AI–66–149

EFFECTS OF HIGH-ENERGY PROTONS ON SELECTED CELLS

Final Report

June 1966 to August 1966

Prepared for

Jet Propulsion Laboratory

Under Contract No. 951648

NASA

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC.

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By

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I. SUMMARY

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Experimental silver-cadmium and nickel-cadmium cells containing commercial battery electrodes and aqueous potassium hydroxide electrolytes were exposed to 60 and 137 Mev protons in the Harvard Cyclotron. Total integrated proton fluxes were twice the maximum values anticipated from solar flare activity during travel to Venus in 1967-69. Irradiated and control cells were examined for gas evolution, loss of electrode materials, and changes in discharge capacity. With the exception of low-level, rapidly-decaying radioactivity, no proton effects were detectable.

Author

II. INTRODUCTION

High-energy protons originating from solar flares are encountered by space vehicles in the Mariner programs of the Jet Propulsion Laboratory. An integrated exposure approaching 1×10^{10} protons/cm^2 is anticipated in travel to Venus during 1967-69. This report describes an experimental study of silver-cadmium and nickel-cadmium cells which was conducted to determine the effects of such proton exposures on commercial battery electrodes in the usual aqueous potassium hydroxide electrolyte solutions.

Proton showers equivalent to twice the above exposures at energies of 60 and 137 Mev were produced in the Harvard Cyclotron in exposure times of approximately one-half hour. Following irradiation, the experimental cells were examined for gas evolution, loss of solid materials, and changes in discharge capacity.

III. EXPERIMENTAL

The experimental procedures were generally similar to those employed in a concurrent program for the study of gamma radiation effects on silver and zinc battery electrodes. Techniques and circuitry are described in recent reports.[1] The proton irradiations were conducted at Harvard University. Pre- and post-irradiation work was performed at Atomics International in Canoga Park, California. Certain modifications in procedures that were made to satisfy time and transportation requirements are indicated below.

A. CELLS

As in previous work, the inner cells were constructed of radiation-resistant polystyrene, with fritted quartz separators. To prevent spillage in shipping, these cells were provided with sealed lids, as shown in Figure 1.

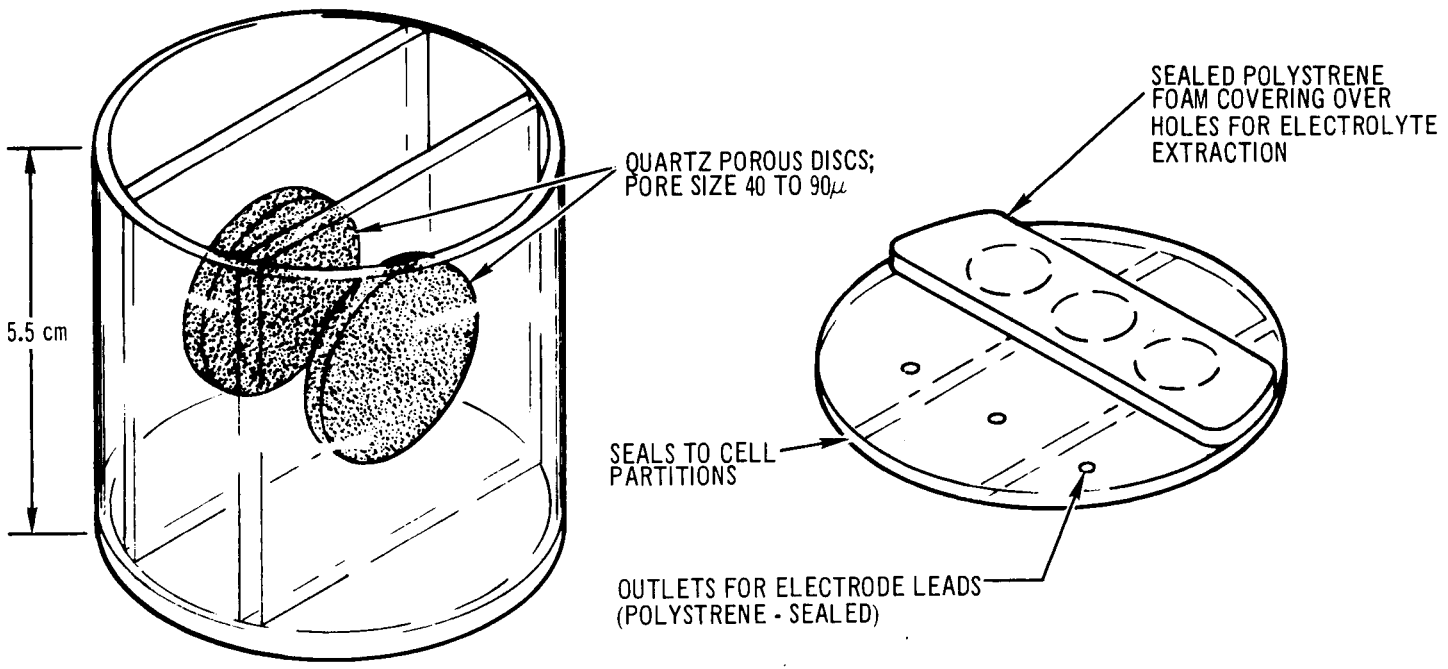

FIGURE 1. POLYSTYRENE CELL AND LID

The openings above each compartment were closed with a sealed foam covering that could be punched out for easy removal of liquid and detached solids. This precaution was taken to facilitate remote handling of the cells, in the event that they retained a hazardous level of radioactivity after exposure to protons. Small openings were made in the foam covering immediately prior to irradiation to permit the collection of gases in an outer cell container. Black spray paint was applied to the outer surfaces of the plastic cells that contained silver electrodes to avoid exposure to light.

The absorption of protons in dense materials is significant, even at high energies. Hence, it was undesirable to use the stainless steel outer cell cases that are suitable for gamma radiation studies. Penetration distances for protons in several materials employed in the present work are given in Table I. Pyrex glass outer containers of the type shown in Figure 2 were furnished by the Jet Propulsion Laboratory to replace the steel cases in the proton experiments. This design permitted access of most of the protons to the chemical system under study and provided for the direct visual observation of pressure.

TABLE I

PENETRATION DISTANCES OF PROTONS IN IRRADIATED MATERIALS[a]

Proton Energy Mev	Penetration Distance in Centimeters				
	Air	Quartz	Polystyrene	40% Potassium Hydroxide	Silver
20	400	0.22	0.40	0.41	0.083
80	510	2.59	5.02	4.91	0.87
140	1400	6.94	13.5	13.1	2.21

[a]Information used in the compilation of this table was supplied by Dr. R. A. Holroyd of Atomics International. Proton ranges in g/cm^2 were obtained by the application of equations in Ref. (3).

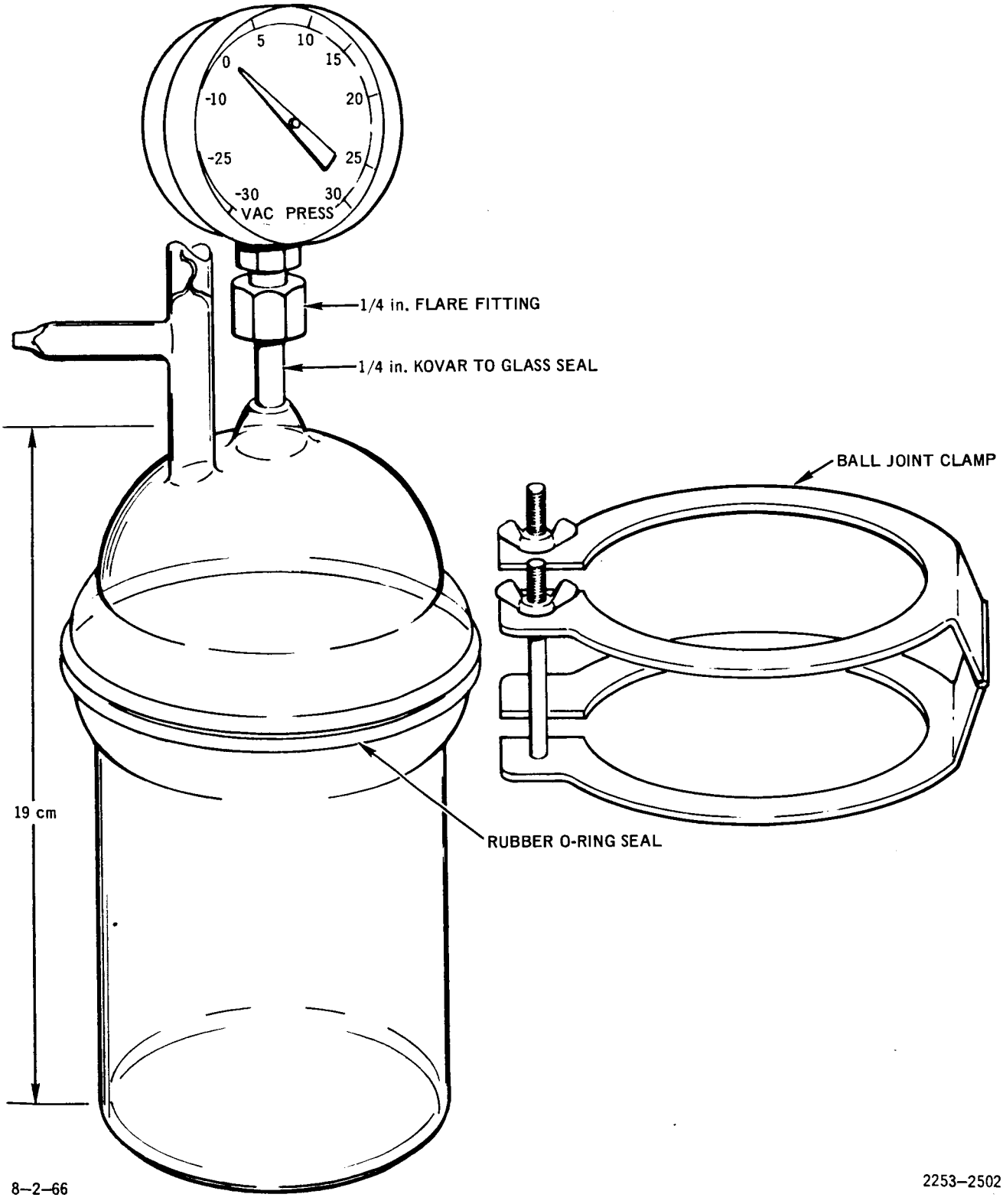

FIGURE 2. GLASS CONTAINER FOR CELLS

B. ELECTRODES AND ELECTROLYTES

The types and configurations of electrodes used in the proton study are given in Table II. The silver and cadmium electrodes were the kind recently used in gamma radiation work on silver-limited cells.[1] Although nickel and cadmium electrodes of the types investigated in an earlier gamma radiation program[2] were desired, they could not be obtained in time to meet the schedule at Harvard. Eveready R-2 electrodes were therefore used in the cells that were intended to have cadmium-limited capacities. The silver-cadmium cells were assembled with the single silver plate in the central compartment and the two parallel-connected cadmium plates in the outer compartments. In the nickel-cadmium cells, the cadmium plate occupied the central position, with a nickel plate in each of the outer compartments.

TABLE II

ELECTRODES FOR PROTON IRRADIATION CELLS

Experimental Cell	Anode	Cathode
Silver-cadmium	Two parallel-connected Eveready R-2 cadmium plates, total nominal capacity 1.0 amp-hr	One Yardney silver plate, trimmed to nominal capacity of 0.4 amp-hr
Nickel-cadmium	One Eveready R-2 cadmium plate, nominal capacity 0.5 amp-hr	Two parallel-connected Eveready R-2 nickel plates, total nominal capacity 0.8 amp-hr

The electrolyte was 40% potassium hydroxide in the silver-cadmium cells and 30% in the nickel-cadmium. These are the concentrations most frequently used in the gamma radiation studies.

C. PROCEDURES

The sequence of experimental steps is outlined for the silver-cadmium cells in Figure 3 and for the nickel-cadmium in Figure 4. The current density for the measurement of discharge capacities was 7.25 ma/cm^2 on the silver electrodes and 9.6 ma/cm^2 on the nickel electrodes, which proved to be capacity-limiting in the nickel-cadmium cells. Cycling currents in the preconditioning stages were chosen to give a 5% capacity change in 15 min.

It was impractical to transport the cycling equipment to Harvard for short-term use. The cells were therefore irradiated at a fixed state of charge. In the silver-limited cells the charge was adjusted accurately to 90% immediately before exposure to protons. Because of their erratic behavior in pre-irradiation stages, the nickel-cadmium cells were fully charged at Atomics International and exposed to protons at Harvard without further adjustment of the charge. The open-circuit potential of the central electrode plate against each of the outer plates was checked in all of the cells before and after shipment.

Immediately before irradiation, a pin-hole was punched in the foam covering above each cell compartment, the cell was returned to a glass container, in which it had been shipped, and the atmosphere inside was changed to nitrogen by repeated partial evacuation and filling, without boiling the electrolyte solution. Finally, the side-arm was sealed with a torch. The cell then remained sealed until the break-off tip was broken for gas analysis after return to Atomics International.

Two runs were made in the cyclotron--one at an energy of 60 Mev and one at 137 Mev. In each case, a total integrated flux of 2.1 x 10^{10} protons/cm^2

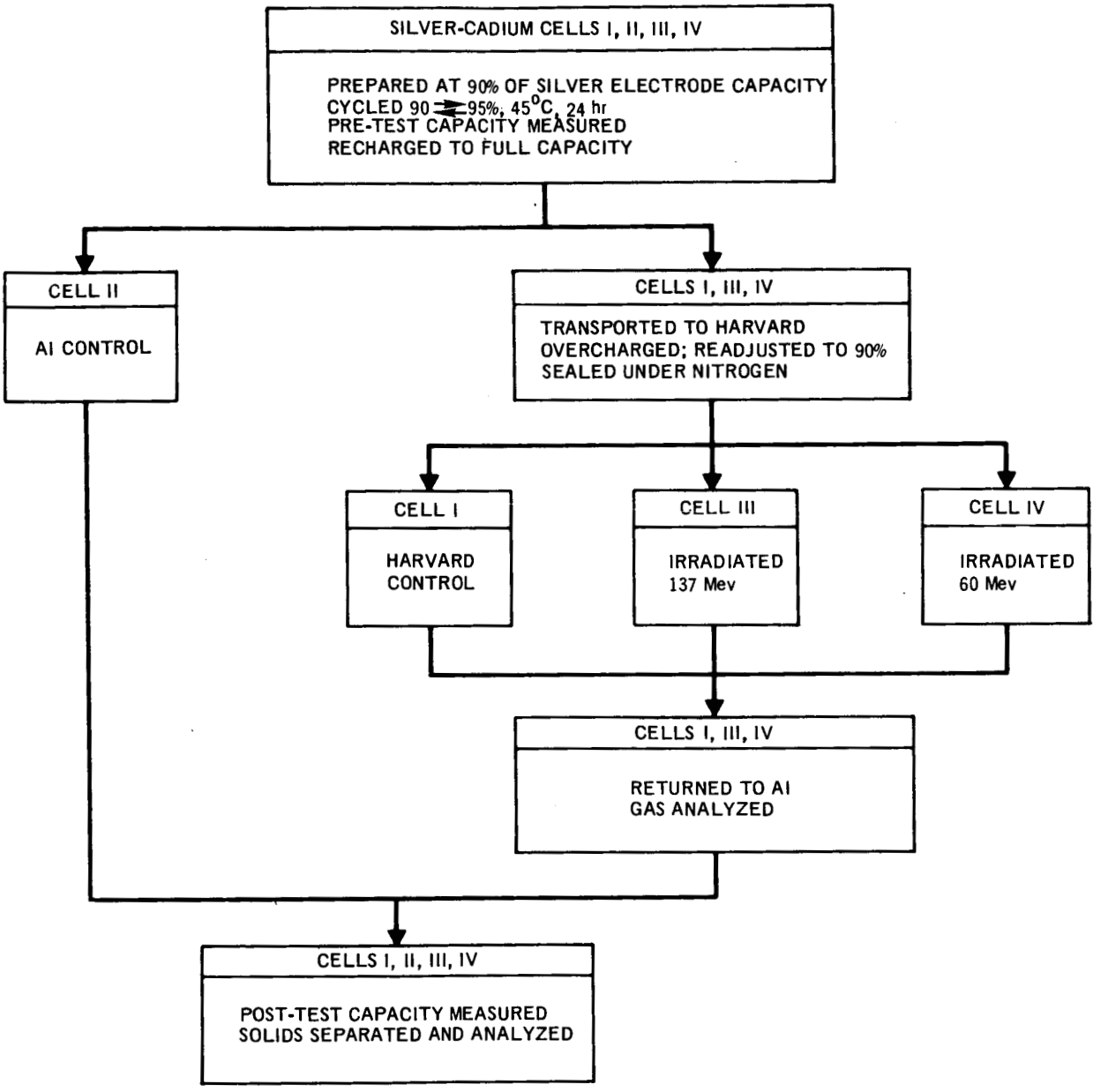

FIGURE 3. EXPERIMENTAL PROCEDURE FOR SILVER-CADMIUM CELLS

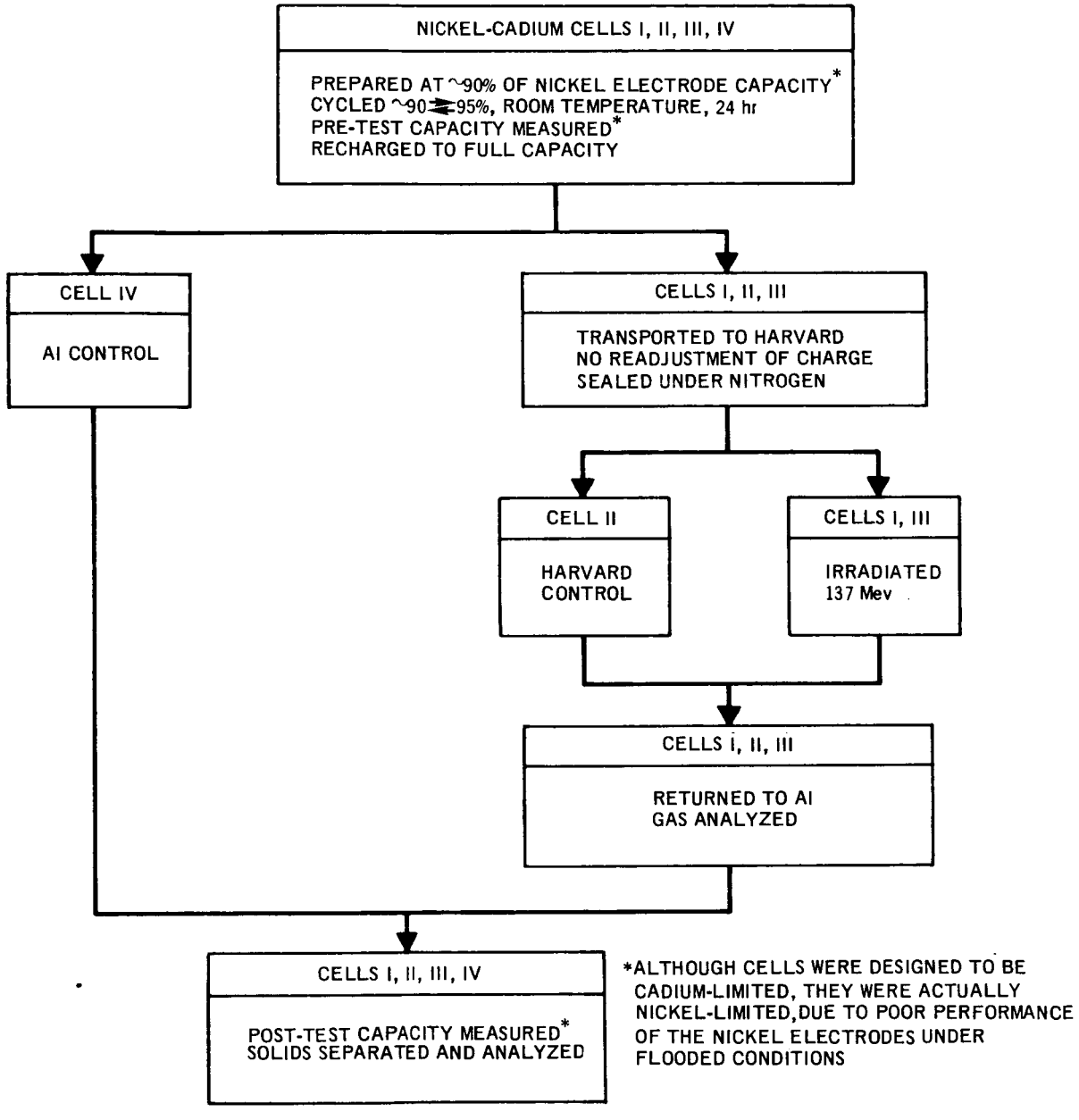

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FIGURE 4. EXPERIMENTAL PROCEDURE FOR NICKEL-CADMIUM CELLS

impinged on the cells.[a] These exposures were produced by the summation of intermittent proton pulses of several minutes duration. The experimental cells exposed in each run are identified in Figures 3 and 4 in subsequent tables. The nickel-cadmium cells were exposed at only one proton energy because of the variability already known to exist in the capacity data. A photograph of the cells positioned in the beam for the 137 Mev run is reproduced in Figure 5. The attached pressure gages were readable on closed-circuit television during the cyclotron runs.

IV. RESULTS AND DISCUSSION

A. PRELIMINARY OBSERVATIONS

Pre-irradiation capacities of the silver-cadmium cells were determined to $\pm$ 1% or better. The nickel-cadmium cells showed erratic behavior, however, which was traced to the nickel electrode by the use of a mercury-mercuric oxide reference half-cell. Although the total capacity of the two parallel nickel plates was nominally 0.8 amp-hr, and that of the cadmium counter electrode was only 0.5 amp-hr, the cell capacity, in practice, was limited by the nickel system. This problem was attributed to poor performance of the nickel plates when operated in a submerged, or flooded, condition. The powdered nickel oxide was dislodged within the perforated metal frame by gas evolution during the charging and discharging processes, and some of it was lost to the bottom of the cell in this way. Since the desired electrodes could not be obtained in the time available, the work was continued with the faulty cells.

Open-circuit potentials of the various pairs of electrode plates, before and after shipment, are recorded in Tables III and IV. In the silver-cadmium

[a] After corrections for meter error and distances from the center of the beam, the exposures in protons/cm^2 at 137 Mev were: Ag/Cd III (2.07×10^{10}); Ni/Cd I (2.05×10^{10}); Ni/Cd III (2.06×10^{10}). At 60 Mev the exposure was Ag/Cd IV (2.10×10^{10}).

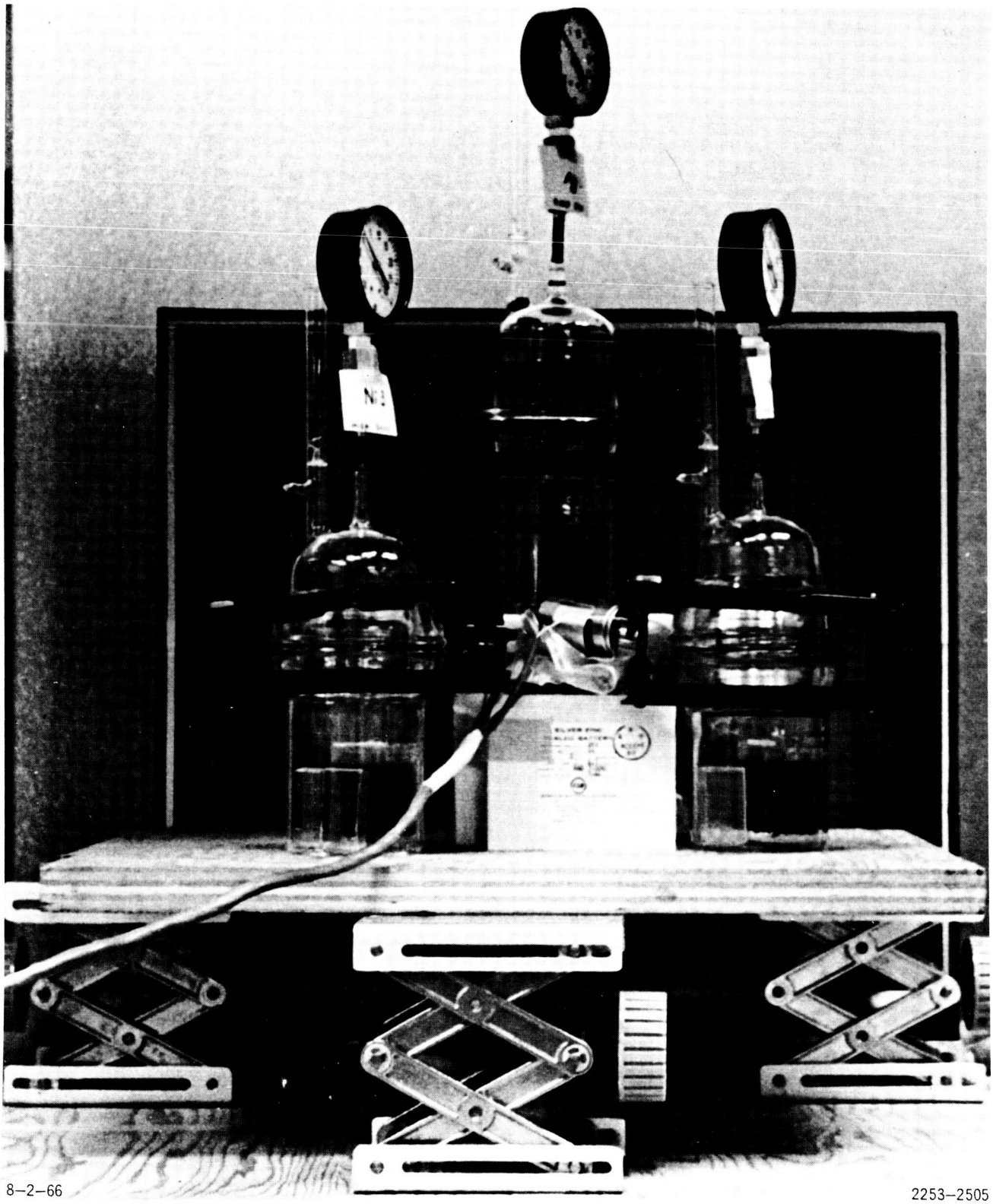

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FIGURE 5. CELLS POSITIONED IN CYCLOTRON BEAM

cells, the potentials at Harvard agreed quite well with those observed before shipment. The nickel-cadmium potentials were somewhat unstable in both cases, but all of the connections remained intact.

TABLE III

OPEN-CIRCUIT POTENTIALS IN SILVER-CADMIUM CELLS[a]

		At AI		Four Days Later at Harvard	
Cell	No.	Cd(1) volts	Cd(2) volts	Cd(1) volts	Cd(2) volts
Harvard Control	I	1.40	1.38	1.41	1.41
137 Mev	III	1.39	1.40	1.41	1.41
60 Mev	IV	1.39	1.38	1.41	1.41

[a]Potential of silver electrode versus the indicated cadmium plate; AI values were determined at full charge; Harvard values were observed before adjustment to 90%.

TABLE IV

OPEN-CIRCUIT POTENTIALS IN NICKEL-CADMIUM CELLS[a]

Cell		At AI		Four Days Later at Harvard	
Cell	No.	Ni(1) volts	Ni(2) volts	Ni(1) volts	Ni(2) volts
Harvard Control	II	1.25	1.11	1.29[b]	1.15[b]
137 Mev	I	1.10	1.25	1.33	1.24[b]
137 Mev	III	1.32	1.30	1.24[b]	1.34

[a]Potential of the indicated nickel plate versus the cadmium electrode; cells were fully charged prior to the AI measurements, and no further adjustment was made.

[b]Unsteady when cell was tapped

B. DISCHARGE CAPACITIES

Discharge capacities before and after exposure to protons are reported for the silver-cadmium cells in Table V and for the nickel-cadmium in Table VI. Also included are corresponding data for control cells, which were not irradiated. The capacities of the silver electrodes increased, on the average, by 10% between the initial and final measurements, but the changes in the irradiated cells were not significantly different from those in the controls. This result was not unexpected, since much higher total energy doses from gamma radiation have failed to change the discharge capacities of silver electrodes.[1]

For the reason mentioned above, the capacity data on the nickel electrodes were badly scattered. With the average uncertainty of $\pm$28%, radiation effects on capacity were not discernable. The greatest capacity loss was actually sustained by the control cell that remained at Atomics International; from its behavior in the initial measurements, this one was considered the least reliable of the four nickel-cadmium cells prepared.

C. GAS COMPOSITIONS

No measurable pressure changes resulted from the proton irradiation. Subsequent gas analyses, reported in Table VII, confirmed that the cell atmospheres were essentially all nitrogen, exclusive of water vapor content. Variation in the latter probably was caused by the sampling procedure and is not considered significant. The oxygen content of the irradiated nickel-cadmium cells was about twice that in the control, but the percentages of oxygen and hydrogen are quite small in all cases and may be residual amounts from the preceding electrochemical treatment.

TABLE V

SILVER ELECTRODE CAPACITIES

Cycle	Cell II, AI Control				Cell III, Irradiated with 137 Mev Protons			
	Pre-Test Capacity		Post-Test Capacity		Pre-Test Capacity		Post-Test Capacity	
	amp-hrs	Δ	amp-hrs	Δ	amp-hrs	Δ	amp-hrs	Δ
1	0.425	+0.002	0.472	+0.006	0.427	-0.002	0.485	+0.004
2	0.423	0.000	0.464	-0.002	0.432	+0.003	0.477	-0.004
3	0.422	-0.001	0.460	-0.006	0.427	-0.002	0.476	-0.005
Average	0.423	±0.001	0.466	±0.005	0.429	±0.002	0.481	±0.004
	Change + 10% (±1%)				Change + 12% (±1%)			
	Cell I, Harvard Control				Cell IV, Irradiated with 60 Mev Protons			
1	0.422	-0.004	0.475	+0.008	0.427	-0.002	0.484	+0.008
2	0.427	+0.001	0.467	0.000	0.425	-0.004	0.476	0.000
3	0.427	+0.001	0.459	-0.008	0.435	+0.006	0.472	-0.004
Average	0.426	±0.002	0.467	±0.005	0.429	±0.004	0.476	±0.004
	Change + 9% (±2%)				Change + 11% (±2%)			

TABLE VI

NICKEL ELECTRODE CAPACITIES

Cycle	Cell IV, AI Control: Pre-Test Capacity amp-hrs	Δ	Post-Test Capacity amp-hrs	Δ	Cell I, Irradiated with 137 Mev Protons: Pre-Test Capacity amp-hrs	Δ	Post-Test Capacity amp-hrs	Δ
1	0.302	-0.008	0.194	+0.023	0.306	-0.041	0.220	-0.016
2	0.367	+0.057	0.194	+0.023	0.435	+0.088	0.257	+0.021
3	0.257	-0.053	0.123	-0.048	0.304	-0.043	0.234	-0.002
Average	0.310	±0.039	0.171	±0.031	0.347	±0.057	0.236	±0.013
	Change - 45% (±22%)				Change - 32% (±20%)			
	Cell II, Harvard Control				Cell III, Irradiated with 137 Mev Protons			
1	0.439	-0.018	0.412	+0.071	0.394	-0.049	0.496	+0.104
2	0.564	+0.107	0.340	-0.001	0.530	+0.087	0.357	-0.035
3	0.370	-0.087	0.276	-0.065	0.409	-0.034	0.323	-0.069
Average	0.457	±0.071	0.341	±0.046	0.443	±0.057	0.392	±0.069
	Change - 25% (±26%)				Change - 12% (±28%)			

TABLE VII

GAS COMPOSITIONS AFTER IRRADIATION STAGE[a]

Cell	No.	Mole Percent						
		N_2	H_2O	O_2	Ar	CH_4	CO_2	H_2
Silver-Cadmium								
Harvard Control	I	98.44	0.54	0.28	0.06	0.07	0.07	---
137 Mev	III	95.85	3.44	0.26	0.09	0.07	---	---
60 Mev	IV	95.18	3.43	0.04	0.07	0.09	---	---
Nickel-Cadmium								
Harvard Control	II	96.83	2.68	0.26	0.07	0.04	0.04	0.03
137 Mev	I	94.00	5.47	0.53	0.06	0.06	0.02	0.05
137 Mev	III	94.76	4.76	0.41	0.06	0.05	0.05	---

[a]Mass spectroscopy

D. LOSSES OF SOLID MATERIALS

The quantities and compositions of solid materials recovered from the electrode compartments are given in Tables VIII and IX. The average net loss from the cadmium electrode in the silver-cadmium cells was twice that in the nickel-cadmium. This is consistent with the fact that the former contained two cadmium plates, while the latter contained only one. The silver electrode losses in both irradiated and control cells were in the range of those found for control cells in recent gamma radiation studies.[1] Material losses from the nickel electrodes accounted for only small fractions of the capacity variations, although the least stable cell, number IV, did show the greatest material loss. In no case did the protons have a detectable influence on the quantity or composition of the solid recovered.

E. RADIOACTIVITY

Immediately after the 137 Mev cyclotron run, the radiation level outside the glass containers exceeded 20 mr/hr. The activity decayed rapidly, however, and was well below 20 mr/hr for all cells in less than 24 hours.

V. CONCLUSIONS

As indicated previously, the cells in this program were subjected to proton exposures at least twice those anticipated for Mariner missions in 1967-69. It is of interest to compare the total energy incident on the cells through proton bombardment with the gamma radiation dose of 7×10^7 rads that has been applied in related programs.[1,2] The latter dose, in the form of 1.32 and 1.15 Mev gamma rays from Co^{60}, results in an absorbed energy of 7×10^9 ergs per gram of water, or 2.9×10^{11} ergs/cell, based on the water content. If attentuation by the

TABLE VIII

SOLIDS RECOVERED FROM SILVER-CADMIUM CELLS

	Cell	No.	Total Wt mg	Wt%SiO_2 [a]	Net Wt mg	Identified [b]	WtAg/WtCd [c]
Silver Compartment	AI Control	II	5.7	8.6	5.1	Ag	3.3
	Harvard Control	I	3.7	--d	--d	Ag	2.8
	137 Mev	III	4.0	--d	--d	Ag	3.6
	60 Mev	IV	3.9	--d	--d	Ag	4.7
Cadmium Compartments	AI Control	II	15.4	1.1	15.2	$Cd(OH)_2$, Ag	0.54
	Harvard Control	I	22.4	1.1	22.2	$Cd(OH)_2$, Ag	0.44
	137 Mev	III	21.0	4.3	20.1	$Cd(OH)_2$, Ag	0.42
	60 Mev	IV	24.6	2.1	24.1	$Cd(OH)_2$, Ag	0.46

[a] Emission spectroscopy

[b] X-ray diffraction

[c] X-ray fluorescence

[d] Insufficient sample

TABLE IX

SOLIDS RECOVERED FROM NICKEL-CADMIUM CELLS

	Cell	No.	Total Wt mg	Wt%SiO_2[a]	Net Wt mg	Identified[b]	WtNi/WtCd[c]
Nickel Compartments	AI Control	IV	41.2	1.1	40.8	$Ni(OH)_2$, $Cd(OH)_2$	5.1
	Harvard Control	II	19.4	21	15.2	$Ni(OH)_2$, $Cd(OH)_2$	5.9
	137 Mev	I	16.3	6.4	15.3	$Ni(OH)_2$, $Cd(OH)_2$	6.0
	137 Mev	III	24.1	6.4	22.6	$Ni(OH)_2$, $Cd(OH)_2$	5.6
Cadmium Compartment	AI Control	IV	10.4	19	8.4	$Cd(OH)_2$	0.49
	Harvard Control	II	9.3	--d	--d	$Cd(OH)_2$	0.56
	137 Mev	I	10.1	6.4	9.5	$Cd(OH)_2$	0.84
	137 Mev	III	14.8	4.3	14.2	$Cd(OH)_2$	0.52

[a] Emission spectroscopy

[b] X-ray diffraction

[c] X-ray fluorescence

[d] Insufficient sample

glass and polystyrene is neglected, the filled portion of each cell in the proton study received approximately 4.0×10^{11} protons. This number of protons corresponds to an incident energy of 8.8×10^{7} ergs/cell at 137 Mev, and 3.8×10^{7} ergs/cell at 60 Mev. Only fractions of these energies were absorbed, according to Table I.

The total energy incident on the cells in the proton experiment was thus three to four orders of magnitude lower than that absorbed in the gamma radiation studies. From these energy considerations alone therefore, no detectable proton effects were anticipated, and none was observed. Unpredicted radiation effects of a specific nature are sometimes encountered, however, and this program was undertaken as a precaution against such an occurrence with battery electrode systems in critical space missions. Parallel work on complete batteries in flight configuration, which was performed at the same time, will be reported by the Jet Propulsion Laboratory.

ACKNOWLEDGEMENTS

The outer glass containers for the cells were designed and supplied by Mr. G. L. Juvinall of the Jet Propulsion Laboratory. Thanks are due also to the Jet Propulsion Laboratory for coordinating the arrangements at Harvard University and for providing the photograph in Figure 5. Dr. C. D. Bingham and Dr. R. A. Holroyd of Atomics International were consultants on this program.

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