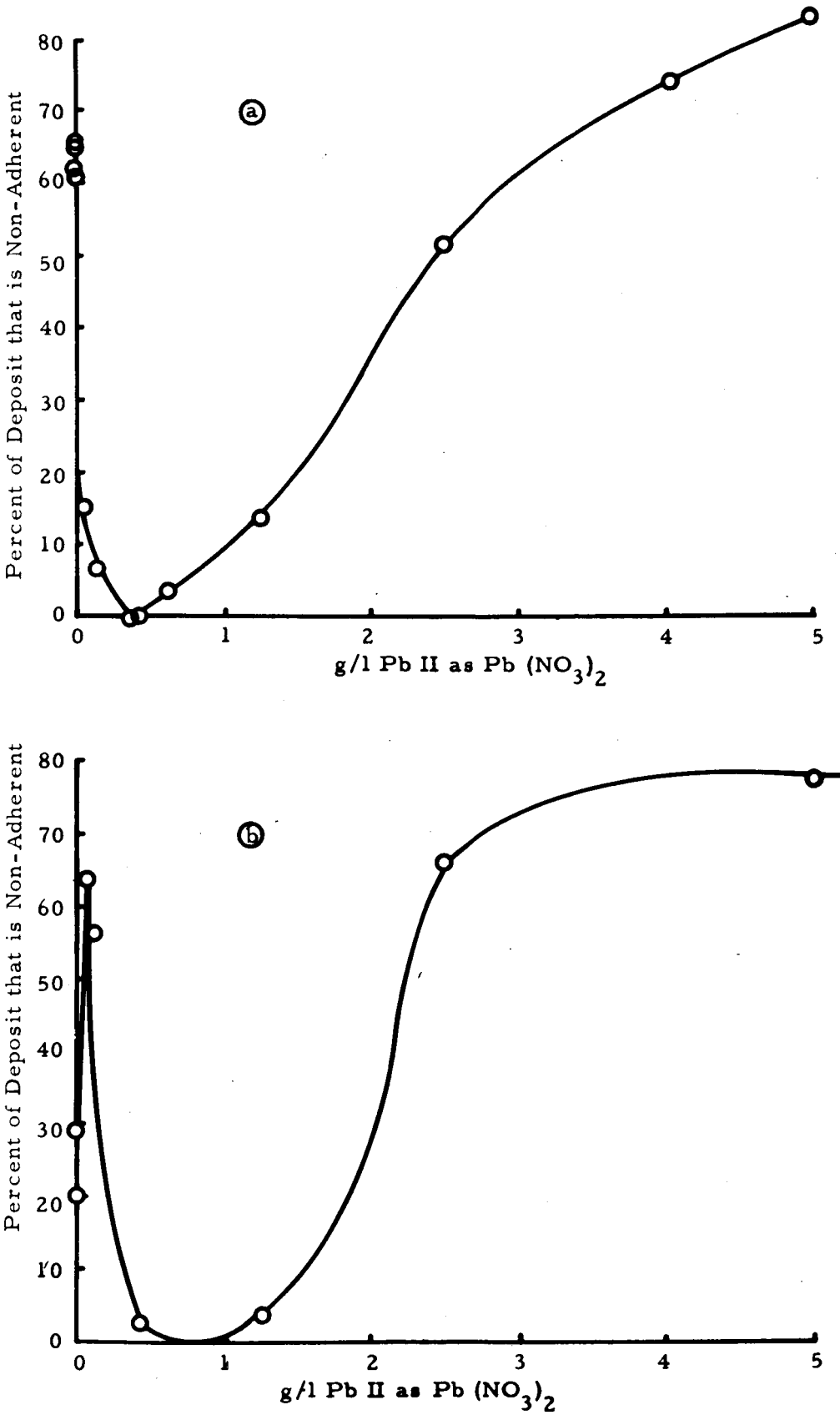


Figure 4

EFFECT OF LEAD ION CONCENTRATION ON ADHERENCY OF ZINC DEPOSIT. (a) 15 mA/cm^2, (b) 30 mA/cm^2

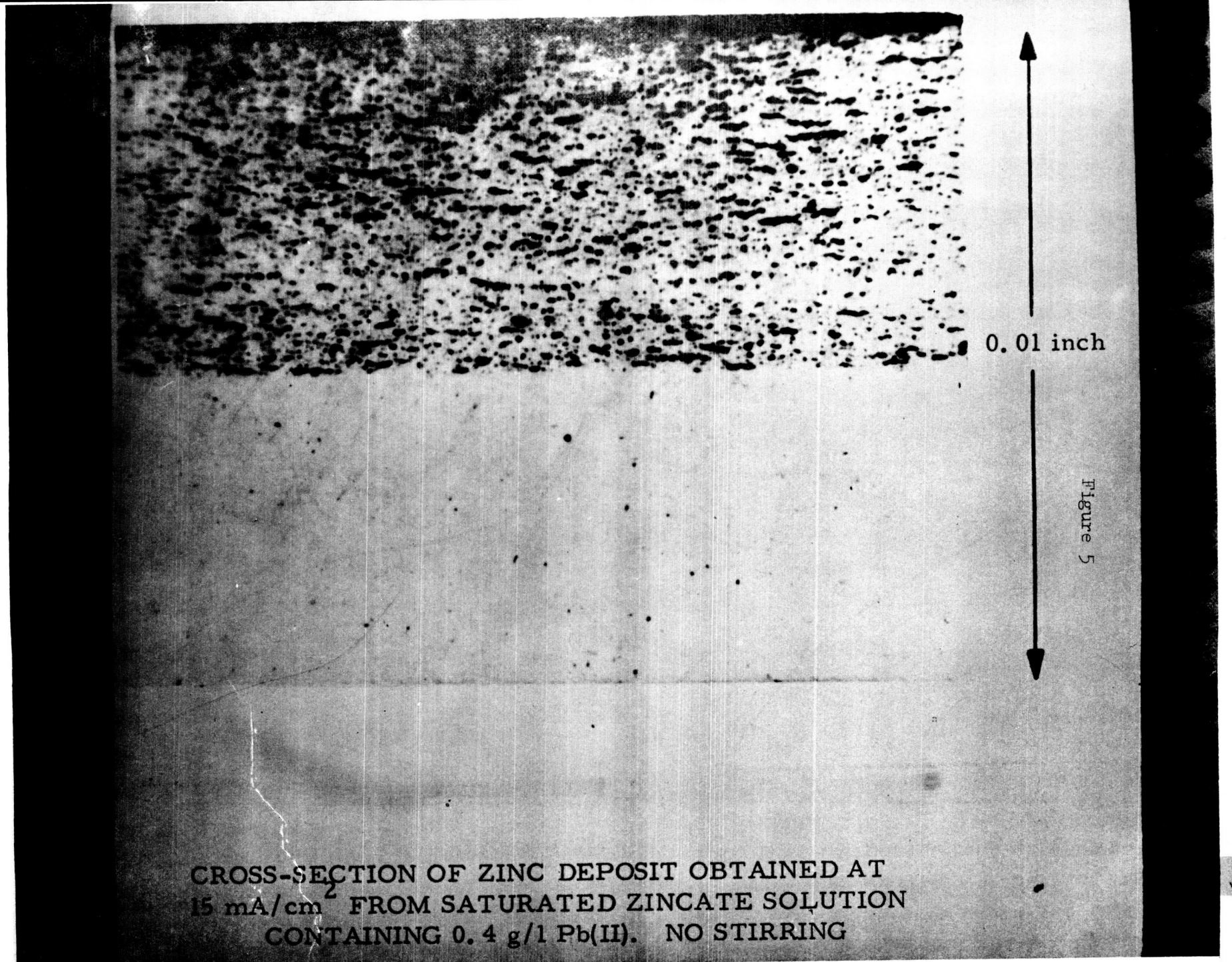


Figure 5

CROSS-SECTION OF ZINC DEPOSIT OBTAINED AT 15 mA/cm^2 FROM SATURATED ZINCATE SOLUTION CONTAINING 0.4 g/l Pb(II). NO STIRRING

These black portions here represent holes. The black at the top disappearing just off the board is the end of the deposit.

I would like to conclude by summarizing a few recommendations as to how the zinc charging process or rather the difficulties in the zinc charging process could be minimized or limited.

Firstly, to minimize any available reservoirs of electrolyte which could provide available zincate, it could be possible, I suppose, to minimize the velocity of silver electrodes while maintaining its good charge/discharge characteristics.

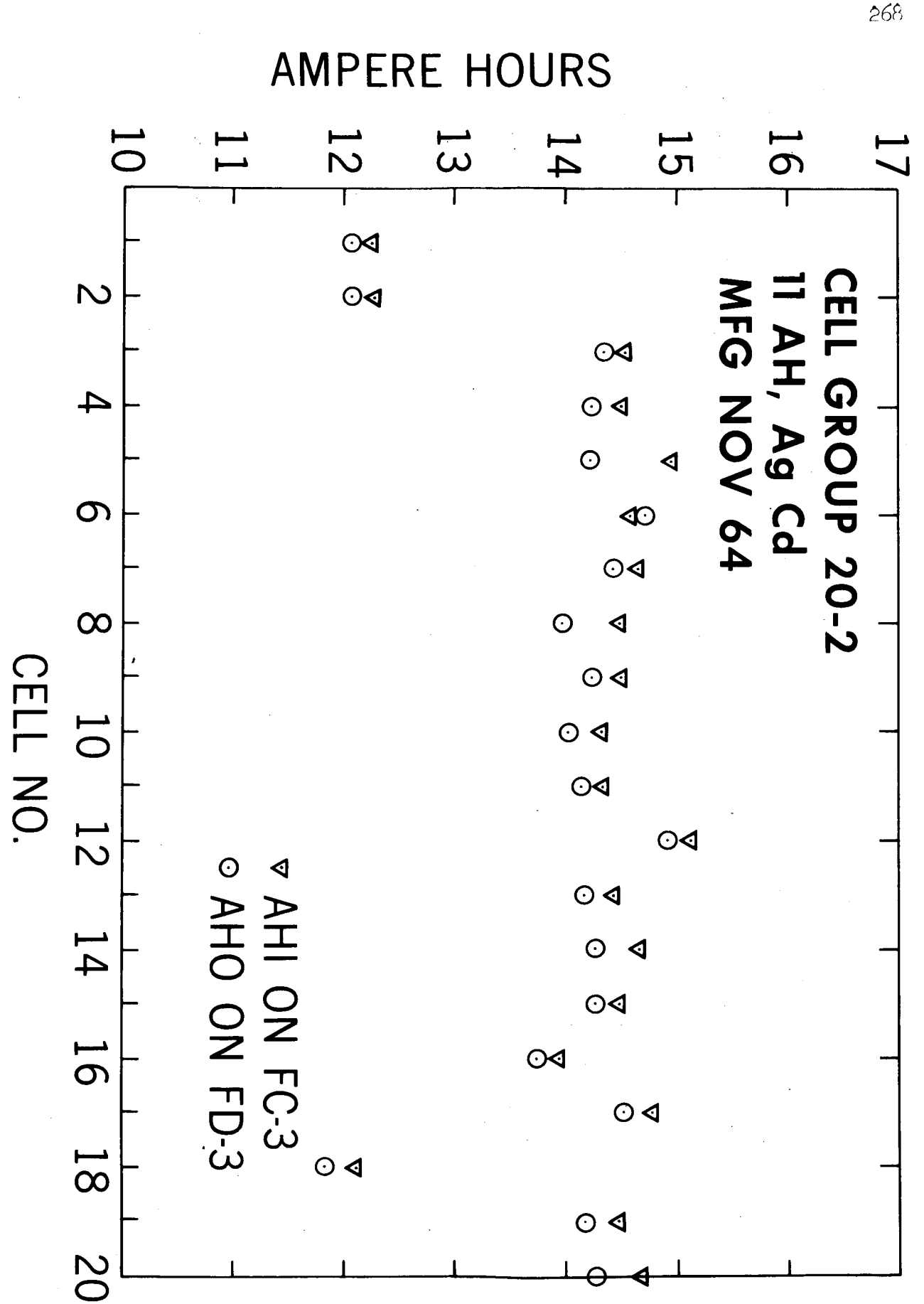
Secondly, to minimize the onset of concentration polarizations by either on/off charging or as restricting the voltage rise.

Thirdly, the possible use of lead.

Thank you.

MR. HENNIGAN: I would like to thank all the speakers this morning for their presentations. I think some of the things which have been pointed out here in component testing, whether it be separators, zinc electrodes and so forth, that it is quite a tedious process. Some of this work takes a year or two to do it, to test our additives, electrodes, different structures and so forth.

This is the type of thing, I think, that is just as


AMPERE HOURS
10
11
12
13
14
15
16
17
CELL GROUP 20-2
11 AH, Ag Cd
MFG NOV 64
2
4
6
8
10
12
14
16
18
20
CELL NO.
AHI ON FC-3
AHO ON FD-3

important, if not more important, than cell testing.

I am sure that many people here have taken apart silver zinc cells after they fail. They are quite confused at the mess you find inside one of these things, and just what went wrong in the cell -- I mean, everything going every which way.

Before I go on here, I would like to show a couple of slides of what we get out of very close controlled Quality Control.

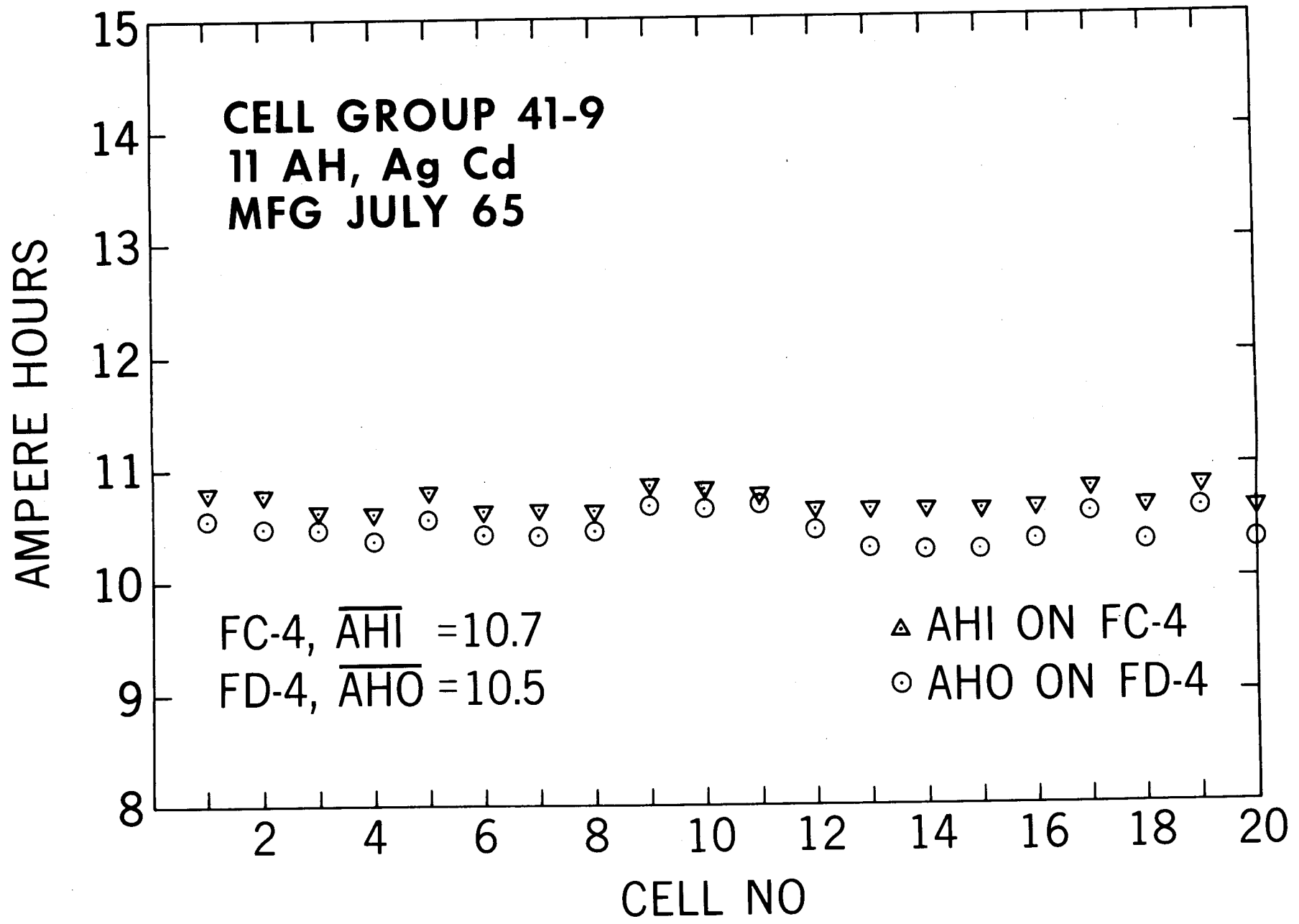
(Slide.)

What we do, we get these cells from the contractor and they are dry. We fill the cells and we form on automatic equipment. We try to eliminate as much as possible personnel. I am quite surprised. We go to the battery company and they are still forming cells and checking these things out with probes and voltmeters. This is all well and good, but you get a lot of personnel areas and I don't think -- it takes a lot of time to form cells when somebody isn't there at the right time.

So this is done on automatic equipment. This is a lot of cells that we got some time ago that we just went out and bought. This is the type of capacity that we got.

By the way, in this formation procedure we are mainly trying to match cells and capacities. This is the type of capacity variation we have got anywhere from the 12 ampere hour range down here, to the 14-1/2 type cells.

Triangles are input on the third formation charge, and the circles are the output on the third formation discharge.


CELL GROUP 41-9
11 AH, Ag Cd
MFG JULY 65
AMPERE HOURS
CELL NO
FC-4, $\overline{AHI}$ =10.7
FD-4, $\overline{AHO}$ =10.5
AHI ON FC-4
AHO ON FD-4
15
14
13
12
11
10
9
8
2
4
6
8
10
12
14
16
18
20

This is one of the better plots we have got. Some of them went up and down, and it looks like buckshot hit the screen. We did make a battery out of these, to try to select out of here, but the battery didn't work and we ruptured the seal after 30 or 40 cycles.

So that after this type of experience, we did go to the Yardney Company and ask them to see what we could do about this. We did go to a procedure of 100 percent inspection, which George Dalin has covered in some detail.

(Slide.)

This next chart shows what we gain from this type of inspection, plus this super-duper formation treatment we give it. You see here the cells are very close together, and the capacity is easy to match, to take 13 cells out of this slot and make a battery. We want 13 out of 20.

We have flown this battery, the 13 cells, and hope it works. But our experience with batteries of this type has been quite rewarding.

One of our biggest gains, I think, is when we take the battery down all the way to .9 of a volt or lower -- and we do this on satellites -- the cells do not imbalance and in fact on these cells here we have taken them down to zero across a resistor without getting a reversal problem. I don't know if we can do this all the time or not. I'm not guaranteeing this, but it has been done.

So these are some of the results we are getting from this very close quality control. But one thing here, we did sacrifice the capacity here. I don't know whether it would fit, these cells up in here. I don't feel that total capacity is that important. Well, we can sacrifice the lower capacity as long as we get a good battery.

That's all for this slide.

Some of the problems, of course, with this QC -- number one, it is very expensive. I think we have planned to have an increase in the price two or three times with this type of QC. It pays off in the end. You just don't lose batteries and whole satellite systems.

The usual problem in the company is a continuous battle between QC and engineering production. We try to QC these things too much and the other two groups are really fighting this type of operation.

The third thing is what you really control in these batteries when you make them. We are controlling many physical parameters and not doing too badly, but what shall we do to control these plates chemically.

I would now like to lay this open for discussion. We have 15 or 20 minutes. Do we have any comments on quality control or component testing?

MR. HARDY (Battelle): This question is directed to

Dr. D'Aftostino.

On your percent Gel formation test, the dissolution implied to me possibly there are areas where there is crosslinking and areas where there is no crosslinking. Is that so, and if so, what effect does that have on the stability of the separator -- In other words, are there points that might be weak?

DR. D'AFTOSTINO: As you know, in a radiation process you have two things taking place. You have both a crosslinking and a degradation of the film taking place simultaneously. So that what one could do in fact with radiation is to get some small fractions inside the membrane material.

At the same time you have a build-up of three-dimensional network. So you do have both of these things taking place simultaneously.

The net effect, the overall effect that one sees is a crosslinking effect, because the ratio of a crosslinking decision is a favorable ratio for crosslinking in polyethylene. When you extract with xylene, you in fact extract out extremely low molecular materials.

DR. FLEISCHER: Would you mind explaining how you use the term "pores"? As I understand it, you start with polyethylene sheets, which is not porous at all. It would be interesting to understand how porous structure develops in this thing as a result of the crosslinking.

DR. D'AFTOSTINO: We are not here really talking of a pore as a hole, as you see in most materials. We don't know too much about this pore structure at all.

I know that if you do take a polyethylene material and graft it, and subject this to -- and try to run a desalinization of water on it, you can in fact stop some of the salt from coming through.

What we are saying here with the crosslinking, is that we are tying the linear chains tighter together so that you can cut down the confusion which we have seen. For instance, if one takes a crystalline polyethylene, diffusion of water vapor to a crystalline polyethylene, it is slower than through an _____polyethylene. The reasoning behind this appears to be the crystal structure is a tighter packing, so that one has a tighter or smaller pore size. One could refer to this.

What we are doing in the crosslinking, we are also inducing into it a tie between the linear polymer and saying that these are, in effect, a smaller pore size.

MR. FLEISCHER: What I don't understand about this is how does it become iron-permeable, which is what you are seeking. Actually, it is the iron-permeable capacity that you are trying to increase, in going from polyethylene to a crosslinked membrane.

DR. D'AFTOSTINO: It is true that we want to increase the iron permeability, but we don't want diffusion of silver

through it.

So what we are saying, in effect, is we could go through it in a tighter network and selectively prevent the diffusion of one material that is closer to another.

MR. HARDY (Battelle): I think Dr. Fleischer is overlooking the fact that you grafted iron exchange material on to the membrane.

DR. D'AFTOSTINO: Let me point that out. After we crosslinked the material, the material was then grafted so that we have acrylic acid or metacrylic acid grafted on to the crosslinked material. It is a volume-type graft.

DR. FLEISCHER: I am going to continue to be stupid. As I gather the picture, you are only talking about cross-linking on the surface that has the change sticking out.

What I am interested in is how do you get all this crosslinking all the way through the film which is, we will say --

DR. D'AFTOSTINO: It is about 1 mil thick.

DR. FLEISCHER: One mil. So that would be 20,000 strands?

DR. D'AFTOSTINO: Using gamma radiation, you have no problem at all for penetration into the film. You, in effect, form a crosslinked size throughout the total film, not only on the surface.

If one were talking of something like UV, where you can't get much lower surface, this is a different story. But

with beta or gamma radiation, you can permeate up to 200 mils in polyethylene, depending upon the radiation you are using. You are doing, in effect, a crosslinking throughout.

As a matter of fact, your grafting is also a volume-type grafting. In this sense it is a misnomer, that we are not only grafting the surface but we are grafting throughout the whole film.

DR. DALIN: On the materials we have seen, the bulk of the graft seems to be on the surface.

I would like to raise the question as to how an acrylic acid residue, or the molecule, gets inside the film, unless the hole bored by the gamma particle going through is large enough for the acrylic acid to pass into it.

DR. D'AFTOSTINO: There are no holes bored by the gamma, per se. What you have is something like this taking place. This can be seen, by the way, in numerous books on radiation grafting -- one by Charlesbe and another one by Shapiro.

If you have a polyethylene film (drawing on board), and you have gamma radiations, and you initiate sites on the surface, once the sites are initiated and you start grafting to the surface, what happens now is that the membranes have solubility deeper into the film to the grafting solution. You get diffusion into the film and grafting proceeds in depth throughout the film.

You can also show this by taking the grafted film and impregnating it with dyes and slicing the film and looking through the thickness area of the film. You see that the dye penetration is throughout the whole film, not only in the surface.

This is not only done on 1 mil film, but it can be done on materials up to 40 or 50 mils. So it is, in effect, this volume graft. There is no question about it.

MR. SHAFFER (AMF): I have a question about slicing the films.

When you slice the film and dye it, is the grafting or the dyeing effect uniform as you go through the film? Is it pretty uniform through it?

DR. D'AFTOSTINO: If one takes the proper precautions to remove all homo-polymer from the film, and one slices the film, you do get a uniform graft throughout the films. This can be shown by going through very thick materials to where you don't have to worry about small surface effects of contamination. In effect, you can show that the grafting throughout the film is in fact homogenous.

MR. SHAFFER: I am amazed to hear this because when polyethylene film is made, the surface is inherently different from the interior on account of the process that is used.

DR. D'AFTOSTINO: In the exclusion of polyethylene film, they do use slip agents on the surface of the film. When we specify a film for our process, we get material which has

no slip agents and which has no additives in the film material itself.

MR. SHAFFER: Is the polyethylene film -- okay, leave out the slip agents. But is the polyethylene film uniform? We have looked at polyethylene films, electron micrographs, before doing anything to them. I mean, as received, unpack it, slice it, and look. The surface is different and I never thought it was entirely due to slip agents, chilling, or some other process. In other words, there is a difference in structure, not just chemical composition.

DR. D'AFTOSTINO: This I can't -- In fact, this may be true, that the surface may be different because of the exclusion process, and also because during the exclusion process there are other polyethylenes which may be slightly different.

This is on the takeup wheels, when you are making the polyethylene film, and this thing is, in effect, stretched in one direction as opposed to two directions. You can get a biaxially-oriented material which is stretched in both directions. So that you, in effect, have no difference in stresses on the film

MR. SHAIR (Gulton Industries): We have seen a lot of the films that you have produced primarily for use in the silver-cadmium and silver-zinc type cells.

I have two questions: Precisely what do you propose

that your separator material does in a silver-type cell; what is the mechanism whereby it does it?

DR. D'AFTOSTINO: Both questions I can only answer "I don't know." All I know is that it just works to an extent now, and I think it can be improved on by certain procedures which I have given in the talk. I don't know exactly what it is doing here. If you are asking for mechanisms, I don't know what it is.

I would appreciate it if anybody could tell me what the mechanism is.

MR. SHAIR: Going back to the question before the mechanism, what is it contributing to the silver cells that is making them better cells?

DR. D'AFTOSTINO: One, the polyethylene, per se, the _____material, is much more resistant to oxidation than any material used, particularly cellulosics.

You see what we can do in the grafting process is to tailor-make or control the amount of graft that we put on to the film; we can control the density of the film to start with; we can control the crosslinking through which we initially set the film. Once we find out what the effect of all these parameters are on improving the properties of the membrane, per se, we can then go ahead and make a membrane material which has in effect the exact parameters that we want.

DR. STRIER (Douglas): Would you say that the effect of crosslinking is to cut down the conductivity, whereas the effect of grafting the acrylic is to improve the conductivity? So that you have in a sense two opposing effects in which you are able to achieve a better control that you were seeking eventually?

DR. D'AFTOSTINO: I think basically this is true. What we are doing, we are grafting -- as we increase the graft we can lower the resistance of the film. If you increase the crosslinking, you also find you have another effect which makes the grafting operation more difficult. Once you come up to a comparable graft level, the conductivity seems to be about the same.

This may be a leveling effect here. You may get up to a certain graft level and achieve a certain conductivity, no matter how much higher you go. We see no increase in conductivity, so it could be a leveling effect at this point.

DR. LANDER (Delco Remy): I have a comment here that crosses both Dr. Oxley's paper and Mr. D'Aftostino's.

We could add a fourth thing to that list of things that Dr. Oxley mentioned as a means for discouraging the growth of zinc to separator materials. If we could achieve a pore size small enough, then we could discourage the growth of dendrites to the pores simply because of the fact that _____ dendrites probably have to have a critical dimension large enough

in order to be able to perpetuate itself. This is somewhat due to the fact that if you get a crystal_____and it is too small, it is going to dissolve rather than continue to grow.

Then in terms of the separator materials that we have tested, namely 2-2-XH, which was prepared for us by RAI under an Air Force contract, I think there is resolved in our reports that these cells receive something like 24 to 3400 cycles at .5 percent_____dendrites, where we could match any zinc beyond the first layer.

This, I think, is suggestive of -- In spite of the fact we did get a diffusion of zinc due to this zinc 8 iron, it suggests to me that the pore size of this material is small enough so that the dendrite flows through.

Now, while I am still on the floor, I would like to comment further on Dr. Oxley's effects of lead on the pipe.(?) If you elect to appoint zinc out of a bath containing lead irons on to the -- what do you call the solvent that has _____cell? Also, you will see that there is a wide range of current density over which you get a nice, shiny and smooth zinc plate. This is not necessarily the kind of zinc deposit that we want to regrow in the negative zinc battery, because my feeling is that it_____ earlier as a result of this decreasing surface area.

The other item was that we have tried lead and tin

and a couple of other metals as a good material. The worst material we have ever seen for this was lead. This was our private source. What happened was that the lead very shortly appeared up in the separator in large quantities and short circuits appeared in maybe 30 or 40 cycles.

That's all.

MR. HENNIGAN: Thank you.

Dr. Oxley?

DR. OXLEY: If you have got too much lead there, then you have got the lead dendrites, of course. We did observe that in our concentration. The lead particles come from the substrate and they are not in contact with any other particle lead surface.

In answer to the remark concerning the small pore size of the dendrite, I am very interested in this in this particle, because anything deposited to the present would be so _____ of opinion, that the resistance of it would be very high. It would discourage further _____.

MR. HENNIGAN: Dr. Dalin?

DR. DALIN: On this question of pore size and the critical size of the zinc dendrite -- rather the critical radius of the zinc dendrite tip for continuous growth -- I would certainly agree with Sam, that this would appear to be valid in solution. But I raise the question as to whether this would pertain to the separator itself.

Now Bakerus (?) has compared the growth of the dendrite to the situation in the growth of crystals, where the critical size is related to the vapor pressure. As the size of the dendrite -- as you select a smaller and smaller dendrite for examination, the vapor pressure of the tip goes up to the point where the rate in which you lose metal from the tip is comparable to the rate at which you are depositing it. Of course, the dendrite then stops growing. But I do raise the question as to whether this would prevail in the separator itself.

In the paper which Chapman gave to me in Brighton -- I don't know how many of you were present -- we pointed out there were some peculiar things going on, particularly in the cellulose membrane, which was studied in much more detail.

(Drawing on blackboard.)

This represents the percent on a concentration of zincate in the external solution. This same thing in the internal solution with the membrane.

Now, if this were the same in both -- rather if the endurance coefficient were 1 -- and the scales are different here, then this line should be something like this (indicating).

Instead you get a big increase. I guess this should go up a little higher like that (drawing). You get a big increase absorbed on the membrane, and we attribute this to absorption over here, and then it levels off. Then as you

continue to increase the external zincate concentration, it rises again up to another plateau. This is saturation within the membrane. Consequently, there are other phenomena going on.

Now, we have found similar curves -- not quite the same but showing this initial absorption in PVA. I think the third material we also ran was an RAI material. So that there are other effects which must be taken into account, rather than the gross penetration in the pores.

MR. HENNIGAN: Ernst Cohn had a question.

MR. COHN (NASA): I would like to ask Dr. Oxley what happened to -- I believe it was the acetate portion of the lead during prolonged cycling. Was it stable, or did it decompose? And if it did decompose, how did it show it?

DR. OXLEY: We only did half a cycle, just charged it up. So the acetate presumably was oxidized and the silver would be oxidized for that purpose. If you used lead, you would form CO_2, probably carbide, perhaps.

MR. COHN: So that, in effect, this was no solution because after one cycle you're short?

DR. OXLEY: You are using iron, presumably, acetate.

MR. HENNIGAN: This problem of uniformity of separators is quite a problem. I wonder if anybody would care to comment on the uniformity of cellophane.

(No response.)

Well, if you don't have any comments in this area --

DR. LANDER (Delco Remy): I would comment in this regard, that fibrous acetate appears to be on the basis of resistance modulus, uniform by ± 5 percent. So we measure a circular area which has a diameter of about 1/4 inch. We make 10, 12 or 20 of these over, maybe 100 feet or so. If you can use this resistance, _____I think you could use that as a criterion. It is uniform within about ± 5 percent.

MR. HENNIGAN: Thank you.

Dr. Fleischer?

DR. FLEISCHER: I just recalled that Dr. Casey, in one of his projects at the Ottawa Defence Research Establishment, examined cellophane with polarized light and he discarded all portions which showed any stress.

As I remember, the cells that he made with the cellophane that he selected out-performed any of those which were just assembled in cellophane that had not been examined.

MR. HENNIGAN: Thank you.

I would like to comment on the same thing. I worked with cellophane with the polarized light. I don't know what the changes mean, but it certainly is not in uniformity. I don't know what percent you could attribute to it.

If we don't have any more questions or further discussion here, let's take a ten or fifteen minute break and come back at about a quarter of.

(A short recess was taken.)

MR. HENNIGAN: We have one more speaker in the area of Standardization, which will be followed by a discussion period. This discussion period can include anything that went on, any topics that went on during the entire meeting.

Our one and only speaker now is Karl Preusse, of Gulton Industries, whose topic is "The Evolution of a Standard Line of Space Cells."

THE EVOLUTION OF A STANDARD LINE OF SPACE CELLS

MR. PREUSSE: Good morning, gentlemen.

I have changed somewhat my topic of discussion. Rather than discussing the evolution of a standard line of space cells, I think the subject of standardization itself could afford some review and some analysis.

I would like to point out, in making some of my basic feelings on standardization, to probably tie it in with the design of a nickel-cadmium cell, and possibly look at the philosophy of standardization. I am just wondering if it is standard practice to have a topic of standardization put last in a program, as it was in the last meeting.

Man-made standardization is not just confined to weights and measures for energy or power or language. It is not also confined to other material commodities or services subject to purchase.

One finds standardization in folklore, mythology,

witchcraft -- as was mentioned yesterday -- social customs, ceremonies, codes, and also practices, procedures, specifications and times.

Standardization is important to life. It is important, for instance, to geography, topography, chemistry and pharmacy, games and sports. It is also important to the eligibility of professions. It is important to ethics and religion. No matter where you look, we find standards are available. There are standards for aircraft and airport construction, bridge construction; there are standards for air conditioning, heating and ventilation, and insulation systems. There are even standards for living and standards for success.

Just look at your morning's activities for this morning. You arose from a bed which has been standardized either as a twin, double, queen or king-size bed. You slip into a pair of shorts which have been standardized by waist size. You put on a shirt which has been standardized by collar size and sleeve length. You brush your teeth with a toothbrush which has probably been standardized or classified as medium, soft or hard. And the toothpaste comes from a tube which is either labeled medium, economy size or large economy size.

Society has set up standards for the individual from the point of prenatal care to the burial rites. So, gentlemen, standardization is here and is something we must live with. In some cases I think it is important that we live with it, and I

think in some cases there may be problems associated with the standardization.

I had considered bringing slides, but they were not of the standard size.

(Laughter.)

When one fabricates or produces a commodity which can be purchased on the market, standardization is an important concept of fabrication technique. Standardization within a particular manufacturer, I think, is more important than -- from my point of view -- than standardization over a gamut of manufacturers. I will point out my reasoning a little later on in this case.

Let's just look at standardization within a particular manufacturer when he designs a particular product. You can have standardization of design; you can have standardization of materials; you can have standardization of fabrication processes.

For instance, when we design the hermetically-sealed nickel-cadmium cell, when we look at these ceramic to metal seals, we look at the material tolerances between the actual terminal posts, ceramic and covering assembly. We try to apply that particular design under those particular tolerances and those particular tolerance relationships -- and not to just ceramic to metal seals, of a particular size cell, let's say a 6 ampere hour size, but try to apply that particular design over the whole range of cells.

Similarly, when we design our electrodes for a particular cell, we try and keep the plate relationships the same from cell to cell.

If we have a certain number of plates in one particular cell, we try and keep that type or amount or quantity of plates the same in the whole series of cells.

When you look at your separator material to design your dimensional tolerances on your separator material, the amount of compression to the separator material within the cell, you try to design that amount of compression the same from cell to cell to cell.

When we design methods of cell closure for a particular cell, the final well, from the cover to the container itself, we try to keep that design standard from one cell to another cell.

We can extend the standardization into the material areas. This morning we had discussions on component testing within a particular cell. For instance, when you test the separator, you test for its dimensional stability, maybe its possible electrolyte retention characteristics, its probable inertness to the electrolyte itself.

Once you actually establish a history of performance on a particular material with respect to the environment in which it is supposed to operate, you try to use that material in the whole range of cells which you are going to be utilizing in the particular product.

Similarly, when you look at it again, the hermetic seal, you have a combination of materials between the terminal, the cover, the ceramic and the braze material. You run component tests to understand the main effects of these individual materials as well as the combination of these materials in different environments which you expect to operate in. You have got a feeling and a handle on this performance, and knowing this thing, you would like to keep that knowledge standard amongst or across the whole spectrum of cells you are fabricating.

Utilizing the same materials and utilizing the same design from cell to cell to cell, offers certainty and offers you a higher reliability and offers you a high quality product. When you go into the actual fabrication of the cell itself, the process control is important and standardization is a necessary criteria.

Again, when you fabricate the ceramic to metal seal, it is important for the operator not to be confused with the different fabrication techniques. They must be trained in the sequence of operations and perform those operations identical from cover to cover, and from cell to cell, immaterial of what size cell is going to be applied.

The formation process of the electrodes for the cells, the formation process is somewhat similar except for rates. The duration of rates, the number of cycles put on, are somewhat the same for cell to cell to cell.

The electrode fabrication techniques are identical. The actual mating of the electrode to the cover assembly, the technique is the same from cell to cell to cell.

The leak detection techniques in the fabrication of the cell are performing the same time, by the same individuals, and in the same fashion, as well as the electrical testing. All this serves to give us a uniformity of the product in this case.

Knowledge of the process becomes specialized along narrower lines. There is a tendancy because of this to constantly improve the product. If the process or steps of fabrication become standardized, it enables one to introduce automatic equipment. This automatic equipment tends to improve the quality. It tends also to give you quicker delivery, lower costs, and again a more reliable item.

There are some problems associated with standardization also. If we look at standardization, let's say, over several manufacturers, one of the problems could be a loss of individuality. Maybe I can give you a little story or occurrence which happened to me in England to, let's say, pinpoint this concept of individuality.

As you know, there is a "Mod" fashion going on in England, and all the boys are letting their hair grow long. The girls are letting their hair be cut short. The boys are wearing gayly colored pants and gayly colored silk shirts,

and the girls are wearing gayly colored pants and gayly colored silk shirts. So as a result, it is really difficult to establish which sex they are.

Well, we were riding on the metro one evening, standing next to an individual, and I nudged him and I said "What is that over there; a boy or girl?" The reply was "That, sir, is my son." I said "I'm sorry. I didn't know you were his mother." The reply was "I am not his mother; I'm his father."

(Laughter.)

You see there is confusion that could become involved.

I think it is difficult to change a product which has been standardized by a particular manufacturer. There are things right now where we can actually change the actual cell and probably improve its capacity for volume relationship. But it can't be done because other things have been designed around that particular cell, where if we would make a change in that cell, these other items would have to be changed. So we are inhibited right now in the sense that we cannot incorporate new technologies in our listed product.

It is difficult to do this within one particular manufacturer. But when you standardize size volume capacity to other manufacturers, I think there may be a problem to change much more. I think there is more inertia in this case. I think it eliminates competition between manufacturers. We may be able to market a particular cell with a certain volume

and a particular capacity that is more competitive than, let's say, another manufacturer.

If you standardize across the manufacturing process, I think it sort of eliminates some sort of competition. Some times standardization offers a dead end to these designs, or stagnation in development. Once a product has been standardized in the industry, people say "Well, that is the ultimate." If standardization can be looked at as a continuing process to establish measurable degrees of uniformity and excellence, this has merit on an industry-wide basis.

As Henry Ford said, "If you think of standardization as the best that you know today, but which is to be improved tomorrow, you get somewhere."

Thank you very much.

MR. HENNIGAN: Dr. McCallum?

DR. MCCALLUM (Battelle): Just a quick question about standardizing. I understand they are more or less standardizing now 6, 12, and 20 ampere hours. I was wondering if there was any reason for this being picked out.

MR. PREUSSE: I think this standardization as to the size of the cell came originally from the requirement, and the cell was designed for that particular requirement.

I think you are speaking of prismatic cells. I think the first cell that was developed essentially was a 6 ampere hour cell which may have been closely related to the

5-1/2 ampere hour spiral cell at that time. So essentially, maybe the first prismatic cell that was looked into was the 6 ampere hour cell.

The next cell which was developed was a 20 ampere hour cell, and that was based on a particular satellite requirement itself. At that time I think that was the only -- let's say the basic need. Well, there are other needs for this particular cell, but the 20 ampere hour cell was developed basically for satellite application.

Another satellite requirement came out thereafter requiring a 12 ampere hour cell. From that point the 12 ampere hour cell was developed. So it is not that these things were arbitrarily set up originally. The requirements were there, and the cells were designed for these particular requirements.

Right now at this point the sizes have been somewhat standardized. And so, when a particular manufacturer of the satellite requires a cell of some kind, these particular cells have a vast background of reliability data now -- both in vibration, thermo-vacuum and life cycling data, and as a result not to re-evaluate and go through another qualification for a cell which may have an 11 hour ampere hour capacity and 13 ampere hour capacity.

There is a trade-off here. Let's say they would select a 12 ampere hour cell which is available. I think these sizes were developed based on requirements, rather than

setting up prior to the requirements.

MR. HENNIGAN: It seems like most of the satellites flown today are using these size cells. They seem to be satisfied with them.

Occasionally you find -- I did see one spec one time for a 7-1/2 ampere hour cell. But you just can't build ampere hours by units of one all the way up.

MR. COHN (NASA): Let me get back to the original purpose for putting this topic on the program today.

In the two meetings we have had previously, people have asked whether we would do something about standardizing batteries and/or associated equipment. I don't remember exactly how this thing was phrased.

We decided that since it came up twice in succession at NASA meetings, we would devote some time and thought to this. I have collected a number of standards of batteries, including lead acid batteries, SLI, and other kinds of commercial batteries as well as whatever may be available in the way of alkaline batteries.

The more I look at these things and the more I have thought about these things, the more I come to the conclusion that the Office of Advanced Research and Technology at NASA has no place in the standardization program. This is what Waite pointed out, too. It is not up to us to standardize anything.

We may do something about trying to raise performance.

If you want to set up standards in terms of performance criteria rather than in terms of materials, physical dimensions and things like that, then indirectly we are involved in standardization -- but only indirectly.

I am pretty sure, unless somebody comes up with a very good argument that I am not aware of, that we will not engage in any activities of standardization through OART.

MR. HENNIGAN: Well, that finishes that.

(Laughter.)

What else would you like to talk about?

MR. COHN: Let me talk about something else.

There was another point that I wanted to talk about before the intermission but didn't get a chance to do so, and that had to do with quality control and selection of materials.

I have had at least two instances where people have chosen materials or have proposed to choose materials that were somewhat cheaper than other materials that could be used and that were being used which were considerably better.

One case would be a matter of using a bakelite case for a battery instead of, for example, a polystyrene case. The second example was a proposal to run some experiments on using copper grids and comparing them with silver grids in batteries. In both cases this is a very laudable attempt, for commercial reasons, to come up with a commercially-competitive product. This has absolutely no place in the space

program, and I wish that the people who have something to do with picking materials for space would please realize that we are paying between $3,000 and $5,000 a pound for getting a pound of material into orbit or on the way in manned missions.

If you add to that the question of reliability -- and as somebody pointed out yesterday, of having a live TV performance that millions of people all over the world are looking at -- then please don't come to us with bakelite cases and copper grids for batteries that may just make -- in one case a $60 mission -- go to pot. We can't afford it.

MR. WAITE: Although Mr. Cohn has sort of closed the door on standardization, he left it open a little bit by saying -- unless someone could think of something else. I was very surprised not to hear something on standardization. On the design and review staff of RCA for space satellites, one of the things that worried me the very most was the cost of reliability, and this I believe is on the first -- as far as the list of NASA criteria is concerned -- and this cost really was reflected in some instances by all the different ways of doing the worst casing.

I must have looked at thousands of worst casings analyses on all levels of small circuits, of sub-components, and they are all done differently.

I think it would be much easier and much cheaper if someone would standardize something like that, by how you do

your worst case calculations.

There are a lot of things, especially in space, where reliability costs tremendous moneys, where standardization of procedures might really pay off. And so I would like to inject this in that door before it gets closed.

Thank you.

MR. HENNIGAN: One thing I would like to bring up here is on these formation types of work that we do, that Gulton does.

I would like to ask the Gulton people: You say it is automatic. What do you mean by this?

MR. PREUSSE: I didn't say it was automatic. It was standardized. It is semi-automatic.

MR. HENNIGAN: I think this is one place -- I don't think we need a computer here. We simply need some good data acquisition equipment that is automatic and that can read out these parameters that we want to read out. I think that is one of the big troubles we are having, a lot of this is taken manually, and we can't correlate this. These records are piles of papers and it is very difficult to correlate this information with cell testing.

MR. COHN: Just because Tom mentioned the computer, I thought I would give you an example of where a computer was used for precisely this purpose.

It happened to be in fuel cells instead of batteries.

This concerned the Allis-Chalmers program, where we are getting stacks made for testing to see what the reliability and what the probabilities are. These are stacks of 33 cell pairs in series.

What they have done is to set up a computer program where they measure and weigh -- that is, measure the dimensions and weigh the anodes, the cathodes, and the asbestos separators. They have a computer program by which they calculate exactly the amount of electrolyte that has to be put in each cell.

The cells are matched with each other. Remember now, these are a series of construction. They are matched with each other. The anodes are hand picked; the cathodes are hand picked; the asbestos is hand picked. And from the computer program they get within a fraction of a cc the amount of KOH that they are going to put into each cell. We hope that by using this computer program we will get very uniform stacks. So there is an application of computers even in making cells for batteries.

MR. HENNIGAN: We have a question here.

MR. MAGISTRO (Picatinny Arsenal): One of the things that has been brought out here is that you people have the same problem that the Army has when it develops a new system or new weapon. We have a small lot, and you have a very limited history of materials. If you change design in dealing with small lot statistics, you don't have infinite populations to

gather information from. It would seem, if we worked in this area, and devised techniques that would be applicable to small lots, we would get a tremendous improvement.

I wonder if anyone in the audience -- I think this is an area where standardization would be fruitful -- has worked with intermittent lots. I am sure you all have. Each program comes along and you make a lot. A program dies and you get a new program. It has a different design and you start all over again. So by the time you have made your last lot, you finally have enough history to say what you should have done when you did your first lot.

We have an Army Research Office inquiry, and they are looking into this problem on a limited nature for one-shot devices for us.

I wonder if anybody would be interested in expanding this area of activities?

MR. HENNIGAN: I understand the lead acid business, on large samples, large lots, their capacity control is quite good. I suppose they do sample testing. But I understand -- maybe Dr. Fleischer could put me down in this line -- but it is about a ± 3 percent capacity to get a lead acid battery run. I don't know if that is reasonable or not.

The data I showed before on a small lot, we had a spread of 3 and about 12 -- 3 ampere hours and 12 ampere hours.

DR. FLEISCHER: I can't answer your question about

what they get in manufacturing lead acid batteries.

Is John Lander still here? John Lander may be able to answer that question. But one of the things I have been thinking about while sitting here, what Karl talked about, he implied that in standardization he was including what we really need as a science, and that is battery engineering. This is one of the things that concerns me a good deal, because I want to start things off in a laboratory and do it on a scale which is reasonable from the standpoint of cost. Then I want to extrapolate my laboratory results and say "how do I design the battery."

The first thing that you run into -- and this has been my experience in the battery industry -- you start with an electrode. You might take one square inch; you might take five square inches; put it into a cell with maybe 3 electrodes, 2 counter-electrodes or whatever design you want. You get results, you find out what the voltage current density curves are, and now you want to say "I want to build a 5 ampere hour cell," or you want to build a 10 or a 100.

Now, when you start to extrapolate, all practical battery men will tell you "Oh, you can't go from one plate to 17 plates. You can't go -- the minimum you start with is 6 or 7." Well, what about the size? Does it make a difference whether they are one inch tall or ten inches tall? Well, we know this makes a big difference.

In fact, one of the early surprises I got was to turn the cell upside down and open the can -- and it happened to be a pocket-type battery -- and I discharged the battery at 1,000 amps and measured the voltage of the plates at the bottom, and it was the open circuit potential. This convinced me that you just can't design this way.

I am bringing out that we do need to program, or we need a lot of programs to develop what I call the science of battery engineering, so that the laboratory man can do his work and with some degree of confidence go up to a large scale or to these various sizes of batteries that are need.

In Karl's work he talked about very carefully adjusting plate sizes -- I think he meant this -- in going from small cells of 6 ampere hours, 12 ampere hours, to 20.

The first thing that happens is that the area that you have of your cans, in relation to the capacity, goes down. So now all your heat transfer problems become different. But if you are going to test different things -- if you say you have standardized and you have made this line of cells so that they are equivalent, then this comes to a matter of incongruity in our scaling up. I think the first time I ran into this was on the design of an autoclave which had operated at 200° Centigrade, and I wanted to know what the reaction mechanism was. This was a long time ago.

I had a small, continuously operating autoclave at 200° C., where I was using steam as my heating medium. Well, the results that I got in that were completely different in the 4-inch autoclave than they were in the 12. It took me a long time to discover that although I had gone to the trouble of adjusting all my flows, that I forgot that the heat transfer was completely different. So that my design was completely off and the results I got were completely different.

So my point here is that we do need -- and when I say we need a science of battery engineering, we need it in the form so that the men who come along after us will find the place where they can read it and learn it, besides having them stuck away in files which are reduced to empirical rules.

MR. PREUSSE: I may have forgotten to mention this, but there has been some work performed at the Gulton laboratories which takes the thermal considerations of the battery into account. We have tried to characterize the _____tropic characteristic of thermal conductivity of the cell, and based on this, we have tried to say that minimizing the heat transfer resistance in the three dimensions and establish cell geometry based on this. What we have found, for instance, would be that we take the cell as a source, a heat-generation source, and then dissipate its energy, let's say, in the Z direction -- (drawing) let's say in the X direction and in the Y direction. Of course, there is equal resistance in the other three planes.

We found that there is a thermal conductivity which is different in each one of these directions.

Now heat transfer is a function of the area, the temperature differential, as well as the length of the path in which this heat is going to be transferred through.

So, based on this resistance parameter, we set up an equation where we actually predict the heat transfer phenomena and actually maximize or minimize that equation and found an adverse set of cell dimensions which will give you, let's say, the maximum temperature grading from the skin to the center of the cell.

I find in the worst case dimensions that you could design away from these dimensions. We were hoping to find the optimum set of cell dimensions which would have been modular heat transfer. But the function is one which just increases -- And intuitively, if you look at this thing, the optimum set of heat transfer dimensions would be one rather infinitesimally thin and, of course, large, wide flat plate. So thermal considerations are also included in cell design, rather than just basic electrodes relationships also.

This is how our 100 ampere hour cells are designed, by the way. We designed this to minimize heat transfer with temperature gradients throughout the solar cells.

MR. HENNIGAN: Thank you, Karl.

We have another question.

MR. JOHNS (Atlantic Research): This is completely an irrelevant question, but maybe somebody can answer it and save NASA some money.

I have a project with NASA/Ames which deals with building a piece of equipment which will be tested at Zero-G. Does anyone know what power is available on these fighter planes that make this test, how well regulated it is?

MR. HENNIGAN: Power on the fighter planes?

MR. JOHNS: You know, when you test equipment at Zero-G, you do it in a big parabola with the fighter. Now NASA/AMes doesn't know. I wonder if anyone here knows what power is available on such a plane and how well regulated is it.

MR. HENNIGAN: Some of the fuel cell people have tested this. Marty, do you have that number?

MR. SULKES (USA Electronic Command): Having some experience in working with batteries which would supply power to these planes, it has been determined that the generators on the planes usually run from 24 to about 32 volts, depending on the type of plane you use. It can be anywhere from 300 amps to several thousand.

MR. JOHNS: There is no current drain to speak of, but I am wondering about voltage and regulation.

MR. SULKES: It is not too good. Your figure is about 24 to 32 volts.

MR. JOHNS: Are the planes used in the Zero G test

equipped with any other power that you know of?

MR. SULKES: Your best place to find it would be at Wright-Patterson Air Force Base.

MR. JOHNS: Do you know anyone there who I could ask?

MR. SULKES: Jim Cooper.

MR. JOHNS: Jim Cooper at Wright-Pat. Thank you very much.

MR. BRODD (Union Carbide): I hate to let you off so easy, by saying that standardization is not a good thing to have in this particular administration of space. Perhaps in the near future it is very expedient to say, because each battery and each mission has a particular size available for power requirements, that you are fairly justified in saying that today, for the next two or three or four years you will probably not need to have a standardized type of battery.

However, in the future -- I am sure that if you work in space you tend to think mostly of the future and the wide horizon -- then I think you must also be prepared to have a line which is standardized in character as much as the other batteries are standardized. It is only then that I think we can get to the more significant problems which Dr. Fleischer mentioned of proper battery design, the problem of existing boundary plates. These are problems which come by which standardization will also help to focus attention on these problems.

MR. COHN: Please let me make clear that what I was talking about was not NASA's decision but the OART decision. NASA has four offices, three of which I think should be -- whether they are or not I don't know -- very much interested in standardizing.

The Office of Advanced Research and Technology should be doing something to upset these standards all the time, and we should have minimum standards of performance that we try to improve.

I fully recognize there are great advantages to standardization in hardware programs. We do not have any hardware programs.

MR. HENNIGAN: We have a question from Jim Oxley.

DR. OXLEY: I would like to go to the blackboard.

I would like to make a few remarks as an extension of what Dr. Lander mentioned, with regard to the porosity of the separator materials.

This is in regard to the current distribution in the zinc electrode. Such problems have been treated recently by Ralph Brown of Pratt & Whitney, and the General Electric Chemical Society has also treated it in a fairly detailed manner in a report from the Lessona Moos Laboratories to the Air Force a few months ago.

One imagines the foreign situation of a very thin wire enlisted to electrolyte, the wire having a fairly

large resistance, and carrying out a process of this type with a reduction of the cadmium metal (drawing on board). When one calculates the current distribution along the wire, one finds that the highest current densities are obtained here. If the wire is sufficiently long and of sufficiently high resistance, the current at the bottom here is almost negligible. Exactly the same situation exists in the silver zinc electrode.

Now, we consider the zinc electrode being as follows; with current collection, of course, up here, separating the two going down here (indicating).

One now imagines the growth of dendrites through these very small pores of the membrane. This is the same situation as previously; it is operative.

When this little dendrite which has wound its way through the membrane is of sufficient length and sufficient high resistance, the growth will inevitably stop because of the current distribution.

Since the current density at the end is almost vanishingly small, and if the pore size as Dr. Lander pointed out is small enough, then the distance of the zinc fiber which is going through is large enough. So it is obviously a very good thing to separate the materials of minimum porosity.

MR. HENNIGAN: We had a question right here.

MR. THEIRFELDER (RCA): Referring back to the slides that Mr. Hennigan showed on the silver-cadmium capacity of

the different cells, and how the capacity was improved from a scatter to an 11-ampere hour cell, I was wondering how much of that improvement was due to the election process and how much was actually due to an improvement on the processes in making these cells.

MR. HENNIGAN: You mean in the formation and purchase--

MR. THIERFELDER: Yes. In other words, we could select out a group of 11-amp hour cells without changing the fundamental processing. That would also bring the price up, as you indicated.

MR. HENNIGAN: I really couldn't tell you. I mean this is a complete program that we run through. It works.

MR. THIERFELDER: Do they actually have the same recovery from the 100 cell starter? Do they recover the same number of cells, or do they reject larger numbers of cells to give you this improvement?

MR. HENNIGAN: They reject about 50 percent of the negatives. The electrodes -- they may have to make twice as many negatives.

MR. THIERFELDER: So it was a prior election process, actually, that they could make better negatives but they rejected more negatives?

MR. HENNIGAN: Right. The silver isn't too bad; I guess a 5 or 10 percent rejection.

I would just like to bring up some -- Go ahead.

DR. FLEISCHER: In that test, did you have two lots of 20 cells, one which you received originally? You tested the whole 20 cells, the whole lot?

MR. HENNIGAN: These were two lots, 20 each.

DR. FLEISCHER: The first lot of 20 was what the battery manufacturers delivered to you for performing?

MR. HENNIGAN: Right.

DR. FLEISCHER: Then when you insisted the quality control be placed in these components, then the second point is that all the cells were satisfactory; is that the point?

MR. HENNIGAN: Right -- well, the point that I don't know, it wouldn't drop either technique. On the 100 percent quality control or information, I don't know which is distributed the most. Was that your question?

MR. THIERFELDER: I wondered what the improvement was due to.

MR. HENNIGAN: I can't tell you. I wouldn't dare do it any other way.

MR. THIERFELDER: By the selection process we could always get them all the same. Just throw them all away and keep the one percent.

DR. FLEISCHER: You had a reject in the first one out of a lot of 20. You had to reject in order to get an 11-cell battery?

MR. HENNIGAN: Right. A 13-cell battery -- it is

harder to get a 13-cell battery out of 20, 13 out of 20. The second time it didn't make any difference as to which cells you picked.

MR. THIERFELDER: Would your supplier select out better the second time than the first time?

MR. HENNIGAN: Oh, sure.

DR. DALIN: But the cells were on the basis of the components. You asked whether the components were actually better, and the answer was Yes.

For instance, we get into the actual way in which we were molding all those cadmium oxide plates, and we found by our standard techniques of molding we were getting a slight variation in thickness from one end of the plate to the other, slight variations in density.

We actually made a study of how we were distributing the cadmium-oxide powder in the mold, and how to hold the plates parallel to each other. So we wound up with a much more uniform product in the manufacturing process, let alone by selection. Then on top of that we went into selection to pick out the most uniform plates.

MR. HENNIGAN: Do we have any more questions?

MR. CLARK (LTV Aerospace): I have a question again about this standardization, the thing we have been discussing this morning.

The thing that keeps bugging me in design, that which

I am interested in, is the fact that when we are working on a design our process is to -- from the program that we are involved in -- we ascertain first what the power requirement is for that mission. Having established this power requirement, we then essentially go to the literature searching for a battery that will fulfill our requirements.

This usually results in establishing a requirement for a battery that -- for instance, if you need one with safety factors thrown in, say of a 2-ampere hour capacity, then we are forced to go to a 3-ampere hour capacity which almost invariably results in over-design in the battery weight in space.

A little further examination with the manufacturer will show you that, in fact, a one ampere hour cell is not a one ampere hour cell, but it may be a 1.8 ampere hour cell. I think to a large degree that this is for testing into an over-design situation.

Therefore, my comment is this: I am not so sure that standardization is not something that should not be looked into.

Furthermore, you mentioned this business of matching secondary cells if we are getting optimum cycling performance in space satellites. Many programs do not have the requirement for thousands of cycles. They have a requirement for one cycle.

In our own case, of which we are associated, we have this SCOUT vehicle in which we have an approximate capacity or need for less than a half-hour. So we would like to size our batteries for optimum performance. The result is we are designing essentially as well as possible to standard cells as produced by the manufacturer, whereby you are going to the select process.

It would seem to me that if we had a standard cell of which all the characteristics and dimensions were known, that the whole industry would be more able to design for these standards.

Another subject which I would like to bring up at this time -- it is just a pointed remark regarding the qualification cells. At this point I would like to throw out a bouquet to the manufacturers.

On the SCOUT vehicle we have processed into batteries over 40 flights some 8,000 cells. These cells were bought to the manufacturer's specifications. Obviously, I dare say we have had less than half of one percent of any type of trouble -- and all this trouble was on the ground. Most of the troubles, I might add, were those things which we, as a user, are responsible for.

This remark that Mr. Fowler made yesterday regarding broken grids or broken wire in testing, in our experience we have found most of our testing has been due to over-testing.

We had one case where the battery which we were using, we packaged the cells into a battery and we found in actual vibration we were putting an application factor of something like 8, which we really didn't realize until we got to looking at the situation.

Therefore, I would caution that in qual testing articles it would be beneficial to find out just exactly what is being put into these tests.

MR. HENNIGAN: These flights you are talking about, this is primary batteries?

MR. CLARK (LTV Aerospace): Yes.

MR. HENNIGAN: Of course, we fly quite a few primaries -- rockets, balloons, odds and ends. We really don't do much testing of these batteries. We take a couple and discharge them at the rate a fellow wants to use that, and tell him this is how many ampere hours he has got.

This primary business is not too tough, although I have seen some.

(Laughter.)

Now, who wants to comment on that?

MR. MCCALLUM (Battelle): I wanted to ask Dr. Oxley something. I have three or four points of clarity, three or four kinds of questions.

I am not sure I understood some of the interesting things you were talking about. You ended up with a recommend-

ation of minimizing available electrolyte, and you were talking about diffusion and the minimum of electrolyte. I couldn't quite follow you there.

DR. OXLEY: Can I answer these questions one by one?

MR. MCCALLUM: Certainly.

DR. OXLEY: When I say minimizing electrolyte, I mean minimizing the electrolyte which is external to the zinc electrode. I recognize you have got to have electrolytes throughout the separator and the silver electrode down to these electrodes.

Of course, zincate, which is formed within the surfaces of the zinc electrode structure, can do no damage whatsoever when one is talking in terms of dendrite formation. So I think one wants to minimize any reservoirs at the bottom of the cell, for example.

I did mention perhaps the possibility of limiting the porosity of the silver electrode while hoping to retain the current voltage charge and discharge characteristics.

MR. MCCALLUM: You brought up these two factors about dendrites and non-adherence. I wondered if there was any connection. That is, you don't get dendrites everywhere. You get different numbers and different sizes.

Is there any relationship here between the adherence problem or the dendrite problem, or your tree problem?

DR. OXLEY: I should point out the method of

determining the adherency was primitive to say the least. We just wiped off the surface with a tissue.

Now the most non-adherent type of deposit is the mossy type of growth formed in the activation control region; i.e., low current density. But also the actual dendrites are non-adherent, depending upon their thickness, which does depend on the current density of this _____polarization. But all of this does refer to the whole shooting match.

Now, using lead in the solution, we found that the deposits were nearly 100 percent adherent in both the activation and diffusion control regions.

MR. MCCALLUM: But when you add more adherence you have less trees? There was no relationship between trees and adherence?

DR. OXLEY: To an extent there was, at least in the presence of lead. As you saw on the photograph, the top section was a deposit of lead. The surface at the top was quite smooth, although retaining I would hope an acceptable reference factor from the point of view of getting a good discharge rate.

MR. MCCALLUM: With your lead addition, you qualified that. It seems like you gave it to us and then took it back. I wondered what you mean by possible.

DR. OXLEY: We were interested in half a cycle for those initial measurements. And we threw in lead acetate

because we knew we would get lead irons.

As Mr. McCallum pointed out, of course, the acetate will be oxidized with the other electrodes.

MR. MCCALLUM: The lead oxide is fairly soluble and caustic?

DR. OXLEY: Yes. The dendrites -- the lead would then presume to have some _____iron, which will operate in the same way, from the point of view of reduction in the zincate iron.

MR. MCCALLUM: Do you have data on that?

DR. OXLEY: The data I would like to mention -- which I didn't mention before -- was that we were able to show the lead did deposit to a certain extent with the zinc. But during the subsequent discharge of lead during oxidation of the zinc, it becomes attached in the form of small particles on the electrodes. Since there is oxygen present to a finite extent within the electrolyte, the corrosion process would take place after each little lead particle, and it will wind up back at_____iron ready for the recharge process. So presumably you can go into successive cycles, retaining the same effect of lead concentration in the electrolyte.

MR. MCCALLUM: Which brings up the last point.

I didn't understand from your talk about the effects of cycling. It is my understanding that we are talking about the trees growing at the outside that keep getting longer, but

when you oxidize them they don't necessarily oxidize back like they build up.

As a consequence, you might have a nice plate on one cycle. So you have gotten rid of your trees but by two or three or eight cycles -- there they are.

Do you have any information about cycling?

DR. OXLEY: On the point of view of cycling, I mentioned on/off charging with the ratio of on/off to time, which is 1.5 seconds off and 1.5 seconds on.

The time shown is rather arbitrary. It is important to a time at which the concentration or the diffusional thickness was still of the same order of magnitude as surface irregularity.

MR. MCCALLUM: Yes, but you are talking about discontinuous discharge; that is, pulse discharging. But I am talking about --

DR. OXLEY: Charging, discontinuous charging.

MR. MCCALLUM: Discontinuous charging, excuse me.

I am talking about many cycles of complete discharge and charge, what the whole conference is about -- secondary batteries.

DR. OXLEY: We could speculate over the long run that you might be better off if you didn't have this discontinuing charging process.

MR. HENNIGAN: Thank you.

We have a question back here.

MR. DUNCAN (Astroelectronics Div, RCA): When I left yesterday two things were on my mind. I stopped by the National Archives and did a little research. I was sure that there was something in our literature that would express my view, and I found a limerick on the first subject. I found a limerick there I would like to present:

"There was an old man of the Cape, who made himself garments of crepe; when asked do they tear, he replied 'Here and there', but they're perfectly splendid for shape.- Robert Louis Stevenson."

The point is here that reflection was made, and it appears to be accepted unanimously, that our space cells don't wear out.

The implication is that they are so bad, the quality is so lousy, that some defect shows up before it can wear out. I would have to say that in my own experience this is not the case. We note a normal infant mortality in normal life in wear out, which I would like to characterize as wear out -- maybe I don't know the definition exactly.

As further substantiation, my experience has been that many times when we disassemble and run, say, an analysis on these cells, we can't find out exactly what caused this failure. The implication earlier was that we could always find a monkey wrench that was left between the plates or

something inside the cells. This isn't really true in my experience. But I felt that I must point this out.

The second item that came up yesterday, my good friend Karl Preusse attacked our short-test method. I use the word "our" advisedly, because I think everybody probably uses the same short test. I feel a little like the guy who was walking down the street and he saw his buddy there, and he said "You look pretty bad. What's wrong?" He said, "Well, I lost my paycheck down at the poker game again." He says "Why do you keep going back to those guys? You know they are cheating you." And he said "Well, it's the only poker game in town."

The point here is, I am trying to elicit from this group any suggestions, any ideas you may have of another short-test method that may be superior to the one that I characterize as "ours".

Thank you.

MR. HENNIGAN: I don't know if anybody is familiar -- I am not going to call it "our" short-test method, but another short-test method -- where the cells are taken down and shorted out for, I think, 16 hours. Then the shorts are removed and we wait for voltage recovery. It has to recover to over 1.15 volts.

Does anybody like that one?

MR. PREUSSE (Gulton): I didn't mean to have my comments looked upon as an attack, because I am a very mild man and I shy

away from fights.

My question yesterday was what is so sacred about 1.15 as compared to 1.14, as compared to 1.13 as an acceptance criteria? In a true short the voltage decays immediately within 4 to 6 hours well below one volt. You can see this.

My question is, what about those cells which exhibit 1.13 and stay at this voltage continuously? We take cells apart and we look to see what is going on on the inside. We can't find one darn thing. I say is there any way we could correlate a true voltage, to give you true significance of what is going on inside the cell. For all we know this 1.13 or 1.10 may be a valid voltage, and then again it may not be. But how can we determine if it is or isn't. That's the thing I wanted to point out.

MR. SCHEEL (Sonotone): One of the things we found is that any type of cell we have has a characteristic voltage. It may be 1.15 or 1.17, 1.20 or 1.24. But the point is that I think any system -- and perhaps maybe even any different manufacture, depending on his process -- has a characteristic on the open circuit voltage.

If you make the short test that Karl referred to, and use your own characteristic voltage as a reference, you have a good key for detection of two types of defects.

One is the mechanical failure; the other may be a chemical failure. I think both of them may show up. It has

been our experience that this is true.

MR. HENNIGAN: Thank you very much.

Is there any more comment on types of short tests that are available, or any comments on the types of short tests that are used?

MR. PREUSSE: We found that the results of the short test depended on the initial previous cycle. We find cells that would exhibit a voltage of 1.13 or 1.14 and would give a little slow, long-range charge, and then go through the shorting procedure and then give it a five-minute energy input and it would pass on the next short test.

It may not be inherent mechanical characteristic. It is dependent on the electrical history of the cell also. These are things that should be pinned down, I think.

MR. HENNIGAN: Mr. Duncan, RCA.

MR. DUNCAN: This is our problem, Karl. In other words, I could take a cell that we would all agree is shorted, and I can charge that cell to see -- to discharge it and run a short test again, and it will pass.

What we are trying to do is pick out these ones before we put them in a cell like that. These short tests come out any way we want. There is no doubt about that.

MR. PREUSSE: That's right.

MR. HENNIGAN: We have got some data here. I just happened to get this this morning from Bill Ingling of Dayrad,

which used to be Inland. We have been running some cells out there since '62. We aren't pushing these cells too much, 10 percent type of discharge, maybe 25. But they just started to pass the state of loans here, minus 10. Of course, the other cells are of higher temperatures fail.

It was very interesting to see here that we have ten cells of company "A", nonfailures at 20,000 cycles, and a capacity check run at 20,000 cycles. These were not necessarily capacity checks in the 20,000, I don't think. They might have been taken down once or twice. The capacity, just eyeballing this stuff, is greater than the initial -- some of the cells by as much as 25 to 30 percent.

Now we have company "B", which shows similar results. They are getting about the same capacities they started with. These cells are leaking and have been bad leakers all along. But still they are doing 18,000 cycles without loss of capacity.

Another company "C", initial capacity about 3, and either a gain capacity or same capacity and the end of 20,000 cycles. No failures in any of these cells.

So I just thought I would pass this on to show that the temperatures we picked should run the cell out is low temperature. We said this before.

Of course, the curious thing about this, if we have got such lousy cells, why are these running so well at minus 10. I suppose these shorts wouldn't tend to show up -- they are

aggravated by temperature, of course, but they really were that bad. I don't think we got this kind of data on the cells that were made four years ago.

Would anybody like to make a comment on this?

MR. BELOVE (Sonotone): I believe that this short test arose many years ago when we first started making satellite batteries. I don't remember whether it was RCA or APL. But we did find one thing, that the short test picked out -- we ran into trouble at that time with proper particles, and we had to try to find those cells that had the copper on them. And the short test picked these out completely.

I believe, in my opinion, this is the beginning of this particular test. Since that time most users of batteries have incorporated this in their specifications. It is my opinioin it has always been that you people in the satellite user field, you must, of necessity, because of our ignorance, use families of cells.

I don't think it matters whether 1.13 volts is the level, or 1.15 volts. I think what is important is that when you make a battery of 20 cells, each of the cells should be the same in their characteristics -- as far as capacity and as far as the short test, too.

This is our feeling, that the differences between cells tends to aggravate the life cycling results obtained.

MR. HENNIGAN: Do we have any more comments on the

short test or in general on the meeting?

MR. BANES (JPL): It took a while for me to collect my thoughts on this primary battery situation.

(Laughter.)

Now that I have got them, maybe I can say something.

We fly generally primary-type batteries. We are on a very limited cycle life as opposed to the very long cycle life that you do in your satellite work. We find that it is necessary to be very selective in our battery, and to be rather strenuous in our qualification. I think we covered that yesterday in the things we do.

It includes areas of environmental testing and some of the other things.

But one thing involving the standardization, I guess, that I would like to throw out here at this time is on missions run for a matter of a few days going to the moon, or a matter of several months going to the hear planets, I suppose eventually in a matter of years going to the farther out planets.

We have a problem right now, we have a task right now of modifying a spacecraft which was made as a spare to go to the planet Mars, and modifying it to go to the planet Venus. On your way to Mars you start out from Earth and your thermal control is set up to be, shall we say, warm in the vicinity of Earth, and get cooler as you approach Mars. Going to Venus it is the reverse. You start out cool and you approach warm.

In 1962 our Mariner started out warm and approached hot. So we can't even standardize between the same type of spacecraft going to different planets, because we have to do different things in order to make a battery that will flow charge, warm to cool or cool to warm, over these periods of time. We find that there are subtle differences that we can make, and make an improvement on the battery over these two different types of missions.

MR. HENNIGAN: Thank you.

I would like to mention here, of course, that our primary batteries are 15-20 minute type operation in rockets, and they would be a couple of hours on a balloon -- which we don't seem to have any trouble with this scheduled usage.

Is there anything else that you would like to bring out. Ernst, any comments?

MR. COHN (NASA): The only comments I have is that I haven't gotten all the illustrations yet. If you have some to hand in, I would be happy to have them. If you want to send them in real soon, with your names and figure numbers on the back, we will try to include them in the proceedings if they come in on time. Otherwise, we just can't hold up the proceedings to wait for the illustrations.

In order to make it as complete as possible, I would appreciate it if you would do that. Thank you.

MR. WEINSTEIN: When do you intend to have them available

MR. COHN: The proceedings?

MR. WEINSTEIN: Yes.

MR. COHN: As quickly as possible, after we get the Multilith plates and have something like 200 or 300 copies run off, and have the secretary address them according to the addresses you gave me here. It is the administrative and secretarial time that determines how fast this goes.

It should be within a matter of, hopefully, two to three weeks.

MR. HENNIGAN: We did have one comment from Mr. Banes, of JPL.

MR. BANES: I would like to throw out more of a question than anything else. As a hardware manufacturer, hardware producer here at JPL, we have a situation where our own in-plant quality control and any quality control that we put into our battery manufacturers plant -- in other words, any other source inspection is by people who are basically either electronics-oriented or in respect to electronic parts and electronic assemblies, or they are mechanically-oriented.

Some of the problems we some times have is trying to instruct our inspectors on the area of inspecting batteries. Do other hardware-oriented organizations have their own battery qualified quality control procedures, manuals, and this type of document? This has been somewhat necessary at JPL, and I wondered if other people have run into similar problems as far

as setting up source inspection of batteries.

MR. HENNIGAN: If any of the battery manufacturers would like to comment on that --

MR. BANES: I would welcome anybody.

MR. GANDEL (Lockheed): What I am going to say probably is familiar to all of you I have done business with. We have acceptance test procedures which are the criterion for procurement of batteries. The acceptance test procedure has the document along with the design control drawing specification by which our quality assurance representative at the vendor's facility buys the battery for us.

All of the assurance representatives that we usually get are men who are not engineers -- I wouldn't call him directed toward the electrical or mechanical or chemical or what have you. These are men who have gained, by the seat of their pants, experience, and I find that somehow these guys have been hanging around assembly lines most of their lives. They see a lot of things that the engineer doesn't.

We find that as time goes by, this man is more important to our operation for some engineering help, or for the more formal reliability or quality assurance people.

The inconsequential item that this man may pick up, as in the past, on more than one occasion saved our lives.

I don't know more I can say specifically to answer your question. Would you have any other questions on that line?

MR. BANES: No.

MR. HENNIGAN: If there are no further questions, and I don't see any hands, we might as well adjourn the meeting.

Do you have anything else you would want to say?

MR. COHN: No.

MR. HENNIGAN: I would like to thank all the speakers who came here. I wish you all a safe trip home.

(Whereupon, at 12:10 p.m., the Battery Workshop Conference was concluded.)