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THE EFFECTS OF RADIATION ON NICKEL-CADMIUM BATTERY ELECTRODES. I

Final Report

June 1963 to April 1965

Prepared for Jet Propulsion Laboratory

Under Contract No. 950514

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By

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TABLE OF CONTENTS

TABLE OF CONTENTS

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES

LIST OF TABLES

I. INTRODUCTION

Batteries represent the source of secondary power on almost all space vehicles. On any mission these vehicles and thus the batteries are subjected to various types of radiation from cosmic rays or the Van Allen belts. Future missions may incorporate nuclear reactors as the primary power source in the vehicle with batteries acting as the secondary power for start-up, standby and peak power requirements. The batteries may thus be in high radiation fields in this application. To study the effects of high radiation fields on these batteries, the nickel-cadmium system was chosen from the current types of rechargeable systems being used.

Previous studies[1,2,3] of nickel-cadmium batteries in radiation fields have been limited to an examination of the voltage and capacity before and after irradiation of the whole battery. A loss in capacity was evident from the data in one paper but was not discussed.[3] This present report describes a study of the behavior of the nickel and cadmium electrodes of cells operating in a flooded condition in a radiation field, and presents information on (a) the loss of material from the electrodes, (b) the radiolytic decomposition of the electrolyte, and (c) some electrochemical changes which were observed, including capacity loss by the cadmium electrode.

Irradiation of the nickel-cadmium cells to $\sim 10^8$ rads (gamma) was taken as the upper limit in the present study. The variables investigated included effects of dose rate, total dose, temperature and state of charge.

II. EXPERIMENTAL PROGRAM

A. MATERIALS AND EQUIPMENT

1. Electrode Selection and Pretreatment

Gulton Industries' nickel-cadmium type VO-.8 flat plate cells were chosen for this study, mainly because of their relatively small size and ease of separating the individual electrodes for use in our test cells. Upon receipt, these commercial cells were charged according to the manufacturer's specifications, i.e., 0.060 amperes for 17 hours. The size of these electrodes is 4.2 x 3.8 cms. The cells were disassembled and two of the three cadmium electrodes and the two nickel electrodes were then used to make two of our laboratory cells.

The laboratory cells were then discharged at 0.20 amperes to the break in the discharge curve. To insure 100 per cent charge of the cells they were charged for two and one half hours at 0.20 amperes which is equivalent to 25 per cent overcharge. Using the same current, they were then discharged to the predetermined state of charge, e.g., 75 per cent of full charge. This procedure was used for all cells. The cells were then cycled, e.g., between 75 and 70 per cent of charge, for a period of 24 hours before irradiation treatment.

2. Cell Designs for Gamma Radiation

A diagram of the type of cell used for the initial experiments is shown in Figure 1. Individual electrodes were placed in holders so that electrode spacing was a constant for all runs. The cell and holders were of quartz which was employed because of its resistance to strong alkali

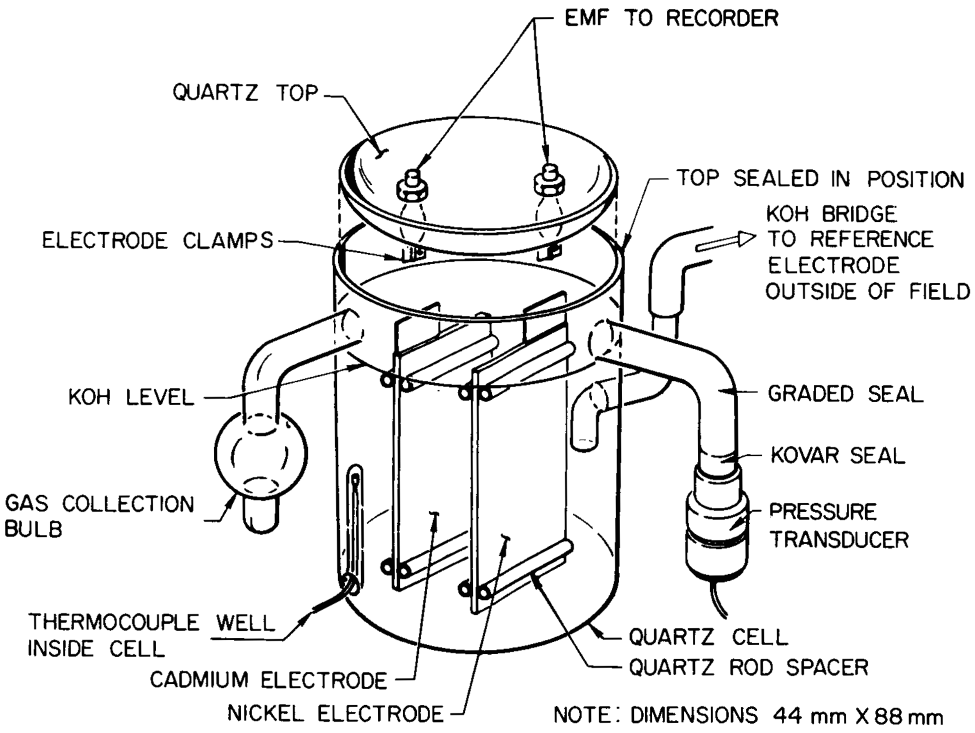

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Figure 1. Quartz Cell for Irradiations

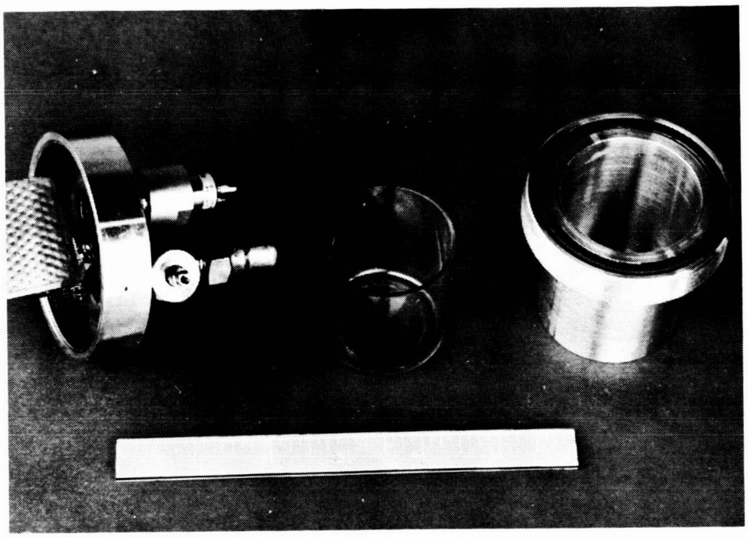

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Figure 2. Stainless Steel Cell with Quartz Liner for Irradiations

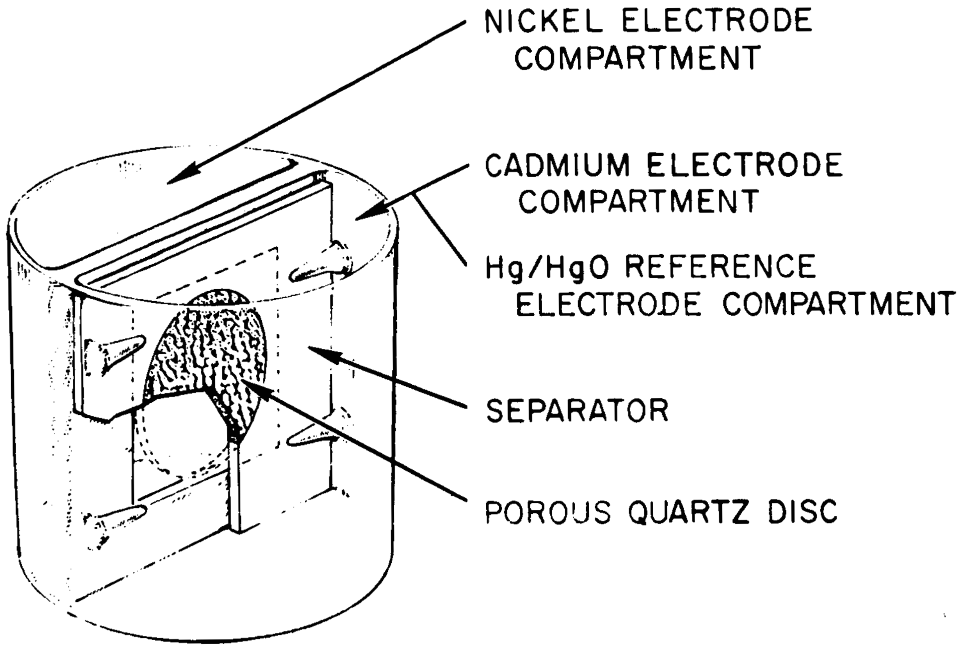

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Figure 3. Quartz Cell Liner with Porous Quartz Separator

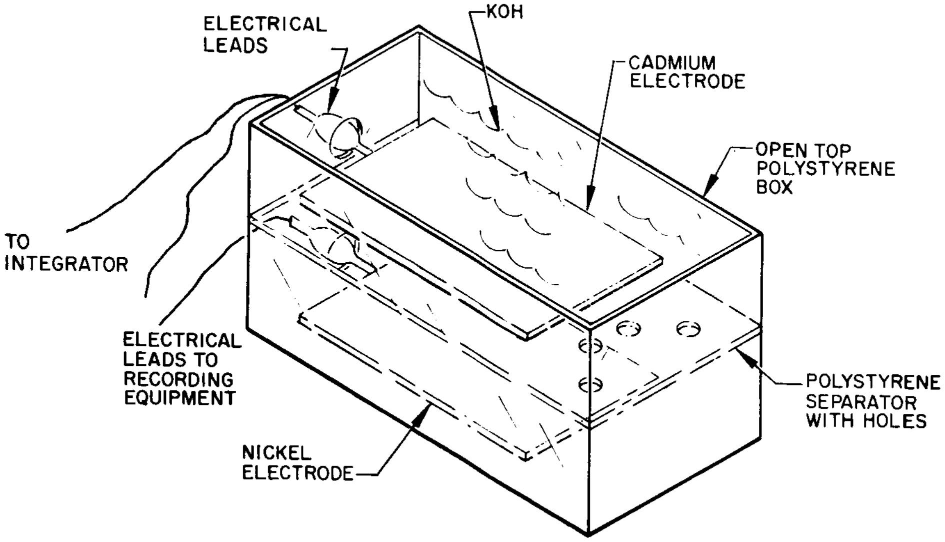

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Figure 4. Nickel-Cadmium Cell Used in 2 Mev Electron Accelerator Experiment

solutions and to radiation. This cell contained a provision for a salt bridge to a reference Hg/HgO electrode outside the radiation field. The cell also contained a small bulb for collection of gases formed during irradiation. Connected to the cell inside the radiation field was a pressure transducer of the diaphragm type, sensitive to 0.1 psi.

A later cell design is shown in Figure 2. This stainless steel cell has a quartz liner to contain the electrodes and electrolyte. This type of cell was introduced to prevent the gas leakage encountered in the quartz cell design. The reference electrode had to be incorporated inside the cell in this design. Comparison of electrode potential data from these cells and those of the earlier design obtained during irradiation runs indicated no effect on the reference electrode potential by the radiation. A cell identical to this was used for the standard 45°C bath runs. The quartz liner with divided compartments, shown in Figure 3, was used during the studies concerned with material loss from electrodes.

3. Cell Designs for Electron and Neutron Radiation

The two compartment polystyrene cell used for electron irradiation is shown in Figure 4. Since the electron beam had very little penetrating power (0.95 gm/cm^2), the electrode to be irradiated was placed in the top compartment perpendicular to the beam and was barely covered with KOH. The cell shown in Figure 1 was modified for later runs by removing the top section of the cell and irradiating the cell and electrodes with them in a vertical position.

The cell design shown in Figure 1 was used for the neutron irradiation. The physical arrangement of the four such cells as used is

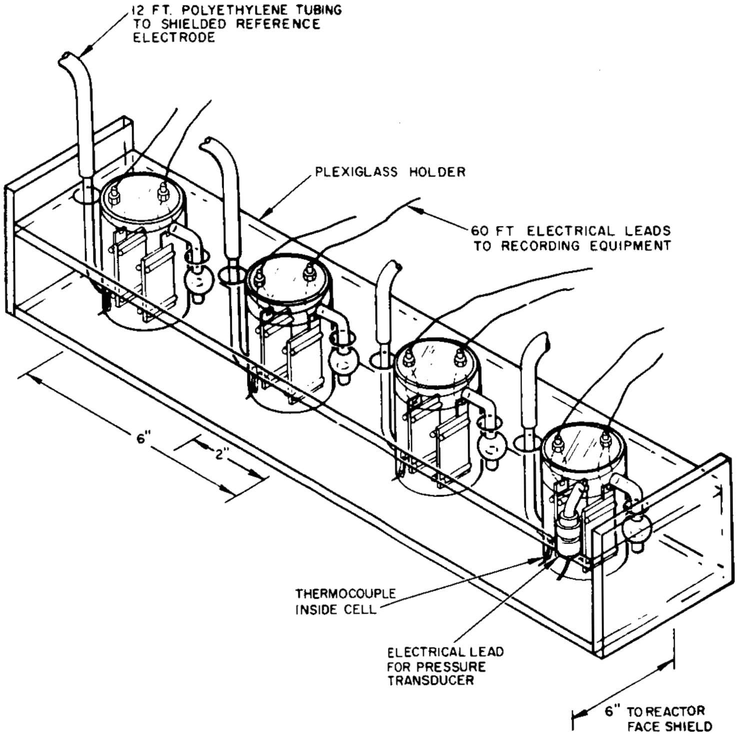

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Figure 5. Quartz Cell Used in Fast Neutron Irradiation Experimemts

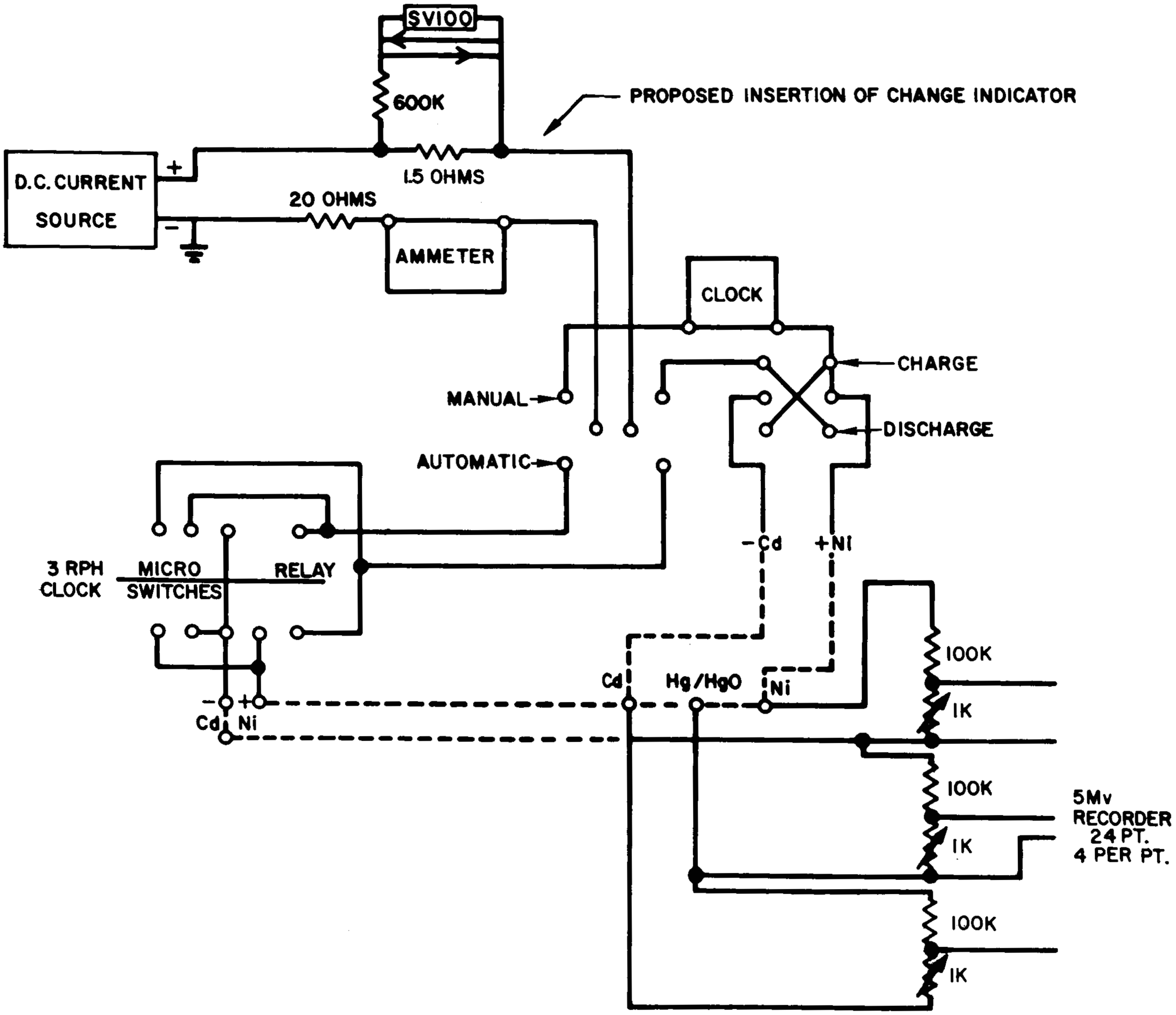

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Figure 6. Circuitry for Ni-Cd Cell Cycling

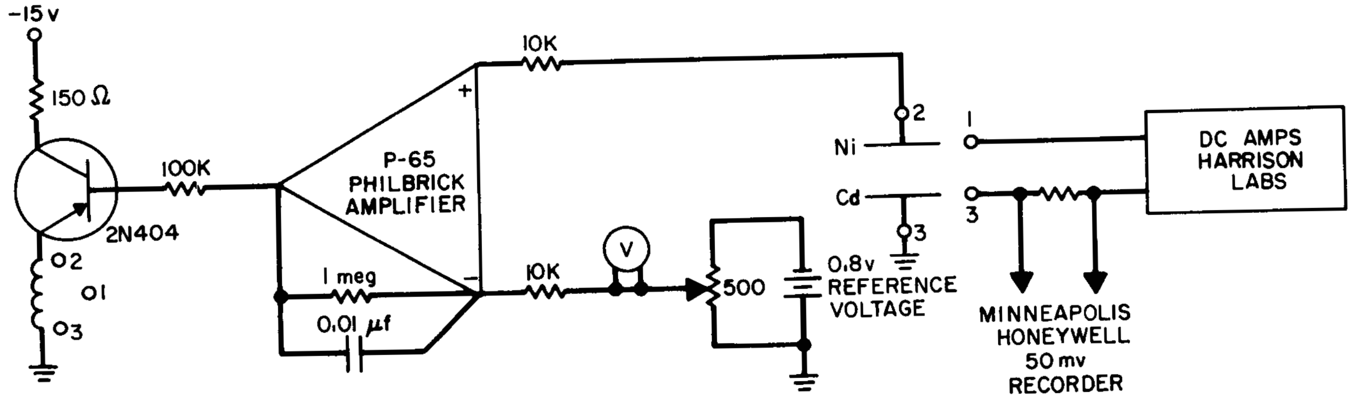

Figure 7. Capacity Measuring Circuit with Automatic Low Voltage Cut-off

shown in Figure 5.

4. Electrical Circuitry

The electrical circuit shown in Figure 6 was used to produce the cycling regime and to measure electrochemical effects during irradiation. The recorder was a Minneapolis-Honeywell Universal 5 mv instrument with ±50 mv suppression. The constant current-constant voltage source was a Harrison Lab Model #855, the timer was Kelelet Model K213 and the multicam timer was assembled from an Industrial Timer Kit #MCK. A solion device Model #SV100 from Self Organizing Systems was used to give a state of charge indication. Two completely portable electrical power and recording systems were made for convenience in taking data.

The circuit shown in Figure 7 was used to automate the capacity measurements. A two hour clock timer assembled from the Industrial Timer Kit #MCK was used so that two hours of charge could be introduced into the cells. After two hours of charge, microswitches reversed the current so that two hours of discharge current could be passed. If the cells became discharged below 0.8 V before this period, the relays cut the current off through the cells. One network of this type was used for each cell making necessary the use of two constant current supplies. The currents from these supplies were checked continuously by monitoring the voltage across a resistor. One system of this design was built and used.

B. RADIATION SOURCES

1. Co-60 Gamma Sources

Two Co-60 gamma sources were used in this investigation. Source I

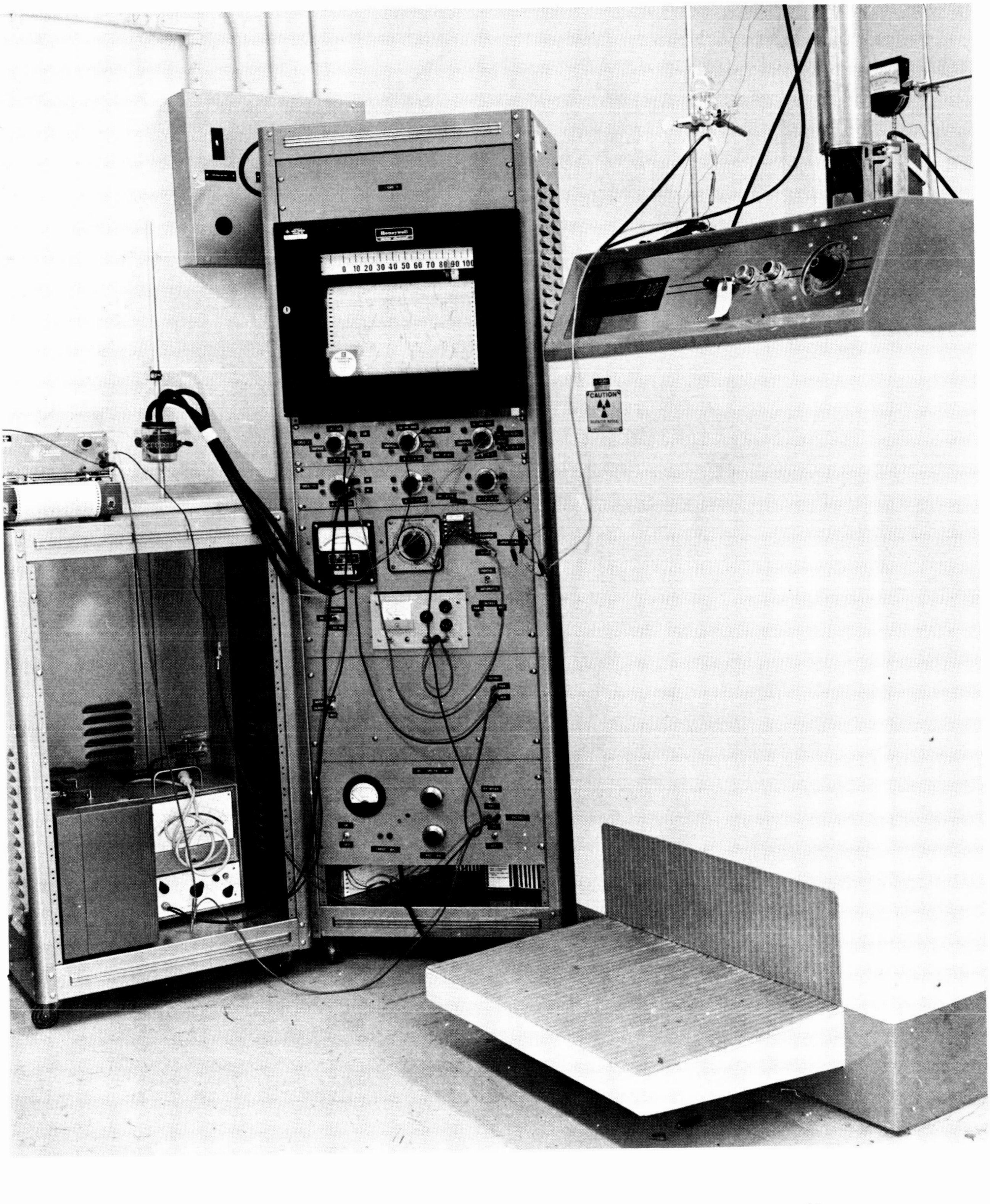

Figure 8. Test Cell Installed in NAA Science Center Co^{60} Source.

gave a dose rate of 8 x 10^4 rads (H_2O) per hour* at the position of the cell in the source.

Source II is rated at 1.4 x 10^6 rads (H_2O) per hour. This source was used for most of the runs. A picture of it and one of the consoles with measuring circuits is shown in Figure 8. The cell is placed in a well 3 inches in diameter x 5 inches deep. Leads are taken out through stainless steel spiraled tubes coming up the column from the well. The salt bridge was also brought up through one of these tubes. After hookup, the well is closed with a stainless steel cover and can then be lowered automatically into the source. When the stainless steel cell was used, the salt bridge was not needed as the reference electrode was inside the cell. A lift, attached to a timer, is available to automatically raise the sample after a predetermined dosage.

2. Electron Source

The electron source was a Van de Graaff accelerator capable of producing 2 Mev electrons at 5 μa. The dosage was monitored by integrating the current resulting from the collection of the electrons on the electrodes.

3. Neutron Source

The neutron source was a small swimming pool reactor in which a port was available for sample irradiations with either thermal or fast neutrons. The fast neutron dose rate was 6.6 x 10^3 rads (H_2O)/hour accompanied by gamma radiation of 8 x 10^3 rads (H_2O)/hour. The radiation dosage varied less than 10 per cent from the center to the outermost of the cells in the rack.

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*It is assumed for this work that the energy absorption of the electrochemical cell system is that of water.

C. EXPERIMENTAL VARIABLES

1. Introduction

Selection of specific values of variables to be employed and establishment and standardization of their effect on nickel-cadmium cell behavior outside the radiation field were established in the laboratory with respect to the following variables: current density, type of cycle, length of cycle, state of charge about which to cycle, temperature, and concentration of electrolyte.

2. Type of Cycle

The effects of radiation on the electrochemical behavior of the electrodes were investigated by following the voltage behavior of the cells during a cycling regime. A 20 minute cycle was chosen, with 6 minutes of discharge, 4 minutes open circuit, 6 minutes charge, and 4 minutes open circuit. In some early experiments this cycle was reversed. With this short cycle several cycles could be completed even during short irradiations.

3. Current

The effect of current on the cell voltage and other parameters of cell behavior was tested by operating cells at several currents. A high current, e.g., 0.40 amperes, resulted in the electrodes becoming full of bulges and pockets due either to excessive local heating or to excessive local gas evolution. Low currents, such as 0.10 amperes, were not practical because of the time involved in measurement of the cells' ampere hour capacity. An intermediate current of 0.20 ampere (25 ma/cm^2) was then chosen for use on all experiments. A Luggin capillary placed at various positions between the electrodes and behind the electrodes in a laboratory cell was used to determine that all the polarization was due to the resistance of the electrolyte. Several cells were cycled in the laboratory for extended periods of time at 0.20 ampere current with no ill effects. This constant current value was then used for all subsequent studies.

4. State of Charge

The current and cycle were chosen so that a 5 per cent change in state of charge occurs on either the charge or discharge portion of the cycle. Since normally the nickel-cadmium batteries on space missions are not discharged very deeply due to cycle life limitations, a moderately discharged condition of the cells was selected as the point about which to cycle. Initially, all cycling was carried out between 70 and 75 per cent of full charge. Later studies involved cycling cells between 95 and 100 per cent, 50 and 55 per cent, 20 and 25 per cent states of charge.

5. Electrolyte Concentration

Aqueous solutions of 30 and 35 per cent KOH have been described in the literature[3] as suitable concentrations for nickel-cadmium batteries. In our preliminary irradiation experiments, negligible variations in IR drop, polarization and total capacity of the cells were observed over the range of 25 to 40 per cent KOH. Therefore, 30 per cent KOH solution was used for all subsequent experiments. A fresh solution was prepared for each experiment in order to keep carbonate contamination to a minimum.

6. Temperature

The logical temperature for the laboratory experiments was laboratory ambient temperature which varied between 22 and 25°C. It became apparent early in the study that temperature did cause large changes in voltage characteristics of the cells. A laboratory cell in Gamma Source II achieves a temperature of 45°C, so laboratory runs were made at this temperature also. Although voltage reproducibility, upon temperature cycling a cell from 25° to 45°C and back to 25°C, was poor after 2-3 hour periods at each temperature, behavior was quite reproducible after 24 hour periods at each temperature. Because of the effect of temperature on the voltage of these cells, a reference nickel-cadmium cell was usually run outside the source at the same temperature as the cell being irradiated. No sloughing off of material from the electrodes was ever observed in these external cells during the test period.

D. EXPERIMENTAL PROCEDURE FOR CADMIUM ELECTRODE CAPACITY STUDIES

After one long (215 hrs. = 3×10^8 rads) irradiation at 75 per cent state of charge, the cell capacity was found to be limited by the cadmium electrode. As no such effect had been observed on the nickel electrode, it was concluded that the radiation had resulted in a decrease in cadmium electrode capacity. In order to study effects of radiation on cadmium electrode capacity, the cadmium electrode was made the limiting electrode using two different types of experiments. In the first type, two nickel electrodes were used. The cell size required that these two electrodes touch each other. This close proximity of the two electrodes made it difficult to extract charge from the inner sides of the electrodes due to concentration polarization and the diffusion kinetics. Nevertheless, this method was used with fair success in Run #A-1. The second approach to making the cadmium electrode limiting was to cut about one-third off the cadmium electrode. This was the more successful technique and was used in Runs A-2 through A-27.

The cells with the cadmium electrode limiting capacity were charged and discharged completely several times to get an accurate value for the cadmium electrode capacity. A current of 0.2 ampere for 120 minutes (150 minutes in Run A-1) was found to charge the cadmium electrode sufficiently to generate hydrogen on overcharge. This current and time schedule were used for charging all the cells before and after the experiments. This resulted in all cells being overcharged to some extent.

After the capacities of the cells were measured, the cells were charged at 0.2 ampere to full capacity. In Runs A-1 through A-27 the cells were then discharged to the prescribed per cent of full charge. All the cells were then run at a constant current of 0.2 ampere through a cycle of 6 minutes discharge, 4 minutes open circuit, 6 minutes charge, and 4 minutes open circuit for 24 hours prior to irradiation and the cycling was continued during the irradiation.

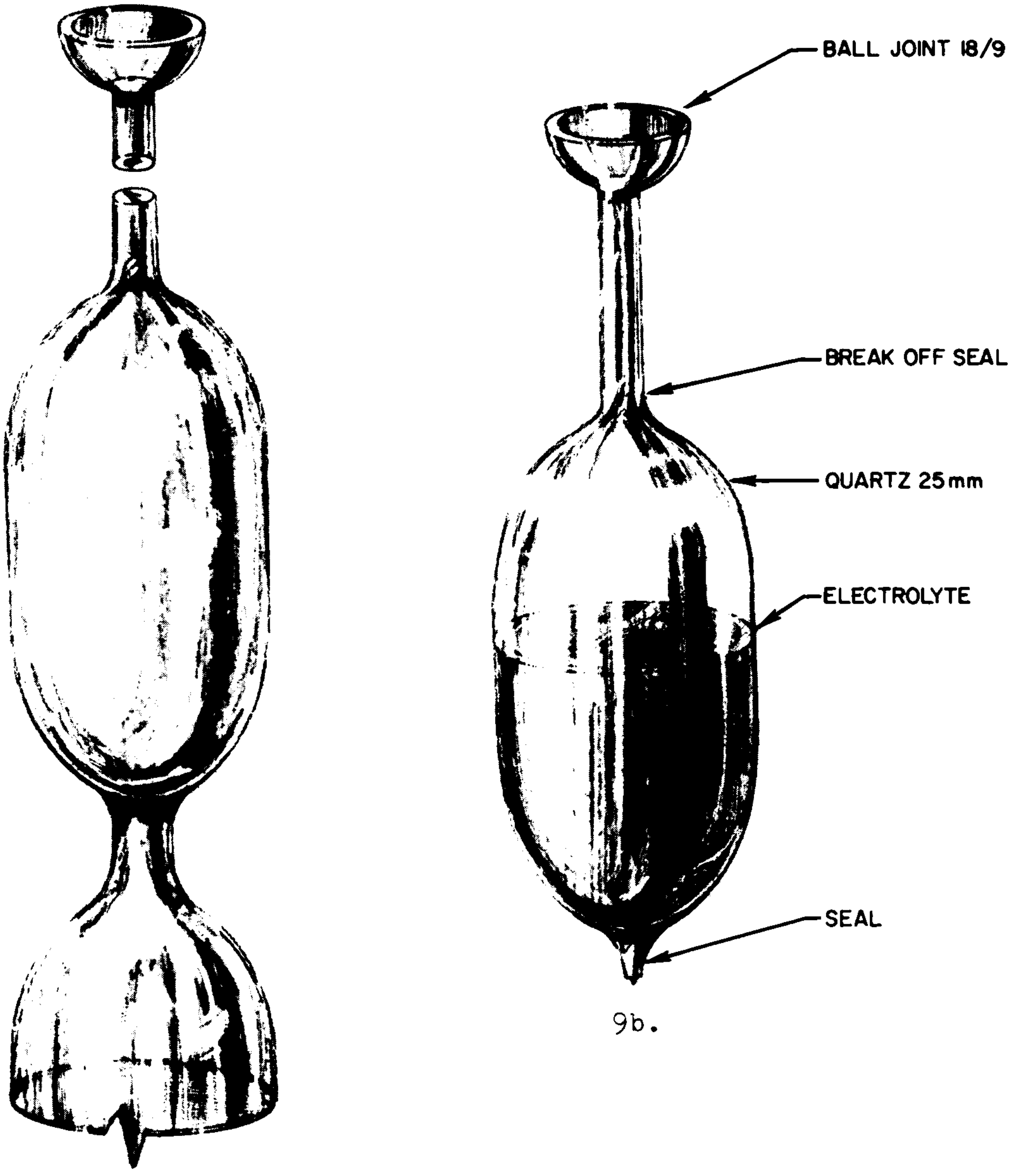
In an attempt to restore lost capacity after Run A-3, the cell, at room temperature, was fully charged and then a trickle charge of 0.050 amp passed through the cell overnight. The cell was then completely discharged and recharged several times in succession. Finally, the cell was cycled at 75 per cent of full charge for 24 hours.

E. RADIOLYSIS OF AQUEOUS KOH

Various concentrations of aqueous KOH solution from 0.5 per cent to 40 per cent were irradiated in the Co-60 gamma source to determine the radiolytic products and their dependence on the concentration of KOH. Several runs using 30 per cent KOH (the concentration used in almost all the nickel cadmium cell work) in contact with either a nickel or a cadmium electrode were made to determine the effect of the electrode material on the radiolysis process. The all-quartz cell used in this work is shown in Figure 9. Figure 9a shows the cell prior to filling. Figure 9b shows the cell after sealing. The electrolyte was put in through the open tube (Figure 9a). The cells were evacuated and back-filled with helium four times before sealing the open tube. The break-off tip of the cell facilitated removal of the gas for analysis.

The cells, after gas analysis, were left under negative pressure. Analysis was then carried out for peroxide in the electrolyte. This was done by taking aliquots of the solution, diluting them with H_2SO_4, and adding ceric sulphate. The amount of ceric ion converted to cerous by the peroxide was measured with a Beckman DU spectrophotometer; this technique has a sensitivity for peroxide of 1 μg/cc.

Similar cells were used to study the effect of electrode material on the products of the radiolysis of KOH. The electrodes were cut in strips and slipped into the cell through the narrow opening. Duplicate runs were made in all cases. In order to separate temperature effects from radiolysis effects, some duplicate cells were run for the same time without irradiation in the 45°C constant temperature bath. Two cells were irradiated containing 1 per cent peroxide in 30 per cent KOH to check on the peroxide stability.



9a.

9b.

Figure 9a. Quartz Capsules for Radiolysis Experiments
9b. Capsule Filled and Sealed

III. IRRADIATION RESULTS

A. ELECTROCHEMICAL EFFECTS

1. Voltage Changes

In Run #3 the voltages of the cell being irradiated and the 45°C reference cell diverged progressively to a difference of 10 mv at the end of 62 hours as is shown by the open circuit voltage in Figure 10. Unfortunately, in the longer run of 215 hours, #5, a similar measurement could not be made due to failure of the reference cell. This effect, because of its small magnitude, was not pursued in the later studies.

2. Capacity Changes

After the 215-hour run in Gamma Source II (Run #5), the cell was discharged at the 0.2 ampere rate. It was noted that the cadmium electrode became the electrode limiting the total capacity of the cell. This is shown in the discharge curve of Figure 11, recorded after a complete discharge and charge cycle of this cell. Tests on such cells before irradiation invariably have shown that the nickel electrode limits the cell capacity at about 0.4 ampere-hour (120 minute discharge at 0.2 ampere). During the initial discharge of the cell after the 215 hour irradiation (Run #5), the cell and specifically the cadmium electrode, went through a 70 mv voltage step downward after approximately one-third discharged. Upon recharging the cell, this step did not appear nor did it reappear on subsequent discharge. This step function was subsequently observed in every cell which was exposed to

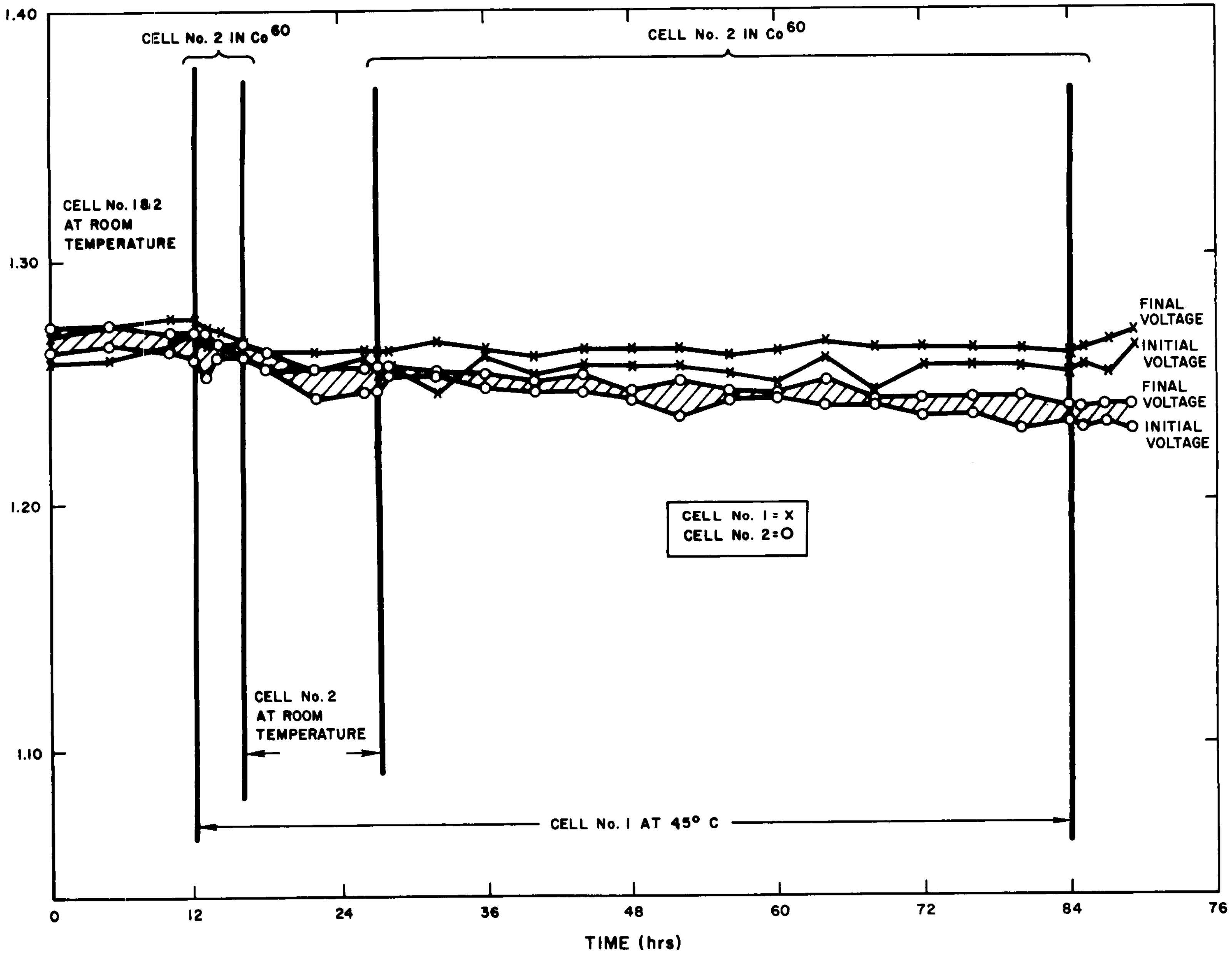


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Figure 10. Open Circuit Cell Voltage During Third Co-60 Gamma Irradiation

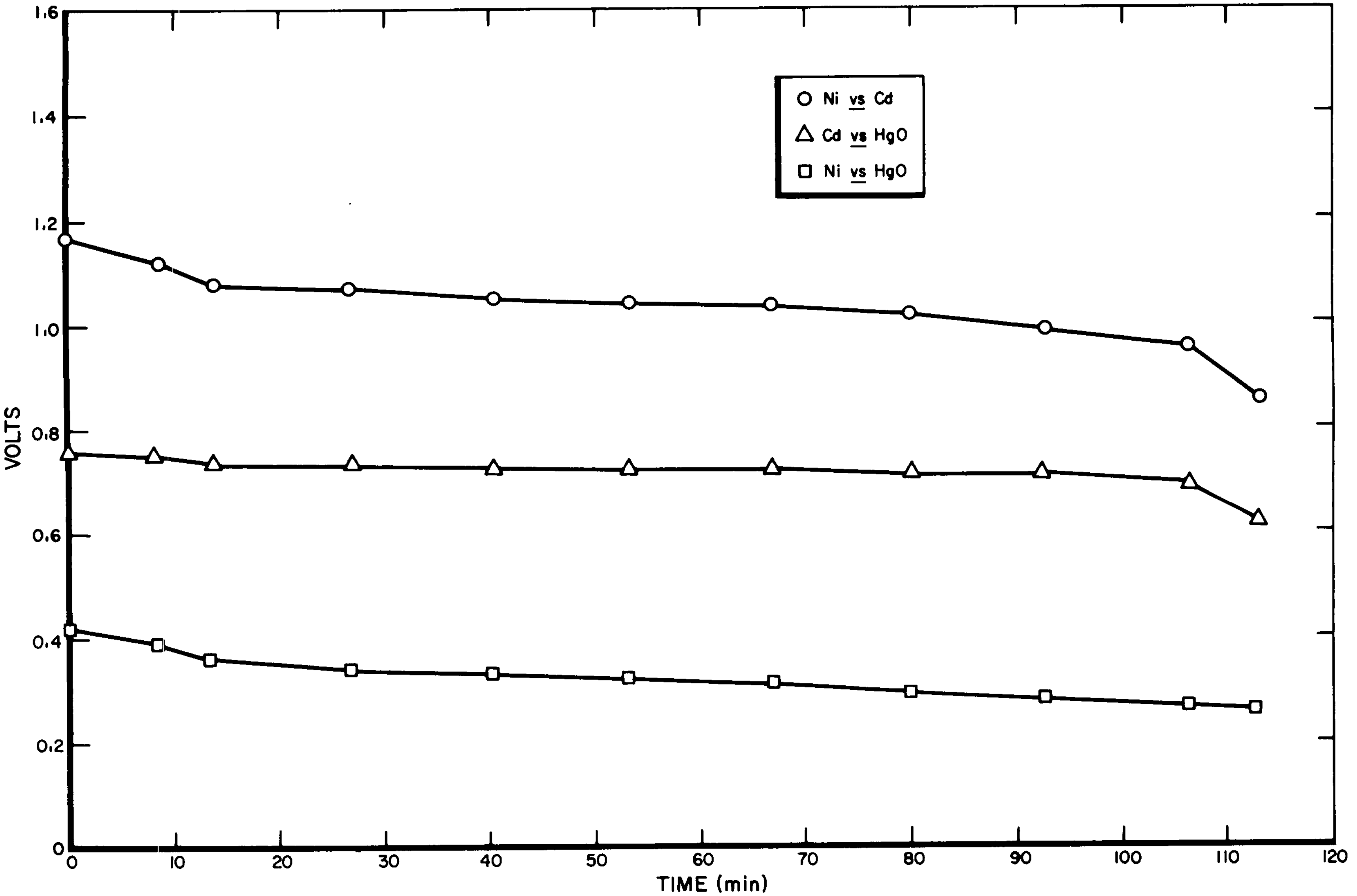

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Figure 11. Discharge Characteristics of Nickel-Cadmium Cell After Co-60 Gamma Irradiation No. 5

TABLE I. RESULTS OF CADMIUM ELECTRODE CAPACITY EXPERIMENTS: GAMMA IRRADIATION RESULTS

Run #	% of Full Charge	Initial Capacity Min. @ .2 Amp	Final Capacity Min. @ .2 Amp	% Change	Overall Average	S.D.
A-2R	100	93	88	- 5.4		
A-5R*	100	96	86	-10.4		
A-11R	100	106	111	+ 4.7	-4.5	-4.5±3.4
A-14R	100	98	91	- 7.1		
A-18R*	100	80	77	- 3.8		
A-19R*	100	97	92	- 5.2		
A-1-R	75	134	112	-16.4		
A-3R	75	107	92	-14.0		
A-13R*	75	104	97	- 6.7	-10.9	10.9±5.0
A-15R	75	100	95	- 5.0		
A-16R	75	96	89	- 7.3		
A-17R*	75	94	79	-16.0		
A-7R	50	104	100	- 3.8		
A-12R	50	103	103	0	-3.4	-3.4±2.3
A-21R*	50	77	72	- 6.5		
A-22R*	50	95	92	- 3.1		
A-23R*	25	82	81	- 1.2	+0.7	+0.7±1.9
A-24R*	25	81	83	+ 2.5		

*Separated cells

TABLE II. RESULTS OF CADMIUM ELECTRODE CAPACITY EXPERIMENT: 45° BATH RESULTS

Run #	% of Full Charge	Initial Capacity Min. @ .2 Amp	Final Capacity Min. @ .2 Amp	% Change	Overall Average	S.D.
A-2B	100	98	93	- 5.1		
A-5B	100	100	102	+ 2.0		
A-11B	100	102	100	- 2.0	+0.3	+0.3 ± 3.8
A-14B	100	103	103	0		
A-18B	100	87	89	+ 2.2		
A-19B	100	100	105	+ 5		
A-4B	75	99	97	- 2.0		
A-13B	75	101	99	- 2.0		
A-15B	75	101	98	- 3.0	-2.1	-2.1 ± 1.5
A-16B	75	108	104	- 3.7		
A-17B	75	96	96	0		
A-6B	50	105	102	- 2.8		
A-7B	50	110	115	+ 4.5		
A-12B	50	94	94	0	+1.8	+1.8 ± 1.7
A-21B	50	94	95	+ 1.1		
A-22B	50	106	104	- 1.9		
A-23B	25	88	84	- 4.8	+4.2	4.2 ± 8.8
A-24B	25	83	94	+13.0		

TABLE IIIA. RESULTS FROM CADMIUM ELECTRODE CAPACITY EXPERIMENTS: GAMMA IRRADIATION RESULTS OF CELLS UNDER SPECIAL CONDITIONS

Run #	% Full Charge	Initial Capacity Min. @ 0.2 Amp	Final Capacity Min. @ 0.2 Amp	% Change
R-25*	75	71	73	+ 2
R-26*	75	94	93	+ 1
R-27**	75	101	84	-17
R-28**	75	92	83	-10

*Open circuit cells

**Cells cycled at 0.2 amp with a cycle three times as long as normal

TABLE IIIB. RESULTS FROM CADMIUM ELECTRODE CAPACITY EXPERIMENTS: 45°C BATH RESULTS OF CELLS UNDER SPECIAL CONDITIONS

Run #	% Full Charge	Initial Capacity Min. @ 0.2 Amp	Final Capacity Min. @ 0.2 Amp	% Change
R-25*	75	74	74	
R-26*	75	90	90	
R-27**	75	Lost bath run due to temp control failure		
R-28**	75	84	79	

*Open circuit

**Cells cycled at 0.2 amp with a cycle three times as long as normal

45°C, even without radiation. Thus the behavior is a consequence of temperature alone. The hump always disappeared after the initial discharge. Two runs were accidentally discharged before the cells had cooled down to room temperature. In each case, excess capacity was observed on the initial full discharge. This trend disappeared also upon subsequent discharges.

The loss of capacity by the cadmium electrode was considered an important radiation effect and was the subject of an extensive study. Studies at 75 per cent of charge of the cadmium electrode showed that the cadmium electrode lost an average of about 11 per cent of its capacity. Studies of cadmium electrode at 100%, 50% and 25% states of charge showed little or no loss in capacity. The data on capacity loss for irradiated cells are shown in Table I. The corresponding 45°C bath data are shown in Table II. A plot of capacity loss vs state of charge is shown in Figure 12.

In contrast, two irradiation runs at 75 per cent state of charge, with the cells on open circuit, rather than the normal cycling regime showed no loss in capacity of the cadmium electrode. Thus, cycling played some part in the capacity losses observed. Two cells at 75 per cent, using a cycle three times as long, were irradiated and both lost capacity.

3. Experimental Voltammetry Data

Fast anodic and cathodic voltage sweeps were made on both the nickel and cadmium electrodes relative to the respective rest potentials, i.e., the voltage of the electrode with reference to the Hg/HgO electrode,

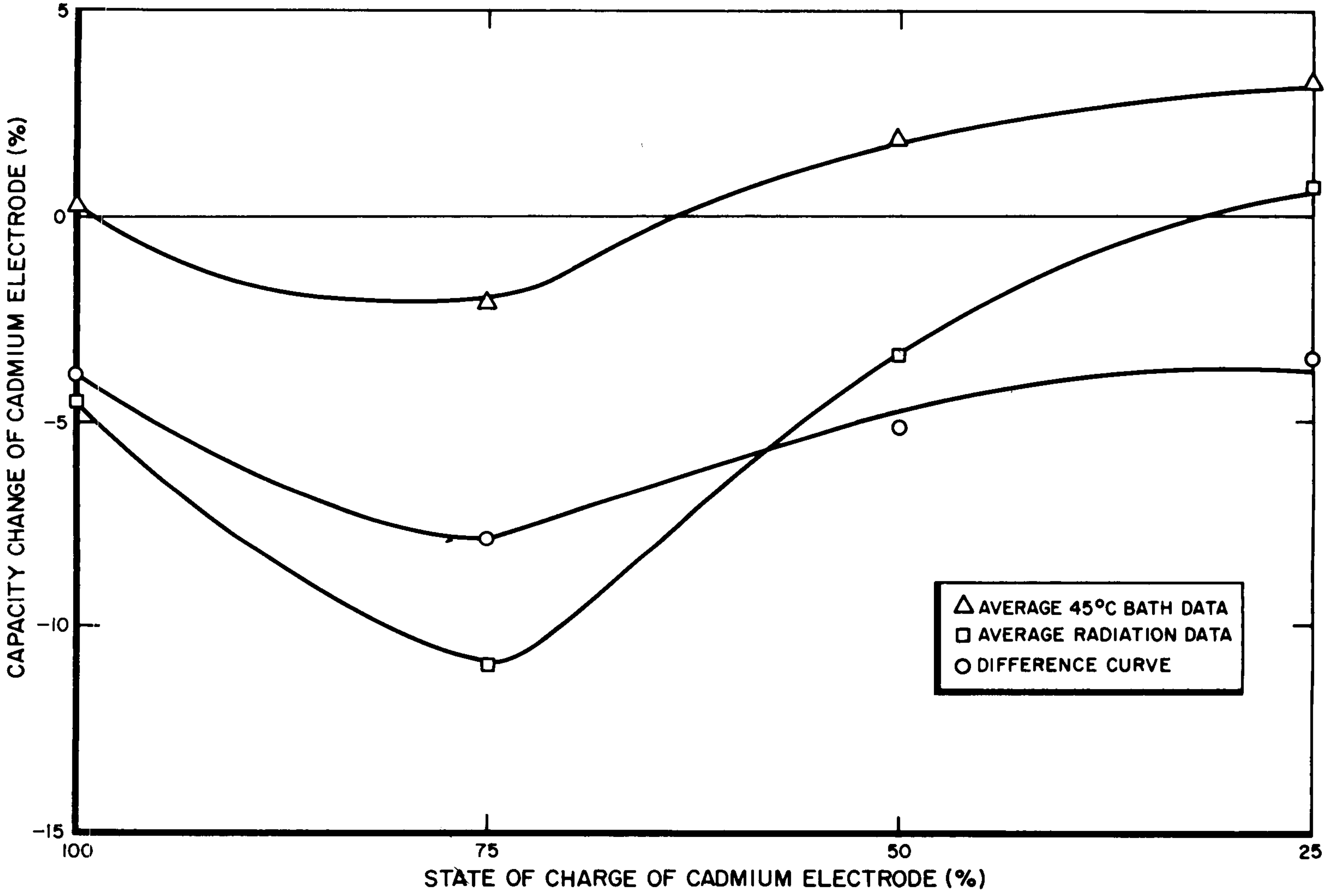

Figure 12. Capacity Loss of Cadmium Electrode *vs* State of Charge

at various times before, during and after the irradiation. The data, as shown in Figures 13 and 13A for the nickel electrode and in Figures 14 and 14A for the cadmium electrode, were calculated from the pictures of the voltage sweeps obtained from the oscilloscope. The linear IR drop was subtracted from the voltage in each case. To get the anodic and cathodic data for each case, two pictures were required; these are combined in the calculated figures to show the complete current-voltage characteristics of the electrodes. The shape of the curves indicate that other than a change in IR drop with temperature, the polarization effects were small.

B. MATERIAL LOSS FROM THE ELECTRODES

It was apparent from the very first run that some physical damage was occurring to the electrodes in that solid material was found on the bottom of the irradiated cell. This material was collected by filtration. The electrodes were washed using a wash bottle and the dislodged solids were combined with the precipitate. (An effort to insure complete removal of this loosened material by ultrasonic cleaning proved to be unsatisfactory. Ultrasonic treatment of cycled electrodes, whether irradiated or not, resulted in the loss of large amounts of material. No material loss had been obtained from similar treatment of uncharged non-cycled electrodes.) In a later experiment visual observation at half-hour intervals of a cell at open circuit conditions showed that clouding of the electrolyte began after one hour of irradiation in Source II, i.e., 1.4×10^6 rads (H_2O). The lowest total dose for which a weighable amount of precipitate was obtained was 5.8×10^6 rads (H_2O).

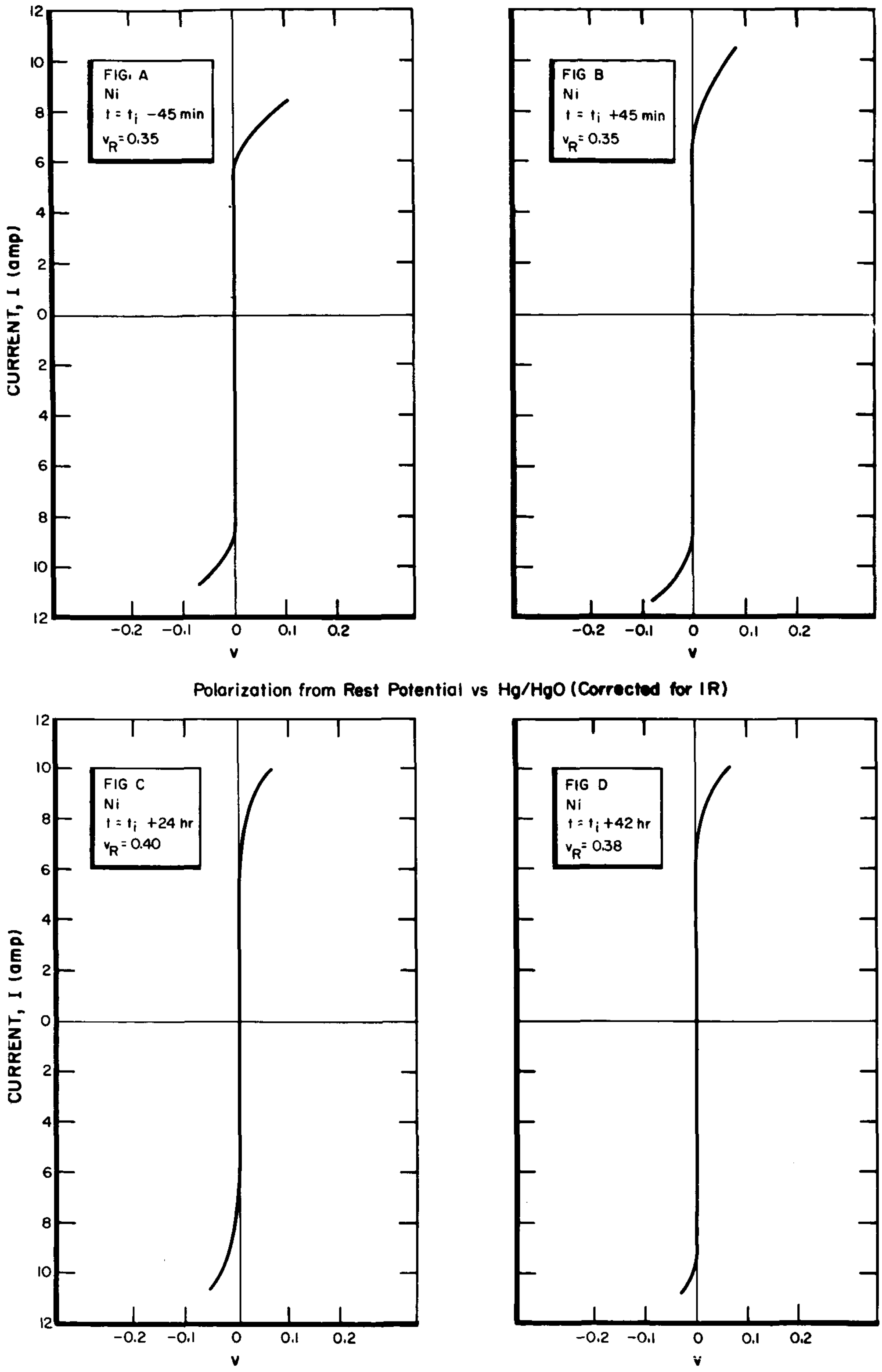

Figure 13. Polarization of Ni Electrode

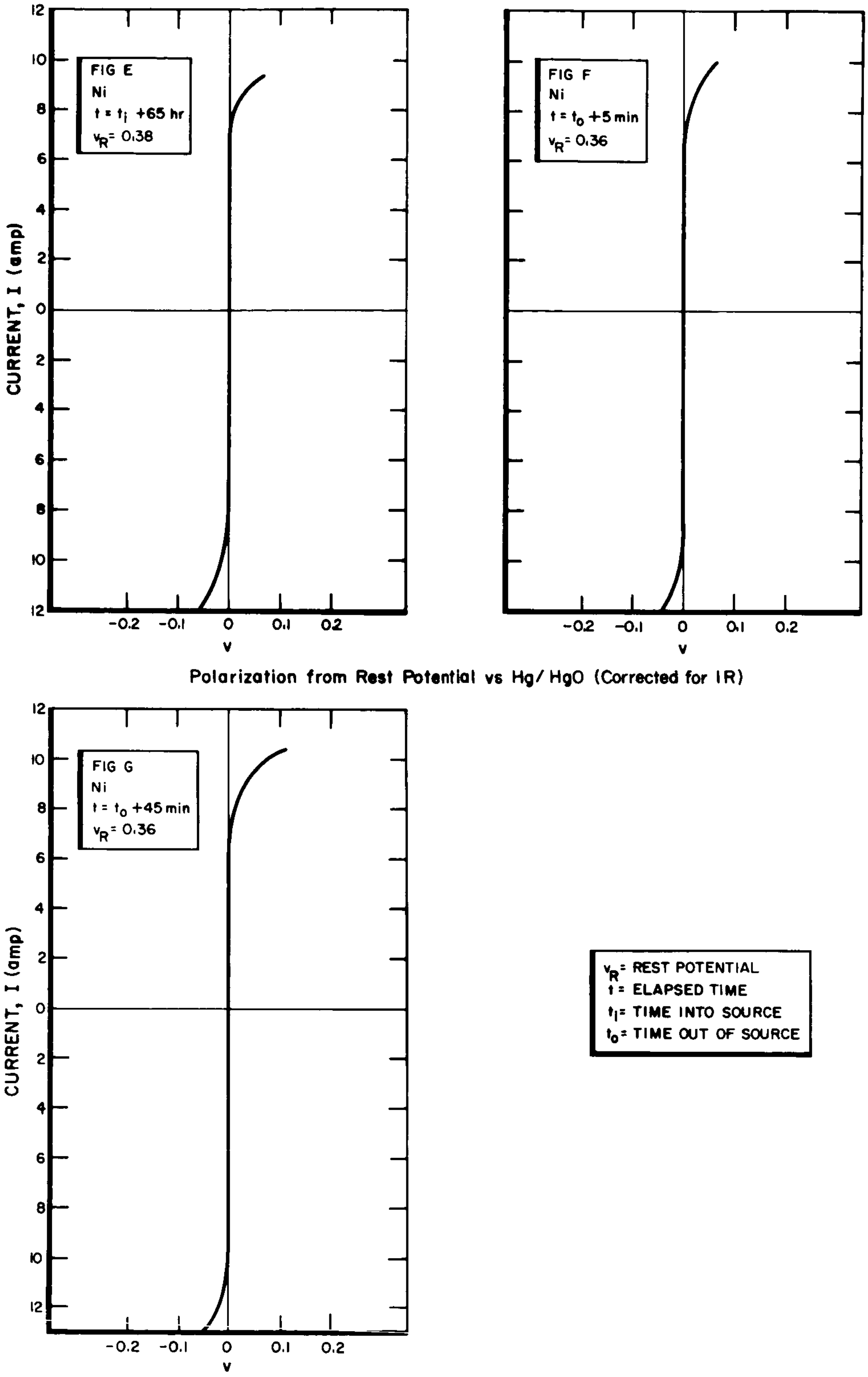

Figure 13A. Polarization of Ni Electrode

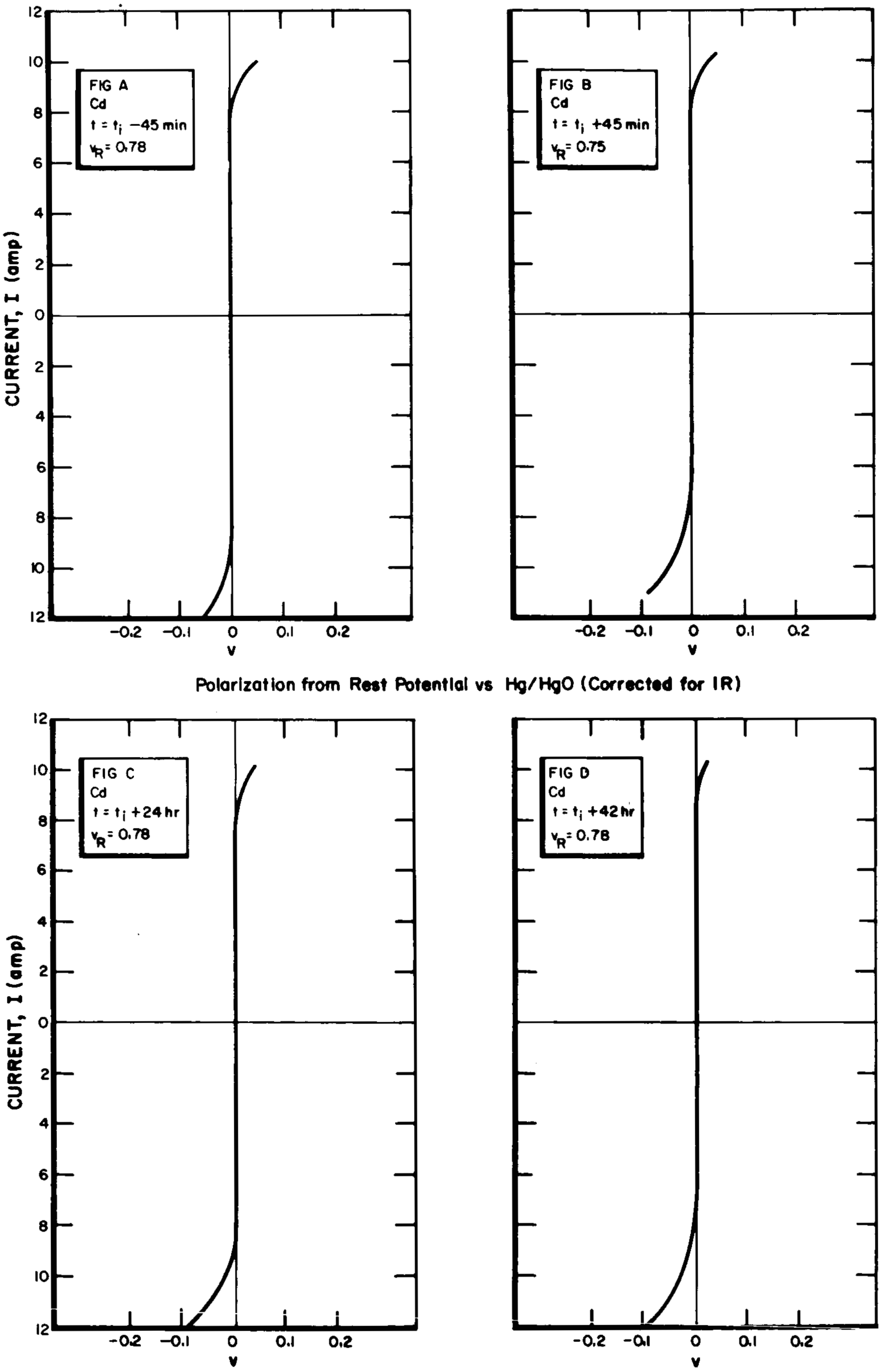

Figure 14. Polarization of Cd Electrode

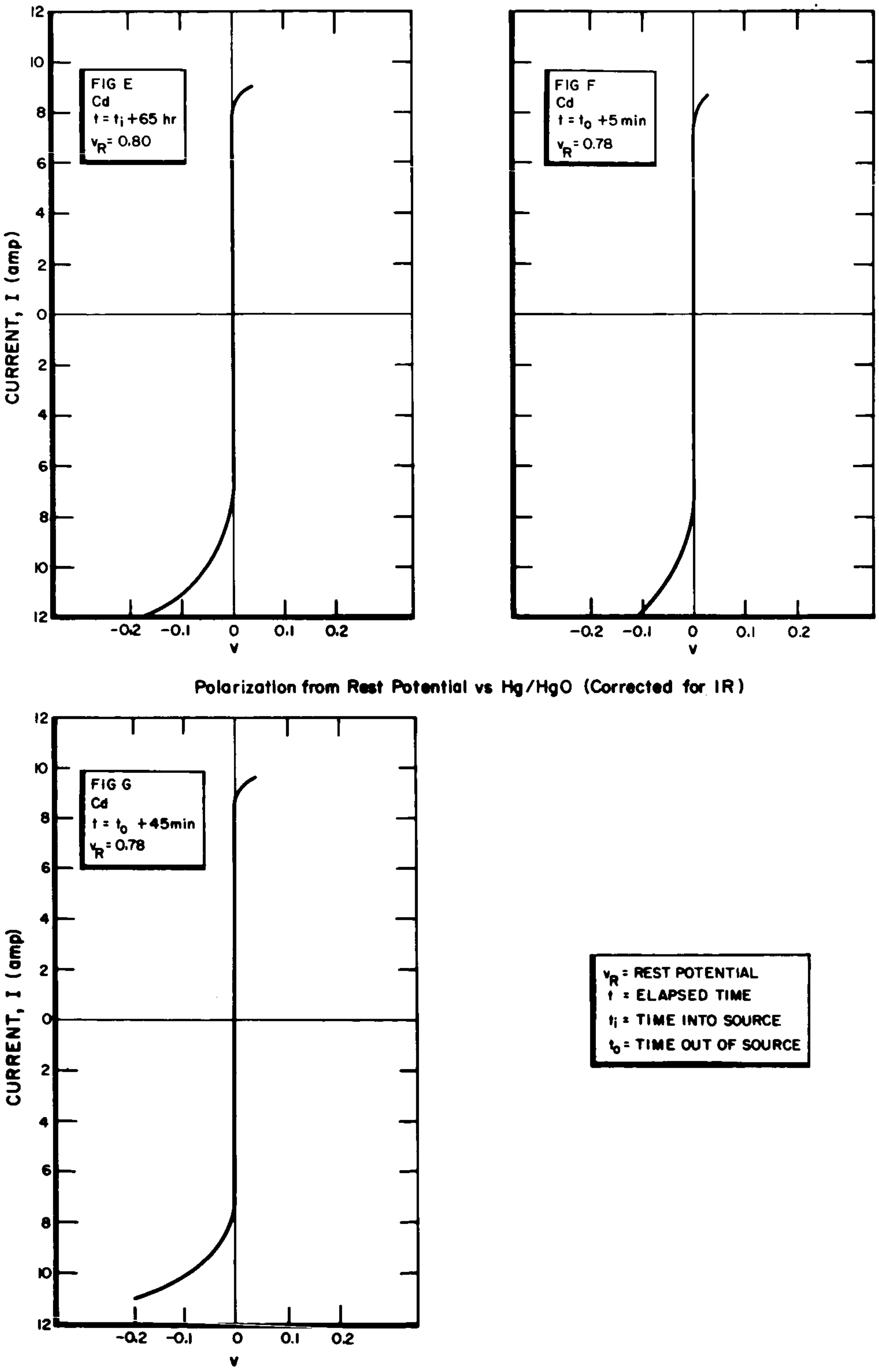

Figure 14A. Polarization of Cd Electrode

TABLE IV. SUMMARY OF RESULTS FROM IRRADIATIONS OF EXPERIMENTAL NICKEL-CADMIUM CELLS AT 75% OF CHARGE

Run #	Radiation Source	Dose Rate (rads/hr)	Length of Run (hr)	Total Dose (rads)	Weight of Material Sloughed (mg)	Cd to Ni Ratio in Sloughed Material	Sloughed Rate (mg/hr)	Temp. (°C)	Type Cell	Remarks
Co-60 #1	Source II	1.4×10^6	12	1.7×10^7	Contaminated	10:1		45	Quartz	On cycling
Co-60 #2	"	1.4×10^6	72	1.0×10^8	35.6	6:1	.50	45	"	" "
Co-60 #3	"	1.4×10^6	62	8.7×10^7	10.1	7:1	.15	45	"	" "
Co-60 #4	"	1.4×10^6	5	7×10^6	.1	NM	.02	45	"	Open circuit
Co-60 #5	"	1.4×10^6	215	3×10^8	77	3:1	.36	45	"	On cycling
Co-60 #6	Source I	8×10^4	96	7.7×10^6	2	NM	.02	30	Lucite	" "
Co-60 #7	"	8×10^4	72	5.8×10^6	.2	NM	.003	30	"	" "
Co-60 #8	"	8×10^4	168	1.3×10^7	.2	NM	.001	30	"	" "
Co-60 #9	Source II	1.4×10^6	111	1.5×10^8	NW			45	Commercial	Open circuit
Co-60 #10	"	1.4×10^6	111	1.5×10^8	5.9	40:1	.05	45	Stainless steel	On cycling
Co-60 #11	"	1.4×10^6	110	1.5×10^8	4.1	3:1	.04		"	" "
Electron #1	Van de Graff	4×10^9	.5	2×10^9	NW				Polystyrene	(this summarizes four runs)
Electron #5	"	4×10^9	.5	2×10^9	6.5	10:1	13.00	50	Quartz	Open circuit
Neutron #1	Reactor	1.5×10^4	52	7.4×10^5					"	On cycling

NM = not measured - amounts too small
NW = not weighed - usually less than .1 mg

The amounts of material lost from the electrodes in relation to the total dose are plotted in Figure 15. The data show a monotonic functional relationship. The rate at which the material was sloughed was greater at the higher dose rate than at the lower. Column 8 in Table V.

Several commercial cells (five electrodes in a plastic case) on open circuit were irradiated in Gamma Source II. (Table IV, Co-60 #9.) These cells were fully charged, discharged to 75 per cent of capacity, and then cycled for 24 hours, as described earlier for the laboratory cells, prior to the irradiation. These cells after irradiation were bulging considerably due to gas buildup in the cell. Upon opening the cells, sloughed material was observed on the separator but only where it was in contact with the nickel electrode. The cadmium to nickel ratio of this material was 2:1. The amount obtained was not weighed. The loss of this material from the Ni electrode appeared to have no measurable effect (±2%) on the capacity of the cell which was determined before and after the irradiation.

Experiments carried out were then designed (a) to obtain more direct evidence as to the source of the sloughed material, and (b) to determine how the sloughing was affected by the state of charge of the electrodes.

C. ANALYSIS OF SLOUGHED MATERIAL

When a sufficient quantity of residue (2 mg) was available from gamma and electron irradiation, it was analyzed using emission spectrography or x-ray fluorescence. In some runs in which there was no measurable amount of residue, all the electrolyte was neutralized and

TABLE V. EMISSION SPECTROGRAPHIC ANALYSES OF RESIDUES FROM CELLS USING ONE NICKEL AND ONE CADMIUM ELECTRODE

Column	1	2	3	4	5	6	7	8	9	10	11	12
Sample #	1st Co-60 Run	2nd Co-60 Run	3rd Co-60 Run	5th Co-60 Run	10th Co-60 Run	Neutron Residue Irrad.	Van de Graff	Residue fm. Rm. Temp. Cycling	Nonirradiated Cd Electrode Material	Nonirradiated Ni Electrode Material	Irradiated Comm'l Cell Residue	Nonirradiated Comm'l Cell Residue
Total Dosage in Rads (H_2O)	1.7×10^7	1.0×10^8	8.7×10^7	3.8×10^8	1.5×10^8	7.4×10^5	2×10^9					
Ag	.02	.02	.3	.03	.01	.001	N. D.	.3	.3	.1	N. D.	N. D.
Al	.3	.4	.3	.2		.2		.3	.5		.003	.002
B	.03	.1	.05	.01	.05	.005		.1			.002	.003
Ba	.3	.01						.3		.03		
Ca	1.	.1	.1	.1	.1	.1		2	.3	.3	.075	
Cd	3	.1	10	M***	.1	.002	.01	10	10	.5	.1	.02
Cr	.01	.05	.05	.01		.01		1	.01	.1	.001	
Cu	.3	.03	5	1	.1	.01		.3	.05	.05	.02	.01
Fe	.1	.2	.2	.3	.03	.01		.2	.05	.1	.05	.008
Li	.01	.01										
Mg	.02	.005	.05	.2	.1	.002		.01	.05	.05	.005	.002
Na	3	.5	.2		.001	.002	.003	.3	.8	.4	.1	.1
Ni	.05	.05	1	1	.1	N. D.	.001	3	10	10	.1	.03
Pb	.1	.01	.5	.3	.1			.05		.05	.004	.005
Si**	4	10	2	1	.1	.05	.02	.3	.2	.2	.03	.02
Sn	.05	.01	.05		.001							
W*	2	.5										
Zr	.05	.5	.05									
Co			.1	.5	.05					.2	.03	

*** Major constituent - the later ratio determination does not give specific values for Ni or Cd

** Silicon high in almost all samples because evaporation and filtration carried out in Pyrex glassware

* Tungsten lead used and it etched through

Column 6 is the analysis of a representative evaporated residue from the neutron irradiations. Column 8 is the analysis of the material found under the cadmium electrode after the 17 day room temperature cycling was complete. Columns 9 and 10 are analyses of electrode materials exclusive of the steel skeleton of the electrode. Columns 11 and 12 are materials washed from the separator in the commercial cells; both were charged, discharged to 75% and cycled identically. The material described in 11 was from a cell which was irradiated and the material in 12 was from a non-irradiated cell. The separator from the irradiated cell was black from this material whereas the non-irradiated separator was not discolored.

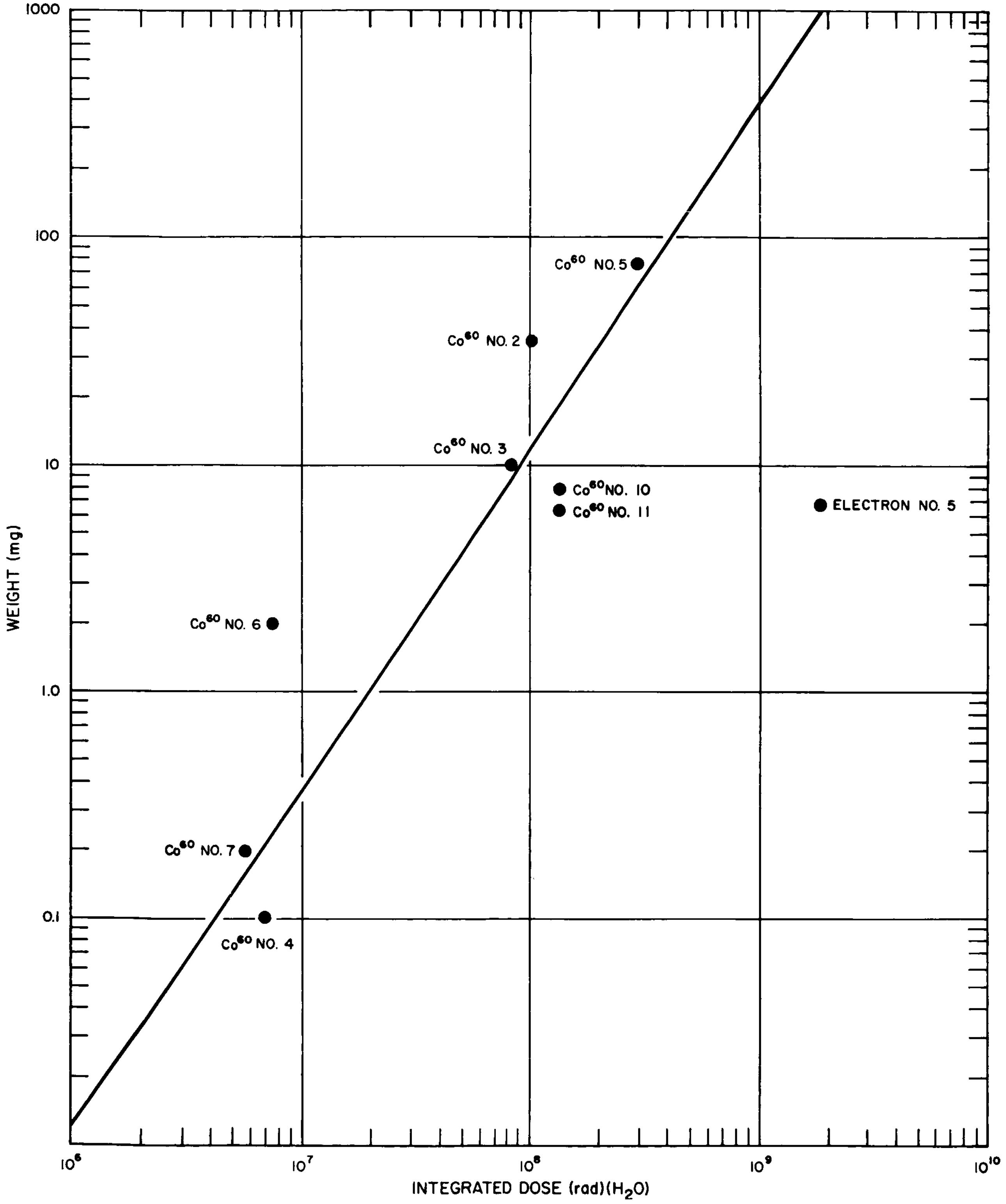

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Figure 15. Weight of Sloughed Material vs Integrated Dose

evaporated to dryness. Representative samples of these evaporated residues were then analyzed. Results of these analyses are shown in Table V. Some sacrifice in precision of the nickel and cadmium analyses was made in the preliminary runs in order to include all the trace elements in the determination. Where sufficient material was available the samples were analyzed again specifically for the cadmium to nickel ratio, as this quantity seemed to be significant. These results are given in column 7 in Table III. The trace elements found in the residues correspond to those expected from the materials used in cell manufacture. The high percentage of cobalt found may be ascribed to the high cobalt content usually found in nickel. X-ray analysis of the materials from Run #5 and the materials from the subsequent A series runs showed $Cd(OH)_2 >$ Ni metal > CdO > Cd metal. There were some unidentified lines in the x-ray pattern. Figure 16 shows the material in the bottom of the separated cell after a typical irradiation run.

A significant correlation is found if the cadmium to nickel ratios in the sloughed material of runs at 75 per cent state of charge using one Ni plus one Cd electrode are compared to the weight of material lost. Table VI shows these results. It should be noted that the greater the amount of material lost, the lower the ratio of cadmium to nickel. The electron irradiation results again are included and follow the trend.

Since cadmium and nickel were known to exist on both electrodes, a decision as to which electrode was the major contributor could not be made from the above data. A cell liner containing a quartz porous disc separator was designed for use in the stainless steel cells to help

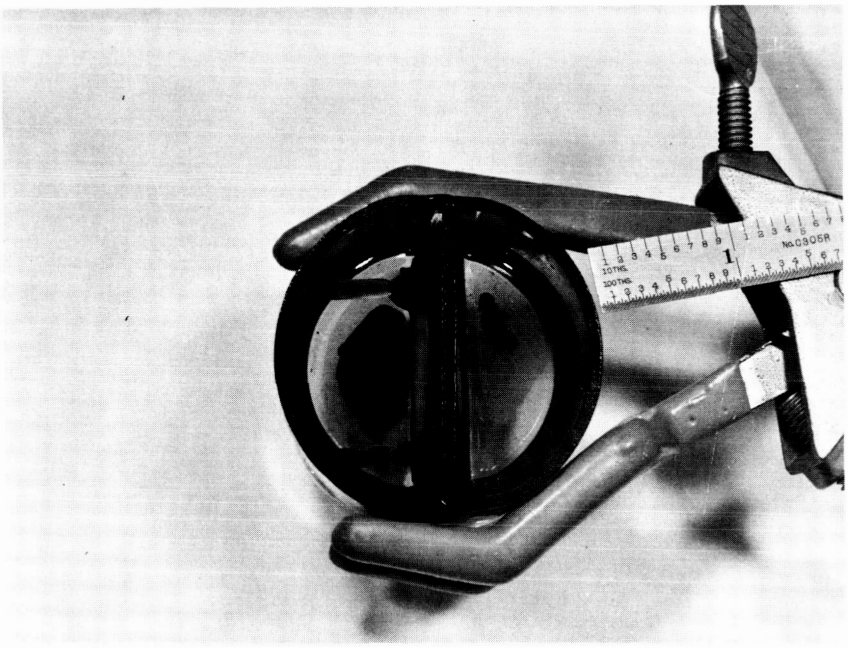

Figure 16. Material Lost from Electrodes in Bottom of Separated Cell

TABLE VI. CADMIUM/NICKEL RATIO OF SLOUGHED MATERIAL FROM CELLS USING ONE NICKEL AND ONE CADMIUM ELECTRODE

Experiment	Cd/Ni Ratio	Wt. of Mat'l (mg)	Total Dose (rads)
Co-60 Run #10	40:1*	5.9	1.5×10^8
Co-60 Run #11	3:1*	4.1	1.5×10^8
Co-60 Run #1	10:1	low+	1.7×10^7
Electron Run #5	10:1	6.5	2×10^9
Co-60 Run #3	7:1	10.1	8.7×10^7
Co-60 Run #2	6:1	35.6	1.0×10^8
Co-60 Run #5	3:1	77	3×10^8

* Only rough analyses were possible on these samples - therefore, the ratios are not as reliable as those of the other runs.

\+ Contaminated by tungsten but amount was less than 5 mg.

determine which electrode was disintegrating the more and what the effect of state of charge had on this weight loss. The data in Table VII clearly show that the cadmium electrode is losing by far the most material. Figure 17 shows a plot of the weight loss from the cadmium electrode as a function of state of charge.

D. GAS EVOLUTION IN THE ELECTROCHEMICAL CELLS

A stainless steel cell with a quartz liner (Figure 2) was constructed to measure gas evolution, and resulting pressure buildup in the cells. The pressure transducer in these measurements was a diaphragm type which has a voltage output of 5 mv per psi. The sensitivity of the transducer was 0.1 psi over 0-20 psig. Run #10 was the first run with the stainless steel quartz-lined cell. Figure 18 shows the variation of the measured cell pressure with time during this run. The important features of this curve are: (1) the initial drop in pressure, due to oxygen uptake by the cadmium electrode, (2) a rapid increase in pressure upon placing the cell in the source, due to two factors, (a) the temperature rise and (b) the radiolysis of the solution giving oxygen and hydrogen gas, (3) a further steady pressure increase due to radiolytic gas production and (4) a pressure decrease on removal of the cell from the source due to temperature decrease and oxygen uptake by the cadmium electrode.

During the run the cadmium electrode continues to take up some of the oxygen so that the resultant pressure is due to a variety of factors. The constant pressure region towards the end of the irradiation is, at present, difficult to explain. A steady state between radiolysis, producing

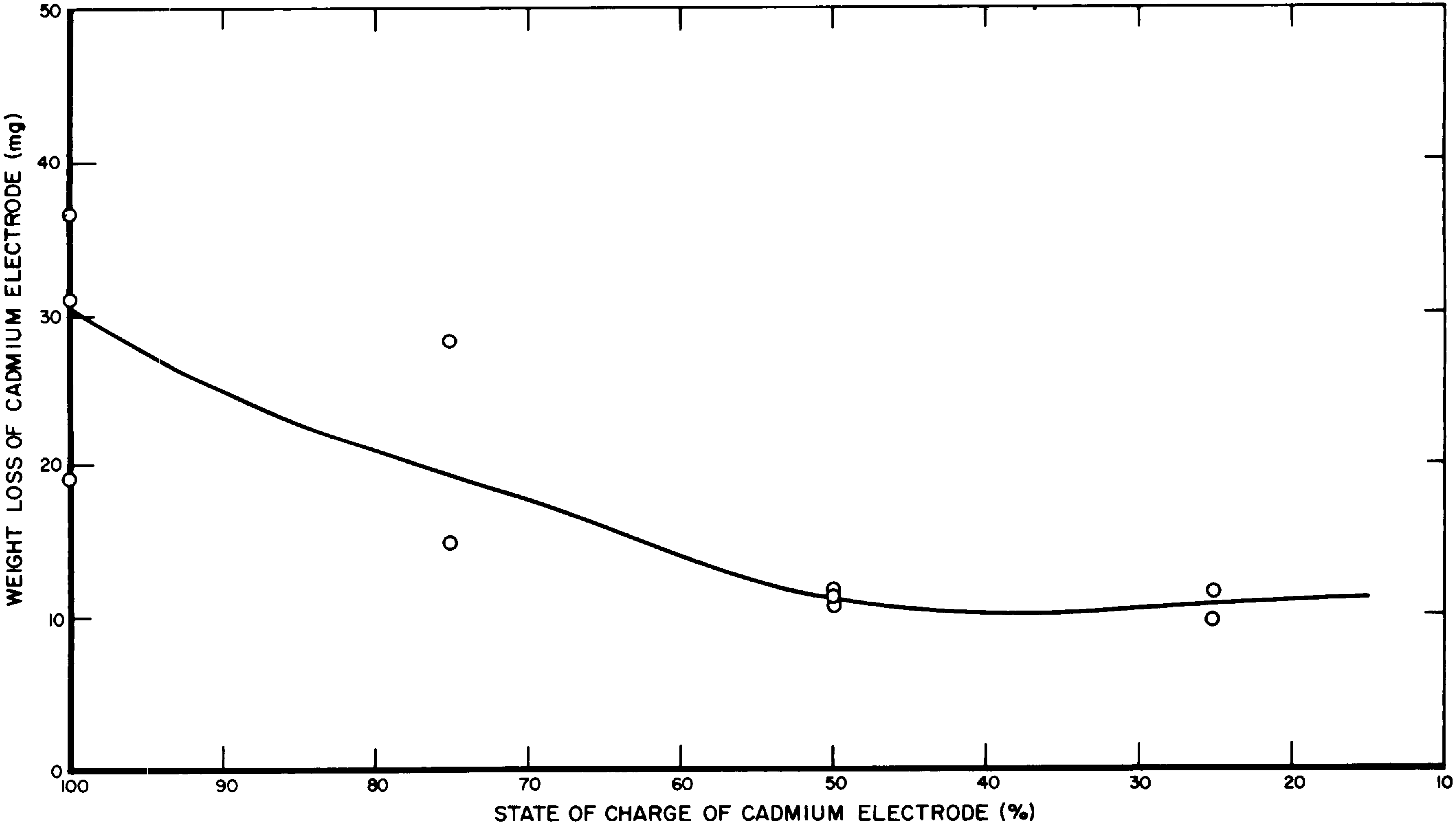

Figure 17. Weight Loss from Cadmium Electrode vs State of Charge

TABLE VII. MATERIAL LOSS FROM ELECTRODES IN DIVIDED CELL STUDIES

Run #	State of Charge of Cd Electrode	Wt. Loss from Cd Electrode	Cd/Ni Ratio	Wt. Loss from Ni Electrode	Cd/Ni Ratio	Total Wt. Loss
A-5R	100	30.7	3:1	11.1	1:10	41.8
A-18R	100	19.2	40:1	0.8	1:3	20.0
A-19	100	36.9	25:1	12.0	2:1	48.9
A-13	75	14.7	16:1	2.0	1:1	16.7
A-17	75	28.3	50:1	2.3	1:1	30.6
A-25*	75	4.4		1.3		5.7
A-26*	75	4.6	3:1	1.5		6.1
A-7	50	11.7	5:3	3.5	1:1	15.2
A-21	50	10.9	10:1	1.1	1:5	12.0
A-22	50	10.7	11:1	.1	1:10	10.8
A-23	25	11.7	8:1	2.8	1:20	14.5
A-24	25	9.7	20:1	1.7	1:1	11.4

*Data from open circuit cells

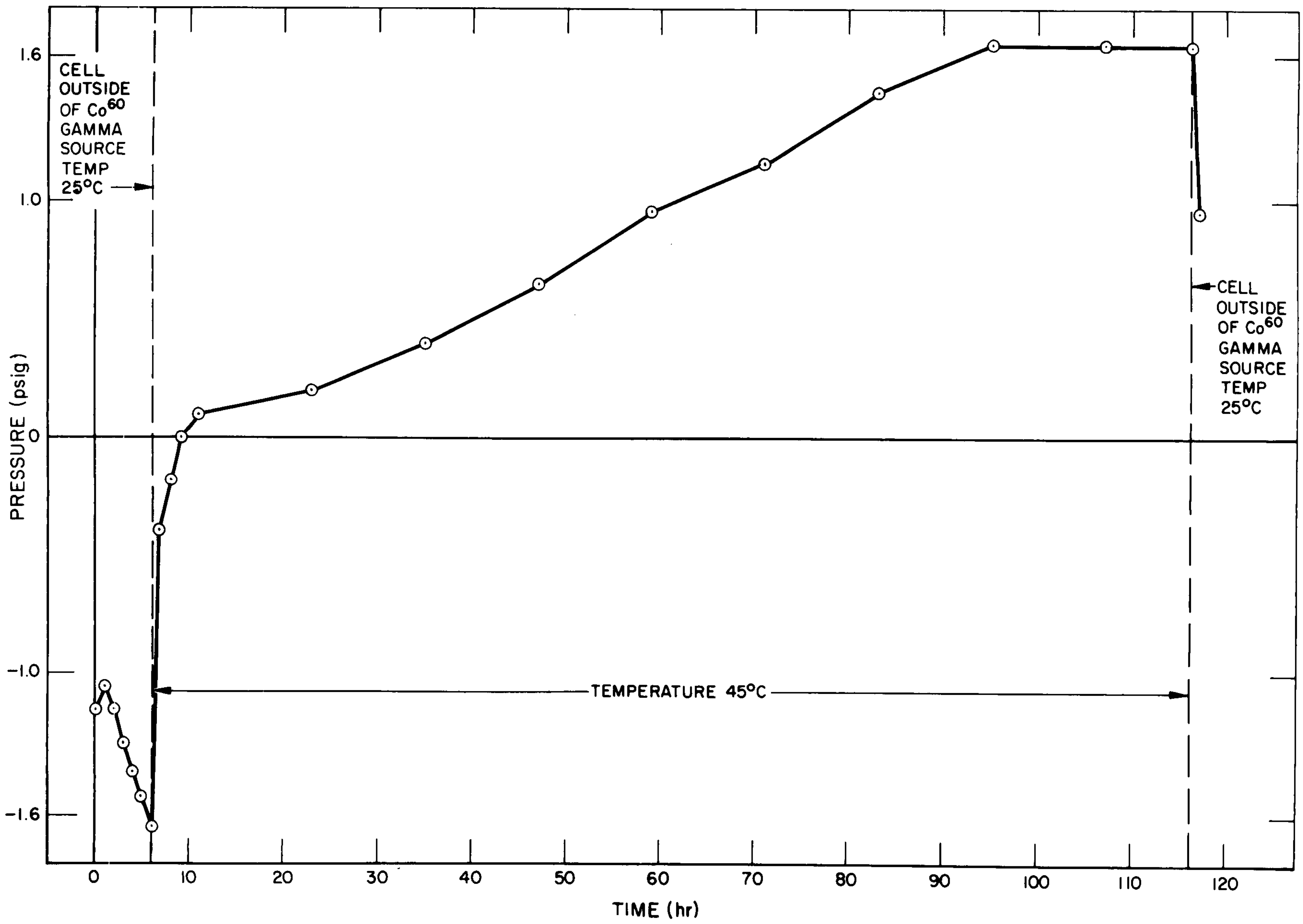

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Figure 18. Pressure Changes During Gamma Irradiation No. 10

oxygen, and cadmium electrode reaction with oxygen is a possible explanation but this is only conjecture. The final decay of pressure due to temperature drop and the cadmium electrode-oxygen reaction, after the cell was removed from the source, was also measured.

Table VIII summarizes the results of the gas analyses from the two runs. A valve leak and air contamination occurred at the conclusion of Run #10. This occurrence probably decreased the hydrogen result and may have lowered the CO and CH_4 concentration below the detection limit. In Run #11 the methane and carbon monoxide probably arise from the action of radiolytically produced hydrogen atoms on some carbon-containing compound. The origin of the carbon-containing compound has not been determined but may arise from carbonate in the electrolyte, from the electrode binder or from the neoprene "O" ring seal in the stainless steel cell. The pressure rises of 2-2.5 lbs. appeared to be a minor effect so further experiments along this line were suspended. The mechanism which caused these pressures was of concern since KOH is a common electrolyte to several rechargeable battery systems.

E. RADIOLYSIS OF KOH SOLUTIONS

Various concentrations of aqueous KOH were irradiated in a Co-60 source to determine the products produced, the quantity of each, and the effect of the materials from the nickel and cadmium electrodes on this production. Hydrogen and oxygen were the only products detected. No hydrogen peroxide (less than 1 μg/cc) was detected in any of the samples examined approximately 24 hours after removal from the field. "G" values for the production of these gases were calculated. (The

"G" value is defined as the number of molecules produced per 100 ev of radiation absorbed.) The data from these studies are given in Table IX. "G" values for H_2 and O_2 in 30 per cent KOH in the presence of nickel or cadmium electrodes were also obtained and are shown in Table X. These data are represented graphically in Figure 19.

TABLE VIII. PRESSURE INCREASE AND GAS ANALYSES OF GAMMA RUNS #10 AND #11

	Pressure Increase (corrected for temp.)	Gas Analysis (Vol. %) H_2	O_2	N_2	CH_4	CO
Run #10	2.6 lbs.	2.1	18.4	79.6	0	0
Run #11	2.3 lbs.	8.1	1.2	90.2	.17	.05

F. RESULTS FROM ELECTRON IRRADIATIONS

Instrumentation of the electron source required that the cells be left on open circuit during these irradiations. A decrease of about 30 mv in this voltage occurred but was thought to be entirely due to the increase in temperature, which reached 52°C. A reference cell was not used for comparison during these short runs because of the uncertainty in temperature across the cell.

Table XI summarizes the results of these runs. In Runs #1 through 4 only one electrode was irradiated per run and, due to absorption by the electrode, the penetration of the electron beam was small. In the fifth run, the electron beam impinged primarily on the electrolyte. Thus, in the first four runs, the upper electrode was covered with only a little electrolyte, and the amount of radiolysis occurring was small. In the

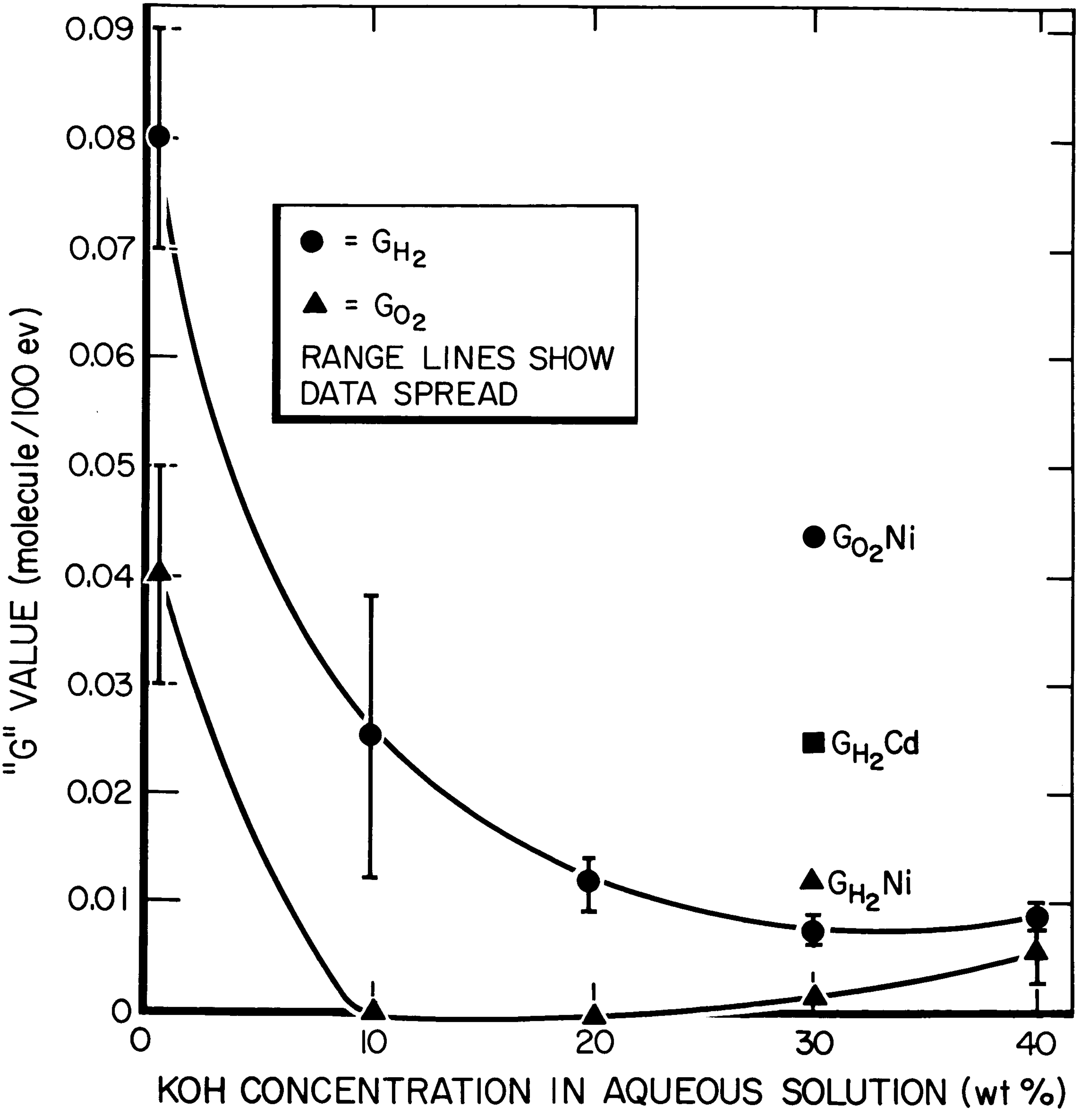

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Figure 19. "G" Values for $H_2 + O_2$ as a Function of KOH Concentration

TABLE IX. RADIOLYSIS PRODUCTS AND CALCULATED YIELDS FROM CO-60 GAMMA IRRADIATION OF VARIOUS CONCENTRATIONS OF KOH (Dose = 6.6×10^7 rads; Temp. = 45°C; He Cover Gas)

Run #	% KOH	Gas Phase Composition % H_2	 % O_2	 % N_2	Sample System* Pressure (mm Hg)	$G_{(H_2)}$	$G_{(O_2)}$
R-8-9	0.5	22.4	12.0	0.04	56	0.09	0.05
R-10-2	0.5	11.4	7.7	.84	74	0.07	0.04
R-10-3	0.5	19.1	9.2	.85	44	0.07	0.03
R-6-1	10	2.2	0	0.34	22	.038	0
R-8-F	10	0.8	0.16	0.30	19	.012	0
R-6-2	20	5.9	0	0.31	28	.014	0
R-6-3	20	3.5	0	0.77	28	.009	0
R-8-C	30	2.0	0.8	4.0	39	0.008	0.002
R-8-D	30	4.1	1.5	4.1	19	0.008	0.002
R-8-2	40	5.9	2.0	0.2	21	0.009	0.003
R-6-4	40	16	3.4	5.6	5	0.008	0.009
R-10-4	40	5.3	1.9	1.5	39	0.01	0.005

*Sample system pressure measured when cell connected to chromatographic sampling system. Variations in this parameter in the runs with He cover gas probably arise from variable expansion of the gas during cell sealing prior to irradiation.

TABLE X. RADIOLYSIS OF 30% KOH CONTAINING Ni or Cd ELECTRODES

(Dose = 6.6×10^7 rads; Temp. = 45°C; He Cover Gas)

Run #	Electrode	Gas Phase Composition % H_2	% O_2	% N_2	Sample System*** Pressure (mm Hg)	$G_{(H_2)}$	$G_{(O_2)}$
R-8-4*	Ni	9.9	52.3	0	16	0.014	0.044
R-10-6	Ni	3.8	25.1	0	27	0.009	0.052
R-8-3	Cd	16.1	0	0.44	21	0.025	0
R-10-5	Cd	6.0	.01	1.2	51	0.025	0
R-8-5**	Ni	0	16.1	1.1	17	---	---

*$G_{(O_2)}$ corrected for apparent self discharge to produce O_2 as observed in R-8-5

**These samples were not irradiated but rather were stored at 45°C for a period equal to the irradiation time

***See footnote Table VI.

TABLE XI. ELECTRON IRRADIATION RESULTS

Run #	Electrode Exposed	Sloughed Material (mg)	Dosage (rads H_2O)
1	Ni	None	5×10^8
2	Cd	"	5×10^8
3	Ni	"	2×10^9
4	Cd	"	2×10^9
5	Both	6.5	2×10^9

last run, the electrolyte received more radiation and sloughing was observed. The results of Run #5 are consistent with the hypothesis that radiolysis of the electrolyte playing a role in the loss of material from the electrodes. The weight and analysis of the material sloughed in Run #5 correlates reasonably well with that obtained in the Co-60 irradiations as is shown in Figure 14 and Table IV.

G. RESULTS FROM NEUTRON IRRADIATION

Figure 5 shows the physical arrangement of the cells for our neutron irradiation. The cells were irradiated for 52 hours for a total dosage (γ and n) of 7.4×10^5 rads. No sloughing of material from any of the electrodes was observed. Some transmutation reactions had occurred. The post-run gamma spectra, indicating the predominant peaks, are shown in Figures 20 and 21. The energy calibration line is included since it is required to determine the energy of the respective peaks. The area under the peaks is a measure of the amount of isotope present. The nuclides formed and their mode of production are summarized in Table XII. The post-run examination of the electrolyte showed only the beta radiation due to potassium 41. Evaporation of the electrolyte and subsequent spectrographic analysis showed a trace of cadmium present but no evidence of any nickel.

The fact that no sloughing was observed is consistent with the results obtained from Co-60 irradiations in which a dose of 1.4×10^6 rads (H_2O) was required to observe any effects associated with sloughing. This source did not provide neutrons only; however, from the very limited information available, it would appear that fast neutrons are not a great

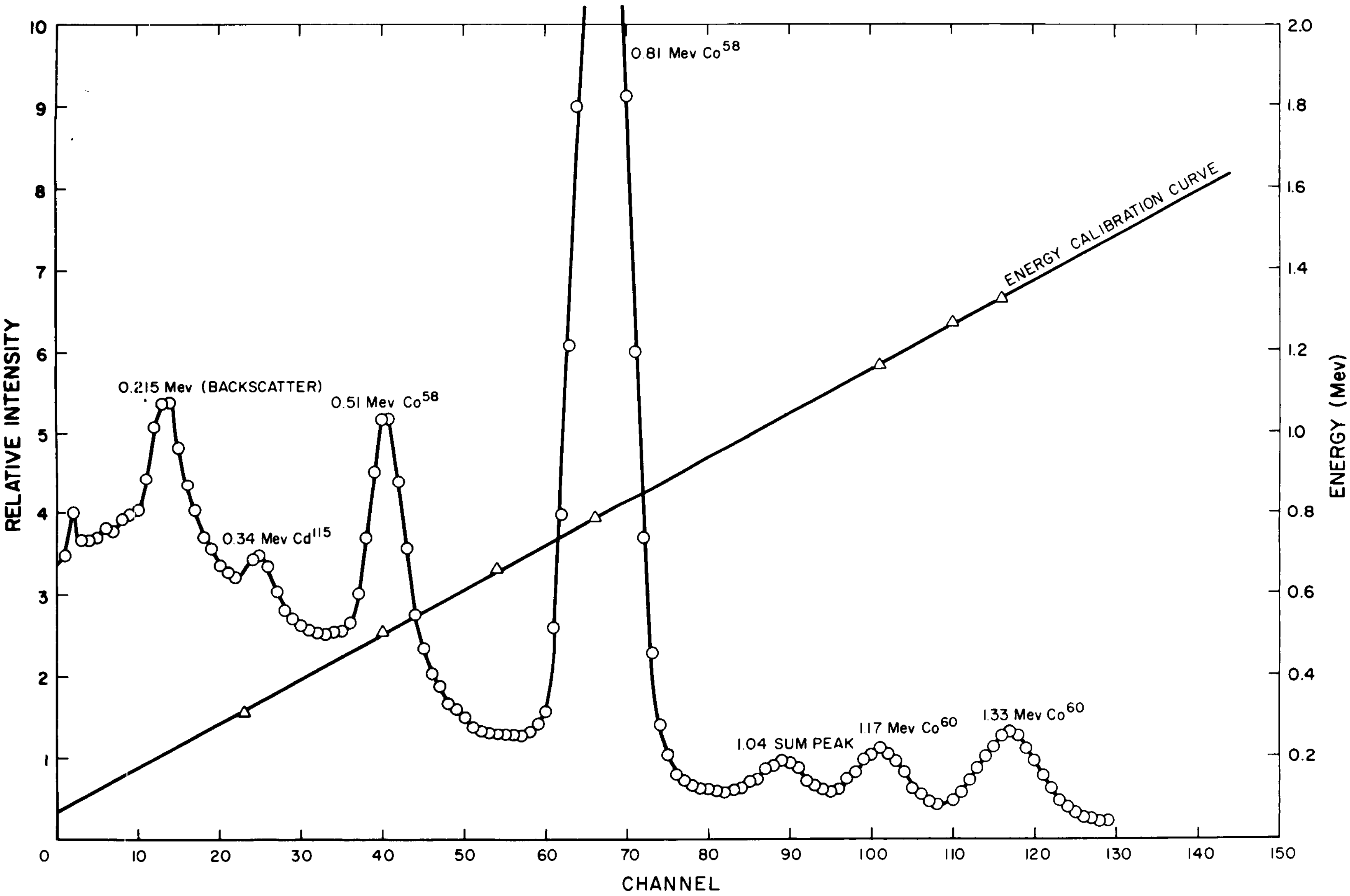

Figure 20. Gamma Counting of Nickel Electrode After Neutron Irradiation

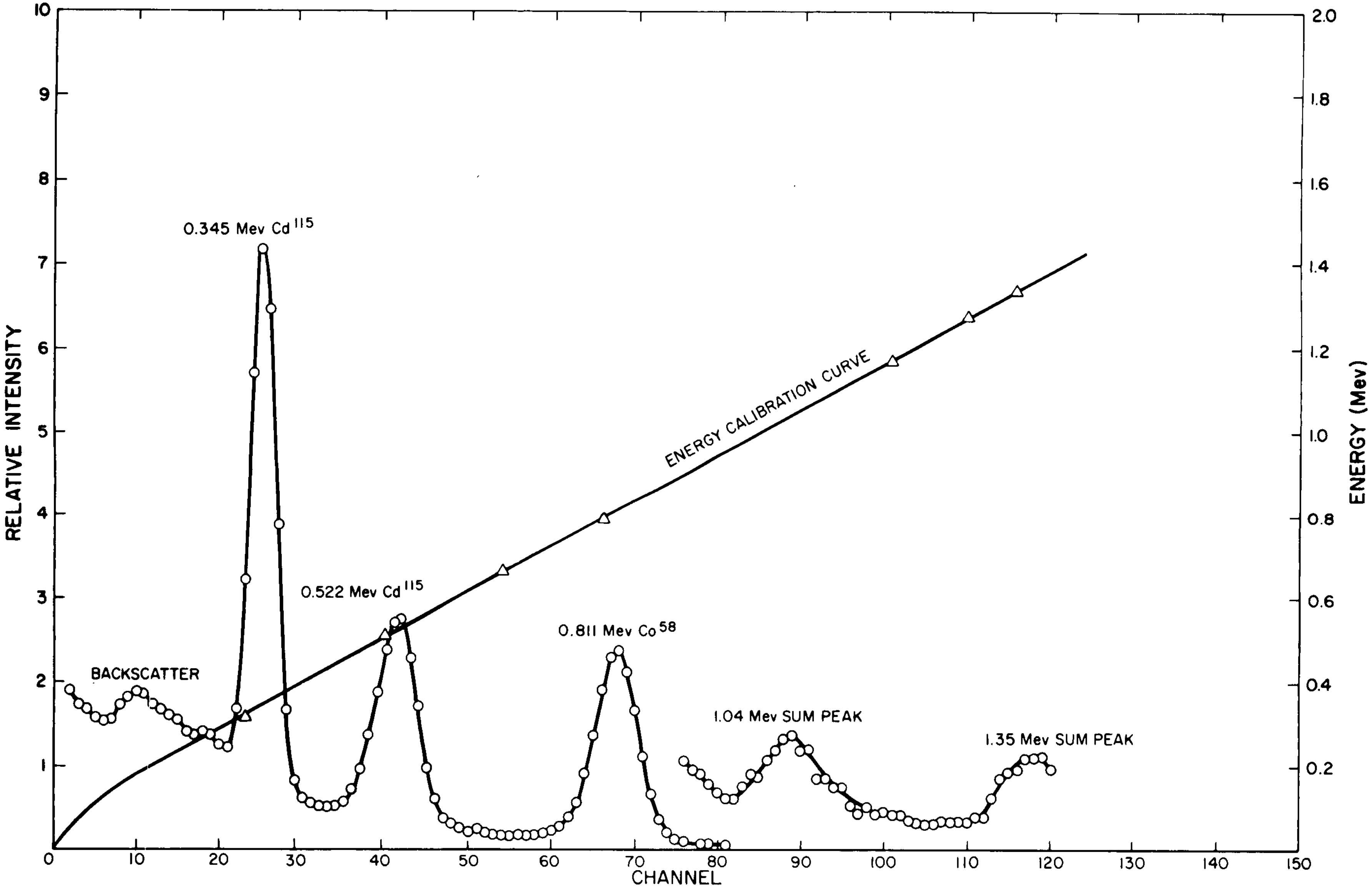

Figure 21. Gamma Counting of Cadmium Electrode After Neutron Irradiation

deal more damaging than gamma radiation with respect to material loss from the electrodes.

TABLE XII. NUCLIDES AND THEIR MODE OF PRODUCTION

Electrode	Nuclide	Half Life	Mode of Production
Cadmium	Cd^{115}	53 hrs.	Cd^{114} (n,γ) Cd^{115}
	Cd^{107}	6.7 hrs.	Cd^{106} (n,γ) Cd^{107}
	Co^{58}	71 days	Ni^{57} (n,γ) Co^{58}
Nickel	Ni^{65}	2.56 hrs.	Ni^{64} (n,γ) Ni^{65}
	Co^{58}	71 days	Ni^{58} (n,γ) Co^{58}
	Co^{60}	5.26 yrs.	Co^{59} (n,γ) Co^{60}
	Cd^{115}	53 hrs.	Cd^{114} (n,γ) Cd^{115}

IV. DISCUSSION OF GAMMA IRRADIATION RESULTS

A. ELECTROCHEMICAL EFFECTS

1. Voltage Characteristics

Voltammetry experiments on Ni-Cd cells during Co-60 irradiation showed that the irradiation had little if any effect on the polarization characteristics of the electrodes. During a 62 hour run (8×10^7 rads), a ten millivolt drop in the open circuit potential of a cell was observed. This was not explored further to determine the mechanism.

2. Loss in Cadmium Electrode Capacity

One important parameter in the capacity loss phenomenon appears to be the electrode state of charge. The data shown in Table I and Figure 11 indicate that at 100 per cent and 50 per cent state of charge very little capacity is lost by the cadmium electrode, while at 25 per cent of charge no loss is observed. On the other hand, at 75 per cent of charge the cadmium electrode lost capacity when the electrodes were cycled through a charge-discharge regime. The fact that a loss in capacity greater than the standard deviation occurred at 75 per cent state of charge during every run at 75 per cent of charge is evidence that the effect is real. The data spread may be due to either or both of two factors: (a) variation in structure of the electrodes themselves due to variations in manufacturing variables, or (b) dependence on whether the cell cycled higher or lower than 75 per cent state of charge. The fact that irradiated cells in the open circuit mode at 75 per cent state of charge did not lose capacity shows that cycling is another parameter associated with this capacity loss phenomenon.

This loss in capacity may mean changes in composition or structure of the cadmium electrode are occurring during the irradiation of a cycling cell. Formation of one or more of the following cadmium species may be responsible for the observed phenomenon:

(a)	α, β or γ cadmium	(4)
(b)	CdO	(5)
(c)	$CdO_2 \cdot n\ H_2O$	(6)
(d)	Inactive $Cd(OH)_2$	(7)

Present data are insufficient to permit a choice between these or other possible cadmium species as being the electrochemically inactive form.

B. MATERIAL LOSS FROM ELECTRODES

1. Mechanisms of Material Loss

The amount of material lost from electrodes in irradiated cells ($\sim 10^8$ rads) is normally about ten times greater than that lost from unirradiated electrodes operating at 45°C, the temperature in the gamma source II. Obviously, then, radiation or a product of irradiation is interacting with the electrode material in some way to cause this effect.

Two mechanisms appear as possible causes for the sloughing phenomenon observed to accompany irradiation of the nickel-cadmium cells. Either or both of these may be causing this phenomenon. These mechanisms are:

a. The Mechanical Effect of Rapid Gas Evolution

Hydrogen and oxygen are formed in the electrolyte by radiolytic action. Hydrogen is also formed at the cadmium electrode on charging at or near 100 per cent state of charge. The oxygen and hydrogen thus evolved, either inside or outside the electrodes, may mechanically dislodge material from them. The evolution of gases during irradiation would be likely to occur throughout the electrolyte, including regions within the pores of the electrodes. This could then lead to extensive sloughing of weakly adherent material. The cadmium-bonded to the nickel plaque of the cadmium electrode is probably more easily dislodged than is the active nickel species on the nickel electrode. The electrochemical evolution of hydrogen at the cadmium electrode near 100 per cent state of charge probably accounts for the larger loss of material at this state of charge.

b. The Chemical Action of Free Radicals

Hydroxyl, hydrogen and oxygen free radicals, may react with the materials of the electrodes. The reaction would release large amounts of energy and could in themselves be responsible for dislodging the material from the electrodes. While some cause of the sloughing phenomenon other than those associated with the radiolysis of the electrolyte is possible, it does not appear as likely.

2. Effect of Cycling on Material Loss

Some light on the place of attack leading to sloughing was shed by the results of tests on cells run at 75 per cent state of charge on open circuit. These cells produced smaller amounts of sloughed material than those undergoing current cycling. This fact would tend to indicate that the radiation or products thereof affect the active material being cycled through successive charges and discharges. This affected material becomes dislodged, and is that which is sloughed. This appears reasonable as this cycling material would be the most chemically active in the entire cell system and thus would act as the catalytic centers for gas evolution or radical reactions. Also, more rapid gas evolution at these sites would lead to large amounts of material being sloughed by mechanical action.

3. The Electrode of Origin of the Sloughed Material

It was observed Table VI that the higher the total gamma dose the greater the amount of material lost from the electrodes. From the Cd/Ni ratios of the sloughed material, it is evident that more cadmium than nickel is dislodged. Wet analysis of the electrodes, exclusive of the steel skeletons, showed that cadmium constitutes 2.5 per cent of the nickel electrode and about 25 per cent of the cadmium electrode, with nickel making up the remaining percentages of metals. Cadmium is placed near the surface of the nickel electrode to act as an oxygen getter in overdischarge. The nickel on the cadmium electrode, on the other hand, is only present in the sintered plaque. In both cases, material dislodged first would be richer in cadmium than in nickel for either electrode. The data in Table VII show that almost all the material sloughed comes from the cadmium electrode. The Cd/Ni ratios are exceedingly high in the material from the cadmium electrode while the Cd/Ni ratio of the material from the nickel electrode is of the order of 1:1. This composition is consistent with the cadmium to nickel ratio obtained for the material found on the nickel electrode side of the separator from as-delivered cells which had been irradiated. Since no dislodged material was found on the cadmium side of the separator, the conclusion was drawn earlier in the present investigation that the nickel electrode contributed most of the sloughed material; this has now been shown to be not the case for cells in the absence of separator material. Just why the cadmium electrode sloughs only in the open cell configuration and not in the closely packed commercial cells is not known, but may involve reaction of radiolysis products with the separator or perhaps is attributable to the small amount of solution present in the commercial cells.

The largest amount of cadmium metal lost from any electrode tested was less than the 77 mg of total sloughed material observed on a 75 per cent state of charge run. In no case was the amount of material loss sufficient to account for the loss in capacity.

C. RADIOLYSIS OF THE ELECTROLYTE

The very low "G" values for hydrogen and oxygen given in Tables IX and X suggest that at a total dose of 6.6 x 10^7 rads (H_2O) the radiolysis of the KOH solutions is in a steady state condition, i.e., very little, if any, net formation of products is occurring. This would mean that the "G" values reported are apparent yields. To determine the initial "G" values for the radiolysis of KOH solutions, irradiations of lower total dosage should be made. This would enable the course of build-up of products to be determined, and would yield true "G" values as well as more data on the mechanism of the process.

At 30 per cent KOH the yield of O_2 and H_2 is very small. The nickel electrode affects the yield of O_2 in a striking manner as shown by the 20-fold increase in the "G" value for O_2. The radiation appears in some way to be discharging the nickel electrode, or the nickel electrode is catalyzing the decomposition of or reacting with an intermediate, e.g., hydrogen peroxide. (While hydrogen peroxide was not detected in radiolyzed electrolytes, it may still be produced as an intermediate in the process.) The effect of the nickel electrode on $G_{(H_2)}$ is considered negligible.

As expected, no oxygen was detected in the presence of the cadmium electrode. The large increase in $G_{(H_2)}$ due to the presence of the cadmium electrode is not surprising. This is to be expected as removal of one product will enhance the production of another. For example, reaction of cadmium metal with OH radicals would permit the formation of hydrogen gas as was shown previously(2) in the radiolysis mechanism presented.

This postulated effect of the electrodes on $G_{(H_2)}$ and $G_{(O_2)}$ would produce on them a form of self discharge. It would be of interest to leave a charged cell on open circuit in a radiation field to determine how much self discharge actually occurs.

A detailed proposed radiolysis mechanism has been previously presented.(2) In reference to this mechanism, no O_2 or H_2 <u>should</u> be formed in the radiolysis in the absence of an impurity since the radicals produced ($G_H = 3.7$ and $G_{OH} = 2.7$) will destroy the molecular products ($G_{H_2} = 0.4$ and G_{O_2} 0.35) by the reactions:

Neutral Solution	Basic Solution
$H + O_2 \longrightarrow HO_2$	$e^-_{aq} + O_2 \longrightarrow O_2^- \xrightarrow{\text{2 steps}} \tfrac{3}{4}\, O_2$*
$OH + H_2 \longrightarrow H_2O + H$	$O^- + H_2 \longrightarrow e^-_{aq}$

However, a small steady state concentration of H_2 and O_2 is observed in the proper 2/1 ratio at 0.5 per cent KOH indicating some solute other than KOH must be present which reacts either with e^-_{aq} or O^- or both. This solute may be a trace impurity, especially a +2 cation, in the H_2O. The decrease in yield of H_2 and O_2 with increasing basicity leads us to suggest that we are observing here a direct decomposition of KOH by radiation and that this decomposition of OH^- yields O^- and e^-_{aq}. This enhanced yield of radicals further reduces the gaseous evolution. That is the mechanism:

$$H_2O \xrightarrow{\gamma} H_2,\ O_2,\ e^-_{aq},\ O^-$$
$$OH^- \xrightarrow{\gamma} O^-,\ e^-_{aq}$$

Overall Primary Processes

$$O^- + H_2 \longrightarrow e^-_{aq}$$
$$e^-_{aq} + O_2 \longrightarrow O_2^-$$
$$O_2^- + \tfrac{1}{2}\, H_2O \longrightarrow OH^- + \tfrac{3}{4}\, O_2$$

Subsequent Reactions

predicts

$$H_2 \text{ yield} = G_{H_2} - G_{O^-}$$
$$O_2 \text{ yield} = G_{O_2} - \tfrac{1}{4}\,(\text{net yield of } e^-_{aq}) = G_{O_2} - \tfrac{1}{4}\,[G\, e^-_{aq} + G_{O^-}]$$

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*That is normally one talks of H and OH but these are now known to exist as e^-_{aq} and O^- in basic solution.

It is recognized that in addition to O^- and e^-_{aq}, H_2 and O_2 might also be formed by this "direct" radiolysis of KOH, but smaller yields are expected than in the radiolysis of water. Recent experimental verification for the above mechanism comes from the observation of e^-_{aq} in frozen (below -50°C) 10 M NaOH and KOH solutions by ESR techniques. Also, the G value of trapped electrons was observed to increase, as proposed, from ~0.2 at 2 M to 2.6 at 16 M NaOH. The increase in yield of H_2 and O_2 at 40 per cent KOH may again be an effect of impurities in the KOH which consume the radicals and allow H_2 and O_2 production.

Reactions of radicals with H_2O_2 (or HO_2^-) should not be considered in the mechanism since H_2O_2 has not been detected in the products. Further experimental data are needed to refine this proposed mechanism.

D. VOLTAMMETRY OF NICKEL AND CADMIUM ELECTRODES

Polarization effects were expected on both the cadmium and the nickel electrodes from surface coverage by the radiolysis products. The measurement made after 45 minutes in the source seemed to indicate this effect at the nickel electrode but the effect diminished during later measurements.

The effects observed on the cadmium electrode can be attributed to temperature since the polarization decreased upon entering the source while returning to normal when removed from the Co-60 radiation and 45°C environment.

V. CONCLUSIONS AND RECOMMENDATIONS

The purpose of this study was to determine the effects of radiation on nickel-cadmium electrodes and their magnitude. The conclusions and recommendations coming from this study should be concerned with nickel-cadmium batteries and their use in space vehicles using SNAP reactors or isotope sources for power.

The effects observed and our conclusions and recommendations about these effects are summarized below.

A. ELECTROCHEMICAL EFFECTS

1. Voltage-current relationships of nickel-cadmium batteries are not affected by gamma radiation in the short run.

2. Radiation causes the cadmium electrode to lose capacity, when undergoing charge-discharge cycling. It is thus recommended that unnecessary cycling of batteries in radiation fields be avoided.

B. MATERIAL LOSS

Material is dislodged from the irradiated electrodes, with the most being lost at 100 per cent of charge. This phenomenon may not be of great importance in commercial cells as their closely packed configuration appears to oppose this effect.

C. GAS PRESSURE CHANGES

Only two to two and one-half pounds per square inch were the highest observed pressures attained by cells in radiation fields. This effect is of little consequence, since cells are designed to retain gases up to 100 psig.

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