NASA CR-54937

INTERIM REPORT # 1

DEVELOPMENT OF IMPROVED CADMIUM ELECTRODES FOR SEALED SECONDARY BATTERIES

by

H. H. Kroger

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NASA Lewis Research Center
Cleveland, Ohio
Mr. William A. Robertson

GENERAL ELECTRIC COMPANY
Battery Business Section
P. O. Box 114
Gainesville, Florida

ABSTRACT

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Physical properties, impregnability, and electrochemical behavior of experimental nickel fiber plaques were compared to those of currently available nickel powder sinter plaques.

Contrary to expectations, the new plaques did not prove to be a better material for the negative electrode of the nickel-cadmium couple than the controls.

The unfavorable pore size distribution of the fiber plaques was the reason for excessive losses of active material during capacity testing and led to numerous short circuits inside the cells.

Author

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1.0 SUMMARY

This interim report contains the results of the first phase of a program planned to investigate the applicability of nickel fiber plaques for support of the negative electrode of the nickel-cadmium couple.

An investigation of the physical properties of the experimental fiber plaques revealed inhomogenities with respect to thickness, density, weight per area, specific pore volume and pore size distribution. Large portions of the fiber materials were found to be out of the specification limits.

For the subsequent impregnation study, the electrochemical cleaning and formation process, a representative sample of the materials was employed to obtain gain in weight and preliminary capacity data. However, these data were not conclusive with respect to the optimum number of impregnation cycles for a given material.

In two capacity tests consisting of some 50 to 60 charge-discharge cycles considerable loss of active material from the experimental plaques was observed. These losses were greater by a factor of 2 to 4 than those encountered by the corresponding control plaques which were tested simultaneously and under identical conditions.

The reason for this inferior performance of the experimental plaques can be found in its considerably greater mean pore sizes. These values and the overall pore size distribution can only be slightly affected by a compression of the materials.

In general, the tests conducted have shown that the experimental plaque materials are inferior to the currently available control materials in retention of active material during gassing and may therefore be more subject to short circuit factors.

Regardless of the substrate material employed the utilization of the active material steadily declined with increasing numbers of test cycles. However, when at the end of the test program the losses of theoretical capacity due to losses of active material were taken into consideration, the interesting fact was revealed that the utilization of the active material still within the pores of the plaques was hardly changed at all with increasing number of cycles.

2.0 INTRODUCTION

2.1 General

The objectives of the Phase I of "Development of Improved Cadmium Electrodes for Sealed Secondary Batteries" were:

1. Check the physical properties of the experimental nickel fiber plaques with respect to the uniformity of specified thicknesses and densities, its computable ranges of weight per area and specific pore volume, and determine mean pore sizes, pore size distribution and internal surface areas.

2. Select a representative sample and submit to a systematic impregnation study to obtain gain in weight data as a function of the number of impregnation cycles.

3. Submit this sample to a sequence of electrochemical cleaning, electrochemical formation and capacity tests, the latter at different current densities, to obtain information about the utilization of the active materials.

4. Process an adequate sample of GE plaque material under identical conditions and use it as control material.

5. Compare performances of experimental and control materials and make recommendations for the impregnation and processing of materials designated for Phases II and III of the program.

2.2 Materials Studied

The experimental material was received from the Huyck Metals Company and consisted of five different items, namely:

Item	Huyck Designation		Test Designation
1	AX1	10%	1-10
2	AX1 modified,	10%	M-10
3	AX2	10%	2-10
4	AX1	20%	1-20
5	AX1 modified,	20%	M-20

Items 1, 2, 4 and 5 were each delivered as seven 12 1/2 x 13 inch plaques which were called master plaques (M.P.). Item #3 was received in two separate shipments each consisting of seven 12 1/2 x 6 1/2 inch plaques.

For the purposes of this program, the original master plaques of each group were cut to 70 smaller plaques of 6 1/2 x 2 1/2 inch which were designated triple plaques (T.P.), inasmuch as they contained enough material to process them into three electrodes of the size selected for the phases II and III of the program.

The control material was taken from the current GE production line and had the designation "GE VO Negative."

2.3 Material Distribution

The 70 triple plaques of each experimental material were to be used in four different portions of the program, namely:

1. 14 T.P. for physical testing
2. 20 T.P. in Phase I (Impregnation Study)
3. 6 T.P. in Phase II (Single Electrode Study)
4. 30 T.P. in Phase III (Sealed Cell Study)

In order to minimize a possible influence of deviations among the master plaques and of the original location of a given triple plaque, respectively, on the results of the different phases, the selection of the triple plaques for a given portion of the program was done for all experimental materials according to Figure 1.

The seven rectangles represent the seven master plaques of each kind. They are numbered I through VII in the same order as they were removed from the shipping wrappers. Upper and lower half were randomly assigned as packed. The two shipments of Item #3, AX2-10, were dealt with as upper and lower halves of seven master plaques again in the order of unpacking.

The 70 GE control plaques were assigned to the different phases of the program at random.

2.4 Technical Meetings

During Phase I of the program two technical meetings were held with Mr. W. A. Robertson of NASA-Lewis Research Center, at Gainesville, Florida, on 28 December 1965 and 17 February 1966, respectively.

Principal General Electric Company personnel attending were Drs. R. L. Hadley and H. H. Kroger.

PLAQUE DISTRIBUTION FOR THE PHASES OF THE PROGRAM

I

P	1	1	1	3
3	3	2	3	P

II

3	3	3	3	P
P	1	1	1	2

III

3	P	2	3	3
1	1	1	P	3

IV

2	3	3	P	3
3	P	1	1	1

V

1	3	P	3	3
2	3	P	3	1

VI

1	1	1	P	2
3	3	P	3	3

VII

P	3	1	1	1
3	3	3	3	P

P = Physical Testing
1 = Phase I
2 = Phase II
3 = Phase III

FIGURE 1

3.0 PHYSICAL PROPERTIES

3.1 General

The evaluation of results obtained from the experimental plaques designated for the physical testing indicated an unexpectedly wide spread in data. It was therefore decided to extend all non-destructive testing methods to the total of all experimental and control materials regardless of their original assignments.

Only the specifically designated materials were to be used in destructive testing, such as in porosimetric and internal surface measurements.

3.2 Thickness Measurements

3.2.1 Apparatus

Lhomargy thickness measurement device gives direct readings in 10^{-2} mm and permits interpolation to 10^{-3} mm.

3.2.2 Procedure

Each triple plaque was submitted to ten measurements at locations uniformly distributed across its surface of slightly greater than 100 cm^2 (16.25 sq. in.), however, excluding the immediate edge areas. Averages for each plaque and each material were calculated and considered to be typical.

3.2.3 Results

Table 1 contains the results for each experimental and the control material together with specified thickness ranges, deviations and a simplified distribution scheme.

As can be seen, the average thicknesses of the experimental materials are rather close to the upper limit of the specified range of 72 to 80 x 10^{-2} mm (.030 inch ± .0015 inch), and considerable percentages of material trail across that upper border.

Evaluating individual triple plaque measurements for each material did not indicate any preference for extreme thickness values as far as the original locations of the T.P. in a given master plaque were concerned. However, in many instances, systematic trends in thickness changes across the surface of master plaques and/or the upper and lower halves could be observed.

The two shipments of the AX2-10 material actually behaved like two different samples, with the one called "lower" half being completely above the upper limit of thickness.

TABLE 1

THICKNESS ANALYSIS OF PLAQUE MATERIALS

Item		Specification		Average	$\pm 1\sigma$	Percentage		
						Below	Within	Above
AX1	10	72	80	79	2.0	0	81	19
AX1 M	10	72	80	78	2.5	0	87	13
				80	.8		74	26
*AX2	10	72	80	84	1.0	0	0	100
AX1	20	72	80	80	1.4	0	53	47
AX1 M	20	72	80	79	1.6	0	85	15
GE Control		84	94	87	1.7	0	100	0

Thickness expressed in 10^{-2} mm

*The AX2 10% material was delivered in two shipments

3.3 Density Determination

3.3.1 Apparatus

Analytical balance
Steel scale
Lhomargy instrument

3.3.2 Procedure

The area of a triple plaque was calculated from the averages of length and width measurements. Multiplication with the appropriate thickness yielded in the apparent volume of the plaque. Division of the plaque's weight by that volume resulted in the apparent specific weight which divided by the true specific weight of the material results in the apparent density of the experimental material.

In the case of the control material, corrections for the steel support structures had to be made.

3.3.3 Results

Table 2 contains the results for each experimental and the control material, together with pertaining data as to specified limits, deviations, and distribution. As can be seen, the experimental materials tested exceeded the specified limits in either direction.

An evaluation of individual plaque data revealed no correlation between extreme values of density and the original plaque location within a given master plaque. However, in analogy to the thickness measurements, pronounced trends in density changes across the surface of individual master plaques and/or their upper and lower halves could be observed.

3.4 Weight per Area Determination

3.4.1 Apparatus

Analytical balance
Steel scale

3.4.2 Procedure

The weight of a triple plaque was determined on an analytical balance and then divided by its area computed from averages of length and width measurements.

TABLE 2

DENSITY ANALYSIS OF PLAQUE MATERIAL

Item		Specification		Average	± 1 σ	Percentage Below	Percentage Within	Percentage Above
AX1	10	9	11	9.7	.9	21	70	9
AX1 M	10	9	11	10.0	.9	8	82	10
AX2	20	9	11	9.9	.8	7	87	6
AX1	20	19	21	19.0	1.6	52	38	10
AX1 M	20	19	21	20.1	1.9	28	47	25
GE Control		13	15	13.9	.3	0	100	0

Density expressed in percent

3.4.3 Results

Contrary to thickness and density of the experimental material, the weight per area was not explicitly specified in the material procurement. The term is, however, of importance in judging the uniformity of a plaque material, and also has certain bearings on battery design considerations.

The nominal value of the weight per area S of a given experimental material and its tolerable deviations can be calculated as follows, when

W = weight of plaque

A = area of the plaque

T = thickness of the plaque

ρ_r = real specific weight

D = apparent density

are known:

$$W = A \times T \times \rho_r \times D$$

$$W/A = \underline{T \times \rho_r \times D = \ } S$$

Inserting the specified nominal values and their limits results in the ranges given in Table 3, together with the computed results, using real data deviations, and distributions.

As can be seen, the experimental materials in all instances exceeded the calculated limits in either direction.

Evaluation of individual plaque data revealed no correlation between extreme values of weight per area and triple plaque location within a given master plaque. However, again in many instances, pronounced trends in changes of weight per area values across the surfaces of the master plaques and/or the upper and lower halves were encountered.

TABLE 3

WEIGHT PER AREA ANALYSIS OF PLAQUE MATERIAL

						Percentage		
Item		Specification		Average	$\pm 1\sigma$	Below	Within	Above
AX1	10	5.77	7.83	6.86	.66	3	89	8
AX1 M	10	5.77	7.83	6.97	.57	1	91	8
AX2	10	5.77	7.83	7.24	.68	4	77	19
AX1	20	12.18	14.95	13.49	1.17	10	79	11
AX1 M	20	12.18	14.95	14.14	1.39	4	71	25
GE Control		13.76	16.48	14.80	.15	0	100	0

Weight per area expressed in g dm^{-2}

3.5 Specific Pore Volume Determination

3.5.1 Apparatus

Analytical balance
Steel scale
Lhomargy thickness measurement device

3.5.2 Procedure

The weight and the dimensions of the sample plaques were determined as outlined before.

3.5.3 Results

The specific pore volume of the experimental plaque materials was not explicitly specified in the procurement of the materials. This term, however, plays an important role in calculating the degree of pore filling with active material and can be related to utilization estimates.

Nominal values of the specific pore volumes V_{ps} and its tolerable limits can be calculated as follows, with

V_p = pore volume

A = area of the sample

T = thickness of the sample

P = apparent porosity

D = apparent density

ρ_a = apparent specific weight

ρ_r = real specific weight

W = weight of the sample

S = weight per area of the sample

$$V_p = A \times T \times P$$

$$V_p/A = V_{ps} = T \times P \quad ; \quad P = 1 - D$$

$$V_{ps} = T\,(1\text{-}d) \quad ; \quad D = \rho_a/\rho_r$$

$$V_{ps} = T - T \times \frac{\rho_a}{\rho_r} \quad ; \quad T \times \rho_a = W/A = S$$

$$V_{ps} = T - S/\rho_r$$

Inserting the corresponding nominal values and their limits results in the ranges of specific pore volumes given in Table 4, together with the calculated results, deviations and distribution.

As can be seen, the experimental materials exceeded their upper limits in all cases, in some instances rather considerably.

As stated previously, no correlation between extreme values and original triple plaque location were detected. However, again pronounced trends in changes of specific pore volume across the surface of master plaques and/or their upper and lower halves were observed.

A thorough evaluation of the individual data of the experimental plaques revealed that the specific pore volumes of all plaques could very well be brought into the computable limits, providing that the thickness of the experimental plaques was reduced to its nominal value of 76×10^{-2} mm (.030 inch) by a carefully monitored compression. The results of this additional processing step are given in Table 5 and do not require any comments.

TABLE 4

SPECIFIC PORE VOLUME ANALYSIS OF PLAQUE MATERIAL

Item		Specification		Average	± 1 σ	Below	Within	Above
AX1	10	6.32	7.35	7.10	.19	0	90	10
AX1 M	10	6.32	7.35	7.02	.21	0	4	4
AX2	10	6.32	7.35	7.39	.22	0	50	50
AX1	20	5.52	6.63	6.51	.18	0	67	33
AX1 M	20	5.52	6.63	6.31	.20	0	99	1
GE Control		7.07	8.38	7.56	.16	0	100	0

Specific pore volume expressed in $cm^3\ dm^{-2}$

TABLE 5

SPECIFIC PORE VOLUME OF COMPRESSED PLAQUE MATERIAL

Item		Specification		Average	± 1 σ	Percentage Below	Percentage Within	Percentage Above
AX1	10	6.32	7.35	6.81	.08	0	100	0
AX1 M	10	6.32	7.35	6.82	.07	0	100	0
AX2	10	6.32	7.35	6.78	.08	0	100	0
AX1	20	5.52	6.63	6.08	.13	0	100	0
AX1 M	20	5.52	6.33	6.01	.15	0	100	0
*GE Control		7.07	8.38	7.56	±.16	0	100	0

Specific Pore Volume expressed in $cm^3 \ dm^{-2}$

*All materials but GE Controls compressed to nominal thickness of 76 10^{-2} mm

3.6 Porosimetric Measurements

3.6.1 Apparatus

Aminco Winslow mercury intrusion porosimeter with a .2 cm^3 penetrometer.

3.6.2 Procedure

Samples were taken from the triple plaques designated for the physical testing program. Each sample consisted of three circular punches with a total area of 2.11 cm^2. Three such samples were taken from each triple plaque with the punches evenly distributed across the whole surface of the plaque.

Prior to the Hg intrusion procedure, the density of each sample was determined as outlined previously. Then samples for the actual test were selected so that the whole spectrum of densities observed was covered.

The volume of mercury intruded was measured at a variety of absolute pressures and plotted versus pore size.

3.6.3 Results

In Table 6 the final results are given; the numbers represent average values calculated for each material tested.

As can be seen, the difference between the experimental materials and the control material is striking.

In Figure 2, typical pore size distribution curves are shown for the materials tested.

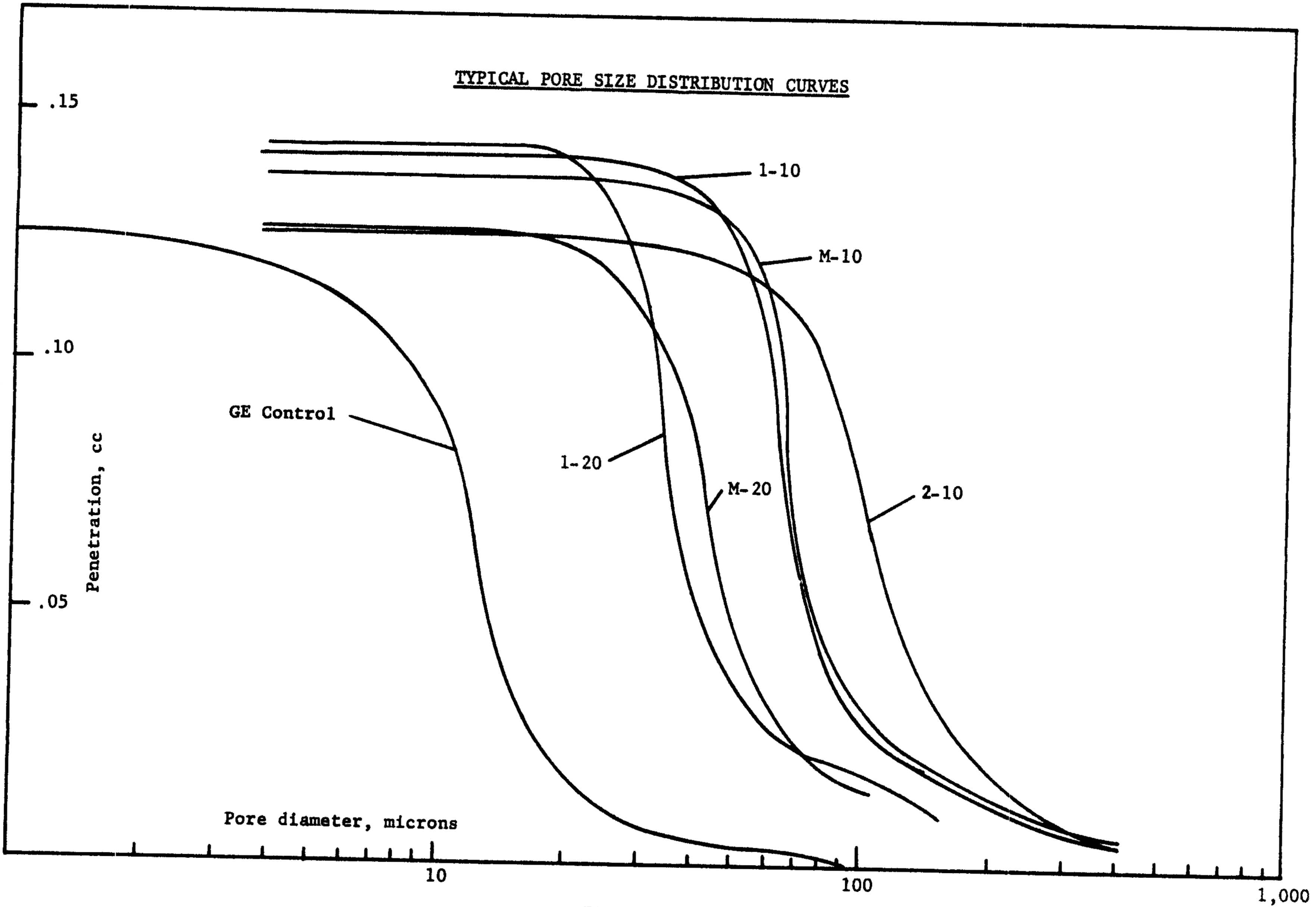
3.7 Internal Surface Area Measurements

3.7.1 Apparatus

Perkin-Elmer Sorptometer 212 C
Leeds-Northrop Speedomax G recorder

3.7.2 Procedure

Samples were taken from triple plaques designated for physical testing. After being baked-out overnight at 110°C, the adsorption and desorption of a flowing nitrogen gas stream with helium as carrier gas was measured. This procedure is a variation of the original BET method.



TYPICAL PORE SIZE DISTRIBUTION CURVES

FIGURE 2

TABLE 6

PORE SIZE ANALYSIS OF PLAQUE MATERIAL

			Pore Size			
Item		Average Density	-1σ	Mean	$+1\sigma$	% $V_p > 100\mu$
AX1	10	10.9	53	65	110	18
AX1 M	10	11.5	56	70	128	22
AX2	10	11.3	75	88	164	38
AX1	20	18.5	31	39	76	12
AX1 M	20	21.4	31	46	92	13
GE Control		14.2	8	14	20	0

3.7.3 Results

According to the corresponding final Huyck report, NASA CR 54,777, pages 37 and 48, the specific surface areas of the plaque materials under consideration were determined by means of the air permeability method. They were found to be in the range of .03 to .06 m^2 g^{-1}.

The Perkin-Elmer sorptometer has a sensitivity of about .3 m^2, which would require sample weights of about 10 grams for the kind of material on hand. As corresponding sample holders were not available, the tests were conducted with samples of standard weights of about one gram. No significant results were obtained.

3.8 Metallographic Examination

3.8.1 Apparatus

A Reichert Zetopan microscope was coupled to a Leitz Aristophot camera with Polaroid film holder. A Leitz steroscopic microscope was also used for visual examination.

3.8.2 Procedure

One sample of each type of fiber plaque was taken, with a piece of General Electric Type VO negative plaque for comparison. The samples were vacuum-impregnated with transparent epoxy resin and given a normal metallographic preparation. All fiber plaque sections were perpendicular to the felting plane; the GE plaque was cut longitudinally and perpendicular to the surface. A photomicrograph in the unetched condition was taken at a magnification of X210. This was chosen to match the magnification of Figs. 5 to 8, 22 and 23 of NASA Report CR-54777.

3.8.3 Results

Fig. 3A shows a typical microstructure of General Electric Type VO negative plaque as used currently for flat plate cells, except that the substrate carrier strip does not appear in this section. Some variation in pore size may be observed. The Huyck fiber plaque samples (Figs. 3B to 3F) are all much coarser in both particle size and pore size than the GE sample. The difference between the nominally 10% and 20% dense materials is quite clear, but the differences within a nominal density group are slight. Agreement with the photomicrographs in NASA Report CR-54777 is good.

Examination of the polished sections with a low power steromicroscope was found to be advantageous, it being possible to look through the transparent resin. Under these conditions, the AX1-modified 10% appeared to have the most open structure suggesting that it was the least dense of the nominally 10% dense samples.

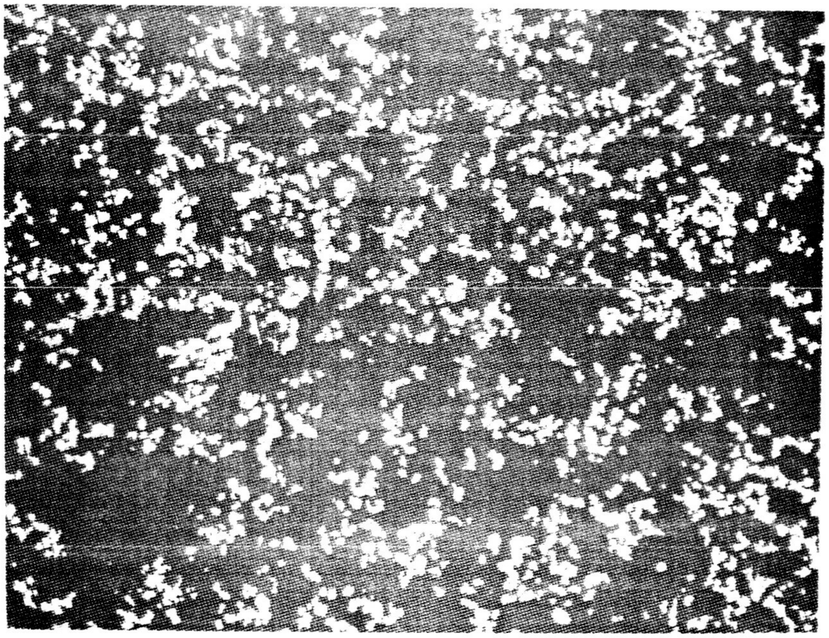


FIGURE 3A MICROSTRUCTURE OF GENERAL ELECTRIC TYPE VO NEGATIVE PLAQUE X210

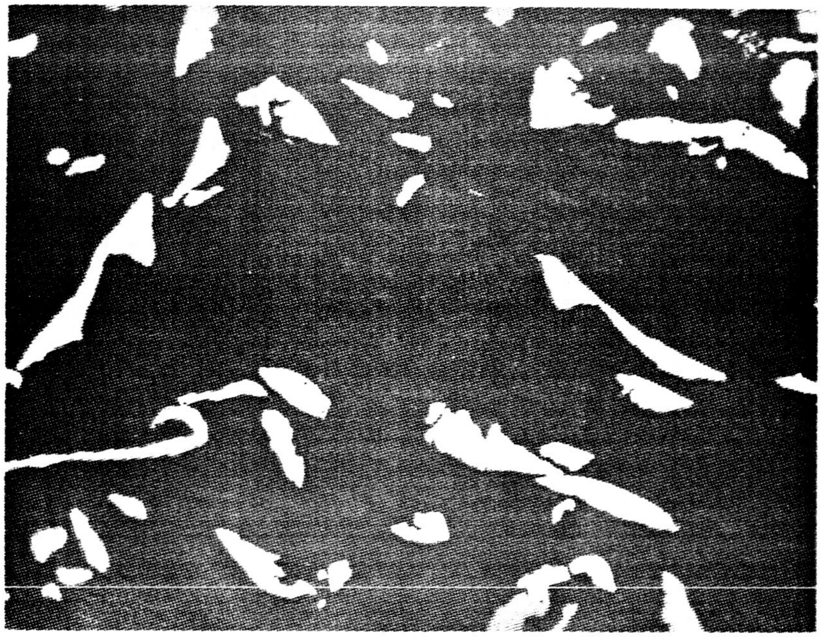


FIGURE 3B MICROSTRUCTURE OF HUYCK FIBER METAL PLAQUE TYPE AX1 (10% DENSE) X210

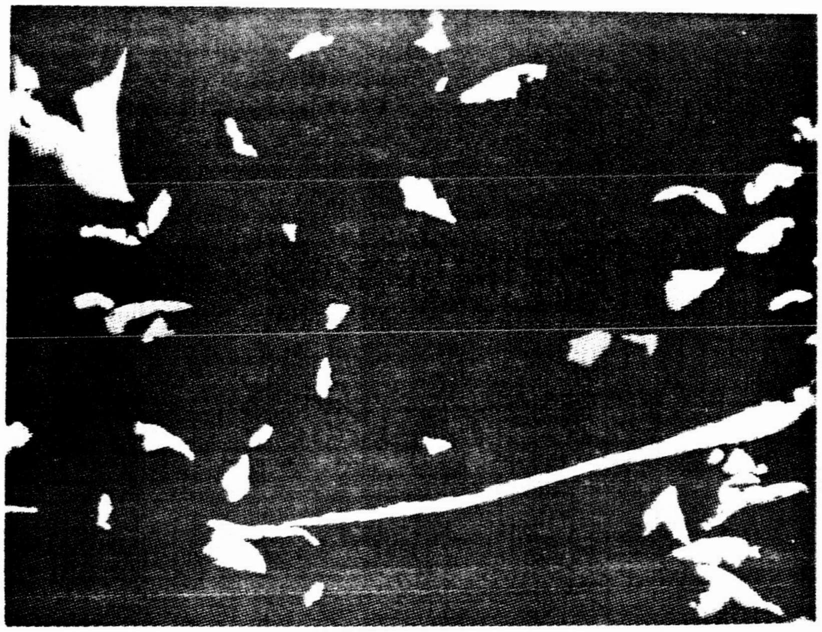


FIGURE 3C MICROSTRUCTURE OF HUYCK FIBER METAL PLAQUE TYPE AX1-MODIFIED (10% DENSE) X210

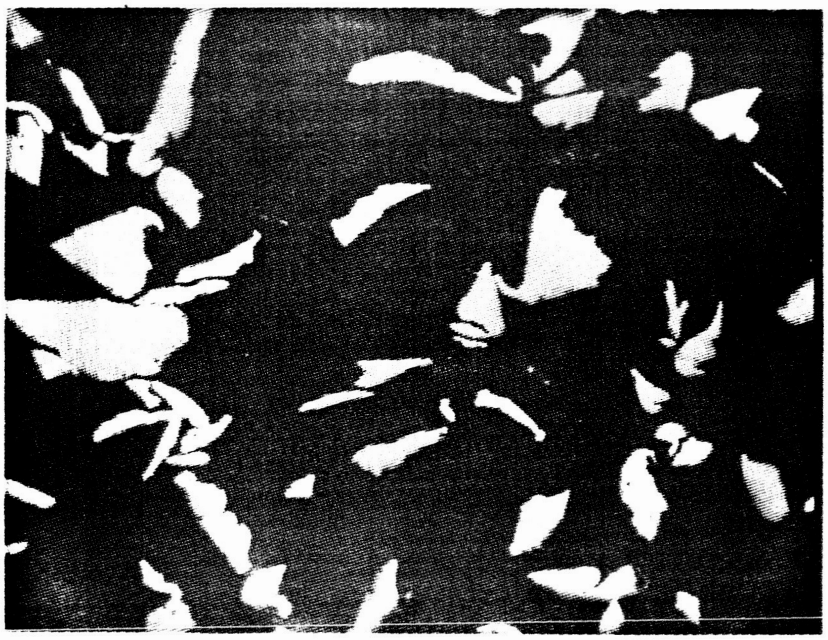


FIGURE 3D MICROSTRUCTURE OF HUYCK FIBER METAL PLAQUE TYPE AX2 (10% DENSE) X210

FIGURE 3E MICROSTRUCTURE OF HUYCK FIBER METAL PLAQUE TYPE AX1 (20% DENSE) X210

FIGURE 3F MICROSTRUCTURE OF HUYCK FIBER METAL PLAQUE TYPE AX1-MODIFIED (20% DENSE) X210

3.9 Conclusions

Nearly all the methods employed in the investigation of the physical properties revealed substantial inhomogenity in the experimental plaque materials.

1. The mean thickness values were close to the specified upper limit, and consequently, large portions of the experimental materials were above the limit.

2. The values observed for the densities of the experimental materials in many cases exceed either upper or lower specified limits.

3. The weight per area values fell likewise in many instances outside the computed limits.

4. The specific pore volume was generally too high. However, a compression of the experimental plaque materials to nominal thickness brought this term back well into tolerable limits.

5. The mean pore sizes of the experimental plaque materials were found to be 3 to 5 times greater than those of the control material. This fact sheds serious doubt upon the applicability of the experimental material as an electrode material.

6. The specific internal surface area was obviously too small to be detected by the gas flow sorption method. This holds true for both the experimental and the control materials.

7. Microscopic investigations resulted in no unusual aspects.

8. The fact that the evaluation of individual triple plaque data of the four basic terms investigated, revealed pronounced trends in changes of those values across the surfaces of given master plaques, seems to indicate that the manufacturing process contains inherent variations.

4.0 IMPREGNATION AND ELECTROCHEMICAL CLEANING

4.1 General

The objective of this part of the program was to find an optimum number of impregnation cycles for each of the experimental materials, and in connection with capacity test results, to determine the influence of the degree of pore filling on the electrochemical utilization of the active material.

According to Figure 1, 20 out of the total of 70 triple plaques per kind of material were selected for this part of the program. They were submitted to from one to ten impregnation cycles in the following mode:

Number of cycles	1	2	3	4	5	6	7	8	9	10
Number of T.P.	1	1	1	2	2	3	3	3	2	2

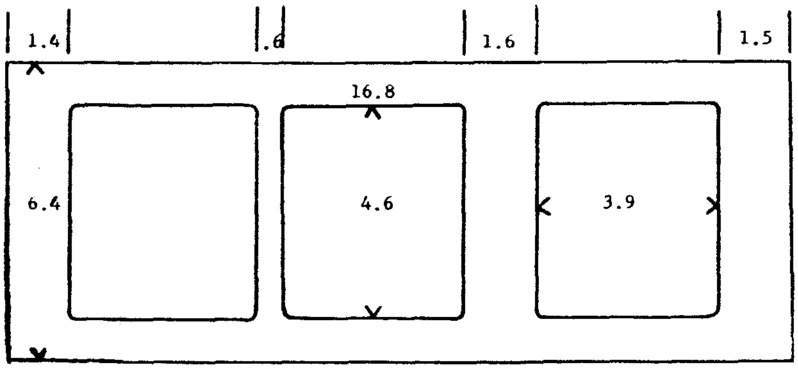
This arrangement reflects the anticipated areas where optimum numbers of impregnation cycles might be expected.

Including the 20 control plaques, a total of 120 triple plaques were processed.

4.2 Coining Operation

Coining is used as an expression for compacting certain areas of plaques in order to make them less accessible for the active materials. It is a general experience that coined plaque areas contain only about 30% of the active material that would be found in the same area if uncoined.

The control material was coined in the factory, while a specially designed die was used for the experimental plaques.



Dimensions on the coined experimental plaques can be taken from the schematic drawing on the left. The numbers given are in centimeters.

The effective area A_{eff} can be calculated by measuring the uncoined portions A_{open} and the coined portions A_{coin} and using the equation

$$A_{eff} = A_{open} + 0.3 \times A_{coin}$$

This results in values of 68.1 cm^2 for the experimental and of 70.8 cm^2 for the control material.

For practical considerations, these values can be assumed to be identical.

Regardless of the kind of experimental plaque material submitted to the operation, a total force of 14.5 metric tons was applied for 30 seconds on the 51 cm^2 surface to be coined.

4.3 Compressing Operation

The evaluation of specific pore volume data yielded that the numerical values were generally too large. However, it was found that by compressing to the nominal thickness of 76 x 10^{-2} mm (.030 inch) the specific pore volumes of all experimental plaque materials could be brought back well into the calculated limits; compare Table 5.

A rectangular, open shim was machined to that nominal thickness and then put around the plaque to be compressed. The total area of the shim and the uncoined area of the plaque was approximately 120 cm^2. The following table gives the forces applied on that area in metric tons and the length of application time in seconds.

Material	Force	Time
AX1 10	4.5	5
AX1-M 10	4.5	5
AX2 10	2.7	5
AX1 20	14.5	30
AX1-M 20	14.5	30

Spot checks proved that the objective of permanent compression was achieved.

4.4 Coding Operation

Each of the three uncoined sections of a triple plaque was permanently identified by spot-welding three coded 1.25 x .8 cm nickel markers to appropriate locations of the adjoining coined area.

Beside this identification purpose, the markers were also intended to serve as electrical tabs during the pertinent capacity test sections of the program.

After application of the markers, the plaques were re-weighed and the new plaque weights were recorded.

4.5 Plaque Holder Design

To facilitate the handling of the plaques during the impregnation process, one well-identified triple plaque of each kind of material comprised a group.

The plaques were placed with their upper rims in a holder consisting of an array of small rectangular nickel plated metal pieces which could be tightly secured by nuts and bolts. The distance between two adjacent plaques was about one centimeter which proved to be more than enough to prevent any build-up of deposits during the impregnation.

Each holder was clearly marked with the number of impregnation cycles anticipated for its plaques and in addition carried the letter A, B, or C to distinguish among parallel impregnation runs.

The design of the holder can be seen in Figure 4.

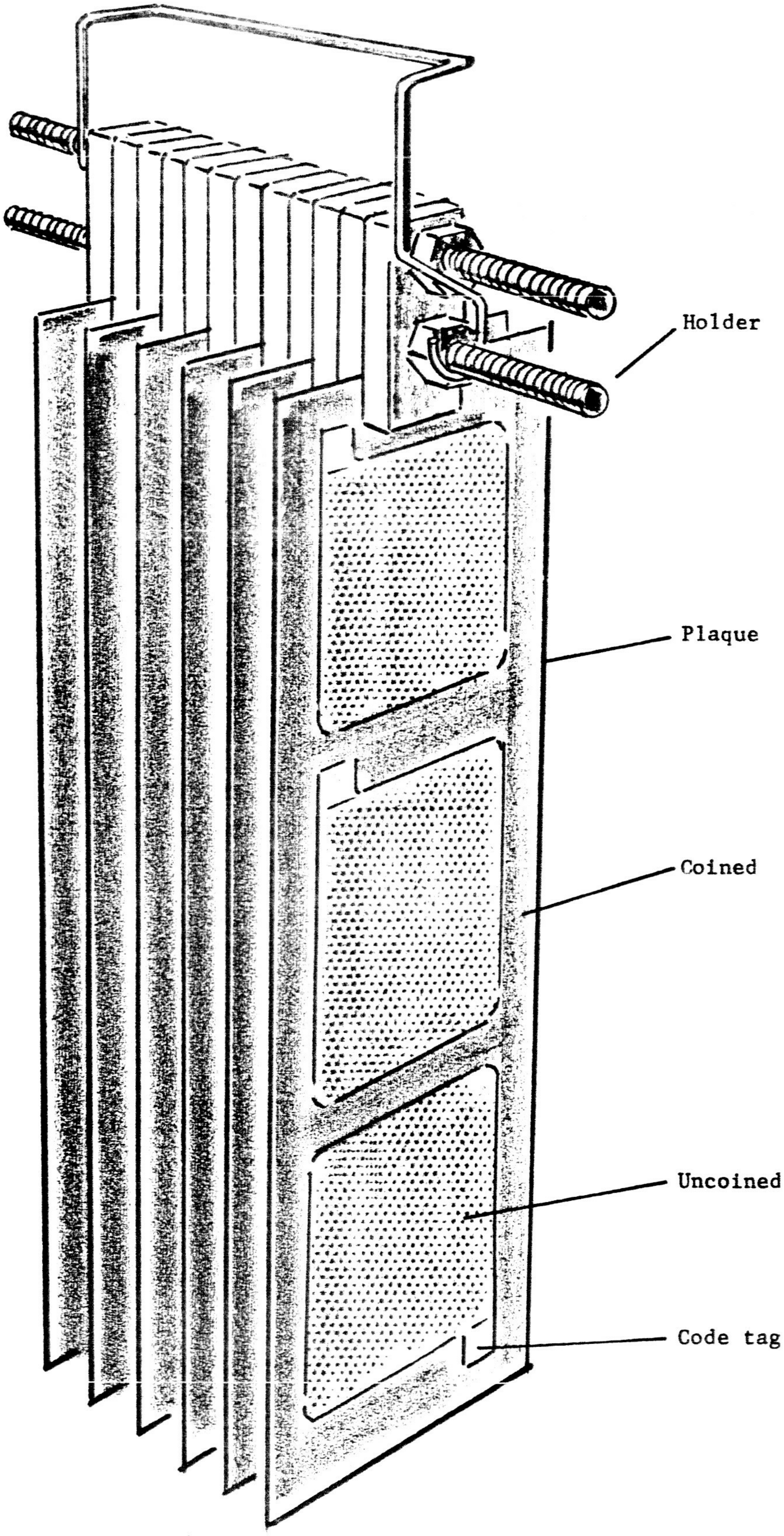


FIGURE 4 PLAQUE HOLDER DESIGN

4.6 Impregnation Procedure

Initially, it was planned to conduct the impregnation of the experimental materials in the factory with control and regular production materials. However, tests with advance samples and employing a different plaque holder revealed the fact that the experimental plaques became extremely stiff and brittle in the course of impregnation. The turbulency of the processing solutions caused so many cracks and breaks in the plaque material that a laboratory bench type impregnation was chosen instead.

The conditions employed were exactly the same as in the factory process. While processing data with respect to times, temperatures and concentrations are outside the scope of this contract, the following flow sheet, P1A-PB-104, describes the process steps:

An impregnation cycle consists of the following steps:

1. Impregnation of the plaques with aqueous cadmium nitrate solution.

2. A dripping phase to get rid of excess liquids, specifically from the outside of the plaques.

3. Drying of the plaques at elevated temperature.

4. Converting of the cadmium nitrate into cadmium hydroxide by means of a treatment of the plaques with hot sodium hydroxide solution.

5. Washing with hot deionized water to remove sodium nitrate and any excess of precipitation solution.

6. Drying of the plaques at elevated temperature.

The steps 1 through 6 were repeated as often as necessary to treat all materials as planned.

The stiffness and brittleness of the experimental materials as mentioned with the advance samples was observed again. First signs of it appeared after the first drying operation and the maximum state was reached after not more than three complete cycles. The materials then became so stiff that touching them with a nickel spatula produced a distinct metallic sound.

The extent of the brittleness acquired can be seen in the fact that an accidental dropping of the holder #7C resulted in the total loss of three experimental plaques due to breakage, and in damage to the two other experimental plaques of this holder. The corresponding control plaque survived this mishap without any damage.

GENERAL ELECTRIC

NO. P1A-PB-103

BATTERY PRODUCT SECTION PROCESS

TITLE: FLOW CHART
ELECTROCHEMICAL CLEAN PHASE - SPECIAL PLATES

REVISIONS

ELECTROCHEMICAL CLEAN PHASE (P4A-PB-103)

1. MECHANICAL BRUSHING
2. CHARGE HIGH RATE IN SOLUTION
3. WASH DEIONIZED WATER - ELEVATED TEMPERATURE
4. DISCHARGE HIGH RATE IN SOLUTION
5. WASH DEIONIZED WATER - ELEVATED TEMPERATURE
6. DRY - ELEVATED TEMPERATURE

72
75N 2
71PD 2

PRINTS TO

MADE BY MARCH 24 '66 ISSUED	APPROVALS	Battery Bus. Section GAINESVILLE, FLORIDA	P1A-PB-103 CONT ON SHEET SH NO.

(3/62)

4.7 Electrochemical Cleaning

In the preparation of the program, it was initially planned to perform the electrochemical cleaning of the experimental and control materials using manufacturing process facilities. However, when the results of the impregnation of the advanced samples became available, it was decided to substitute not only the impregnation in the factory, but also the cleaning of the materials in the factory by a laboratory bench type process.

In essence, the electrochemical cleaning process consists of a sequence of mechanical brushings of the impregnated plaques, a charge and discharge regime, and an extended washing procedure. The current involved was adjusted to the amounts of active material present inside the plaques in order to avoid any damage to the material due to excessive current densities. The electrochemical cleaning flow sheet, P1A-PB-103, follows:

The objectives of the electrochemical cleaning are manifold, namely:

1. It is a mechanical cleaning of the outside of the plaques by means of brushings.

2. It is a removal of loose particles of active materials from the interior by means of regulated gas evolutions.

3. It is a considerable reduction of the inherent nitrate content of the active material by means of electrochemical reduction and simple washings.

4. and finally, it is the first step of the formation process of the electrode materials.

It was found that the plaques lost between 0.1 and 0.3 grams in weight during the cleaning process.

Furthermore, and even more important, it was observed that at least partially, the initial flexibility of the experimental materials was restored.

GENERAL ELECTRIC

NO. P1A-PB-104

BATTERY PRODUCT SECTION PROCESS

TITLE: FLOW CHART
IMPREGNATION PHASE - SPECIAL PLATES (NEG)

REVISIONS

IMPREGNATION PHASE (P5A-PB-105)

1. IMPREGNATE SINTERED PLAQUES WITH SOLUTION
2. DRIP EXCESSIVE SOLUTION
3. DRY AT ELEVATED TEMPERATURE
4. CONVERSION OF RESIDUAL MATERIAL FROM NITRATE TO HYDROXIDE
5. WASH DEIONIZED WATER - ELEVATED TEMPERATURE
6. DRY PLAQUES - ELEVATED TEMPERATURE

72
$75N^2$
$71PD^2$

SMF1 (3/62)

MADE BY MARCH 24 '66	APPROVALS	**Battery Bus. Section**	P1A-PB-104
ISSUED		GAINESVILLE, FLORIDA	CONT ON SHEET

72 B72PX-272

4.8 Results

The impregnation procedure was conducted without significant difficulties, and both experimental and control materials developed only traces of outside scaling.

In one instance, e.g., during the tenth impregnation cycle of the plaques in holder 10B, a heavy fall-out of active material from the plaques of this holder was observed during the first moments of the washing process. This phenomenon seems to be the reason for the discrepancies* of weight when identical plaque materials from holders 10A and 10B, respectively, are compared.

The accumulated gains in weight for each plaque material and each impregnation cycle are given in Table 7, and where applicable, the average values for parallel runs were computed.

Considering the fact that accumulated gains in weight for each plaque material were determined by using a variety of different samples at each impregnation cycle, the values obtained appear to be quite reasonable.

Table 8 contains the same data in a different form of presentation. Here the gains in weight per impregnation cycle are listed for each material.

In the extreme right column of the table the incremental gains in weight for each impregnation cycle are listed for the GE control material; where applicable, the averages of Table 7 have been employed.

With the exception of the cycles 7 and 8, respectively, the declining sequence observed is typical for the control material. Such a decline is naturally expected, because the available pore volume, i.e., the volume of pores not yet filled with active material, is decreasing with the number of impregnation cycles accomplished.

The slight break in the normal sequence, however, can be explained by the fact already mentioned that different samples had to be used at each impregnation cycle.

Assuming that the behavior of the control material is considered to be normal,the data of Table 8 have been used to make up Figure 5.

By and large, the impregnability of the experimental plaques followed the behavior of the corresponding control material. Yet, it appears that a certain inconsistency occurred on and around the fourth impregnation cycle. At that very point, the incremental increases of gain in weight dropped considerably.

The data of Table 7 have been used in calculating the degree of pore filling, i.e., to compare the percentage to which the available pore volume is filled with electrochemically active cadmium hydroxide.

TABLE 7

ACCUMULATED GAINS IN WEIGHT (grams) AFTER ELECTROCHEMICAL CLEANING

Number of Impregnations	AX1 10%	AX1M 10%	AX2 10%	AX1 20%	AX1M 20%	GE
1A	2.00	2.23	1.86	2.39	2.44	2.56
2A	4.12	4.28	4.34	4.93	4.78	4.90
3A	6.60	6.53	6.28	6.96	7.32	6.66
4A	7.97	7.81	8.10	7.96	8.50	8.06
4B	7.74	8.57	7.89	8.32	8.58	8.09
Avg.	7.86	8.19	8.00	8.14	8.54	8.08
5A	9.10	9.41	8.94	9.61	10.05	9.13
5B	9.25	9.18	9.53	9.46	9.18	9.00
Avg.	9.18	9.30	9.24	9.54	9.62	9.07
6A	10.16	10.32	10.15	10.96	10.46	9.73
6B	9.81	9.82	10.67	10.47	10.69	10.32
6C	9.42	10.16	10.17	10.40	10.68	10.11
Avg.	9.79	10.09	10.32	10.60	10.60	10.04
7A	11.53	11.06	11.50	11.60	11.84	10.63
7B	10.61	11.54	11.26	11.41	12.11	10.42
7C	-	11.11	11.27	-	-	10.70
Avg.	11.07	11.23	11.33	11.51	11.98	10.57
8A	11.83	11.78	12.22	12.60	12.96	11.59
8B	11.79	12.70	12.03	12.14	13.49	11.42
8C	11.84	12.34	11.99	12.36	12.35	11.20
Avg.	11.81	12.26	12.07	12.35	12.91	11.39
9A	13.11	12.94	13.29	12.80	13.35	12.05
9B	12.78	12.90	11.92	12.53	13.90	11.72
Avg.	12.94	12.92	12.57	12.66	13.62	11.88
10A	12.92	14.00	13.50	12.81	14.92	12.42
10B	12.84	12.56 *	13.41	12.17	13.27 *	12.32
Avg.	12.88	13.28	13.45	12.49	14.10	12.37

TABLE 8

INCREMENTAL GAINS IN WEIGHT (grams) AFTER ELECTROCHEMICAL CLEANING

Number of Impregnations	AX1 10	AX1-M 10	AX2 10	AX1 20	AX1-M 20	GE-Control
1	2.00	2.23	1.86	2.39	2.44	2.56
2	2.12	2.05	2.48	2.54	2.34	2.34
3	2.48	2.25	1.94	2.03	2.54	1.76
4	2.38	1.66	1.82	1.18	1.22	1.42
5	1.32	1.11	1.24	1.40	1.18	.99
6	.41	.79	1.08	1.06	.98	.97
7	1.28	1.14	1.01	.91	1.38	.53
8	.74	1.03	.74	.84	.93	.82
9	1.13	.66	.50	.31	.71	.49
10	- .06	.26	.88	- .17	.48	.49

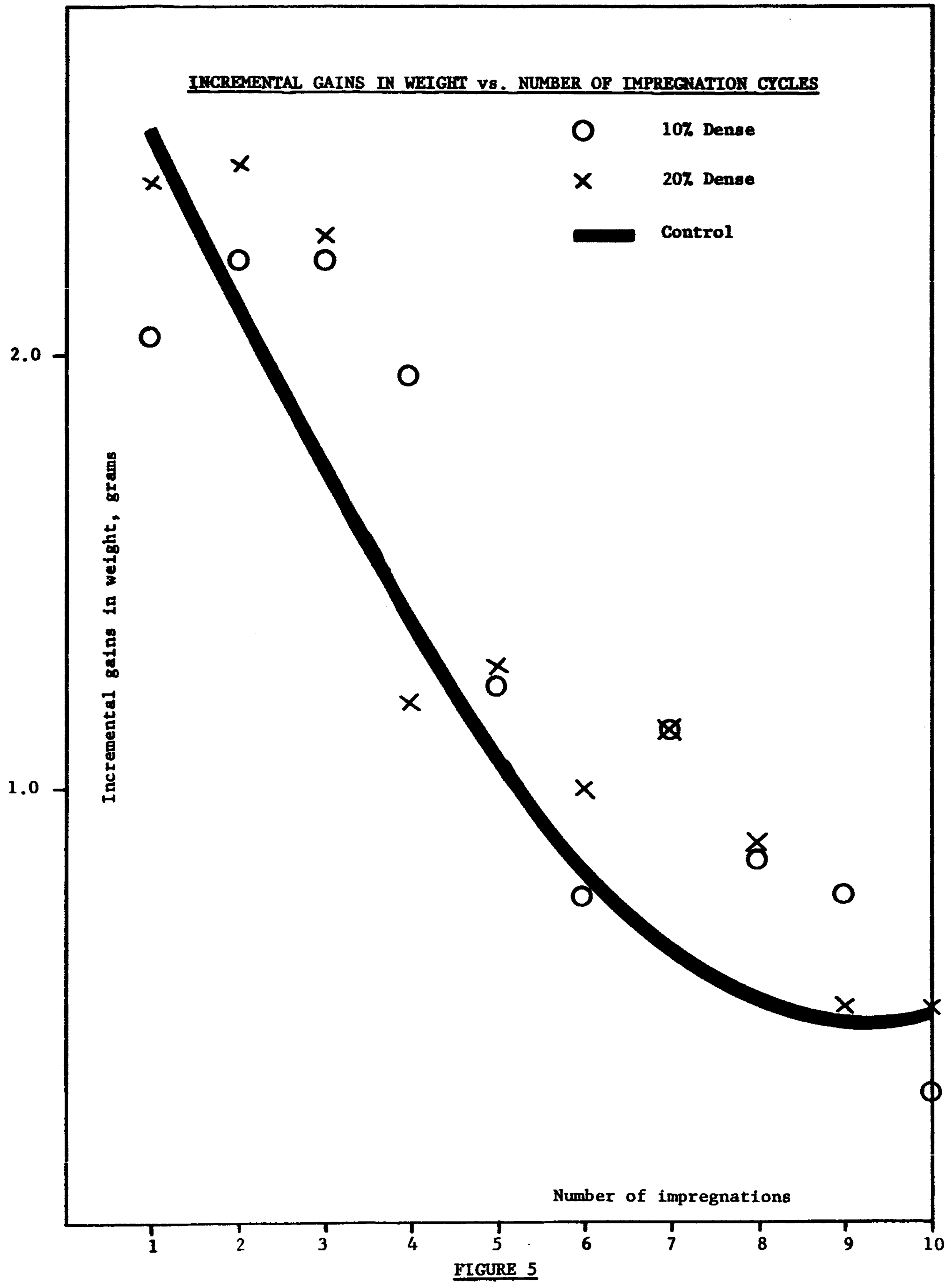

INCREMENTAL GAINS IN WEIGHT vs. NUMBER OF IMPREGNATION CYCLES
○ 10% Dense
× 20% Dense
Control
2.0
1.0
Incremental gains in weight, grams
Number of impregnations
1
2
3
4
5
6
7
8
9
10

FIGURE 5

In computing the numerical values of pore filling, which are given in Table 9, the following assumptions were made:

1. The specific weight of the cadmium hydroxide precipitated within the pores of the plaque materials is the same as the average literature value of 4.8 gr cm^{-3}.

2. The effective areas of plaques can be expressed as outlined in Section 4.2, page 23, of this report.

3. The actual specific pore volume V_{ps} values of the plaque materials are identical with the average values observed.

4. The average of accumulated gains in weight, as given in Table 7, are typical for the plaque materials.

In Figure 6, the average values of degree of pore filling for each of the nominal densities investigated, i.e., experimental plaques with 10 and 20% density, respectively, and GE control material, are plotted versus the number of impregnation cycles.

As can be seen from this figure, for each type of material the degree of pore filling is approaching a terminal value with increasing number of impregnation cycles. Due to the asymptotic character of this approach, the incremental increases in pore filling, and hence in the gains of weight of active material, do not contribute to any large extent beyond 7 or more impregnation cycles.

Therefore, both for practical and economic reasons, an extension of impregnation cycles beyond seven can hardly be justified.

4.9 Conclusions

The following conclusions pertaining to this part of the program can be drawn:

1. All of the experimental plaques developed an extreme and permanent stiffness during the first few impregnation cycles. The resulting brittleness made the handling rather difficult and it took great care to avoid breakage.

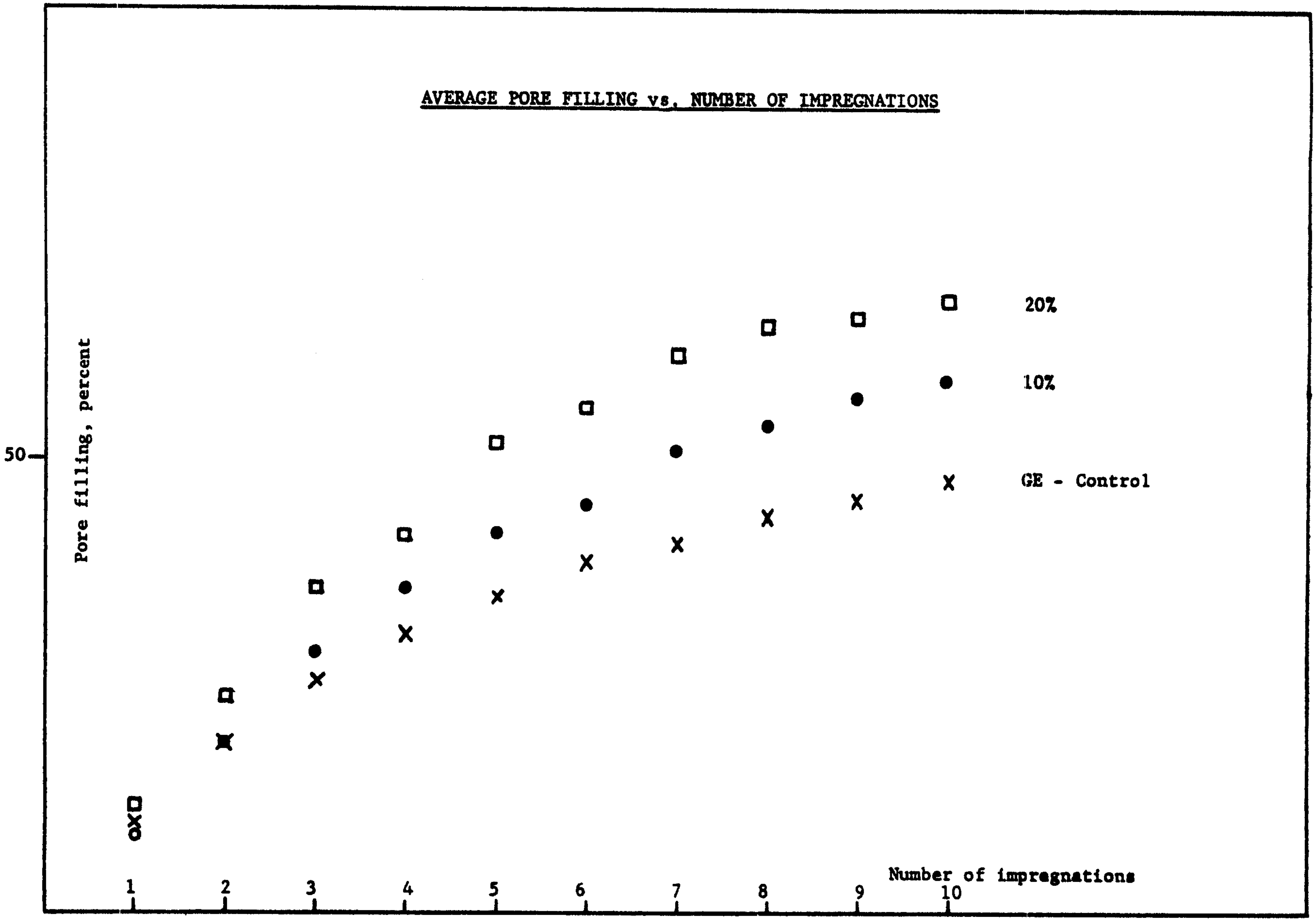
2. The impregnation behavior of the experimental materials was different from the one of the controls. The rather smooth decline in incremental gains in weight with increasing number of impregnation cycles was replaced by sudden change from high to low gains, around 4 and 5 impregnation cycles.

3. For both experimental and control material it could be shown that additional impregnation cycles in excess of seven yield only small incremental gains in weight.

TABLE 9

DEGREE OF PORE FILLING IN PERCENT

Number of Impregnations	AX1 10	AX1-M 10	AX2 10	AX1 20	AX1-M 20	GE
1	9	10	8	12	12	10
2	19	19	19	25	24	19
3	30	29	28	35	37	26
4	35	37	36	41	43	31
5	41	42	42	54	49	35
6	44	45	46	58	54	39
7	50	51	51	63	61	41
8	53	55	54	64	65	44
9	58	58	57	64	69	46
10	58	60	60	63	72	48



AVERAGE PORE FILLING vs. NUMBER OF IMPREGNATIONS

FIGURE 6

5.0 AEROSPACE FORMATION

5.1 General

Upon completion of the electrochemical cleaning process and after the determination of the final gains in weight, the plaques were submitted to a special treatment referred to as "Aerospace Formation Process."

Essentially, this treatment is an extended electrochemical cleaning performed as a batch process. The objectives of this procedure are:

1. To continue the cleaning of the impregnated material
2. To continue the formation of the material
3. To characterize the plate material for comparison with design requirements.

5.2 Procedure

On the attached flow charge, P1A-PB-105, the points pertaining to the current program are grouped as follows:

5.2.1 Assembly Steps

1. Serializing of the plates has already been done and was described in Section 4.4, Coding Operation, page 24, of this report.

2. Storing of the plaques in desiccators took place between the end of the cleaning process and the start of assembling into test cells

3. The test cells referred to as temporary cells were as follows:

Case and cover:	Nylon
Terminals:	Nickel plated steel
Counter electrode:	U-shaped nickel metal sheet
Separator:	U-shaped corrugated perforated PVC

The design is shown in Figure 7. The nickel counter electrode was connected to the positive terminal of the cover, then the test electrode was wrapped in the separator and the electrode/separator package slipped into the U-shaped counter electrode. The test electrode was then tightly clamped to the negative terminal of the cover utilizing one of the coded markers mentioned previously as contact areas.

4. The electrodes/separator assembly was checked for proper alignment and for possible short circuits before it was slipped into a clearly identified case.

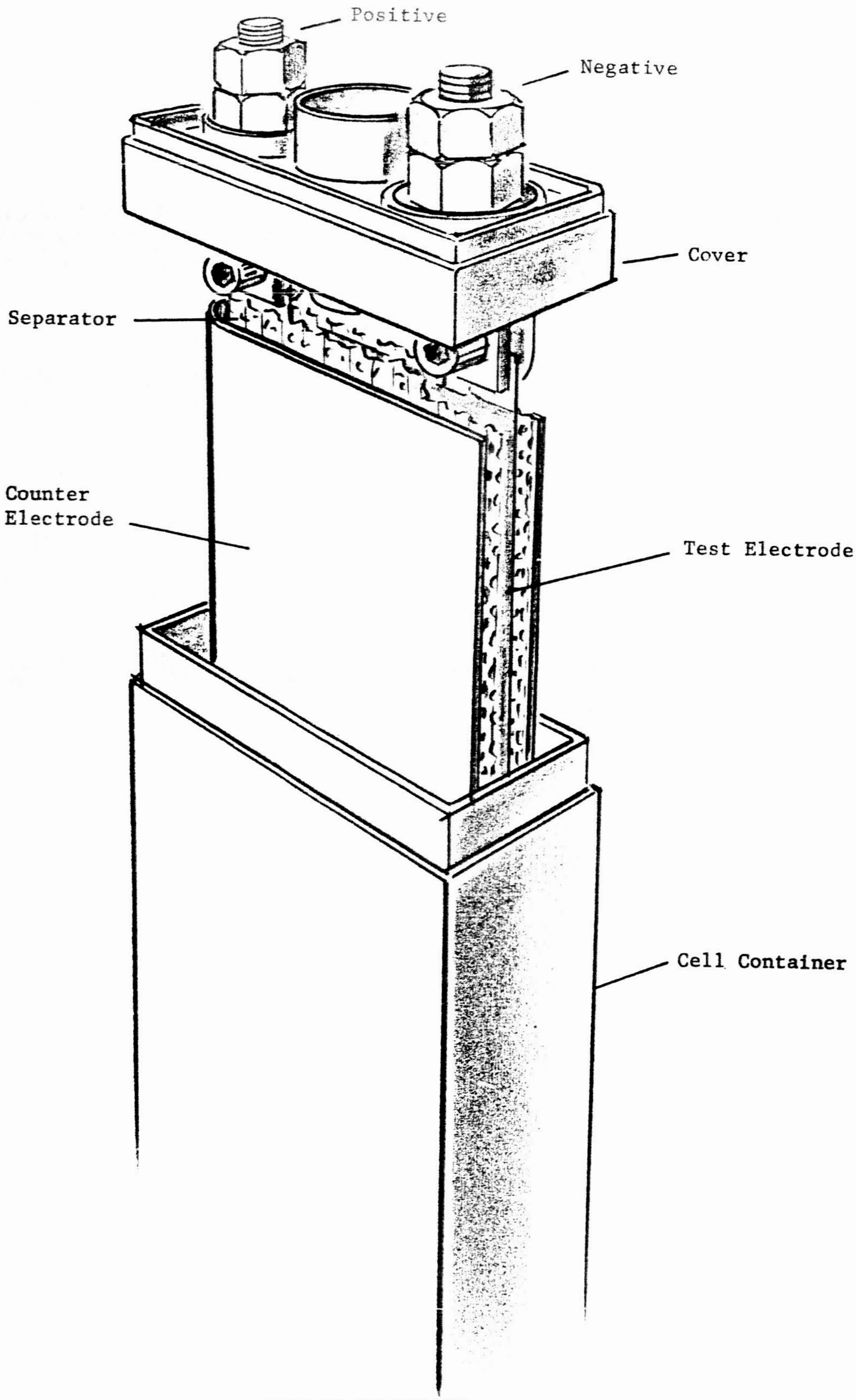


FIGURE 7 DESIGN OF TEMPORARY TEST CELL

GENERAL ELECTRIC

NO. P1A-PB-105

BATTERY PRODUCT SECTION PROCESS

TITLE: FLOW CHART (EXCERPT FROM P1A-PB-101)
AEROSPACE FORMATION - SPECIAL PLATES

REVISIONS

ASSEMBLY STEPS (P23B-PB-101 AND P14A-PB-106)

1. SERIALIZE PLATES
2. CONTROL STORAGE
3. ASSEMBLE TEMPORARY CELLS
4. INSPECT & TEST TEMPORARY CELLS AND ASSEMBLIES
5. ADD TEMPORARY CELL ELECTROLYTE

ELECTRICAL PROCESSING (P3B-PB-103)

1. REVERSE CHARGE NUMBER 1
2. FORWARD CHARGE NUMBER 1
3. DISCHARGE NUMBER 1
4. REVERSE CHARGE NUMBER 2
5. FORWARD CHARGE NUMBER 2
6. DISCHARGE NUMBER 2
7. REVERSE CHARGE NUMBER 3

CONCLUDING STEPS (P4B-PB-101)

1. EVALUATE DATA FOR ACCEPT/REJECT DECISIONS
2. DISCARD ELECTROLYTE AND REMOVE TEMPORARY HARDWARE
3. WASH PLATES (ELEVATED TEMPERATURE DEIONIZED WATER)
4. REASSEMBLE TEMPORARY CELL
5. FILL WITH ELECTROLYTE

72
75N 2
71PD 2

PRINTS TO

BMF1 (3/62)

MADE BY
X H Ullrich MARCH 29, 1966
ISSUED

APPROVALS
X M C

Battery Bus. Section
GAINESVILLE, FLA.

P1A-PB-105
CONT ON SHEET SH NO.

5. 150 ml of 31% by weight aqueous potassium hydroxide solution was added to each cell, enough to cover the electrodes completely. The cells were then allowed to stand overnight for soaking the electrodes with electrolyte.

6. Appropriate wiring for potential monitoring was provided and the cells were connected in series for charge and discharge as test groups.

5.2.2 Electrical processing

The currents used during the second charge and discharge periods were calculated based on the average gains in weight of the plaques of a given test group. A utilization of 90% of theoretical capacity was assumed for the electrochemically active materials.

1. Reverse Charge No. 1 - Performed at the C/10 rate until reversal of all electrodes was achieved.
2. Forward Charge No. 1 - A charge of the active materials at C/10 rate applying a considerable amount of overcharge.
3. Discharge No. 1 - A monitored discharge at the C/2 rate followed by
4. Reverse Charge No. 2 - A deep discharge into reversal using a rate of approximately C/20
5. Forward Charge No. 2 - A repetition of Charge No. 1
6. Discharge No. 2 - A repetition of Discharge No. 1
7. Reverse Charge No. 3 - A repetition of reverse charge No. 2

5.2.3 Concluding steps

1. Evaluating of data
2. Dumping of the formation electrolyte
3. Washing of the plates
4. Re-assembly of temporary cells
5. Refilling of the cells with 31% by weight aqueous potassium hydroxide solution.

5.3 Results

In Table 10 the theoretically expected capacities in mAhrs are given for all plaques. These values were arrived at by multiplying the corresponding weights of active material, given in Table 7, with the conversion factor of 366 for weight of active material in grams into capacity in mAhrs.

The column on the extreme right of Table 10 contains the test group designations O, I, II, III and IV, respectively, and the average theoretical capacity of all plaques of a given test group.

The next Table 11 contains the percentage of capacities actually obtained during the formation process. The left parts of boxes show the percentage obtained at Discharge No. 1, while the right parts show those percentages obtained during Discharge No. 2.

It might be noted here, that in case of the test groups III and IV, respectively, not all plaques submitted to the formation process were monitored for potential and capacity during this phase. The respective locations in Table 11 are marked with asterisks, these cells were only hooked up to the monitoring system when the capacity testing started.

An evaluation of the data in Table 11 reveals the following facts.

1. First Discharge Values
   All materials developed a flat maximum of utilization of the active material in the range of 6 to 8 impregnation cycles applied.

2. Second Discharge Values
   The same observations as in the first cycles were made.

3. First vs. Second Cycle
   Distinctive differences between experimental and control material seem to prevail

TABLE 10

THEORETICAL CAPACITIES IN mAhr AFTER ELECTROCHEMICAL CLEANING

Number of Impregnations	AX1 10	AX1-M 10	AX2 10	AX1 20	AX1-M 20	GE	Theoretical Group Capacity
1	730	820	680	880	890	940	0
2	1510	1570	1590	1800	1750	1790	Ø
3	2420	2390	2300	2550	2680	2440	I
4	2920	2860	2970	2910	3110	2950	2,400
	2830	3140	2890	3050	3140	2960	II
5	3330	3440	3270	3520	3680	3340	3,400
	3390	3360	3490	3460	3360	3290	
6	3720	3780	3720	4010	3830	3560	III 3,920
	3590	3590	3910	3830	3910	3780	
	3450	3720	3720	3810	3910	3700	
7	4230	4050	4210	4250	4330	3890	
	3880	4220	4120	4180	4430	3810	
	-	4070	4130	-	-	3920	
8	4330	4310	4970	4610	4730	4240	IV 4,630
	4320	4650	4400	4440	4940	4180	
	4330	4520	4390	4520	4520	4100	
9	4800	4740	4860	4690	4890	4410	
	4680	4720	4360	4590	5090	4290	
10	4730	5120	4940	4690	5460	4550	
	4700	4600	4910	4450	5860	4510	

Ø No electrochemical tests required

TABLE 11

UTILIZATION OF ACTIVE MATERIAL IN PERCENT

Number of Impregnations	AX1 10	AX1-M 10	AX2 10	AX1 20	AX1-M 20	GE	Test Group
1	No Electrochemical Testing Required						O
2							
3	75 79	74 72	79 80	74 77	75 77	74 73	I
4	73 77	75 79	76 82	70 67	74 79	73 79	
	76 73	80 79	79 77	76 75	76 76	77 76	II
5	77 75	79 77	76 74	75 74	77 77	76 76	
	83 82	83 82	77 76	81 80	80 78	83 81	
6	*	-	87 80	92 85	-	-	III
	87 77	-	-	-	86 79	82 82	
	-	89 83	*	79 74	86 80	-	
7	89 82	*	89 82	*	83 77	*	
	89 82	90 83	*	89 83	86 80	86 83	
	∤	91 80	81 75	∤	∤	87 82	
8	84 76	86 77	86 80	83 78	*	*	IV
	-	*	*	*	-	82 79	
	*	89 82	86 75	76 73	87 82	80 81	
9	*	86 79	85 78	86 80	86 80	82 75	
	86 78	*	-	*	*	*	
10	86 79	*	-	*	74 70	81 73	
	-	-	*	*	*	-	

* = Formation without monitoring
\- = Non-formed spare samples
∤ = Lost samples

1. Experimental material

(1) In test group I, in 8 out of 10 instances, the second discharge resulted in a better utilization of the active material.

(2) In test group II, the utilization during discharge No. 2 was a few percentage points less than the one during discharge No. 1.

(3) Test groups III and IV revealed a pronounced downward trend from discharge No. 1 to discharge No. 2.

2. Control material

(1) Test groups I, II, and III showed about the same utilization during both formation discharges.

(2) This behavior was similar in test group IV where material with 8 cycles appeared to be rather stable.

(3) The materials impregnated 9 or 10 times showed decreases in utilization comparable to those of the corresponding experimental material.

Combining the pertaining data of Table 9, i.e., degree of pore filling, with those of Table 11, i.e., utilization of active materials, permits the plotting of the utilization as a function of the pore filling. The results are presented in Figure 8.

The flat charater of the maxima observed seems to be real, i.e., regardless of the plaque material studied, the utilization of the active material is largely independent of the amount of active materials deposited inside the porous electrode structure.

This seems true for the ranges investigated even if one considers that sample numbers were small for each point of the diagram.

5.4 Conclusions

The following pertinent conclusions could be drawn for this part of the program:

1. Regardless of the nature of the plaque material the second discharge provided a lower utilization of the active material when the number of impregnation cycles increased.
2. Considering each cycle for itself, a flat maximum of the utilization of the active material at seven impregnation cycles could be observed.
3. In general, these maximums were reached at a degree of pore filling of 40 - 50 percent of the theoretically available pores.

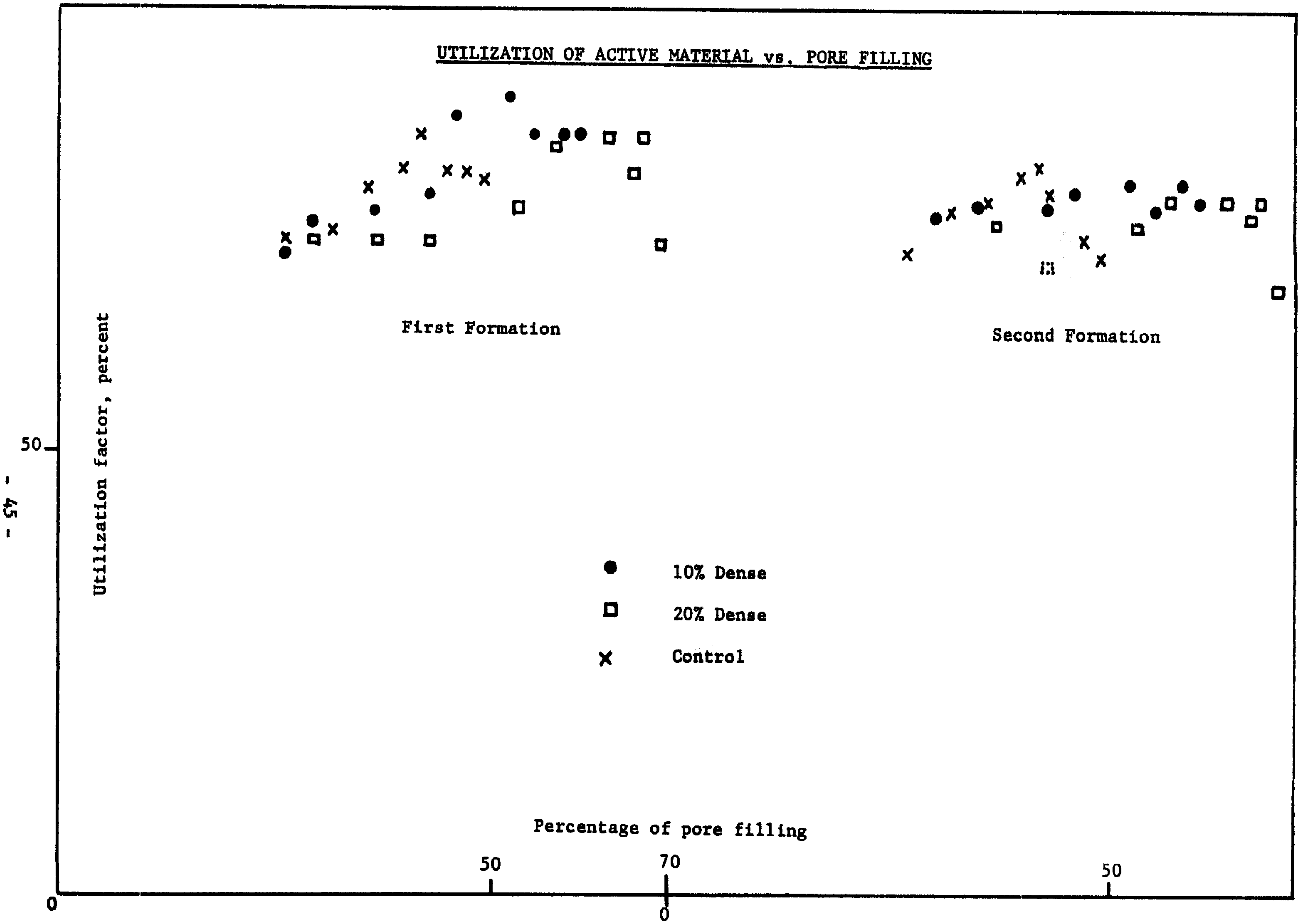

UTILIZATION OF ACTIVE MATERIAL vs. PORE FILLING
First Formation
Second Formation
Utilization factor, percent
50
● 10% Dense
□ 20% Dense
× Control
Percentage of pore filling
0
50
70
0
50

FIGURE 8

6.0 CAPACITY TESTING

6.1 General

The objectives of this part of the program were as follows:

1. To obtain additional information about the correlation between utilization of active material and the degree of pore filling of the plaques.

2. To investigate the repetitive cycling behavior of the plaque material at a variety of discharge current densities.

In order to get as much information as possible in the short time available, severe test conditions were selected. One has to keep in mind that the actual testing of the materials is the objective of Phases II and III, respectively, of the program.

6.2 Test Equipment

Basically, the experimental set-up consisted of two parts, namely:

1. The current circuitry

2. The potential monitoring system

6.2.1 Current circuitry

Cells assigned to a particular test group were electrically connected in series, and by means of timer-controlled relays, were submitted to regular charge, discharge, and rest periods.

Direct current for charging and discharging of the cells was provided by rectifying the AC line and was regulated by means of adjustable resistors. In essence, this system permitted a constant current operation. The monitoring of the discharge currents revealed that during the later phases of the discharge period the current dropped below nominal values due to internal resistance increases inside the cells of a test group as soon as the particular cells were discharged and driven into reverse.

However, in all instances the calculation of capacities discharged was possible because the changes of discharge current as a function of state of charge of the battery could be calibrated.

6.2.2 Potential monitoring equipment

Two independent systems were employed simultaneously for monitoring the test cell voltages, namely:

1. A continuous recording of the battery voltage of the cells of a particular test group during the discharge period. This total voltage was fed into a chart recorder, the sensitivity of which was adjusted so that the completed discharge of any test cell appeared as a distinctive break in the voltage versus time curve. In this manner a permanent record as to the time of any discharge was provided.

2. An occasional measuring of the voltage of each single cell of a given test group. For this purpose each cell could be individually connected to a voltmeter by means of a manually operated selector switch. This system permitted the recording of the cell voltage at any desired time.

By the combined utilization of both systems the length of time required to discharge a given cell could be established with an accuracy of better than 1%.

The test cells employed in this part of the program were the same as described earlier in Section 5.2.1, Aerospace Formation.

6.3 Test Procedure

6.3.1 Current and time requirements

The currents for charging and discharging the cells of a given test group were calculated based upon the average theoretical capacity of that group and considering certain requirements pertaining to other parts of the program.

The lengths of time for which these currents were applied were established by one or more of the following conditions:

1. At a constant charge current, a sufficient amount of charge and overcharge had to be returned to the cells.

2. The amount of charge removed from any cell during the constant current discharge period had to be greater than the practically available capacity, i.e., all cells of a test group had to be driven into reverse.

3. The total length of time for charge, discharge, and rest periods of a cycle was kept to either 8, 12, or 18 hours, thus a reoccurrence of events to be observed at easily predicted times.

The numerical rates for currents and times are given in Table 12 with currents in mA and times in hours.

TABLE 12

CAPACITY TEST OPERATING CONDITIONS

Test Group	Mode	I_{ch}	T_{ch}	I_{dch}	T_{dch}	T_{Rest}
I	High	475	5	640	3	-
	Medium	400	6	320	6	-
	Low	400	6	160	12	-
	High	475	5	640	3	-
II	High	660	5	880	3	-
	Medium	550	6	440	6	-
	Low	550	6	220	12	-
	High	660	5	880	3	-
III	High	800	5	1,100	3	-
	Medium	800	5	550	6	1
	Low	800	5	275	12	1
	High	800	5	1,100	3	-
IV	High	960	5	1,300	3	-
	Medium	960	5	650	6	1
	Low	960	5	325	12	1
	High	960	5	1.300	3	-

6.3.2 Number of cycles

The cells were cycled at a given discharge current for a sufficiently great number of cycles so that a quasi-stationary capacity state was reached.

6.3.3 Test sequence

As can be seen from Table 12, the discharge currents were applied in the sequence high, medium, low, and high repeated.

In the course of testing, test groups III and IV, respectively, were simultaneously cycled prior to the testing of group I and II. However, for reporting purposes, this order will be reversed.

6.4 Results

6.4.1 Capacities and utilization of active material

For approximately 40% of the cycles performed, the capacity discharged was calculated for each test cell. These cycles were evenly distributed over the entire length of the test program and a thorough check of the permanent records of the paper charts, see section 6.2.2, revealed that this quota was more than sufficient to cover the changes of performance as they occur as function of time and discharge currents.

Instead of presenting the experimentally observed capacity, the corresponding utilization factors are given, i.e., the ratio of capacity being discharged to the calculated capacity based upon the gains in weight observed. The advantage of this form of presentation is that it permits the direct comparison of different electrode materials and different amounts of active material. This even holds true for all the test groups under consideration, inasmuch as the currents applied were based upon the average theoretical capacity of the members of a group.

The following three tables contain the utilization factors for all cells tested and they are given in percent of the individual initial theoretical capacity of each cell. The values shown are for the first and last cycle of a given charge-discharge regime.

In presenting these numbers, a differentiation with regard to their reliability was made as follows:

Plain numbers indicate that the cell was completely discharged within the time alloted for the discharge period. Numbers followed by a + sign indicate that the apparent utilization was greater than calculated as the cells were not completely discharged.

TABLE 13

UTILIZATION FACTORS
IN PERCENT OF TEST GROUP I AND II MATERIALS

			High		Medium		Low		High	
Impreg.	**Run**	**Material**	1	16	17	29	30	38	39	54
3	A	1-10	69	57	64 x	55	55	50	42	37
		M-10	59	51	52	45	47	42	36	29
		2-10	72	49	53	38	40	32	26	20
		1-20	61	57	62	55	57	54	48	43
		M-20	64	62	67+x	63	70	55	47	42
		GE	72	59	67	62	66	64	53	47
4	A	1-10	65+	65	65+xx	64	62	57	48	40
		M-10	66+	68+	67+x	64	65	62	52	51
		2-10	64+	66+	64+xx	66+	64+x	65	52	50+
		1-20	57	51	56	52	55	49	42	38
		M-20	61+	63+	61+xx	55	61	59	50	43
		GE	64+	66+	65+xx	67+	65+	66	61+	46
4	B	1-10	70	51	54	46	49	47	40	34
		M-10	69	56	58	50	54	49	43	45
		2-10	71	51	53	45	56 x	45	38	30
		1-20	65	57	60	54	58	56	50	47
		M-20	65	57	59	54	58	55	48	46
		GE	69	59	65	59	68	59	56	50
5	A	1-10	71	59	63	71	73+x	64	53	46
	B		76	70	72+x	59	62	58	49	44
	A	M-10	72	60	62	56	60	57	49	45
	B		74	66	72+x	57	61	61	49	44
	A	2-10	68	52	55	45	49	45	38	36
	B		73	74+	70+x	57	64 x	58	48	38
	A	1-20	69	73+	69+x	56	61	59	50	48
	B		70	75+	70+x	60	65	61	53	49
	A	M-20	71	63	66+xx	60	63	60	53	47
	B		70	62	70+x	62	65	58	52	48
	A	GE	73	56	62	58	66	66	57	49
	B		76	57+	63	58	63	67	57	47

TABLE 14

UTILIZATION FACTORS
IN PERCENT OF TEST GROUP III MATERIALS

			High		Medium		Low		High	
Impreg.	Run	Material	1	18	19	30	31	43	44	62
6	A	1-10	67	58	68	60	62	54	50	44
	B		71	59	69	62	65	57	54	48
	C	M-10	70	59	71	67	77	63	56	57
	A	2-10	69	59	70	87+	81+x	55	52	45
	C		72	59	71	87+	79	63	55	44
	A	1-20	74	65	76	87+	81+x	67	63	62+
	C		66	59	68	61	64	79+	78+	78+
	B	M-20	69	59	72	83+	77+	62	60	54
	C		70	61	72	67	71+	71+	60	55
	B	GE	68	57	69	64	64	79+	62	53
7	A	1-10	70+	63+	77+x	76+	71+	71+	70+x	55
	B		71	62	74	67	70	62	58	52
	A	M-10	66	60	71	61	64	54	56	46
	B		70+	63+	77+x	76+	71+	68	70+x	48
	C		71	65+	80+	79+	74+	62	59	44
	A	2-10	70+	63+	77+x	77+	71+	66	62	x 55
	B		71	64+	79+x	78+	73+x	49	52	41
	C		64	61	79+x	61	69	67	51	43
	A	1-20	63	57	65	59	62	55	53	50
	B		71+	63+	78+	77+	71+	72	64	x 52
	A	M-20	66	61+	68	67	69+	63	59	52
	B		67+	60+	73+	73+	68+	68+	67	x 67+
	A	GE	68	57	66	60	66	64	59	48
	B		68	58	71	65	72	68	62	52
	C		68	56	73	61	69	67	61	67+

TABLE 15

UTILIZATION FACTORS
IN PERCENT OF TEST GROUP IV MATERIAL

Impreg.	Run	Material	High		Medium		Low		High	
			1	18	19	30	31	43	44	62
8	A	1-10	70	72+	89+x	81	77	83+	65	74+
	A	M-10	70	73+	90+x	70	68	60	58	50
	B		64	61	75	81+	76+	66	63	x 50
	C		73	65	83	84+	78+x	71	70	x 52
	A	2-10	70	70+	86+x	85+	79+	69	68	x 52
	C		71	72+	88+x	86+	81+	69	67	x 53
	A	1-20	72	68+	84+x	74	75	66	68	55
	B		65	61	73	66	67	61	63	56
	C		67	60	74	68	68	61	61	53
	A	M-20	69	66+	82+x	71	69	66	65	48
	C		73	62	77	84+	78+	77	75	x 54
	A	GE	64	54	73	66	69	65	61	53
	B		68	52	71	66	69	66	65	48
	C		69	59	82	73	69	71	67	48
9	B	1-10	72	67+	83+x	81+	76+	77+	71 x	50
	A	M-10	70	66+	82+x	80+	75+	64	64 x	53
	B		68	66+	82+	80+	75+x	60	61	49
	A	2-10	72	65+	79+	78+	73+	74+	67 x	68+
	A	1-20	73	68	84+x	72	73	65	64	55
	B		68	68+	84+x	83+	77+	64	64	54
	A	M-20	72	64+	79+x	77+	72+	73+	73+x	51
	B		66	57	76+	74+	70+	70+	70+	51
	A	GE	66	53	70	66	68	66	64	46
	B		67	57	75	69	71	67	65	48
10	B	1-10	70	88+	82+x	81+	65+x	66+	65	53
	A	M-10	66	61+	75+	74+	69+x	59	60 x	44
	B	2-10	67	64+	79+x	77+	72+x	61+	68 x	67+
	A	1-20	63	62	78+	76	73	x 56	61	45
	B		76	70+	87+x	81	80+	80+	81+x	51
	A	M-20	64	57+	71+	69+	65+	66+	66+	49
	B		68	65+	80+x	78+	70	62	64 x	40
	A	GE	67	55	72	66	70	67	63	44

The fact that a cell was not completely discharged does not necessarily mean that its capacity is considerably greater than those of comparable partners. It was observed that a high numerical value of "apparent" utilization factor was almost always related to a peculiar voltage behavior of the corresponding cell. At the beginning of the discharge the potential of a good test electrode was about .22 volts more positive than that of the freely hydrogen gassing inert counter electrode. This difference in potential was slowly increasing as schematically presented in the following table.

% of Discharge Time	Difference in Potential
0	.22
25	.25
50	.29
75	.33
90	.35
98	.40
100	.50
101	1.60

However, in the cases of extremely high utilization this potential vs time schedule was not followed. Those cells showed potential difference even at the end of the scheduled discharge time as if they were only discharged for 25% of their capacities. Upon charge the same cells developed voltages which were considerably higher than those of normally behaving cells.[1]

This deviating behavior was soon to be discovered as caused by internal high resistance short circuits due to cadmium migration and depositing of residues between the electrodes and on the bottom of the cells.

This short circuiting could be overcome, at least temporarily, by a disassembling of the cell and a careful removal of those deposits. The number of times a particular cell had to be cleaned during a given charge-discharge régime is marked by x-marks. As can be seen, unusually high utilization values are in general followed by one or more of these markings. Successfully performed cleaning operation brought capacity and utilization factors back in line with those of comparable cells. However, as mentioned above, in some cases only temporarily.

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1. However, during the intial high discharge rate period, those cells of test group I which received four impregnations were an exception to these rules. The current requirements for that particular test group were based upon the lower theoretical capacities of the plaques which received three impregnation only.

As can be seen from the tables, the utilization of the active material was steadily decreasing with increasing number of cycles accumulated within a given charge-discharge regime. A decrease in the discharge rate was always followed by an immediate, but transient recovery of the utilization factors, so that the general downward trend was not broken. When the testing was concluded with a repetition of the initial high discharge currents, the lowest utilization rates ever were observed.

When the transient recoveries upon decrease of discharge current are neglected, the overall performance of all materials in all test groups can easily be presented as done in the following Figures 9, 10, and 11, respectively. Here the averages of the initial and final utilization factors for each original plaque material in each test group are plotted versus the number of cycles acquired.

With the exception of the 10% dense plaques with a relatively low loading of active material, the utilization of all experimental and control plates dropped almost uniformly from an initial value of 70% to a final one in the vicinity of 50%.

Considering the loss of active material from the plates, a process which is identical to a reduction in theoretical capacity of the respective cells, the final utilization factors had to be corrected. They are shown in the appropriate positions, marked "corrected." The losses of active material and in theoretical capacity were experimentally determined by reweighing the washed and dried plates upon completion of the respective test phases.

If one assumes that the loss of active material and the reduction in theoretical capacity was distributed evenly over the total length of testing time, the interesting observation can be made that the utilization rate as such has not changed significantly over the time of testing.

6.4.2 Material loss and cleaning correlation

In the following Table 16, the percentage of losses of active material from the plates are presented. The numerical values given are average numbers for the electrodes assigned to a given test group. It can be seen from the table that:

1. The average loss of all experimental materials are twice as high as those of the control GE material

2. 10% dense experimental material encountered greater loss than the corresponding 20% dense plaques.

3. The greatest losses occurred with 10% dense lightly loaded plaques.

4. The lowest losses, beside the GE controls, with heavily loaded 20% dense material

5. Item 2-10 as a group lost more than 50% of its initial active material when lightly loaded.

UTILIZATION FACTORS vs. NUMBER OF TEST CYCLES FOR TEST GROUP I and II

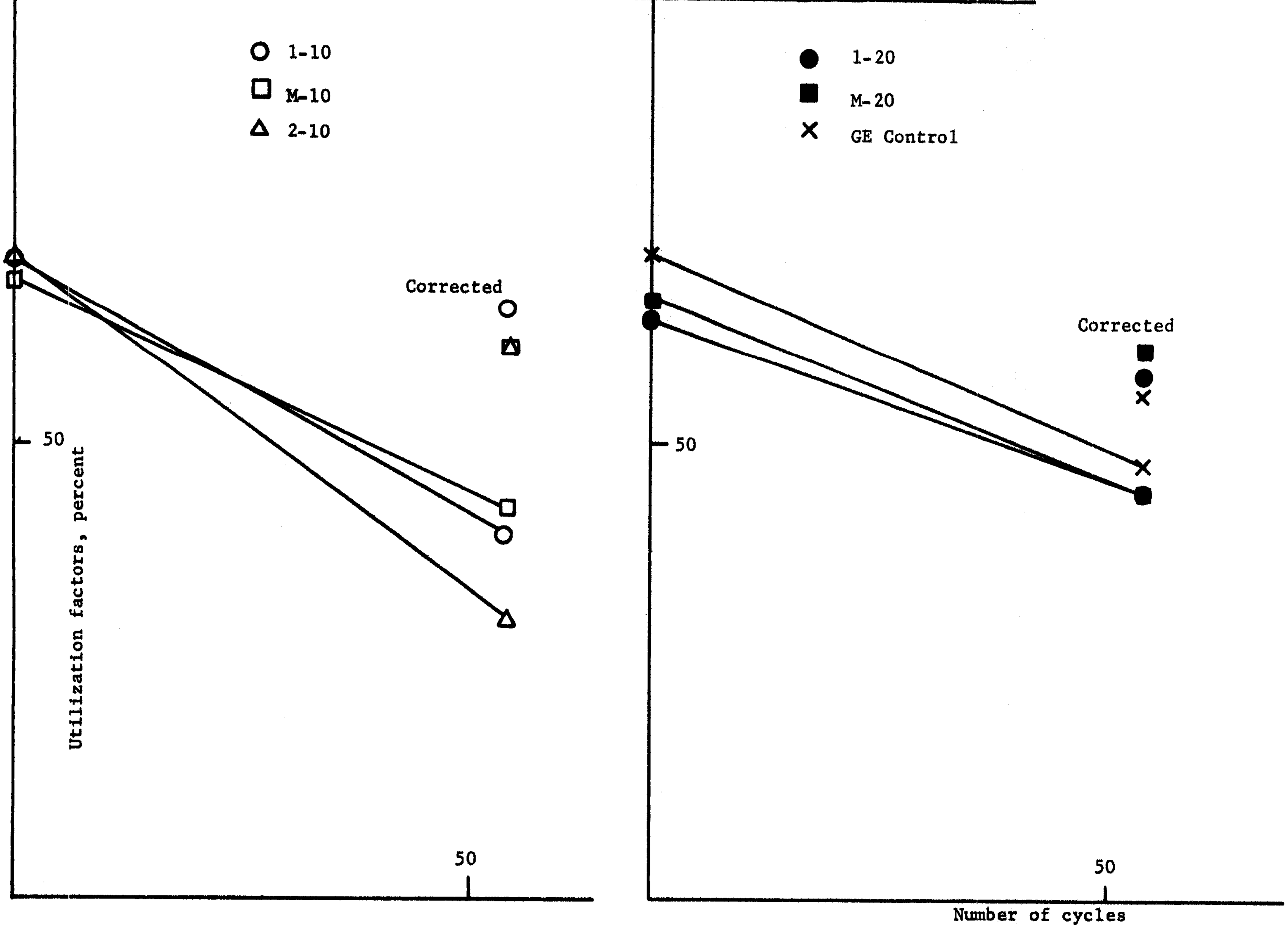


FIGURE 9

UTILIZATION FACTORS vs. NUMBER OF TEST CYCLES FOR TEST GROUP III

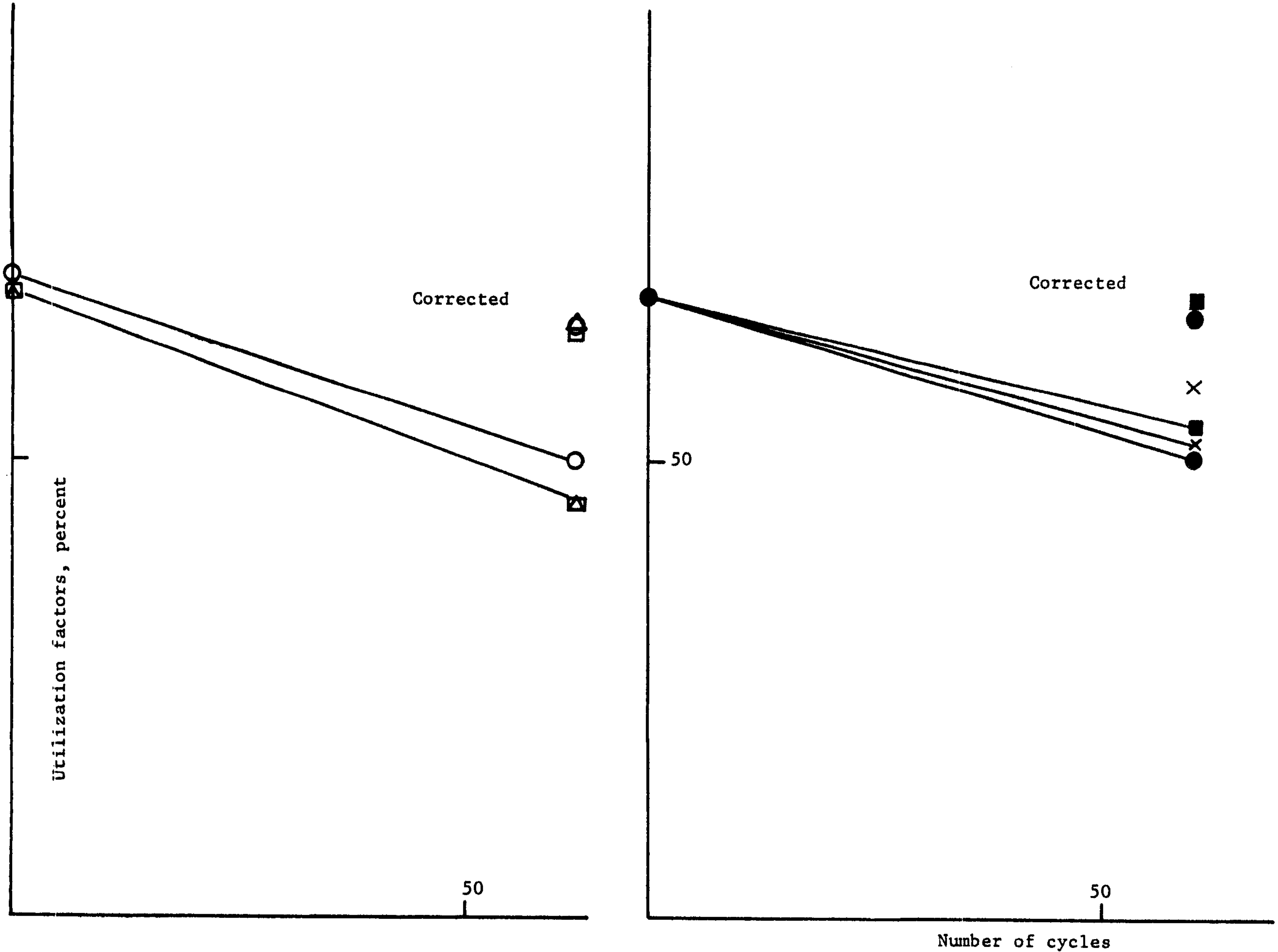


FIGURE 10

UTILIZATION FACTORS vs. NUMBER OF TEST CYCLES FOR TEST GROUP IV

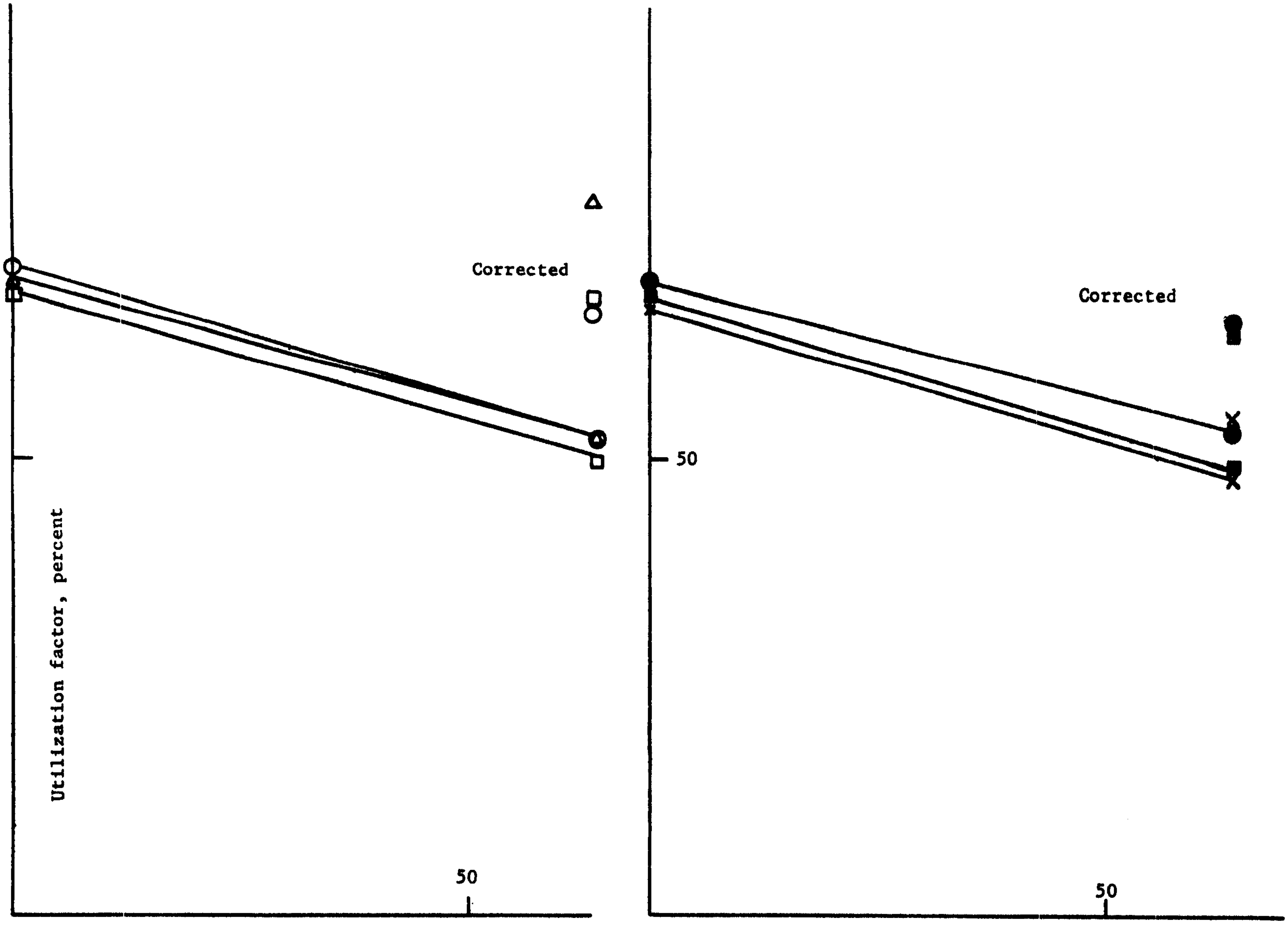


FIGURE 11

TABLE 16

TEST GROUP AVERAGES FOR LOSS OF ACTIVE MATERIAL IN PERCENT OF INITIAL VALUES

	Test Group			
Material	I & II	III	IV	Total Average
1-10	41	27	24	31
M-10	38	27	26	30
2-10	54	35	34	41
All 10	44	30	28	34
1-20	24	26	20	23
M-20	26	23	19	23
All 20	25	25	20	23
All Experimental	37	28	25	30
GE	15	14	12	14

The final Table 17 shows how the number of necessary cleaning operations of cells was distributed among plaque materials and test groups. The most striking observation is the extremely small number of cleanings which was necessary in case of the cells containing GE control compared to those with experimental material.

Recalling the fact that the controls lost about half the percentage of active materials of that of experimentals, this indicates that a given cell design can cope with a limited amount of freely moveable active material before the cell is rendered inoperable due to internal short circuits.

6.5 Conclusions

These following conclusions pertaining to this part of the program could be drawn:

1. The application of identical capacity test conditions resulted in different performance of the experimental and control material with respect to losses of active material from the plates.

2. The heavier losses of active material encountered by the experimental material can be attributed to their different pore size distribution, which obviously favors the cadmium migration.

3. The losses of active materials resulted in a series of internal high resistance short circuits which could at least temporarily be overcome by a careful cleaning of the experimental cells. This treatment is certainly not applicable to sealed cells.

4. The utilization of active material observed were about the same for experimental and control materials, and showed a steady decline with increasing number of charge-discharge cycles.

5. However, when the losses of theoretical capacity due to losses of active material were taken into consideration, the interesting fact was revealed that the utilization of the active material still within the pores of the plaques was hardly changed at all with increasing number of cycles.

TABLE 17

NUMBER OF CELL CLEANINGS

Item	I & II	III	IV	Total
1-10	6	2	5	13
M-10	2	2	9	13
2-10	7	6	8	21
All 10	15	10	22	47
1-20	2	2	6	10
M-20	6	1	6	13
All 20	8	3	12	23
All Experimental	23	13	34	70
GE	2	0	0	2

7.0 GENERAL CONCLUSIONS

1. The investigation of physical properties revealed that considerable portions of all five expermental materials did not conform to the specification of the material procurement.

2. Pronounced trends in changes of physical properties across the surfaces of the so-called master plaques resulted in an unusually wide spreading of data compared to the corresponding values of the control material.

3. The two points just mentioned, seem to illustrate that the manufacturing process for the experimental plaques has inherent inhomogenities when plaques of 1/2 or 1 square foot size, respectively, are involved.

4. In the course of the impregnation procedure the experimental material became extremely stiff and brittle and required great care in handling. However, the previous flexibility was partially restored by the electrochemical cleaning.

5. The most significant and unfavorable deviation of properties from those of the control material is believed to be the larger mean pore sizes and different overall pore size distribution of the experimental material.

6. Consequently, these larger pores obviously favored the inherent cadmium migration which in turn led to greater losses of active material from the experimental plaques, followed by a greater number of high resistance short circuits within the experimental cells under identical test conditions.

7. The utilization of the active material was about the same for both experimental and control material. A rather flat maximum of this utilization factor could be observed when the pores were filled to between 40 and 50% of their theoretical volume. This was ordinarily achieved with seven impregnation cycles under the pertaining conditions chosen.

8. With increasing number of operating cycles, the utilization factors of all plate materials were constantly decreasing and no significant differences could be observed.

9. When final factors of utilization of active materials were calculated, correcting for loss of active material encountered in the course of testing, it was observed that the utilization of the material still inside the pores of the plates had hardly changed at all during the testing.

10. The experimental materials investigated did not show any sign of superiority compared to the currently available controls.

8.0 RECOMMENDATIONS

Based upon the findings of Phase I of the program, we have recommended not to start with the processing of plaque material designated for Phases II and III, respectively.

Instead, an extension of the testing program of Phase I was suggested using the well-characterized material on hand under a variety of pore loadings, current regimes and separator arrangements. The result of this study will definitely prove whether or not the experimental materials have any prospects in the field of negative electrodes for the nickel-cadmium couple.

9.0 APPENDIX

9.1 Compression Study

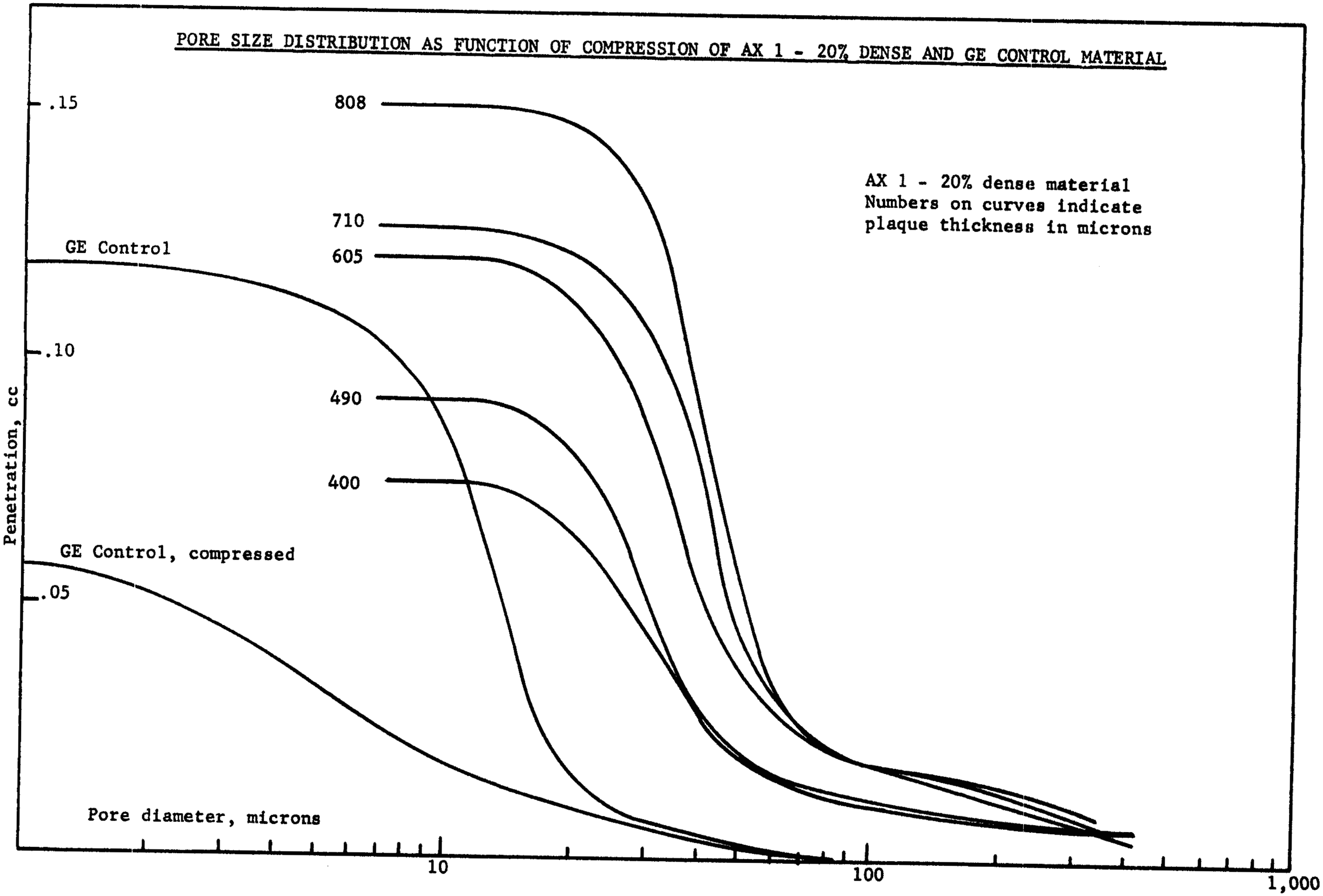
The different pore size distribution of experimental and control material was the obvious reason for the large losses of active material from the fiber plaques.

As a possible remedy for this deviation a compression of the plaque material was suggested. The degree of that compression certainly had to exceed the one used to uniformize the specific pore volumes. In order to investigate this possibility, AX1-10% and AX1-20% plaque material, respectively, were chosen for a consecutive compression. Samples were taken at predefined reductions in thickness and submitted to porosimetric measurements as described in Section 3.6.2.

The results of this treatment are shown in Figures 12 and 13. As can be seen, the compression resulted in the expected reduction in pore volume with decreasing plaque thickness. However, the mean pore size, i.e., the inflection point of the curve, was only slightly shifted towards the smaller region.

For comparison, the test was repeated with GE control material. In this case the compression resulted not only in a reduction in overall pore volume but also in an equivalent shift in mean pore size from 13 μ to about 6 μ.

This different response to the same treatment seems to indicate that profound differences exist inside the porous structures of the experimental and control material.



PORE SIZE DISTRIBUTION AS FUNCTION OF COMPRESSION OF AX 1 - 20% DENSE AND GE CONTROL MATERIAL

AX 1 - 20% dense material
Numbers on curves indicate
plaque thickness in microns

FIGURE 12

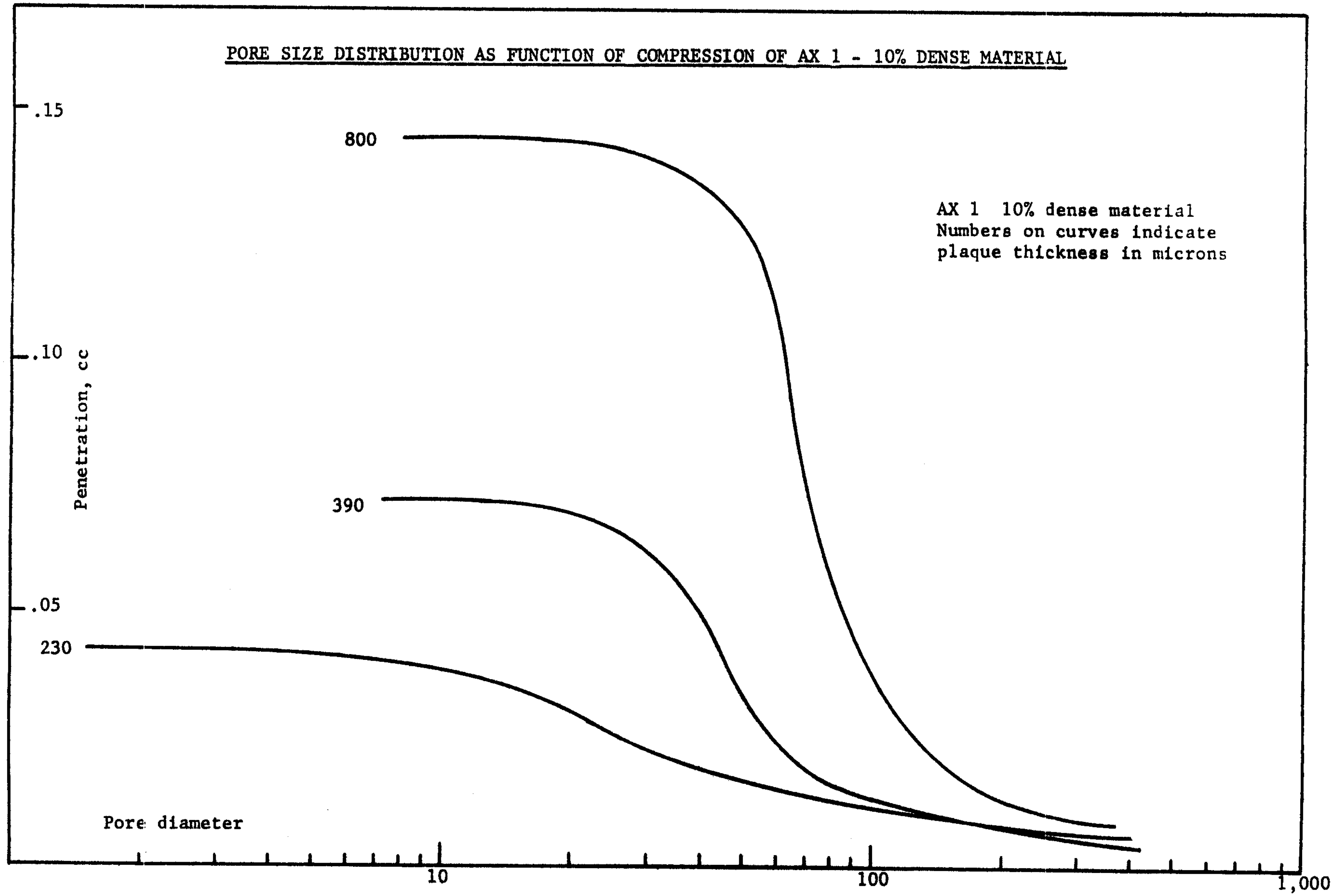

PORE SIZE DISTRIBUTION AS FUNCTION OF COMPRESSION OF AX 1 - 10% DENSE MATERIAL

FIGURE 13