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**ANNUAL REPORT FOR 1979 ON
RESEARCH, DEVELOPMENT AND DEMONSTRATION OF
NICKEL-ZINC BATTERIES FOR
ELECTRIC VEHICLE PROPULSION
Contract No. 31-109-38-4248**

by

Energy Research Corporation

MASTER

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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June 1980

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FINAL

SECOND ANNUAL NON-PROPRIETARY REPORT

CONTRACT NO. 31-109-38-4248

Prepared For:

ARGONNE NATIONAL LABORATORY

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Date:

September 17, 1979

NON-PROPRIETARYTABLE OF CONTENTS

	<u>PAGE NO.</u>
SECTION I	
INTRODUCTION -----	1
SECTION II	
NICKEL ELECTRODE DEVELOPMENT FOR Ni-Zn CELLS (TASK I)-----	6
1.0 <u>INTRODUCTION</u> -----	7
2.0 <u>TECHNICAL DISCUSSION</u> -----	7
2.1 WASHING AND DRYING OF Ni(OH) ₂ -----	7
2.2 CONTINUOUS PRECIPITATION OF Ni(OH) ₂ -----	12
2.3 GRAPHITE ADDITION DURING Ni(OH) ₂ PRECIPITATION-----	14
2.4 CHEMICAL OXIDATION OF Ni(OH) ₂ -----	16
2.5 REDUCED COBALT QUANTITY-----	18
2.6 USE OF COMMERCIAL Ni(OH) ₂ -----	22
2.7 GRAPHITE PARTICLE SIZE-----	26
2.8 OTHER Ni(OH) ₂ MATERIALS-----	26
2.9 COBALT SUBSTITUTES-----	28
3.0 <u>CONCLUSIONS</u> -----	29
SECTION III	
ZINC ELECTRODE DEVELOPMENT FOR Ni-Zn CELLS (TASK II)-----	34
1.0 <u>INTRODUCTION</u> -----	35
2.0 <u>TECHNICAL DISCUSSION</u> -----	36
2.1 SUBSTRATE DEVELOPMENT-----	36
2.1.1 Nickel Exmet-----	36
2.1.2 Proprietary - Type A -----	38
2.1.3 Proprietary - Type B -----	38
2.1.4 Copper Foil, Cd-Plated -----	39
2.1.5 Copper Foil with a Polymer Layer-----	39

	<u>PAGE NO.</u>
2.1.6 Proprietary - Type C -----	41
2.1.7 Silver Foil-----	41
2.2 ADDITIVES-----	41
2.3 KINETICS OF THE ZINC ELECTRODE-----	53
SECTION IV	
SEPARATOR DEVELOPMENT FOR Ni-Zn CELLS (TASK III)-----	60
1.0 <u>INTRODUCTION</u> -----	61
2.0 <u>TECHNICAL DISCUSSION</u> -----	62
2.1 THERMOPLASTIC-BASED SEPARATORS-----	62
2.1.1 Optimum Composition-----	62
2.1.2 Thermoplastic Films as Separator Materials-----	63
2.2 PVA-BASED SEPARATORS-----	68
2.2.1 Optimum Technology for the Production Process-----	68
2.2.2 Calculation of Production Parameters of PVA Films from Solution-----	71
2.2.3 Optimum Crosslinking in PVA-----	74
2.2.4 Experimental Data-----	81
3.0 <u>CONCLUSIONS</u> -----	92
4.0 <u>FUTURE WORK</u> -----	94
SECTION V	
DEVELOPMENT OF SEALED NICKEL-ZINC CELLS (TASK IV)-----	95
1.0 <u>INTRODUCTION</u> -----	96
2.0 <u>TECHNICAL DISCUSSION</u> -----	96
2.1 GROUP I SEALED CELLS-----	96
2.1.1 Cell Design-----	96
2.1.2 Test Procedures-----	98
2.1.3 Test Results-----	99
2.2 GROUP II SEALED CELLS-----	111
2.2.1 Cell Design-----	111
2.2.2 Test Results-----	116

2.2.3	Cells with Recombination Electrodes-----	121
2.2.4	Single Zinc Electrode Studies-----	121
2.2.5	Platinum Recombination Studies-----	123
2.2.6	Cells with Celgard/Pellon Separator System-----	127
3.0	<u>CONCLUSIONS</u> -----	135

SECTION VI

SYSTEM ENGINEERING (TASK V)-----	139
----------------------------------	-----

1.0	<u>INTRODUCTION</u> -----	140
2.0	<u>TECHNICAL DISCUSSION</u> -----	140
2.1	LIFE CYCLE PERFORMANCE OF EV TYPE CELLS-----	140
2.1.1	Design A - Framed Positive-----	141
2.1.2	Design B - Effect of Absorbent Material-----	141
2.1.3	Design C - Effect of Zigzag Wrap & Electrode Geometry-----	141
2.1.4	Design D - Effect of Rectangular Electrodes-----	143
2.1.5	Design E - Au Plated Positive Substrates-----	143
2.1.6	Design F - Proprietary Current Collector-----	144
2.1.7	Design G - Proprietary Positives-----	144
2.2	ELECTROCHEMICAL CHARACTERIZATION-----	147
2.2.1	Charging Curves-----	147
2.2.2	Thermal Response-----	147
2.2.3	Discharge Capacity and Temperature-----	150
2.2.4	Depth of Discharge and Cycle Life-----	154
2.3	CHARGE CONTROL-----	156
2.3.1	Auxiliary Electrode-----	156
2.3.2	Constant Voltage-----	156
2.4	POST FAILURE CHARACTERIZATION-----	158
2.4.1	Zinc Shape Change-----	158
2.4.2	Charge Percentage-----	159
2.4.3	Graphite Loss-----	162
3.0	<u>CONCLUSIONS</u> -----	164

NON-PROPRIETARYLIST OF FIGURES

SECTION III

ZINC ELECTRODE DEVELOPMENT FOR Ni-Zn CELLS (TASK II)

<u>FIGURE NO.</u>	<u>PAGE NO.</u>
II.1 Variation of Cell Capacity with Cycling for Ni-Zn Cells Containing Zn Electrodes with Polymer Laminated Cu Collectors-----	40
II.2 Performance Curves for Cell Z40-1-----	42
II.3 Capacity-Cycle Relationship for Cells Z13 & Z15---	43
II.4 Performance Curves for Cell Z63A with Fe ₂ O ₃ in Zn Electrode-----	46
II.5 Performance Curves for Cell Z48B-----	50
II.6 Effect of Insoluble Zn Compounds in the Zn Electrode (Cell 53A)-----	51
II.7 Polarization Curves from a Typical Uncycled Electrode-----	54
II.8 Polarization Curves from Edge Section of a Cycled Zn Electrode-----	55
II.9 Sectioned Zn Electrode-----	57

SECTION IV

SEPARATOR DEVELOPMENT FOR Ni-Zn CELLS (TASK III)

III.1 Influence of Exposure Time in KOH on Electrical Resistance of PVA Film-----	69
III.2 Residual Solvent Concentration as a Function of Film Formation Time for PVA + Water + Methanol System-----	77
III.3 Formation Time as a Function of Temperature for PVA + Water + Methanol System-----	78
III.4 Activation Energy for Solvent Diffusion as a Function of Residual Solvent Concentration-----	79
III.5 Influence of Ionic Resistivity on Degree of Crosslinking-----	80
III.6 Influence of Degree of Crosslinking on Electrical Resistance in PVA Films-----	83

ENERGY RESEARCH CORPORATION

SECTION V DEVELOPMENT OF SEALED Ni-Zn CELLS - (TASK IV)

<u>FIGURE NO.</u>		<u>PAGE NO.</u>
IV.1	Gas Production for Cell 2D1 at 3A Charge Rate----	103
IV.2	Gas Production for Cell 2E1 at 3A Charge Rate----	103
IV.3	Gas Production for Cell 2D1 at 8A Charge Rate----	104
IV.4	Gas Production for Cell 2E1 at 8A Charge Rate----	104
IV.5	Gas Production for Cell IG1 at 3.67A Charge Rate-	105
IV.6	Gas Production for Cell IG1 at 3A Charge Rate----	105
IV.7	Gas Production for Cell IG2 at 3.67A Charge Rate-	106
IV.8	Gas Production for Cell IG2 at 3A Charge Rate----	106
IV.9	Gas Production for Cell IG1 at 8A Charge Rate----	107
IV.10	Gas Production for Cell IG2 at 8A Charge Rate----	107
IV.11	Gas Production for Cell IH1 at 3A Charge Rate----	108
IV.12	Gas Production for Cell IH2 at 3A Charge Rate----	108
IV.13	Gas Production for Cell IH1 at 8A Charge Rate----	109
IV.14	Gas Production for Cell IH2 at 8A Charge Rate----	109
IV.15	Chemical Recombination Tests for Cell 2B1-----	112
IV.16	Chemical Recombination Tests for Cell 2E1-----	112
IV.17	Chemical Recombination Tests for Cell 2E2-----	113
IV.18	Group 2J Cell Cycle Results-----	120
IV.19	Characteristics of Platinum Catalysts in Electro- lyte Cell at 1A Rate-----	125
IV.20	Performance of Platinum Catalysts in Electrolyte Cell at 1A Rate-----	126
IV.21	Platinum Catalysts on Cycle, Cell 2P-----	128
IV.22	Pressure Buildup During Charge in Cells with Celgard-Pellon Separator System-----	130
IV.23	Pressure Decay on Open Circuit (After Charge) in Cells with Celgard-Pellon Separator System-----	131
IV.24	Open Circuit Recombination with Pure O ₂ -----	132
IV.25	Platinum Recombination Catalyst on Automatic Cycle, Cell 2T(I)-----	135

ENERGY RESEARCH CORPORATION

SECTION VI
SYSTEM ENGINEERING (TASK V)

<u>FIGURE NO.</u>	<u>PAGE NO.</u>
V.1 Cell Voltage-Capacity Relationship for Cells EV23, EV25, EV39 and EVT45-----	142
V.2 Cell Voltage-Capacity Relationship for Cells EV92, Design G, Effect of Formation-----	145
V.3 Charging Curves at Different Rates of Constant Current Charge-----	148
V.4 Capacity-Cell Voltage Relationship During Constant Current Charging at C/6-----	149
V.5 Variation of Cell Temperature During Charging-----	151
V.6 Variation of Cell Temperature During Discharge-----	152
V.7 Variation of Cell Temperature and Voltage During Discharge-----	153
V.8 Cell Voltage-Capacity Relationship During Charge and Discharge at 5°C-----	155

NON-PROPRIETARYLIST OF TABLES

SECTION II

NICKEL ELECTRODE DEVELOPMENT FOR Ni-Zn CELLS (TASK I)

<u>TABLE NO.</u>		<u>PAGE NO.</u>
I.1	Effect of Mulling Nickel Hydroxide Active Material----	9
I.2	Nickel Hydrate Drying Temperature Tests-----	11
I.3	ERC Nickel Hydrate Preparations-----	13
I.4	Addition of Graphite During Hydrate Preparation-----	15
I.5	Further Graphite Addition for Improved Utilization---	17
I.6	Nickel Hydrate Variations-----	19
I.7	5% Cobalt-Nickel Hydrate-----	21
I.8	Comparison of ERC and Commercial Nickel Hydrates----	23
I.9	Commercial Nickel Hydrate (September 1978)-----	25
I.10	Commercial Nickel Hydrate (April 1979)-----	27
I.11	Coprecipitated Nickel Hydrates-----	30
I.12	Coprecipitated Hydrate Formation Capacities-----	31

SECTION III

ZINC ELECTRODE DEVELOPMENT FOR Ni-Zn CELLS (TASK II)

II.1	Design Features of 20 Ahr Ni-Zn Cells-----	37
II.2	Summary of Substrate Study-----	44
II.3	Life Cycle Performance of Zn Electrodes in Ni-Zn Cells Containing Additives-----	48
II.4	Summary of Additive Study-----	52
II.5	Polarization Characteristics of a Selection Zinc Electrode-----	58

SECTION IV

SEPARATOR DEVELOPMENT FOR Ni-Zn CELLS (TASK III)

III.1	Influence of Prolonged KOH Exposure on Electrical Resistance of Thermoplastic Based Films-----	64
III.2	Rate of Electrolyte Diffusion for TP-Based Films-----	64
III.3	Dimensional Change of Separator Films-----	66
III.4	Zinc Penetration Test Results with TP-Based Separators-----	67

ENERGY RESEARCH CORPORATION

<u>TABLE NO.</u>	<u>PAGE NO.</u>
III.5 Influence of Residual Solvent Quantity on Electrical Resistance of PVA Films-----	70
III.6 Influence of Prolonged KOH Exposure on Electrical Resistance of PVA Films-----	72
III.7 Quantity of Residual Solvent in PVA Films Formed at Various Conditions for PVA + Water System-----	75
III.8 Quantity of Residual Solvent in PVA Films Formed at Various Conditions-----	76
III.9 Ionic Resistivity of PVA Films with Varying Amounts of Crosslinking Agent-----	82
III.10 Influence of Temperature on Properties of Cross- linked PVA Films-----	83
III.11 Electrical Resistance of Crosslinked PVA Films-----	86
III.12 Electrical Resistance of Crosslinked PVA Films After Post Treatment at 140°C -----	87
III.13 Degree of Crosslinking in PVA Films-----	89
III.14 Dimensional Change of PVA Films in KOH-----	90
III.15 Zinc Penetration Test Results with PVA Based Separator-----	91

SECTION V

DEVELOPMENT OF SEALED NICKEL-ZINC CELLS (TASK IV)

IV.1 Construction Variables for Group I 20 Ahr Sealed Cells-----	97
IV.2 Test Summary for First Sealed Cell Group-----	100
IV. 3 Group IG Cycle Test Results-----	102
IV.4 Cell Test Results at 3A and 8A Charge Rates -----	110
IV.5 Group II Cell Design Summary-----	115
IV.6 Test Summary for Second Sealed Cell Group-----	118
IV.7 Performance of Sealed Cells with Recombination Electrodes-----	122
IV.8 Single Electrode Test Results-----	124
IV.9 Pressure Controlled Charge Characteristics for Cells with Celgard-Pellon Separator System-----	129
IV.10 Cycle Data For Sealed Cells-----	134

ENERGY RESEARCH CORPORATION

SECTION VI
SYSTEM ENGINEERING (TASK V)

<u>TABLE NO.</u>	<u>PAGE NO.</u>
V.1	Summary of Life Performance of EV Type Cells----- 146
V.2	Temperature Dependence of the Discharge Capacity--154
V.3	Cycle Life Data of 20 Ahr Cells Containing an Auxiliary Electrode-----157
V.4	Comparison of Area Reduction and Cycle Life-----160
V.5	Graphite Loss at the Positive as a Function of Number of Cycles-----163

ENERGY RESEARCH CORPORATION

SECTION I

INTRODUCTION

1.0 INTRODUCTION

The report contained herein is the second annual report which reviews the progress achieved under ANL Contract No. 31-109-38-4248. It covers the report period from 16 August 1978 to 16 August 1979.

The report itself is subdivided into the major areas of activity, e.g., Component Development and System Engineering. The first segment of the overall program entitled, "Component Development" consists of four basic tasks which are proceeding in parallel. They are:

TASK I - Nickel Electrode Development

TASK II - Zinc Electrode Development

TASK III - Separator Development

TASK IV - Sealed Cell Development

Each of these tasks is reported herein on a stand-alone basis along with its own introduction and conclusion.

TASK I: The nickel electrode development program is directed at the optimization of the electrical performance, specifically, in terms of increased cycle life. In addition, emphasis is being placed on low cost manufacturing procedures since the ERC developed non-sintered electrode holds great promise of becoming the lowest cost nickel electrode available.

The work during this report period has concentrated on both the development of pilot plant facilities for the production of nickel hydroxide and on the optimization of manufacturing processes to produce nickel hydroxide with high electrochemical utilization. The pilot plant is now capable of producing in

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excess of 100 lb/week of nickel hydroxide which is equivalent to approximately 12.5 kWhr theoretical capacity.

The baseline nickel hydroxide has been characterized and is now being subjected to optimization via processing variations (e.g., in precipitation procedures, degree of washing, grinding, drying and aging) prior to incorporation into electrodes. Nickel electrodes of optimized construction are now capable of over 500 cycles at the C/2 rate at 100% DOD with no evidence of decay in performance.

With full size nickel electrodes now being routinely manufactured in the pilot plant, it is apparent that there are no barriers to large scale production utilizing ERC's non-sintered process.

During the next twelve (12) month period, efforts will center on reduction or elimination of the Co(OH)_2 additive since its cost is becoming prohibitive.

TASK II. The primary goal of studying the zinc electrode is to increase its cycle life to achieve 400 to 500 deep cycles at the C/2 discharge rate.

This effort is primarily concentrating on the effect of additives on shape change and cycle performance and on the mechanistic processes involved in the shape change. Improved performance has been obtained with various insolubilizing additives.

During the next twelve months, zinc electrode tasks will center on the effects of various additives and constructional variations on electrode stability and cycle life. Work will continue on the development of laboratory procedures for screening

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additives and quantitative determination of shape change.

TASK III: The separator effort has as its major goal the development of a low cost separator which: exhibits stability in the electrolyte, has uniform pores sufficiently small to impede the growth of zinc dendrites, and exhibits low electrical resistance and good flexibility. ERC's efforts involve both in-house manufactured and commercially available separator materials. The in-house manufactured separators consist of self-supporting cast plastic films.

The process itself is now optimized for pilot plant manufacture; hundreds of formulations have been produced and subsequently screened in both the laboratory and in actual cells. Promising formulations which include both thermoplastic based and PVA separators are presently being subjected to additional characterization tests and life cycles. Additionally, any promising commercial separators which become available are immediately placed into screening programs.

During the next twelve months, selected formulations will be tested in full scale EV cells. Studies will be undertaken to improve the mass transport characteristics and new separators will continue to be manufactured and tested.

TASK IV: The goal of the sealed cell studies is to determine the feasibility of sealed cell operation. This task was started later than the other studies and hence has the least amount of available data. The initial exploratory studies involve 20 Ahr size cells where the rates of oxygen recombination, hydrogen generation and electrolyte concentration effects, etc. are being determined.

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TASK V: System Engineering is the second major sub-division of the effort. It includes the design and testing of all cells, the investigation of charge control devices and techniques, and the complete analysis of all cells for failure modes.

TASK V also encompasses the accelerated testing of 20 Ahr size cells. To date, large numbers of these cells (incorporating separator variations, active material additives and internal design variations) have been subjected to this type of testing.

ERC has developed a test facility under this task which is capable of testing large numbers of full scale EV cells under varied test regimes including the simulated J227 test. These test data are now routinely fed into our computer system for data reduction and correlation. The small number of full scale cells tested to date appear to have somewhat lower cycle life capability than 20 Ahr cells.

SECTION II.

NICKEL ELECTRODE DEVELOPMENT
FOR NICKEL-ZINC CELLS - (TASK I)

1.0 INTRODUCTION

During the past 12 months, work has been in progress to optimize the roll bonded positive electrode structure. The technical investigation has centered on:

- the method for precipitation of $\text{Ni}(\text{OH})_2$
- drying temperature for $\text{Ni}(\text{OH})_2$
- graphite addition
- $\text{Co}(\text{OH})_2$ content and substitutes for $\text{Co}(\text{OH})_2$
- particle size of $\text{Ni}(\text{OH})_2$ starting material.

$\text{Ni}(\text{OH})_2$ produced at ERC as well as $\text{Ni}(\text{OH})_2$ from commercial sources was studied.

Positive electrodes were usually evaluated in 20 Ahr size Ni-Cd cells to determine voltage characteristics and active material utilization. Following initial screening, the cells were life cycled to determine capacity maintenance for various positive electrode types.

2.0 TECHNICAL DISCUSSION

2.1 WASHING AND DRYING OF $\text{Ni}(\text{OH})_2$

In the preparation of roll bonded positive electrodes, nickel hydrate, graphite and Teflon are mulled between rollers to develop a cohesive mass. A test was made of the effect of the amount of mulling and resultant Teflon fibrolation on the performance of subsequent electrodes. Active material mixtures used contained 10% cobalt-nickel hydrates, were designated SD and WDW and were made by essentially two different processes. The SD process forms a fine powder while the WDW results in large agglomerates that must be micromilled. The apparent density

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(Scott Volumeter) of the SD hydrate is essentially half that of the WDW hydrate.

These hydrates were used to make nominal 20 Ahr Ni-Cd test cells with positive plate materials mulled "normally", in excess of normal, and less than normal. The cells were tested on an automatic cycler with a six hour charge at 3.7 amperes followed by a two hour discharge at 10 amperes, representing 100% depth of nominal discharge capacity. Giving data for 550 cycles, Table I.1 shows the initial improvement in capacity with cycling and the general superiority of the WDW over the SD hydrate. Two of the SD hydrate cells were discontinued after 300 cycles; the superior overmulled material was continued. The WDW hydrate cells appear equivalent within experimental precision. In this case, the larger particle size of this hydrate is believed to produce additional Teflon fibrolation during the sizing of the layers, resulting in an equalizing effect.

After 550 cycles, the available electrolyte was removed from the WDW cells for analysis and the cells were given a complete discharge to determine the capacity of both the positive and negative plates. The electrolyte showed a buildup of carbonate and a decrease in total alkalinity. The carbonate buildup is believed to be due primarily to the oxidation of graphite and reaction of atmospheric CO_2 with the electrolyte. The decrease in normality is believed to be caused by loss of electrolyte through entrainment and its replacement with water during cell maintenance. Although the cell capacities were only moderately decreased during cycling, there was a large increase in the

TABLE I. 1

EFFECT OF MULLING NICKEL HYDROXIDE ACTIVE MATERIALS
(20 Ahr Ni-Cd Cells)

	SD			WDW		
DEGREE OF MULLING	OVER	NORMAL	UNDER	OVER	NORMAL	UNDER
Cell Voltage	At 1 hour/1 hour + 55 minutes or Cap.(Ahr) to 0.70V					
CYCLE 1	1.116/0.993	1.098/18.5	1.094/18.7	1.132/18.7	1.129/1.006	1.131/19.0
CYCLE 13	1.133/1.019	1.108/0.911	1.102/0.866	1.153/1.065	1.144/1.061	1.148/1.063
CYCLE 61	1.139/1.010	1.056/17.7	1.023/16.3	1.160/1.065	1.137/1.043	1.159/1.061
CYCLE 106	1.135/0.986	1.029/17.5	1.018/17.2	1.164/1.063	1.133/1.036	1.168/1.067
CYCLE 163	1.123/0.948	0.965/15.8	0.953/15.3	1.170/1.039	1.122/0.988	1.175/1.046
CYCLE 205	1.116/0.892	0.924/14.8	0.883/14.0	1.168/1.032	1.122/0.995	1.174/1.044
CYCLE 247	1.101/0.879	-/7.7	-/8.8	1.152/1.012	1.118/1.020	1.160/1.038
CYCLE 301	1.125/0.815	OFF TEST	OFF TEST	1.162/0.888	1.160/0.977	1.172/0.982
CYCLE 403	1.121/16.8			1.152/0.836	1.163/0.955	1.167/0.951
CYCLE 457	1.099/14.1			1.129/0.803	1.165/0.833	1.163/0.894
CYCLE 499	1.080/12.5			1.087/0.778	1.152/0.845	1.145/0.856
CYCLE 550	-/9.2			1.038/14.7	1.155/18.8	1.157/19.8

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distribution of cell capacity between 1.00 and 0.70V. The negative plate capacities were 24 Ahr and represent 50% utilization of the active material. With the complete discharge, there was an improvement in the cell discharge voltage believed to be associated with the memory effect of the cadmium electrode. These capacities were equivalent to those obtained after 250 cycles. The cycling was continued and it was 800 cycles before the cells declined to their pretreatment capacities. Cycling was continued for over 1000 cycles before cadmium penetration of the separator and soft shorts affected the cell capacities to the point where they were terminated.

A preparation objection to WDW hydrate is the relatively long time required for initial drying at 60°C. The hydrate, prior to the initial drying stage, contains chemically bonded water with the nickel hydroxide. To overcome this, experimental samples of hydrate were dried at 60, 80, 100 and 120°C.

Nominal 20 Ahr Ni-Cd cells were made with these hydrates using the overmilled electrode preparative procedure described earlier as the standard. The cells were given 273 automatic cycles as shown in Table I.2. Initially, the midpoint voltage at the C/2 rate showed a decrease with the higher drying temperature which disappeared with cycling. As the discharge cycles increased, the final voltages of the cells with hydrate dried at the higher temperature decreased more rapidly indicating that performance is affected by the higher drying temperature.

In the preparation of WDW hydrate, washing of the $\text{Ni}(\text{OH})_2$ is continued until just before the hydrate takes on colloidal properties. At this point, the liquid and hydrate still have

TABLE I.2

NICKEL HYDRATE DRYING TEMPERATURE TESTS

(20 Ahr Ni-Cd Cells)

CYCLES	DRYING TEMPERATURE, °C			
	60	80	100	120
Formation Cycles	Voltage at 1 hour - Capacity (Ahr) to 1.00/0.70V			
CYCLE 2 at 10 A	1.122-17.7/18.2	1.118-17.4/17.9	1.052-15.9/17.6	1.075-16.1/17.8
CYCLE 5 at 10 A	1.131-19.5/20.1	1.130-19.5/20.2	1.107-19.2/20.2	1.116-19.5/20.4
CYCLE 8 at 10 A	1.140-22.5/23.2	1.136-22.8/23.3	1.127-23.4/24.2	1.130-23.8/24.2
AUTOMATIC CYCLING				
Cell Voltage	At 1 hour/1 hour + 55 minutes or Capacity (Ahr) to 0.80V			
CYCLE 1	1.145/1.072	1.142/1.072	1.135/1.071	1.135/1.072
CYCLE 25	1.157/1.052	1.152/1.052	1.153/1.038	1.152/1.044
CYCLE 42	1.161/1.074	1.158/1.072	1.152/1.064	1.158/1.064
CYCLE 66	1.168/1.071	1.168/1.070	1.168/1.058	1.168/1.060
CYCLE 105	1.178/1.078	1.178/1.076	1.170/1.053	1.170/1.060
CYCLE 147	1.175/1.050	1.171/1.044	1.168/1.014	1.169/1.020
CYCLE 162	1.164/1.044	1.167/1.036	1.158/1.002	1.154/1.008
CYCLE 183	1.169/1.025	1.168/1.025	1.160/0.994	1.158/0.993
CYCLE 204	1.162/1.006	1.158/1.008	1.150/0.964	1.148/0.962
CYCLE 225	1.148/0.892	1.147/0.916	1.128/19.0	1.134/18.0
CYCLE 252	1.152/0.898	1.145/0.914	1.121/19.2	1.128/18.3
CYCLE 273	1.148/0.916	1.136/19.0	1.104/18.3	1.058/16.7

NOTE: All results are the average of two cells. At Cycle 40, the cells were transferred to a different cycler.

excessive amounts of residual sulfate. If the washing is continued until the material is essentially free of sulfate, the hydrate becomes very difficult to filter because it becomes colloidal. The 10% cobalt-nickel hydrates were made by both the single and double washing methods to ascertain the trade offs between the longer filtration time versus the additional washing and drying step.

The 20 Ahr Ni-Cd cells were made from these hydrates and were given 365 standard automatic charge/discharge cycles to determine any difference in behavior. Table I.3 shows that cells made with either hydrate are equivalent.

2.2 CONTINUOUS PRECIPITATION OF $\text{Ni}(\text{OH})_2$

In the batch preparation of nickel hydrate, sufficient 45% KOH is added to the nickel sulfate solution in two equal amounts to give a small excess over the stoichiometric requirement. A more uniform hydrate can be made by the continuous mixing of the nickel sulfate and caustic solutions. An apparatus was set up to continuously pump these solutions into a small reaction vessel where the precipitation took place, facilitated by vigorous mixing. The nickel hydrate slurry was continuously withdrawn through an overflow pipe to the washing container. A 20 lb. quantity of our WDW hydrate made by this method appeared finer than hydrate made by our regular procedure.

Four 20 Ahr Ni-Cd cells were made from this hydrate. Two of the cells were made with 1/4 x 5 mil strip rather than three 16 mil nickel wires as connection to the plates. The intent was to determine if better spot welding between the expanded metal grid and tab would lead to improved cycling. Because it

TABLE I.3

ERC NICKEL HYDRATE PREPARATIONS

(20 Ahr Ni-Cd Cells)

CYCLES	WDW	WD	CONTINUOUS PRECIPITATION		
			Cycle	Normal Tabs	Strip Tabs
Formation Cycles	Voltage at 1 hour Capacity (Ahr) to 1.00/0.70V				
CYCLE 4 at 10A	1.130-20.4/20.8	1.124-20.4/20.7		1.135-19.3/19.8	1.150-18.9/19.1
AUTOMATIC CYCLING					
Cell Voltage	At 1 hour/1 hour + 55 minutes or Capacity(Ahr) to 0.70V				
CYCLE 3	1.134/1.030	1.127/1.028	CYCLE 1	1.133/1.036	1.144/1.038
CYCLE 9	1.152/1.062	1.146/1.069	CYCLE 16	1.149/1.056	1.167/1.071
CYCLE 30	1.142/1.024	1.138/1.020	CYCLE 37	1.155/1.053	1.179/1.067
CYCLE 45	1.130/1.020	1.126/1.021	CYCLE 58	1.157/1.032	1.170/1.078
CYCLE 72	1.130/1.006	1.122/1.020	CYCLE 67	1.162/1.036	1.184/0.992
CYCLE 105	1.126/1.010	1.116/1.012	CYCLE 82	1.162/1.018	1.178/18.8
CYCLE 129	1.118/0.980	1.096/0.981	CYCLE 100	1.163/1.006	1.190/0.961
CYCLE 165	1.101/0.959	1.098/0.962	CYCLE 133	1.146/18.7	1.178/17.4
CYCLE 207	1.091/0.933	1.089/0.933	CYCLE 153	1.155/17.9	1.182/16.9
CYCLE 249	1.087/0.908	1.082/0.899	CYCLE 174	1.158/18.8	1.178/17.0
CYCLE 273	1.084/0.896	1.072/0.879	CYCLE 195	1.160/18.4	
CYCLE 303	1.082/0.811	1.074/0.841	CYCLE 207	1.152/18.0	
CYCLE 324	1.076/0.745	1.068/0.891	CYCLE 216	1.152/18.4	
CYCLE 365	1.090/0.849	1.084/0.882	CYCLE 225	1.156/18.4	

NOTE: All results are the average of two cells.

ENERGY RESEARCH CORPORATION

was not possible to use cell posts with the nickel strip, the tabs were extended above the cell cover for electrical connection. These cells were given 174 and 225 automatic charge/discharge cycles. Table I.3 presents the data for cells with hydrate made by the batch process utilizing WDW and WD procedures for ready comparison with the hydrate made by continuous precipitation. The continuously precipitated hydrate cells had slightly lower formation capacities, although the voltage at one hour was a little higher. On cycling, the cells took several additional cycles to attain their maximum capacity. Capacity maintenance was not as stable as our standard cells. It is believed that this was due to the finer nature of the prepared hydrate. The use of nickel strip rather than wire tabs was beneficial with respect to cell discharge voltage, but it did not aid in cyclic capacity maintenance.

2.3 GRAPHITE ADDITION DURING $\text{Ni}(\text{OH})_2$ PRECIPITATION

To improve the electrode capacity per unit volume, experiments were run to use the graphite more efficiently so that a greater portion of the electrode volume would be devoted to the active hydrate. The procedure involved the preparation of nickel hydrate with a portion of the graphite added during precipitation to achieve contact between the two materials. The final graphite addition during electrode preparation was adjusted to give a total of 25% rather than 30% graphite.

The 20 Ahr Ni-Cd test cells were made with these hydrates along with a WDW hydrate made in a similar manner, but without the graphite addition. The cells were given 163 standard automatic charge/discharge cycles as described in Table I.4.

TABLE I.4

ADDITION OF GRAPHITE DURING HYDRATE PREPARATION
(20 Ahr Ni-Cd Cells)

	GRAPHITE ADDED		
	0 30% GO2	8% GO2 17% GO2	8% G24 17% GO2
Hydrate Precipitation Electrode Preparation Theoretical Cap., (Ahr)	23.4	25.3	25.3
Formation Cycles	Voltage at 1 hour - Capacity (Ahr) to 1.00/0.70V		
Cycle 4 at 1CA	1.117-16.7/19.5	1.124-18.9/19.2	1.129-19.0/19.2
AUTOMATIC CYCLING			
Cell Voltage	At 1 hour/1 hour + 55 minutes or Capacity (Ahr) to 0.70V		
CYCLE 1	1.122/0.716	1.130/1.034	1.134/1.041
CYCLE 19	1.131/0.850	1.144/1.024	1.148/1.024
CYCLE 28	1.132/18.8	1.150/0.985	1.154/1.002
CYCLE 49	1.126/18.8	1.144/0.932	1.144/0.908
CYCLE 79	1.110/19.0	1.154/0.948	1.144/0.871
CYCLE 100	1.098/18.3	1.148/0.918	1.136/0.833
CYCLE 121	1.086/18.3	1.148/0.870	1.140/0.816
CYCLE 133	1.058/18.0	1.146/0.864	1.138/0.818
CYCLE 142	1.029/17.7	1.139/0.872	1.137/0.823
CYCLE 154	0.998/17.3	1.142/0.860	1.136/0.830
CYCLE 163	0.996/17.0	1.138/0.832	1.128/0.804

NOTE: All results are the average of two cells.

ENERGY RESEARCH CORPORATION

These cells behaved poorly compared to the usual standard hydrate indicating that the hot concentrated caustic required to wet the graphite probably caused excessive carbonate contamination. The voltage improvement of the other cells with less graphite does indicate that the approach is a viable way of improving the capacity per unit volume.

Additional hydrates were made to obtain better utilization of the conductive graphite. In one case, 2% colloidal graphites Aquadag and Electrodag 192-A (Acheson Colloids Co.) were added to the caustic during precipitation of the 10% cobalt nickel hydrate. In the second experiment, 2% Shawinigan acetylene black was added during precipitation and 1% to the positive mix prior to mulling. These hydrates were made into positive electrodes using less total graphite as indicated in Table I.5.

The electrodes were made into 20 Ahr Ni-Cd cells by our standard procedures and given 138 automatic charge/discharge cycles as also shown in the table. The cyclic capacity maintenance of all cells was inferior to the standard WDW hydrate cells. A comparison of cells having 30% GO2 and 1% Shawinigan acetylene black plus 20% GO2 graphites with the same hydrate indicates that this approach should be investigated further. The characteristics of hot concentrated potassium hydroxide to absorb carbon dioxide indicate that this condition should be avoided during hydrate preparation by limiting access by air.

2.4 CHEMICAL OXIDATION OF $\text{Ni}(\text{OH})_2$

Another phase of upgrading electrode behavior was to improve the electrochemical activity of the nickel hydrate. One of the variations tried was to oxidize 10 and 25% of the

TABLE I.5
FURTHER GRAPHITE ADDITION FOR IMPROVED UTILIZATION
(20 Ahr Ni-Cd Cells)

Graphite Percent Hydrate Precipitation Electrode Preparation Theoretical Cap., Ahr	GRAPHITE ADDED			
	0 1% Shawinigan 26.8	2% Shawinigan 20% GO2 26.6	2% Electrodag 20% GO2 26.6	2% Aquadag 20% GO2 26.6
Formation Cycles	Voltage at 1 hour - Capacity(Ahr) to 1.00/0.70V			
Cycle 3 at 10A	1.135-22.4/24.8	1.140-21.0/23.0	1.134-21.9/23.1	1.128-16.7/22.1
AUTOMATIC CYCLING				
Cell Voltage	At 1 hour/1 hour + 55 minutes or Capacity(Ahr) to 0.80V			
CYCLE 1	1.142/1.039	1.144/1.036	1.142/1.031	1.138/0.996
CYCLE 12	1.145/1.012	1.148/1.015	1.147/1.012	1.143/1.005
CYCLE 21	1.146/1.006	1.148/1.011	1.148/1.012	1.144/1.003
CYCLE 33	1.141/0.997	1.143/0.996	1.145/1.006	1.140/0.991
CYCLE 39	1.146/0.985	1.142/0.976	1.146/0.982	1.144/0.989
CYCLE 60	1.138/0.977	1.132/0.946	1.136/0.954	1.138/0.975
CYCLE 81	1.126/0.884	1.117/17.3	1.120/0.826	1.133/0.900
CYCLE 96	1.130/0.930	1.118/19.2	1.127/0.860	1.145/0.972
CYCLE 105	1.130/19.0	1.118/18.0	1.122/18.2	1.140/19.0
CYCLE 117	1.129/0.832	1.118/18.3	1.124/19.2	1.140/0.890
CYCLE 126	1.138/0.851	1.132/19.0	1.136/0.910	1.149/0.934
CYCLE 138	1.138/0.861	1.130/19.0	1.129/19.0	1.140/0.953

NOTE: All results are the average of two cells.

10% cobalt-nickel hydrate with potassium persulfate during preparation. Another was to eliminate the addition of cobalt to improve the capacity per unit volume. For possible cycling improvement, potassium sulfate was added to the nickel solution to enhance the introduction of potassium into the nickel hydrate lattice. Except as noted, the hydrates were prepared by the standard WDW procedure and made into standard 20 Ahr Ni-Cd test cells.

Test cells containing potassium persulfate treated nickel hydrate were tested for 437 cycles while those without cobalt were given 238 cycles as described in Table I.6. The cells with 10% persulfate treated hydrate equaled our best results. The cells without cobalt did not cycle as well as those with 10% cobalt. It is probable that satisfactory results could be obtained with an intermediate amount of cobalt. The addition of potassium in the nickel hydrate lattice does not appear to be beneficial.

2.5 REDUCED COBALT QUANTITY

The 10% cobalt-nickel hydrate made by the WDW procedure has met many of the objectives of this program. However the expense and relatively inactive state of cobalt hydrate warrants that its use be kept to a minimum. Utilization of a hydrate preparative procedure not requiring extensive filtration times would improve productivity. Finally, better utilization of the conductive graphite would permit reduction in graphite quantity, thereby increasing the capacity per unit volume. An attempt has been made to incorporate all of these possibilities into these hydrates.

TABLE I.6

NICKEL HYDRATE VARIATIONS
(20 Ahr Ni-Cd Cells)

	10% Co-Ni(OH) ₂		100% Ni(OH) ₂	
Theoretical Cap, Ahr	10% K ₂ S ₂ O ₈ 23.4	25% K ₂ S ₂ O ₈ 23.4	-- 26.0	Added K 26.0
Formation Cycles	Voltage at 1 hour - Capacity (Ahr) to 1.00/0.70V			
Cycle 4 at 1GA	1.134-21.2/22.4	1.133-21.2/21.9	1.154-21.6/22.0	1.155-21.6/22.0
AUTOMATIC CYCLING				
Cell Voltage	At 1 hour / 1 hour + 55 minutes or Capacity (Ahr) to 0.80v			
CYCLE 3	1.134/1.038	1.132/1.034	1.153/1.050	1.154/1.046
CYCLE 51	1.163/1.086	1.166/1.084	1.159/1.115	1.145/1.106
CYCLE 93	1.140/0.962	1.154/1.007	1.134/1.008	1.113/19.0
CYCLE 154	1.145/1.005	1.148/0.992	1.118/18.8	1.106/18.8
CYCLE 199	1.144/0.983	1.148/0.964	1.103/17.5	1.107/18.2
CYCLE 238	1.142/0.960	1.149/0.920	1.100/17.3	1.102/17.5
CYCLE 264	1.149/0.988	1.144/0.942		
CYCLE 306	1.148/0.954	1.133/0.876		
CYCLE 334	1.154/0.960	1.140/0.878		
CYCLE 355	1.162/0.948	1.140/0.854		
CYCLE 376	1.164/0.932	1.140/0.769		
CYCLE 406	1.162/0.901	1.133/18.8		
CYCLE 416	1.162/0.868	1.127/18.2		
CYCLE 437	1.156/19.0	1.091/15.7		

NOTE: All results are the average of two cells.
Cycling stopped for 4 days after the 114th cycle.

Previous experiments have shown that cells without cobalt will maintain their full cyclic capacity for only 100 cycles rather than 500 cycles. Therefore a logical step was to make an intermediate 5% cobalt-nickel hydrate.

The preparative conditions for the 5% cobalt-nickel hydrate were adjusted to avoid the formation of colloidal hydrate. The final variable was to concentrate the cobalt on the outside of the nickel hydrate. This was accomplished by first precipitating nickel hydrate and washing to a neutral pH. Next, 5% cobalt as a solution, was added and precipitated with additional caustic.

A second series of experiments incorporated graphite directly into the precipitating solutions. In previous experiments the graphite was made wettable by boiling it in the precipitating caustic solution. In this case, G02 was treated to make it wettable. The 10% graphite hydrates were made by using graphite in the 5% cobalt-nickel sulfate solution and in the precipitating caustic. All of the 5% cobalt-nickel hydrates were made into 20 Ahr Ni-Cd test cells without any apparent difficulty. The use of 5% cobalt led to cells with a theoretical capacity of 24.7 Ahr. Decreasing the total graphite to 25% for cells with graphite hydrate gave a theoretical capacity of 28.9 Ahr.

After several formation cycles, the cells were given 278 automatic charge/discharge cycles as shown in Table I.7. The formation results were encouraging for cells with externally concentrated cobalt in that these cells exhibited full capacity with the first formation discharge. In the cases of the precip-

TABLE I.7

5% COBALT-NICKEL HYDRATE

(20 Ahr Ni-Cd Cells)

	Added Cobalt	Std.	Std.	Graphite to KOH	Graphite to Ni Solution
Theoretical Cap., (Ahr)	24.7	24.7	24.7	28.9	28.9
Formation Cycle	Voltage at 1 hour - Capacity (Ahr) to 1.00/0.70V				
Cycle 6 at 10A	1.150-20.5/21.4	1.144-20.0/20.5	1.144-19.5/19.9	1.151-19.9/21.4	1.148-18.9/20.9
CYCLE 2	1.162/0.961	1.127/1.020	1.148/19.8	1.154/0.968	1.153/0.944
CYCLE 23	1.157/1.001	1.123/0.946	1.146/1.046	1.156/1.051	1.156/1.032
CYCLE 56	1.129/1.000	1.126/0.908	1.128/1.022	1.141/1.032	1.134/1.021
CYCLE 77	1.127/0.957	1.104/19.2	1.136/0.956	1.136/0.978	1.125/0.907
CYCLE 98	1.132/0.952	1.092/18.5	1.148/0.988	1.145/0.958	1.128/0.885
CYCLE 131	1.111/19.0	1.103/18.2	1.140/0.901	1.132/20.0	1.122/19.3
CYCLE 152	1.110/18.3	1.092/18.5	1.126/0.785	1.128/19.5	1.108/18.8
CYCLE 173	1.106/18.0	1.103/18.2	1.149/19.8	1.126/18.8	1.103/18.5
CYCLE 203	1.104/18.5	1.094/18.5	1.134/0.895	1.116/19.5	1.086/18.8
CYCLE 224	1.104/18.2	1.100/18.2	1.141/19.8	1.126/19.2	1.092/18.2
CYCLE 245	1.091/17.5	1.086/17.5	1.129/19.2	1.104/18.3	1.073/17.2
CYCLE 254	1.083/17.2	1.080/17.2	1.130/18.7	1.100/18.0	1.072/17.0
CYCLE 269	1.071/17.0	1.069/17.0	1.120/18.8	1.085/17.8	1.052/16.3
CYCLE 278	1.063/16.2	1.066/16.2	1.116/18.0	1.080/17.2	1.048/16.2

NOTE: All results are the average of two cells.

ENERGY RESEARCH CORPORATION

itated graphite hydrate, the additional hydrate capacity was not fully utilized although the voltage level was not affected by the decrease in the graphite quantity.

None of the 5% cobalt-nickel hydrate cells have cycled as well as those with 10% cobalt. Aside from the formation capacities, the results with coprecipitated and externally concentrated cobalt are equivalent. The addition of graphite to the caustic appears to give better results than adding it to the nickel solution. Adding graphite to the caustic also improves the cell voltage with less graphite, implying that the electrode has better conductivity. The next step will be to determine whether graphite addition during precipitation will further improve the cyclic performance of the positive electrode with 5% cobalt.

2.6 USE OF COMMERCIAL $\text{Ni}(\text{OH})_2$

In the present nickel-zinc battery work, considerable quantities of commercial nickel hydrate are used because of its availability in quantity. This material differs from ERC hydrate in that it contains 1.5% rather than 10% cobalt and will all pass through a 200 mesh screen in contrast to the 10 to 20% usually retained by the ERC hydrate. The commercial material received in September 1978 contained a noticeable amount of free alkali and 1.0% sulfate. The hydrate was rewashed, yielding a final product containing no free caustic and 0.5% sulfate.

The 20 Ahr Ni-Cd cells were made using ERC hydrate and as-received commercial hydrate. Table I.8 describes the formation and cyclic capacities for a number of cycles. The discharge voltages of the cells with commercial hydrate were better in part due to the lower cobalt content. The ERC hydrate cells

Table I.8
COMPARISON OF ERC AND COMMERCIAL NICKEL HYDRATES
(20 Ahr Ni-Cd Cells)

	ERC-1	ERC-2	Commercial	Commercial	Washed-1	Washed-2	
Theo. Cap.,Ahr	23.4	23.4	25.3	25.3	25.3	25.3	
Formation Cycles	Voltage at 1 hour/ Capacity (Ahr) to 1.00/C.70 V						
Cycle 2 at 10 A	1.068-16.5/17.8	1.074-16.8/18.0	1.139-18.3/18.8	1.147-19.0/19.2	1.151-21.5/22.0	1.150-21.2/22.0	
Cycle 9 at 10 A	1.126-23.7/25.7	1.129-24.0/26.0	1.153-21.0/22.0	1.151-21.8/23.0			
AUTOMATIC CYCLING							
Cell Voltage	At 1 hour/1 hour + 55 minutes or Capacity (Ahr) to 0.70 V						
CYCLE 4	1.118/1.076	1.120/1.082	1.138/1.078	1.132/1.097	CYCLE 1	1.152/1.06	1.151/1.101
CYCLE 60	1.147/1.029	1.126/1.000	1.095/16.0	1.132/0.771	CYCLE 59	1.175/1.077	1.148/1.057
CYCLE 102	1.129/0.987	1.109/0.942	1.126/17.3	1.113/0.760	CYCLE 95	1.171/1.059	1.137/1.012
CYCLE 141	1.100/0.946	1.086/0.896	1.130/17.0	1.089/0.829	CYCLE 149	1.160/1.023	1.124/0.736
CYCLE 201	1.114/0.910	1.096/0.756	1.141/17.3	1.110/0.815	CYCLE 200	1.132/0.993	1.112/18.7
CYCLE 264	1.094/0.873	1.088/0.820	1.143/17.0	1.106/0.881	CYCLE 206	1.147/0.982	1.129/18.7
CYCLE 270	1.114/0.864	1.092/0.797	1.154/17.3	1.118/0.860		23.5 21.2	23.6 18.7
Positive Plate Cap. Ah	20.7	19.8	17.5	20.3	CYCLE 209	1.158/0.936	1.132/18.0
Negative Plate Cap. Ah	23.5	24.3	24.3	25.0	CYCLE 224	1.153/0.965	1.132/16.5
					CYCLE 242	1.136/0.925	1.113/17.0
CYCLE 273	1.082/0.741	1.088/14.7	1.152/15.0	1.128/0.808			
CYCLE 288	1.065/0.753	0.759/10.5	1.146/16.3	1.114/0.750			
CYCLE 306			1.134/16.3	1.107/19.0			

ENERGY RESEARCH CORPORATION

are poorer than the previous cells and required a greater number of formation cycles than commercial hydrate cells to develop maximum capacity. Washing commercial hydrate allowed the development of full capacity after only two formation cycles.

The cyclic capacity of each of the groups can be considered equal, with each group having a noticeably poorer cell. The individual cell plate capacities were determined by a complete discharge of cells with a reference electrode. These results showed that the ERC and commercial hydrate cells varied because the positive plate limited the capacity, while the washed commercial hydrate cells varied because of the negative plate. Several of the cells had a significant capacity decrease on subsequent cycles, indicating that this discharge produced possible delamination of the electrodes. The poorest cell in each group was taken apart and examination of the electrodes and separator revealed no signs of active material shedding. When individual plates were bent to determine adhesion to the plate grid, there did appear to be some loss of active material.

Six additional cells were made with washed (September 1978) hydrate to determine cell reproducibility under present manufacturing conditions. These cells were given 400 charge/discharge cycles as described in Table I.9. Although there is variation, the results indicate that the roll bonded procedure will produce satisfactory cells.

A new supply of commercial hydrate was received during April 1979. This material showed only a trace of free caustic and had a sulfate content of 0.7%. Five 20 Ahr Ni-Cd test cells

TABLE I.9
COMMERCIAL NICKEL HYDRATE (SEPT. 1978)
(20 Ahr Ni-Cd Cells)

CELL NO.	1	2	3	4	5	6
Formation Cycles	Voltage at 1 hour - Capacity (Ahr) to 1.00/0.70 V					
Cycle 4 at 10 A	1.141-21.0/21.3	1.145-21.3/21.7	1.140-21.8/22.0	1.139-21.5/22.0	1.146-21.2/21.3	1.145-21.2/21.3
AUTOMATIC CYCLING						
Cell Voltage	At 1 hour/1 hour + 55 minutes or Capacity (Ahr) to 0.70 V					
CYCLE 1	1.134/1.090	1.138/1.096	1.131/1.092	1.134/1.082	1.135/1.096	1.133/1.094
CYCLE 58	1.150/1.071	1.166/1.069	1.151/1.072	1.133/1.060	1.158/1.074	1.116/19.0
CYCLE 100	1.153/1.042	1.151/0.973	1.137/1.045	1.116/1.027	1.139/1.043	1.093/18.3
CYCLE 150	1.152/1.036	1.150/0.973	1.128/1.002	1.117/0.972	1.139/0.979	1.096/19.0
CYCLE 201	1.143/0.965	1.147/0.956	1.130/0.963	1.112/0.873	1.142/0.942	1.092/18.7
CYCLE 253	1.135/0.824	1.142/0.824	1.129/0.803	1.094/19.2	1.135/0.804	1.079/17.8
CYCLE 283	1.134/0.881	1.138/0.884	1.125/0.889	0.942/16.0	1.135/0.887	1.075/18.5
CYCLE 304	1.134/0.856	1.140/0.882	1.127/0.847	0.782/14.8	1.135/0.871	1.062/18.5
CYCLE 316	1.134/0.794	1.139/0.838	1.125/0.758		1.136/0.802	1.058/18.0
CYCLE 337	1.131/0.806	1.133/0.844	1.122/0.816		1.132/0.838	1.015/17.3
CYCLE 346	1.127/0.780	1.130/0.819	1.118/0.780		1.126/0.809	1.007/17.0
CYCLE 358	1.124/19.0	1.131/0.794	1.117/19.2		1.128/0.771	0.997/16.3
CYCLE 379	1.108/19.2	1.127/0.790	1.125/0.782		1.123/0.784	
CYCLE 400	1.092/0.762	1.114/0.792			1.112/0.794	

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were made from this material by standard procedures. The formation and cyclic data for these cells are presented in Table I.10. The cells were given an extra formation cycle because these capacities were somewhat lower than for previous cells. The cells, having gone through 249 charge/discharge cycles, are apparently inferior to the previous washed commercial hydrate cells.

2.7 GRAPHITE PARTICLE SIZE

During preparation of some nickel hydrate mixes, the commercial corporation adds both a fine and a coarse fraction of graphite to the nickel hydrate for conductivity. An attempt to use this mix in our roll bonded electrodes was not successful due to the inability to make a cohesive mass. A sample with only 15% fine graphite added was received which could be made into satisfactory electrodes by substituting our G40 graphite for the coarse graphite portion. Comparative tests showed that the technique used by the commercial source to incorporate fine graphite produced no significant difference from our direct addition prior to mulling. A reported decrease in electrode swelling attributable to their technique was not substantiated.

2.8 OTHER $\text{Ni}(\text{OH})_2$ MATERIALS

Nickel hydrate samples were received from a second commercial source. These included the unmixed nickel hydrate and the finished nickel hydrate mix to which fine and coarse graphite had been added. The latter could not be made into a suitable cohesive mass by our mulling procedure. Test cells made from

TABLE I.10
COMMERCIAL NICKEL HYDRATE (APRIL 1979)
(20 Ahr Ni-Cd Cells)

CELL NO.	1	2	3	4	5
Formation Cycles	Voltage at 1 hour - Capacity (Ahr) to 1.00/0.70 v				
Cycle 2 at 10A	1.149-18.5/18.7	1.148-18.7/19.0	1.146-17.7/18.0	1.153-18.5/18.7	1.152-17.7/18.3
Cycle 5 at 10A	1.149-19.2/19.3	1.149-19.5/19.7	1.151-18.2/18.3	1.152-19.2/19.3	1.155-18.3/18.7
AUTOMATIC CYCLING					
Cell Voltage	At 1 hour/1 hour + 55 minutes or Capacity (Ahr) to 0.70 v				
CYCLE 1	1.149/1.089	1.150/1.097	1.153/19.0	1.155/1.101	1.160/19.0
CYCLE 19	1.154/0.815	1.157/0.829	1.158/0.761	1.161/0.809	1.155/0.760
CYCLE 31	1.156/0.814	1.158/0.830	1.162/0.804	1.164/0.815	1.156/0.708
CYCLE 52	1.163/0.843	1.165/0.854	1.170/0.847	1.169/0.834	1.149/0.706
CYCLE 73	1.165/0.806	1.162/0.803	1.165/19.0	1.165/0.761	1.142/18.0
CYCLE 104	1.170/0.823	1.165/0.832	1.161/0.801	1.167/0.790	1.096/17.7
CYCLE 125	1.170/0.802	1.168/0.816	1.159/0.848	1.160/0.844	1.074/18.3
CYCLE 144	1.170/0.813	1.170/0.832	1.127/0.789	1.154/0.787	0.911/12.0
CYCLE 156	1.166/0.832	1.170/0.859	1.123/0.780	1.153/0.787	
CYCLE 177	1.161/0.842	1.164/0.880	1.069/0.777	1.145/0.782	
CYCLE 198	1.159/0.824	1.162/0.858	1.039/18.7	1.135/18.8	
CYCLE 216	1.156/0.831	1.164/0.874	1.031/18.0	1.100/18.5	
CYCLE 231	1.147/0.828	1.160/0.870	1.009/16.8	1.060/17.7	
CYCLE 249	1.141/0.811	1.156/0.856	0.937/15.2	1.047/17.3	

the hydrate were satisfactory but did not maintain their capacity on cycling, indicating that some cobalt must be necessary for cyclic capacity maintenance.

Nickel hydrate samples received from a third source were made by an electrolytic and chemical precipitation method from sulfate salts. Test cells made from both hydrates had capacities essentially 85% of normal.

A sample of nickel hydrate made from a chloride salt was received from a fourth commercial source. Cells made with this hydrate give capacities only 30% of theoretical. The most probable reason for this behavior was the extremely fine particle size of the hydrate.

2.9 COBALT SUBSTITUTES

A series of coprecipitates containing different insoluble metal hydroxides along with nickel hydroxide were prepared using the continuous precipitation WDW procedure. Where possible, the hydrates were precipitated from sulfate salts; otherwise nitrate salts were used. A summary of the coprecipitated hydrates is given below:

- 100% nickel hydrate
- 1 and 5% cobalt hydrate
- 1 and 5% AD hydrate
- 1 and 5% LU hydrate
- 1 and 5% TT hydrate
- 1 and 5% AM hydrate
- 1 and 5% IL hydrate
- 1 and 5% ER hydrate
- 1 and 5% AN hydrate
- 10^{-4} and 10^{-3} M OL hydrate

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After precipitation, the hydrates were diluted to 4.3% solids, agitated with air and allowed to settle. A measurement of the height of the settled hydrate after 16 hours indicated that the slurry contained 10 to 12% solids. In general the hydrates were washed twice a day until the supernatant liquid was neutral. At this point, the hydrates were filtered for several days in a porous polypropylene bag to form a more concentrated slurry containing 20 to 25% solids. In the cases of 1% TT, AM and IL, the prepared hydrate acquired a colloidal state and proved difficult to filter. The heavy slurry was then dried at 60°C and micromilled. It was then redispersed in water to remove the residual anion, filtered and dried. A summary of the powder characteristics which include particle size, anion concentration and water of hydration is given in Table I.11. In the case of the IL hydrate, the anion concentration was extremely low since ammonia was continually being given off during preparation.

The hydrates were then made into 20 Ahr Ni-Cd test cells using standard procedures. The cells were given the usual formation cycles of a 160% charge and a discharge at C/2 to 0.70V as shown in Table I.12. Results indicate that only cells with 1 and 5% cobalt and 1% AD had a utilization of over 90% of theoretical. The cells will be subjected to charge acceptance and capacity retention tests before being placed on automatic cycling.

3.0 CONCLUSIONS

Cells having 10% cobalt-nickel hydrate prepared by the WDW procedure cycled more stably than cells prepared from SD hydrate. The need was demonstrated for maximum Teflon fibrolation

TABLE I.11
COPRECIPITATED NICKEL HYDRATES

ADDITION AGENT	PLUS 200 MESH, %	SULFATE %	NITRATE %	MOLE H ₂ O/ MOLE Ni
100% Nickel	19.3	1.31		0.16
1% Cobalt	22.4	1.22		0.15
5% Cobalt	18.0	1.48		0.12
1% AD	19.3	1.06		0.16
5% AD	17.7	1.24		0.14
1% LU	18.5	1.38		0.18
5% LU	33.2	2.40		0.26
1% TT	17.8		0.40	0.28
5% TT	25.6		1.42	0.18
1% AM	29.0		0.70	0.23
5% AM	25.7		1.46	0.23
1% IL	13.9		0.00	0.19
5% IL	13.6		0.00	0.16
1% ER	26.1	0.90		0.16
5% ER	22.6	1.40		0.11
1% AN	23.3	1.06		0.11
5% AN	22.6	1.08		0.13
10 ⁻⁴ M OL	13.8	1.01		0.11
10 ⁻³ M OL	16.8	1.23		0.10

TABLE I.12

COPRECIPITATED HYDRATE FORMATION CAPACITIES

ADDITION AGENT	CYCLE 2		CYCLE 4	
	CAPACITY @ 10A to 1.00/0.70V	% THEORETICAL to 0.70V	CAPACITY @ 10A to 1.00/0.70V	% THEORETICAL to 0.70V
100% Nickel	18.4/22.4	86.2	19.0/23.0	88.5
1% Cobalt	20.4/23.9	93.0	20.5/24.2	94.2
5% Cobalt	22.6/24.8	100.4	20.8/23.4	94.7
1% AD	19.8/22.8	88.7	21.0/24.0	93.4
5% AD	19.0/22.0	89.1	19.3/19.7	79.8
1% LU	19.6/20.1	78.2	20.6/21.0	81.7
5% LU	19.6/21.3	88.3	18.8/20.4	82.6
1% TT	16.8/17.2	66.9	16.8/17.4	67.7
5% TT	16.2/16.6	67.2	16.5/16.8	68.0
1% AM	16.4/16.8	65.4	16.4/17.2	66.9
5% AM	16.2/16.6	67.2	17.2/17.6	71.3
1% IL	19.0/20.0	77.8	18.8/19.8	77.0
5% IL	19.0/19.4	78.5	17.8/18.2	73.7
1% ER	16.9/19.8	77.0	17.7/19.9	77.4
5% ER	15.4/16.3	66.0	17.0/18.0	72.9
1% AN	17.7/18.3	71.2	17.5/18.2	70.8
5% AN	15.9/16.5	66.8	16.0/16.4	66.4
10 ⁻⁴ OL	18.3/18.9	73.5	18.7/19.2	74.7
10 ⁻³ OL	17.2/17.5	70.9	17.8/19.0	72.9

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through additional working of the mix.

The temperature at which the hydrate is initially dried influences the cyclic behavior of the hydrate. Drying at 60°C appears to be optimum.

Hydrates prepared by either the WDW or WD procedure have equivalent cyclic capacity maintenance.

A hydrate prepared by continuous precipitation has not cycled as well as the standard hydrate. Modifications used with the continuous precipitation procedure may have influenced the hydrate.

Particle size of the hydrate influences the preparation of electrodes and their cyclic capacity maintenance. Jet milling hydrates to form extra fine particles leads to a loss of capacity.

The addition of graphite to the hydrate during precipitation improves the conductivity of the hydrate. The results with colloidal graphites for this purpose were poorer, probably due to the greater surface area and consequent greater oxidation. Pretreatment of graphite has been used to make the graphite wettable.

The use of potassium persulfate to oxidize a portion of the hydrate from the nickelous to the nickelic state during preparation appears to improve its cyclic behavior. The presence of 10% cobalt is necessary for satisfactory cyclic capacity maintenance with ERC WDW hydrate.

Commercial nickel hydrate has produced satisfactory electrodes and cells after being rewashed to remove additional caustic and sulfate.

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A series of insoluble non-cobalt additives were added to nickel to determine their influence on capacity, charge acceptance, capacity retention and cycling stability. Only cobalt and Type AD initially improved the cell capacity.

SECTION III
ZINC ELECTRODE DEVELOPMENT FOR
NICKEL-ZINC CELLS - (TASK II)

1.0 INTRODUCTION

The objective of this task is to develop high performance zinc electrodes capable of 500 deep cycles for use in nickel-zinc cells.

The zinc study is divided into technology development and fundamental studies, both efforts directed at finding effective solutions for such prominent problems as shape change, dendritic growth, passivation and densification.

In the area of technology development, our attention is concentrated on examining two different means to improve the stability of the zinc electrode:

- Substrate - nickel exmet, Cu foil with a polymer layer, Cd plated Cu foil, Ag foil, and three proprietary substrates.
- Additives - Fe_2O_3 , CdO , $\text{Ca}(\text{OH})_2$, Bi_2O_3 , PbO , and insoluble Zn compounds, etc. to the active material mixture or to the electrolyte.

Life cycle data on experimental 20 Ahr size Ni-Zn cells are presented which illustrate the degree of effectiveness of these electrode construction variables.

With regard to fundamental study, work is in progress to determine the electrochemical polarization of Zn dissolution and deposition reactions as a function of several variables such as number of cycles, substrate structure, electrolyte additives, shape changed area, etc.

2.0 TECHNICAL DISCUSSION

2.1 SUBSTRATE DEVELOPMENT

In the ERC process for the manufacture of Zn electrodes, the Teflon bonded active material is laminated onto either side of a current collector and pressed. Normally a thin foil of copper, silver or an expanded mesh of nickel is used as the collector. The effect of the nature of the current collector on the performance of Zn electrodes was investigated since current distribution, nucleation, growth and adhesion of Zn deposits depend on the type of substrate.

A group of substrates including the metallic collectors mentioned above and their modifications were screened. The Teflon laminated collector and metal oxide/Teflon laminated collectors were included in this study since a previous ERC investigation (U.S. Patent 4,022,953) produced some encouraging results.

The design features of the 20 Ahr size Ni-Zn cells used in the zinc study are illustrated in Table II.1.

2.1.1 Nickel Exmet

Nickel exmet as a collector for the Zn electrode was examined by fabricating and testing a 20 Ahr size vented type Ni-Zn cell. The positive and negative electrodes were of the Teflon bonded type. The active material composition at the Zn electrode was proprietary. The cell was cycled on a regimen consisting of charge at C/6 and discharge at C/2. The variation of cell capacity with cycling is tabulated below:

TABLE II.1

DESIGN FEATURES OF 20 Ahr NI-ZN CELLS

<u>ITEM</u>	<u>DESCRIPTION</u>
Cell Type	Vented, Prismatic
Cell Case, inches	Polysulfone, 5.5 x 1.37 x 3.6
Cell Cover	Polysulfone cover which incorporates a vent and two terminals.
Active Core	An electrode sandwich consisting of alternate layers of positive, separator and negative electrodes.
Number of Electrodes	6 positive, 5 full negatives and 2 half negatives.
Positive Electrode	ERC polymer bound type
Positive Theoretical Capacity	25 Ahr
Negative Electrode	ERC polymer bound type
Negative Theoretical Capacity	80 Ahr
Separator	Pellon as electrolyte reservoir in combination with a commercial membrane.
Electrolyte	35% KOH + 1% LiOH

<u>CYCLE NO.</u>	<u>CELL Z46, CAPACITY, Ahr</u>
6	20
24	15
39	14
42	15
51	9

2.1.2 Proprietary - Type A

The substrate was prepared by laminating a thin layer (0.003 in. thick) of polymer bound metallic oxide onto nickel exmet. The active material composition consisting of ZnO and additives was then laminated onto the substrate to form the finished electrode.

Two vented type Ni-Zn cells, Z26A and Z26B (rated capacity 15 Ahr) were fabricated and tested. The variation of cell capacity for Cell Z26A with cycling is tabulated below:

<u>CYCLE NO.</u>	<u>CELL Z26A, CAPACITY, Ahr</u>
6	14.0
25	13.6
40	12.5
49	10.5

Comparing the experimental data, it is evident that the nickel exmet substrate laminated with a polymer bound metallic oxide is only marginally better than the nickel exmet substrate.

2.1.3 Proprietary - Type B

The substrate was produced by laminating a layer of polymer bound metallic oxide onto either side of 0.002 in. thick copper foil.

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Cells Z27A and Z27B were fabricated with such a substrate. Both cells, rated at 15 Ahr, were life cycle tested. The variation of cell capacity with cycling is tabulated below:

<u>CYCLE NO.</u>	<u>CELL Z27A, CAPACITY, Ahr</u>
4	14.5
25	14.0
40	12.0
49	10.0

2.1.4 Copper Foil, Cadmium Plated

The substrate in this case is 0.002 in. thick copper foil plated with cadmium (0.0001 in. thick). Three 20 Ahr size Ni-Zn cells were fabricated with Zn electrodes containing Cd plated Cu as the collector.

One of the cells, Z29, prematurely failed at the 25th cycle. The other two cells, 15 and 16, displayed a cycle life of 53 before the capacity declined by 40%. The variation of cell capacity with cycling for Cell 15 is tabulated below:

<u>CYCLE NO.</u>	<u>CELL 15, CAPACITY, Ahr</u>
10	19.0
20	16.3
35	17.5
53	12.0

2.1.5 Copper Foil with a Polymer Layer

The substrate was produced by coating a 0.002 in. thick copper foil with a polymer suspension.

Four cells (Z43, Z47, Z58 and Z60), fabricated with such a substrate for the zinc electrode, were life cycle tested in an identical manner. The variation of discharge capacity with cycling is illustrated in Figure II.1.

FIGURE II.1 VARIATION OF CELL CAPACITY WITH CYCLING FOR Ni-Zn CELLS
CONTAINING Zn ELECTRODES WITH POLYMER LAMINATED COPPER COLLECTORS

2.1.6 Proprietary - Type C

This substrate was produced by laminating a polymer bound metallic oxide layer onto either side of a metallic foil. The negative electrode active material is then pressed onto this substrate to produce the electrode. Two cells, Z40-1 and Z40-2, were so fabricated and life cycle tested. The variation of discharge capacity with cycling for Cell Z40-1 is given in Figure II.2. The cell capacity was 12 Ahr at the 110th cycle, 10 Ahr at the 127th cycle and 10 Ahr at the 175th cycle (even though the figure only represents performance up to 130 cycles).

2.1.7 Silver Foil

Silver foil as a substrate was tested in the Ni-Zn cell with square electrode geometry. Cells Z13 and Z15 were fabricated with a Ag foil collector and life cycle tested. The results are presented in Section 2.2, Figure II.3.

The substrate study, summarized in Table II.2 is incomplete since it forms part of a parameter study involving substrates, additives and electrolyte type. However preliminary results appear to show that the performance depends on the type of substrate.

2.2 ADDITIVES

Several inorganic compounds were screened as additives by fabricating Zn electrodes and testing in 20 Ahr size Ni-Zn cells. These additives were drawn from the following class of inorganic compounds.

FIGURE II.2 PERFORMANCE CURVES FOR CELL Z-40-1

FIGURE II.3 CAPACITY-CYCLE RELATIONSHIP FOR CELLS Z13 AND Z15

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TABLE II.2

SUMMARY OF SUBSTRATE STUDY

TYPE OF SUBSTRATE	CELL NO.	CYCLES TO 40% DECLINE IN CAPACITY (BASED ON RATED CAPACITY)
Nickel Exmet	Z46	~42
Proprietary, Type A	Z26A	~40
Proprietary, Type B	Z27A	~40
Cd plated copper foil	15	53
Ag foil	Z13 & Z15	100
Copper foil with a polymer layer	Z43 Z47 Z58 Z60	~73 ~32 46 54
Proprietary, Type C	Z40-1	115

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1. Compounds somewhat soluble in 35% KOH (such as Fe_2O_3 , $\text{Ca}(\text{OH})_2$, TiO_2 , and PbO).
2. Compounds insoluble in 35% KOH (such as Bi_2O_3 , CdO , MgO , and HgO).

On the basis of their electrochemical activity, these compounds may be further divided into two classes: electrochemically inactive (such as $\text{Ca}(\text{OH})_2$, MgO , and TiO_2) and electrochemically reducible (such as HgO , Bi_2O_3 , CdO and Fe_2O_3).

Some of these additives form oxy-hydroxy ions in solutions such as ferrate and titanate in addition to the usual zincate. Still others induce passivity to the Zn electrode during discharge, e.g. $\text{Ca}(\text{OH})_2$ and PbO .

CdO as a major additive in a Zn electrode (92% ZnO , 5% CdO , and 3% TFE) was tested in several cells which typically exhibited a cycle life of 50.

Ferric oxide in combination with CdO was also tested in several cells. Figure II.3 shows the capacity-cycle number relationship for Cell Z13 which contained the Fe_2O_3 additive in the Zn electrodes. This figure also shows the capacity-cycle number relationship for Cell Z15 which also contained $\text{Fe}_2\text{O}_3/\text{ZnO}$ electrodes. These cells had a theoretical capacity of 18.2 Ahr at the positive electrode. The electrodes had a square geometry.

Figure II.4 shows the cell voltage-capacity plot for Cell Z63A which also contained the Fe_2O_3 additive in the Zn electrode.

FIGURE II.4 PERFORMANCE CURVES FOR CELL Z63A WITH Fe_2O_3 IN ZINC ELECTRODE

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The theoretical capacity of the positive electrode was 25 Ahr. The cell capacity declined by 40% at the 112th cycle.

Calcium hydroxide in combination with a proprietary oxide was tested in 5 cells. Two of these cells, Z38 and Z51A, were life cycle tested and the experimental results are illustrated in Table II.3.

Another proprietary oxide combination was also tested in 5 cells. Two of the cells were life cycle tested. The other three were set apart for studies such as electrolyte additives and charging procedures. The cell capacity variation with cycling for two of these cells, Z39B and Z50A, is also illustrated in Table II.3.

Bi_2O_3 was tested as an additive in two cells. The variation of cell capacity with cycling is detailed below:

<u>CYCLE NO.</u>	<u>CELL Z49A, CAPACITY, Ahr</u>
8	20
13	20
22	20
36	16
52	8

Gallium oxide was tested in a 20 Ahr Ni-Zn cell. The capacity maintenance with cycling for this cell is tabulated below:

<u>CYCLE NO.</u>	<u>CELL 62A, CAPACITY, Ahr</u>
14	16
20	15
38	12
46	10

TABLE II.3
LIFE CYCLE PERFORMANCE OF Zn ELECTRODES
IN Ni-Zn CELLS CONTAINING ADDITIVES

CELL NO.	ADDITIVES*	CYCLE NO.	CAPACITY, Ahr
Z38A	0.75% Ca(OH) ₂ + proprietary oxide	8	20
		21	20
		42	19
		64	19
		84	15
		91	12
Z51A	0.75% Ca(OH) ₂ + proprietary oxide	8	19
		20	19
		29	17
		41	16
		47	14
		50	11
Z39A	Proprietary oxide combination	8	19
		21	19
		30	19
		42	19
		64	16
		84	12
Z50A	Proprietary oxide combination	8	19
		20	19
		41	19
		47	15
		65	10

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An insolubilizing additive to the electrolyte was tested in 5 cells. Cell Z48B was filled with an electrolyte composition containing this additive. The cell was life cycle tested on a regimen consisting of charge at C/6 and discharge at C/2. The relationship between cell voltage and ampere-hour capacity for Cycles 21, 89 and 114 is shown in Figure II.5. The discharge capacity declined by 40% at the 114th cycle.

The same electrolyte additive in another cell (Cell Z50B) which contained a proprietary additive in the Zn electrode did not enhance the cycle life. The variation of cell capacity with cycling was as follows:

<u>CYCLE NO.</u>	<u>CELL Z50B, CAPACITY, Ahr</u>
8	19
15	19
44	16
62	16
71	14
78	12
81	10

An insoluble Zn compound as an additive was tested in two cells.

The cells were life cycle tested. The relationship between cell voltage and capacity for Cycles 3, 41, and 95 is shown in Figure II.6. There was no decline from the initial capacity until 95 cycles, even though the discharge capacity in each cycle was lower than normal. Capacity declined by 40% of the rated capacity (20 Ahr) at the 105th cycle. The additive study is summarized in Table II.4. To conclude, the additive study involves examination of several variables. The results presented are quite preliminary. Even though Fe_2O_3 and the

FIGURE II.5 PERFORMANCE CURVES FOR CELL Z48B

FIGURE II.6 EFFECT OF INSOLUBLE ZINC COMPOUNDS IN THE ZINC ELECTRODE
(CELL 53A)

TABLE II.4

SUMMARY OF ADDITIVE STUDY

ADDITIVE TYPE	NUMBER OF CYCLES TO 40% DECLINE FROM THE RATED CAPACITY
CdO	50
CdO in combination with Fe ₂ O ₃	112
CdO in combination with proprietary oxide	50/91
CdO in combination with proprietary oxide combination	50/84
Bi ₂ O ₃	40
Ga ₂ O ₃	38
Proprietary Additive (insolubilizing) in the electrolyte	78
CdO in combination with an insoluble Zn compound	105

insoluble Zn compound appear quite promising, the reproducibility of the results have to be checked.

2.3 KINETICS OF THE ZINC ELECTRODE

The electrochemical polarization during deposition and dissolution of Zn in 0.5M zincate electrolyte was determined.

The experimental arrangement consisted of an electrochemical cell involving a working electrode of 1.61 cm^2 geometric area, a very large surface area platinum counter electrode and a Hg/HgO reference electrode. Polarization measurements were done under potentiostatic conditions using a Princeton Applied Research potentiostat. The procedure consisted of increasing the working electrode potential in 10 mV increments and noting the steady state reaction current.

Figure II.7 shows a potentiostatic polarization curve obtained for deposition and dissolution of Zn on a typical uncycled, Teflonated ZnO electrode. This electrode uses a Cu foil as the substrate. The deposition reaction exhibits a Tafel region from -1.325 to -1.380V and the dissolution reaction from -1.350 to -1.315V. The values for $dE/d \log i$ are 35 and 40 mV/decade, respectively.

Figure II.8 shows the polarization curves obtained for deposition and dissolution of Zn on a sample from a Zn electrode edge cut from a cycled Ni-Zn cell. This edge was severely eroded due to shape change in the original cell. The Tafel slope for deposition is 50 mV/decade and for dissolution, 32 mV/decade.

a = Deposition b = Dissolution

Electrode = ERC Teflonated ZnO

FIGURE II.7 POLARIZATION CURVES FROM A TYPICAL UNCYCLED ELECTRODE

a = Deposition b = Dissolution
Electrode = Shape Changed Edge

FIGURE II.8 POLARIZATION CURVES FROM EDGE SECTION OF A CYCLED Zn ELECTRODE

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A change in the values of the Tafel slope for the "shape changed" Zn electrode is indicative of a change in the mechanism of the reactions.

Next, the polarization characteristics of the Zn reaction in a working Ni-Zn cell were determined. This cell was specially constructed using one sectioned Zn electrode (ERC Teflon bound type) and one NiOOH electrode. The cell was assembled in a Plexiglas fixture. The voltage of each section of the Zn electrode was monitored by means of the reference electrode Luggin capillary inserted into a well opposite each section. The cell was cycled 27 times on a cycling regimen consisting of charge at C/6 and discharge at C/3. The polarization characteristic measurements of each section were then determined. During potentiostatic measurements, each section of the Zn electrode was polarized in relation to the entire working surface of the NiOOH electrode. The locations of sections in the Zn electrode are illustrated in Figure II.9.

Table II.5 summarizes the Tafel slope values and the values for current i at the interception of the anodic and cathodic polarization curves. There is a variation in the Tafel slope which is dependent on the location of the section in the electrode. The sections located at the electrode edges clearly show greater polarization.

Experimental analyses using the sectioned Zn electrode are being continued to determine the significance of the Tafel slope values, limiting currents, etc. Experiments are also in progress to determine:

FIGURE II. 9 SECTIONED ZINC ELECTRODE

TABLE II.5
POLARIZATION CHARACTERISTICS OF A
SECTION ZINC ELECTRODE

SECTION NO.	TAFEL SLOPE DEPOSITION, mV/Decade	TAFEL SLOPE DISSOLUTION, mV/Decade	i, Intercept, mA/cm ²
3	40	72	7.2×10^{-3}
6	65	67	6.8×10^{-3}
7	42	52	6.0×10^{-3}
13	40	40	5.6×10^{-3}
19	43	32	3.8×10^{-3}
21	50	55	5.2×10^{-3}
26	60	60	6.3×10^{-3}
27	63	62	3.9×10^{-3}
28	57	65	5.5×10^{-3}
30	58	65	5.6×10^{-3}

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1. the effect of number of cycles
2. reproducibility of Tafel slope values
3. IR effects

In summary, the kinetic study has shown that the edge sections of a cycled Zn electrode are more polarized during dissolution and deposition of Zn.

SECTION IV

SEPARATOR DEVELOPMENT FOR
NICKEL-ZINC CELLS - (TASK III)

1.0 INTRODUCTION

Separators have two primary functions: to keep positive and negative plates physically apart so electronic current will be constrained to flow outside the cell and; to allow ionic transport in the electrolyte between plates, as necessary.

These functions lead to the following separator requirements:

- Physical and chemical stability in the cell environment
- Low electrical resistance
- Ability to retard shape change of zinc electrode and dendritic growth.

The goal of this task in the component optimization program is to develop a low cost separator which can meet the above requirements. The investigation includes both self-supporting and supported cast films utilizing filled and non-filled plastic formulations. Appropriate component ratios and technology of film formation are selected for each plastic based composition. The study for developing improved separators is centered on three different classes of polymers: crosslinked PVA and two different thermoplastics. Initial properties of each polymer should be correct to be suitable for the separator material in Ni-Zn cells.

Separator materials are subjected to both physical and electrochemical screening tests to fully characterize each type of material before experimental cells are fabricated for cyclic testing. The most critical parameters are electrical resistance and stability of physical and chemical properties. Therefore the screening tests include electrical resistance, OH^- diffusion, mechanical durability and long-term stability in KOH.

Promising candidates for separator materials are evaluated in both vented and sealed Ni-Zn cells.

2.0 TECHNICAL DISCUSSION

2.1 THERMOPLASTIC BASED SEPARATORS

Electrical resistance as well as mechanical and physical properties of polymer films depend on composition and technology of production. Therefore the problem of film development was divided into three tasks: 1) determination of the optimum composition of thermoplastic based separator films; 2) development of the optimum technology of the process; 3) evaluation of the thermoplastic based film as a separator material.

2.1.1 OPTIMUM COMPOSITION

The influence of the different quantities of fillers on electrical resistance of thermoplastic (TP) based films was studied. In the first part of these experiments, several fillers were used which gave positive results in work with TP based separators.

The factor of varied quantities of additives was studied in combination with another polymer which swells in KOH. Films which were produced with inorganic fillers showed low electrical resistance, good elasticity and less separation during film formation.

Another method of reducing the separation rate was to increase the formation temperature. Films which were formed in the oven at an elevated temperature had better surface quality with smaller traces of separation. Films exhibited low electrical resistance, smooth surface and relatively good elasticity. Two compositions obtained showed similar acceptable

properties. It is now necessary to test the chemical stability of the films to find the optimum formulation.

Another goal was to find a way to avoid the addition of large quantities of fillers in TP based films. The property of the polymer to precipitate from a solution which contains some quantity of water was utilized. After forming, a layer of the TP solution in methanol was covered with a layer of water or aqueous solution of Polyox. The films contained pinholes if covered by water before film formation was completed, and the system contained an entrapped liquid phase. Electrical resistance of the films in the solid state was very high if coated by water.

2.1.2 THERMOPLASTIC FILMS AS SEPARATOR MATERIALS

Evaluation of TP films has been broken down into five basic tasks:

1) Studying the stability of properties of the TP based film was the first task in this part of the investigation. Systematic measurement of electrical resistance was undertaken and results obtained appear in Table III.1. The data indicates that electrical resistance and appearance did not change during a prolonged period of exposure in KOH (about five months).

2) Measuring electrolyte diffusion at various temperatures was carried out in order to study the behavior of separator material under different conditions. TP based films were tested over a temperature range of 23 to 60°C.

According to the data obtained, the rate of diffusion decreases with increasing temperature (see Table III.2). This finding violates diffusion laws and may be the result of shrinkage of the TP based films at elevated temperatures.

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TABLE III.1

INFLUENCE OF PROLONGED KOH EXPOSURE
ON ELECTRICAL RESISTANCE OF THERMOPLASTIC BASED FILMS

COMPOSITION	THICKNESS, mil	ELECTRICAL RESISTANCE, $m\Omega$ in ² /mil				
		INITIALLY	AFTER 2 Mos.	AFTER 3 Mos.	AFTER 4 Mos.	AFTER 5 Mos.
A	2.0	25	30	32	20	25
B	3.0	185	175	190	170	180
C	3.0	15	25	30	20	25
D	3.5	85	40	50	60	70
E	2.2	20	25	30	35	20
F	3.5	45	50	40	45	35

TABLE III.2

RATE OF ELECTROLYTE DIFFUSION
FOR TP-BASED FILMS

TIME, Min. @ 5 Min. Intervals	TEMPERATURE, °C	DIFFUSION RATE, Mol/Min-in ²
45	(Room Temp.)	1.406×10^{-3}
45	40	6.270×10^{-4}
45	50	4.658×10^{-4}
45	60	2.559×10^{-4}

3) The third task involved measuring dimensional stability at elevated temperatures for TP and PVA based films in order to explain unusual data for temperature dependence on the rate of diffusion. Dimensional change measurements, shown in Table III.3, indicate that the areal dimensions of the films essentially decrease. Shrinkage of the film can explain unusual reduction in the rate of diffusion at elevated temperatures. The degree of shrinkage is a function of inside stress in film with temperature. Therefore this phenomenon should be considered when the design of the separator is finalized.

4) Mechanical durability of TP based films was measured in KOH under constant loading at a temperature of 60°C during the fourth task. The durability of TP based films in 20 and 35% KOH is about the same, averaging 2 months. This is approximately ten times higher than the durability of PVA films under the same exposure conditions and much higher than the durability of any other material tested.

5) During the fifth task, accelerated zinc penetration tests were performed in cells constructed with one separator layer to test the zinc stopping ability. Results obtained (see Table III.4) show that although essential increase of cell cycle life was not achieved, the application of TP based separators leads to a substantial decrease in shape change of the zinc electrode. After about 65 cycles, the zinc electrode did not exhibit shape change and zinc was still spongy, indicating good electrochemical activity. Extended examination of TP based separators in 20 Ahr cells is being performed.

TABLE III.3
DIMENSIONAL CHANGE OF SEPARATOR FILMS

MATERIAL	TIME, min.	INITIAL DIMENSIONS, cm		DIMENSIONS AFTER HEAT TREATMENT, cm	
		LENGTH	WIDTH	LENGTH,	WIDTH
TP	300	9.00	7.3	8.90	7.20
PVA	100	9.05	7.3	8.85	7.10
TP	300	9.00	7.2	8.90	7.15

All samples tested at 80°C.

TABLE III.4
ZINC PENETRATION TEST RESULTS
WITH TP-BASED SEPARATORS

NO.	ELECTRODE TYPE	ELECTRODE SIZE/in.	SEPARATOR CONFIGURATION	CYCLE	FAILURE MODE	COMMENTS
1	2 Full sintered Ni 1 Full Zinc ZnO 88% Bi ₂ O ₃ 10% TFE 2%	H 3-7/8 W 2-7/8 T .07	TP	24		
2	Same	Same	Same	15	Dendrite Growth	
3	2 Full sintered Ni 1 Full Zinc ZnO 93% CdO 5% TFE 2%	Same	TP	12	Resistance high - pinhole	No change in film and zinc electrode
4	Same	Same	TP film + filler	12	Very small pinholes in separator	Dendrites grow through pinholes
5	Same	Same	TP film + filler 20% KOH	10	Big pinhole	Dendrites grow through hole. No shape change observed.
6	2 Full sintered Ni 1 Full Zinc ZnO 93% CdO 5% TFE 2%	H 3-7/8 W 2-7/8 T .07"	One layer (1.8 mil) of TP + filler	66	Pinhole	No change in color of film. Film looks stable. Zinc dendrites don't grow from the sides. No change in shape of zinc electrode.
7	Same	Same	TP coating - (thickness 1.5 mil)	64	Small dendrite spread uniformly on zinc plate	Dendrites grow through small holes in separator. No change in shape of zinc plate.
8	Same	Same	TP coating + filler	48	Resistance too high	Film cracked from sides. Dendrites grow from sides. Depresson in zinc electrode.

Discharge = 2.5A x 1 hr.

Charge/Discharge Ratio = 120%

Theor. Zinc Capacity, Ahr = 14.4

2.2 PVA BASED SEPARATORS

Commercial PVA films which are used in alkaline batteries show low electrical resistance but poor stability in the electrolyte environment. Attempts to improve chemical stability by crosslinking have led to increasing brittleness and cracking of the separator. Therefore, employing a cross-linking agent, which can correct the chemical deficiencies and not aggravate mechanical properties of PVA will increase cycle life of the cell.

2.2.1 OPTIMUM TECHNOLOGY FOR THE PRODUCTION PROCESS

The fact that PVA films exhibit very low electrical resistance in KOH should be examined further in order to optimize production of PVA crosslinked separators. Experimental study of the dependence of electrical resistance on time of exposure of the PVA films in KOH shows a very sharp decrease of electrical resistance during the first 3 to 4 days, (see Figure III.1) These results can possibly be explained from the viewpoint of quantity of the residual solvent (water) in the PVA film. It is possible to assume that if the film contains water, then during the first 3 to 4 days, PVA loses the solvent and electrical resistance decreases. The properties of the film stabilize after the solvent is lost. To check this supposition films were prepared which were oven-dried at constant temperature (70°C) for various lengths of time. Electrical resistance and quantity of the residual solvent in the film were measured, resulting in the data given in Table III.5.

These results indicate that electrical resistance of PVA films depends on the quantity of residual solvent in the

FIGURE III.1 - INFLUENCE OF EXPOSURE TIME IN KOH
ON ELECTRICAL RESISTANCE OF PVA FILM

TABLE III.5

INFLUENCE OF RESIDUAL SOLVENT QUANTITY
ON ELECTRICAL RESISTANCE OF PVA FILMS

NO.	DRYING TIME, min.	RESISTANCE m Ω in ² /mil	RESIDUAL SOLVENT, %
1	180	too high	2.7
2	166	too high	3.1
3	130	1000	3.5
4	110	315	4.1
5	80	40	6.7
6	75	45	8.6
7	60	43	8.9

All samples dried at 70°C and aged at 23°C for 1 day.

film. An increase in quantity of residual solvent (water) results in a sharp decrease in electrical resistance. This dependence is valid up to a quantity of residual solvent approximately equal to 6%. Further increase in quantity of water in PVA film does not result in a decrease of the electrical resistance which reaches an equilibrium value for this film. After these experiments, dry film (with approximately 1 to 1.5% residual water) and wet film (with more than 6% residual water) were tested for 10 days in KOH (see Table III.6). Variation in value of electrical resistance during the first ten days of aging has the same character as shown in Figure III.1. Electrical resistance of wet film (>6% water) does not change during this period.

Therefore our explanation of change in the electrical resistance with time given above was not valid. According to the data, PVA film absorbs water from KOH solution to an equilibrium quantity. This results in a decrease of electrical resistance during the first 3 to 6 days up to this equilibrium level, which does not change over the next 5 to 6 months. This property of the PVA separator is very important for production because it may lead to a dependence of electrical resistance on temperature of film formation, viscosity of the PVA solution and molecular weight of the polymer.

2.2.2 CALCULATION OF PRODUCTION PARAMETERS OF PVA FILMS FROM SOLUTION

Quantities of residual solvent (water) are usually present in the film after completion of the casting procedure. Mechanical and electrical properties of PVA cast films are dependent on the quantity of the residual solvent in the film.

TABLE III.6

INFLUENCE OF PROLONGED KOH EXPOSURE
ON ELECTRICAL RESISTANCE OF PVA FILMS

NO.	DRYING TIME, min.	DRY THICKNESS, mil	RESISTANCE $m\Omega \text{ in}^2/\text{mil}$	AGING PERIOD AT 23°C, Days	RESIDUAL SOLVENT, %
1	130	1.8	very high 45 45	1 4 10	2.7
2	166	2.0	very high 47 47	1 4 10	3.1
3	110	1.8	315 45 45	1 4 10	4.1
4	80	2.1	40 40 40	1 4 10	6.65
5	75	2.0	45 44 44	1 4 10	8.6
6	60	1.9	43 42 42	1 4 10	8.9

All samples dried at 70°C

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Part of our work was to find a kinetic equation which correlated manufacturing parameters with quantity of residual solvent in the film. This was needed to develop a viable casting process and production of films with defined physical and mechanical properties.

According to the thermoactivation theory of diffusion in polymers, the equation is expressed in the following form:

$$t = \beta \exp \left[\frac{Q(c)}{R} \left(\frac{1}{T} - \frac{1}{T_p} \right) \right] \quad (1)$$

Where:

c = quantity of residual solvent in film

$$Q(c) = Q_0 - \alpha C \quad (2)$$

or
$$Q(c) = Q_0 - \alpha \log C \quad (3)$$

Q_0 = activation energy of solvent diffusion

t = time of formation

α = constant of polymer solvent system

β = constant

T = temperature of formation, K

T_p = constant of polymer solvent system

The systems tested included:

a) PVA + water

b) PVA + 15% crosslinking agent + water

c) PVA + water + methanol

Concentration of the residual solvent was calculated by the equation:

$$C = \frac{P_w - P_d}{P_w} \cdot 100\% \quad (4)$$

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Where:

C = concentration of residual solvent in film

P_w = wet weight of the film

P_d = dry weight of the film after drying to constant weight.

The experimental data (Tables III.7 and III.8 and Figures III.2 through III.4) can actually be described by an equation which can be written in the following form:

$$t = \beta \exp \left[\frac{Q_0 - \alpha \log C}{R} \left(\frac{1}{T} - \frac{1}{T_r} \right) \right] \quad (5)$$

Equation 5 is valid for all systems tested over a wide range of temperatures and time of film formation allowing calculation of any component of technology (t,T,C) if two others are given. It is possible to calculate the concentration of the residual solvent in the film by incremental stages during the formation and drying of the film. The essential parameters of the casting machine can also be found by employing Equation 5.

2.2.3 OPTIMUM CROSSLINKING IN PVA

According to data obtained at ERC regarding the influence of residual water in PVA film on ionic resistivity, it is possible to formulate a theory relating the ionic resistivity to degree of crosslinking in PVA based films. Slight increases of crosslinking lead to a decrease in the degree of crystallinity but do not result in reducing the equilibrium quantity of water in film. Therefore small degrees of crosslinking should result in a decrease in the ionic resistivity. Further increase in the degree of crosslinking reduces the equilibrium quantity of water in the film which should result in an increase in the

TABLE III.7

QUANTITY OF RESIDUAL SOLVENT IN PVA FILMS
FORMED AT VARIOUS CONDITIONS FOR PVA + WATER SYSTEM

NO.	TEMPERATURE OF FORMATION, °C	TIME OF FORMATION, min.	QUANTITY OF RESIDUAL SOLVENT, %
1	21	910	9.2
2	21	1450	7.5
3	21	1760	7.3
4	21	2900	6.6
5	30	360	9.4
6	30	960	6.7
7	30	1100	6.4
8	30	2900	4.4
9	40	290	8.0
10	40	400	6.3
11	40	960	4.7
12	40	1080	4.4
13	55	150	7.3
14	55	180	6.0
15	55	210	5.6
16	55	285	6.7
17	55	1250	2.6
18	55	1300	2.2
19	70	60	8.9
20	70	80	6.7
21	70	90	4.7
22	70	110	4.1
23	70	145	3.1
24	70	180	2.7
25	70	240	2.0

Film thickness, $\delta = 2.5$ mil

TABLE III.8

QUANTITY OF RESIDUAL SOLVENT IN PVA FILMS
FORMED AT VARIOUS CONDITIONS

NO.	TEMP. OF FORMATION, °C	TIME, min.	QUANTITY OF RESIDUAL SOLVENT, %
1	21	280	14.5
2	21	380	12.9
3	21	950	10.6
4	21	1000	11.0
5	21	1100	10.5
6	21	1150	10.6
7	21	2400	8.9
8	21	5400	6.9
9	40	125	22.0
10	40	256	11.5
11	40	325	10.2
12	40	400	9.1
13	40	1020	6.6
14	40	1120	6.7
15	40	1200	6.9
16	40	1250	6.8
17	63	90	13.0
18	63	105	12.0
19	63	155	8.3
20	63	180	8.7
21	63	800	3.8
22	63	1120	2.8
23	77	50	13.5
24	77	60	9.5
25	77	80	7.2
26	77	90	7.1
27	77	120	4.7
28	85	42	11.0
29	85	48	9.5
30	85	53	9.7
31	85	63	5.2
32	85	80	3.9
33	85	85	3.6

FIGURE III.2 RESIDUAL SOLVENT CONCENTRATION AS A FUNCTION OF FILM-
FORMATION TIME FOR PVA + WATER + METHANOL SYSTEM

FIGURE III.3 FORMATION TIME AS A FUNCTION OF TEMPERATURE
FOR PVA + WATER + METHANOL SYSTEM

FIGURE III.4 ACTIVATION ENERGY FOR SOLVENT DIFFUSION AS A FUNCTION
 OF RESIDUAL SOLVENT CONCENTRATION

ionic resistivity of crosslinked PVA material. In conformity with this viewpoint, the dependence of ionic resistivity on degree of crosslinking should be minimal. (see Figure III.5)

FIGURE III.5 INFLUENCE OF IONIC RESISTIVITY ON DEGREE OF CROSSLINKING

However achievement of the minimum value of ionic resistivity is not the main goal of crosslinking PVA films for battery separators. From the viewpoint of increasing the chemical stability, the degree of crosslinking should be increased to its maximum. However highly crosslinked PVA films become brittle and eventually crack in the cell environment. Therefore consideration of all described requirements leads to the necessity of selecting the optimum degree of crosslinking. This allows production of PVA films with low ionic resistivity, high chemical stability and physical flexibility.

Another important problem in optimization of separator properties of crosslinked PVA is the presence of residual crosslinking agents which do not participate in the chemical reaction during the process of film formation and post treatment. These agents can react with the polymer during storage and operation of the cell. Such reaction would result in a change of the mechanical and electrical properties of the separator and battery with time. It is necessary therefore to find not only the optimum degree of crosslinking but also the optimum quantity of crosslinking agent.

2.2.4 EXPERIMENTAL DATA

PVA films were prepared at ERC by casting on a metal sheet with a doctor blade to obtain uniform samples. Dry film thicknesses varied from 1.5 to 2.5 mil.

Different amounts of crosslinking agent were studied to determine the optimum quantity for crosslinking. Also, varying conditions were investigated during the drying step. Electrical resistance of the prepared films was measured as a guide to the degree of crosslinking. As Table III.9 indicates, as the amount of crosslinking agent is increased, the ionic resistivity is lowered for the same thickness of film. Again the film dried in the oven had a greater ionic resistivity than the ones dried at room temperature under the same conditions.

TABLE III.9

IONIC RESISTIVITY OF PVA FILMS

WITH VARYING AMOUNTS OF CROSSLINKING AGENT

AMOUNT OF CROSSLINKING AGENT, g	RESISTIVITY, m Ω in ² /mil	TEMPERATURE OF FILM FORMATION, °C
0.8	112	Room Temperature
1.0	108	" "
1.2	105	" "
1.5	80	" "
1.5	130	80
Dry thickness = 2 mil All samples aged in KOH for 2 days		

These results which were obtained before studying the influence of residual water in PVA film on ionic resistivity, can be explained by the position described above.

In another part of this work, PVA was crosslinked separately with a carboxylic acid dialdehyde. After casting, films were heated in an oven at 140°C in a nitrogen atmosphere. The measured electrical resistance of these crosslinked PVA films were equivalent to that of commercial PVA and PVA cross-linked with a single crosslinking agent. Electrical resistance values are between 20 and 50 m Ω in²/mil for films with dry thicknesses of 2 to 2.5 mil.

Tensile hanging tests were performed for commercial PVA and crosslinked PVA with the organic acid and dialdehyde. These tests showed that PVA film crosslinked with the carboxylic acid turned brown and stretched much more than commercial PVA and broke sooner.

PVA crosslinked with a dialdehyde showed improved physical properties. It stretched less and broke after 7 to 8 days in an oven at 65°C. In comparison, commercial PVA broke after only 4 days under the same conditions.

Films crosslinked with dialdehyde at 140°C in a nitrogen atmosphere did not become brittle even after exposure in KOH for about one week. PVA films with 10% dialdehyde were produced at room temperature and then heat treated in a nitrogen atmosphere for 1.5 hours at different temperatures to complete the crosslinking reaction. Electrical resistance and degree of crosslinking were approximately measured. The degree of crosslinking (N) was determined by the formula:

$$(N) = 100 - \left(\frac{P_f - P_d}{P_f} \right) \cdot 100\% \quad (6)$$

Where:

P_f = weight of the film after heat treatment in oven

P_d = weight of the crosslinked film after exposure in hot water (60°C) for one hour

Results of the measurements are given in Table III.10.

However, the method of measuring degree of crosslinking used in our investigation relates to chosen conditions and is not precise enough. It can only be observed that the degree of crosslinking changes when the treatment temperature rises from 85 to above 100°C. According to literature references, the rate of reaction between PVA and this particular dialdehyde composition is noticeable at temperatures above 100°C.

PVA was crosslinked by reaction with different quantities of the dialdehyde. Films were prepared under similar conditions

TABLE III.10

INFLUENCE OF TEMPERATURE ON
PROPERTIES OF CROSSLINKED PVA FILMS

CONDITION CROSSLINKED WITH DIALDEHYDE	% APPROX. WT. CHANGE	ELECTRICAL RESISTANCE, m Ω /in ² /mil	COMMENT
85°C in oven for 1-1/2 hrs.	~30	15	Does not turn brown or get sticky in water.
100°C in oven for 1-1/2 hrs.	~3	45	Does not turn brown, unaffected by hot water.
110°C in oven	~3	60	Does not turn brown.
120°C in oven	~3	125	Turns slightly brown, remains unaffected by water.
140°C in oven	---	85-75	Turns brown and slightly brittle.
Composition Ratio: 20 g PVA + 2 g dialdehyde			
Dry Thickness: 1 mil			

Results indicate that the dependence of electrical resistance on degree of crosslinking is minimal as shown in Figure III.6.

FIGURE III.6 INFLUENCE OF DEGREE OF CROSSLINKING ON ELECTRICAL RESISTANCE IN PVA FILMS

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and were subjected to post treatment in an oven at 125 to 130°C for 2 hours in a vacuum. Electrical resistance measurements in 45 and 20% KOH are given in Table III.11.

Results indicate that the quantity of crosslinking agent at a specific condition does not influence electrical resistance. Probably not all of the crosslinking agent reacts at each selected condition. However films crosslinked by dialdehyde reactions could not be dissolved in boiling water, indicating that the degree of crosslinking is high.

Comparison of the values of electrical resistance after exposure in 20 and 45% KOH demonstrates that electrical resistance in 20% KOH is higher than in 45% KOH. PVA films became brown in 45% KOH after 4 days and in 20% KOH for the same period turned only slightly brown.

PVA based films with various amounts of dialdehyde were subjected to post treatment in a vacuum oven at 140°C for 2 and 3 hours. Weight change in boiling water, capacity to absorb water, and dimensional stability in 45% KOH were determined. Electrical resistance of PVA films crosslinked with various quantities of dialdehyde after post treatment and aging in KOH is given in Table III.12. Results indicate that electrical resistance of PVA films which were crosslinked by dialdehyde does not depend on the amount of crosslinking agent or the time of post treatment. These and previous results can be explained by the dependence of electrical resistance on the amount of water absorbed by PVA film. The rate of absorption is a function of the degree of crosslinking; therefore the electrical resistance of PVA films which are measured after 2 to 3 days in KOH shows

TABLE III.11

ELECTRICAL RESISTANCE OF CROSSLINKED PVA FILMS

COMPOSITION, g	THICKNESS, mil	ELECTRICAL RESISTANCE, $m\Omega$ in ² /mil	
		in 20% KOH	in 45% KOH
20 PVA + 2.5 dialdehyde	2.0	50	20
20 PVA + 2 dialdehyde	1.5	60	30
20 PVA + 1.5 dialdehyde	1.5	45	45
20 PVA + 1 dialdehyde	1.5	40	15
20 PVA + 1 dialdehyde + carboxylic acid	1.5	45	45
20 PVA + 1 dialdehyde + acid	1.5	60-55	45

All samples aged for 4 days at 50°C.

TABLE III.12

ELECTRICAL RESISTANCE OF CROSSLINKED PVA FILMS AFTER POST TREATMENT AT 140°C

COMPOSITION, g	THICKNESS, mils	ELECTRICAL RESISTANCE, mΩ in ² /mil	
		POST TREATMENT FOR 2 HRS.	POST TREATMENT FOR 3 HRS.
PVA + dialdehyde 20 2.5	1.5	20-25	25
PVA + dialdehyde 20 2	1.5	45	40
PVA + dialdehyde 20 1.5	1.5	25-30	25
PVA + dialdehyde 20 1	1.5	25-35	25-30
PVA + dialdehyde + acid 20 1 1	1.5	-	35
PVA (88% hydrolyzed) + dialdehyde 20 15	5.0	-	55

All samples aged for 5 days at 50°C.

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dependence of electrical resistance on degree of crosslinking.

However the equilibrium amount of water absorbed is much higher than 6 to 7% for all films crosslinked after 4 to 5 days of exposure in KOH. Electrical resistances are similar for different degrees of crosslinking.

Degree of crosslinking was measured by determining the solubility of PVA films in boiling water. Results obtained are given in Table III.13. The same degree of crosslinking (97%) was obtained for all films tested. Another independent method should probably be employed to verify these results since 97% crosslinking appears very high in view of the electrical resistance data.

Water absorption and dimensional stability were also determined. PVA films crosslinked by dialdehyde can absorb approximately 60 to 70% water which is much higher than necessary to have low electrical resistance of PVA separators. Crosslinked PVA films swell to some degree in KOH. Results of these measurements, given in Table III.14, indicate that commercial PVA swells much more than PVA crosslinked by dialdehyde and that all films produced by casting from solution swell more in width than in length.

Accelerated zinc penetration tests were carried out in cells with one layer of various PVA films to test the zinc stopping ability of the separators. Results obtained (see Table III.15) indicate that crosslinked PVA works better in the cell than commercial material but that the optimum composition has not been achieved so far.

TABLE III.13
DEGREE OF CROSSLINKING IN PVA FILMS

COMPOSITION, g	WEIGHT, g		DEGREE OF CROSSLINKING, %
	BEFORE TREATMENT IN BOILING WATER	AFTER TREATMENT IN BOILING WATER	
20 PVA + 2.5 dialdehyde	1.0537	1.0258	97.4
20 PVA + 2 dialdehyde	1.2418	1.197	96.4
20 PVA + 1.5 dialdehyde	0.7512	0.7412	96.9
20 PVA + 1 dialdehyde	0.4308	0.4148	96.3
20 PVA + 1 dialdehyde + 1 acid	1.3167	1.2965	98.0

TABLE III.14

DIMENSIONAL CHANGE OF PVA FILMS IN KOH

COMPOSITION, g	DIMENSIONAL CHANGE, % (film swell)	
	LENGTH	WIDTH
Commercial PVA	20.2	22.9
20 PVA + 1.5 dialdehyde	10.8	14.1
20 PVA + 1 dialdehyde + 1 acid	9.1	13.1

All samples exposed to KOH for 24 hrs. at 60°C.

TABLE III.15
ZINC PENETRATION TEST RESULTS WITH PVA-BASED SEPARATOR

NO.	ELECTRODE TYPE	ELECTRODE SIZE/in.	SEPARATOR CONFIGURATION	CYCLE	FAILURE MODE	COMMENTS
1	2 Full sintered Ni 1 Full Zinc ZnO 93% CdO 5% TFE 2%	H 3-7/8 W 2-7/8 T .07	Commercial PVA - 1 layer.	42	Pinhole	Swells too much, turned brown. Shape of zinc electrode changed, dendrite growth.
2	Same	Same	PVA crosslinked with 15% acid.	42	Small pinhole	Film swells less than commercial PVA. Turned slightly brown, cracked from edges.
3	Same	Same	PVA crosslinked with 10%-20% dialdehyde.	60	One small pinhole	Swells, turned slightly brown but still had good strength. Shape changed for zinc electrode and film swell in a similar way.
4	Same	Same	One layer 2 mil thick PVA crosslinked with 12% acid.	52	Dendrite growth	Looks brittle. No change in color.
5	Same	Same	1.8 mil thick film- one layer of PVA. vis. (28-32 cP).	45	Dendrite grow through sides	Film swells, little change in color.
6	Same	Same	1 layer 1.9 mil thick PVA crosslinked with 15% acid and filtered before casting.			
7	Same	Same	1.7 mil thick - one layer of high mol. wt. PVA, vis. (52-65 cP)	56	Very small one pinhole	Swells less, turned less brown, little change in shape of zinc electrode.

Discharge = 2.5A x 1 hr.
Charge/Discharge Ratio = 120%
Theor. Zinc Capacity, Ahr = 14.4

3.0 CONCLUSIONSPVA-Based Separator Materials

During this period of the investigation, it was determined that:

a) Electrical resistance depends on the quantity of water in film up to 6%. A further increase in the amount of water in PVA film does not result in a decrease of the electrical resistance which reaches an equilibrium value for this film.

b) PVA film can absorb water from an aqueous solution of KOH in quantities much greater than 6%. The same amount of water can be kept in PVA as a residual solvent after completion of the casting process. Electrical resistance of PVA films is the same in either case.

c) The quantity of residual solvent in PVA films as a function of casting technology can be calculated by the following equation:

$$t = \beta \exp \left[\frac{Q_0 - \alpha \log C}{R} \left(\frac{1}{T} - \frac{1}{T_p} \right) \right]$$

d) Crosslinking of the PVA by acid leads to increased chemical stability of the polymer but at the same time increased brittleness. Electrical resistance of crosslinked PVA is in the same range as commercial PVA because crosslinked material absorbs more than 6% water from KOH solution.

e) PVA crosslinked by dialdehyde exhibits low electrical resistance and good elasticity.

f) Accelerated zinc penetration tests indicate that cross-linked PVA works better in the cell than commercial film but optimum composition has not as yet been achieved.

Thermoplastic-Based Separator Materials

During the study of a thermoplastic-based separator material, the following results were obtained:

a) Various compositions which contain different fillers and plasticizers were investigated in order to reduce the initially very high electrical resistance of thermoplastic. The optimum ratio of components in the thermoplastic-based system shows suitable low electrical resistance.

b) The main problem in using this thermoplastic as a separator material is extremely high brittleness which leads to cracking of the separator bag. Attempts to find additives for increasing the elasticity of films have not as yet given satisfactory results.

Another Thermoplastic-Based Separator Material

Work with another thermoplastic based separator material has led to the following conclusions:

a) The composition which contains an optimum ratio of fillers and wetting agent has acceptable low electrical resistance, relatively high elasticity and good stability in a KOH environment.

b) Study of the influence of production technology on electrical resistance of these films shows that: dependence of electrical resistance on initial concentration of the solution is minimal at 10 to 12 wt% of the solid parts in solution; and an increase in temperature of film formation leads to a slight increase in electrical resistance.

c) Electrical resistance of films did not change during an aging period of 6 months at 50°C.

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d) Mechanical durability of films was measured in KOH under constant loading and at a temperature of 60°C. The durability of films in 20 and 35% KOH is approximately the same, averaging about 2 months. This is approximately ten times higher than the durability of PVA films under the same exposure conditions and much higher than the durability of any other material tested.

e) Accelerated zinc penetration tests were performed in cells constructed with one layer of separator to test the zinc stopping ability. Results obtained show that although an increase of cell cycle life was not as yet achieved, application of these separators leads to a substantial decrease in shape change of the zinc electrode. After about 65 cycles, the zinc electrode did not change shape and zinc was still spongy, indicating good electrochemical activity.

4.0 FUTURE WORK

During this period, several inorganic/organic separator compositions have been developed which are promising candidates for use in Ni-Zn cells. Therefore the tasks for the next period of work will include:

- Detailed evaluation of plastic based compositions as separator materials for Ni-Zn batteries in 20 and 250 Ahr size cells.
- Improvement of the compositions in order to achieve optimum properties of the separators.
- Advancement of the technology to produce films with uniform properties.
- Development of the optimum design and production technology for separator bags.
- Study of long-term stability of separator materials.

SECTION V
DEVELOPMENT OF SEALED
NICKEL-ZINC CELLS - (TASK IV)

1.0 INTRODUCTION

During the past 12 months the investigation of sealed Ni-Zn cells has centered on: 1) studying rates of oxygen and hydrogen evolution and recombination; 2) determining methods to improve gas recombination; 3) determining the effects of zinc electrode additives, electrolyte quantity, and separator system on sealed cell performance; and 4) determining the cycle-life characteristics of sealed cells.

2.0 TECHNICAL DISCUSSION

2.1 GROUP I SEALED CELLS

2.1.1 Cell Design

Table IV.1 lists the cell designs for the first group of sealed Ni-Zn cells. This group of designs was intended to optimize separator configuration, negative electrode composition, and electrolyte concentration.

The separator materials used in these cells were Celgard, fibrous sausage casing (regenerated cellulose), commercial PVA, ERC crosslinked PVA, and ERC P-64. The P-64 material, a cast polymeric film, was used to protect the PVA and cellophane membranes from oxidation. Fibrous sausage casing (FSC) was used in one group to prevent short circuits through the larger Celgard pores. Celgard is a polypropylene material with pores about $200 \text{ \AA}$ in diameter. This pore size is 10 to 50 times greater than FSC or PVA. Celgard was used in some cells to determine if the increased pore size significantly improves sealed cell performance by increasing mass transport without decreasing cycle life by allowing the growth of zinc shorts.

TABLE IV.1

CONSTRUCTION VARIABLES FOR GROUP I 20 Ahr SEALED CELLS

GROUP NO.	POSITIVE PLATE TYPE	THEO. POS. CAPACITY, Ahr	NEG. PLATE ADDITIVE	*SEPARATOR SYSTEM	ELECTROLYTE CONCENTRATION % KOH IN 1% LiOH
IA	Sintered	25	1% Tl_2O_3 + 2% PbO	(+) 1P/4CG/1Pt (-)	25
1B	Sintered	25	"	"	30
IC	Sintered	26	"	"	35
ID	Sintered	26	Inert conductive 5% CdO layer	"	30
IE	Sintered	26	1% Tl_2O_3 + 2% PbO Inert conductive layer	(+) 1P/2CG/2FSC/ 1CG/1Pt (-)	35
IIA	Rolled	25	5% CdO	(+) 1NY/4CG/1NY (-)	30
IIB	Rolled	25	1% Tl_2O_3 + 2% PbO	"	30
IF	Sintered	26	2% CdO + 1% PbO	1P/1P-64/2-PVA/P	35
1G	Sintered	26	2% CdO + 1% PbO	1P/1P-64/2CN/1P	40
1H	Sintered	26	2% CdO + 1% PbO	1P/3CLPVA/2P	35
2C	Rolled	29	2% CdO + 1% PbO	1P/1P-64/2PVA/1P	35
2D	Rolled	29	2% CdO + 1% PbO	1P/1P-64/2CN/1P	40
2E	Rolled	29	2% CdO + 1% PbO	1P/3CLPVA/2P	35
2F	Rolled	29	1% Tl_2O_3 + 2% PbO Inert conductive layer Inert conductive Layer + 5% CdO	1P/1P-64/2CN/1P 1P/1P-64/2 CN/1P	40 35

*CG - Celgard FSC - Fibrous Sausage Casing
 P - Pellon CN - Cellophane
 NY - Nylon CLPVA - Crosslinked PVA

With regard to the negative plate additives, the $\text{Tl}_2\text{O}_3\text{-PbO}$ binary is a mercury substitute which has proven satisfactory in 850 Ahr Ag-Zn cells which have been fabricated and tested under contracts for the Naval Sea Systems Command. The inert conductive layer and 5% CdO in the negative plate are unique constructions patented by ERC which have shown vastly improved cycle life in 40 Ahr Ag-Zn cells.

Four electrolyte concentrations were selected to establish the optimum concentration for oxygen recombination and to learn how reduced zinc solubility in lower KOH concentrations affects performance.

2.1.2 Test Procedures

The cells were filled with electrolyte and allowed to soak for three days. They were then put through two vented cycles consisting of charging at the C/16 rate for 16 hours and discharging at C/2 to 1.2V. After charging a third time at C/16, the cells were drained of all free electrolyte and sealed, followed by a discharge at C/2 to 1.2V.

The procedure was different for cells containing only Celgard as the separator material. To minimize dendrite growth through the larger pores of the Celgard, the cells were never run flooded. The cells were soaked in excess electrolyte for three days and then drained and sealed prior to running any formation cycles.

Initially, it was planned to divide the cells into two groups, running one group of cells with a slight excess of electrolyte. This was not done because initial test results indicated that the lower portion of the cell pack containing some free electrolyte would carry most of the charge current,

resulting in increased current density and greater chance of shorting due to zinc growth. Because several different separator systems were under investigation, it was impossible to standardize the amount of electrolyte put into the cells.

Once sealed, the cells were tested by monitoring the pressure behavior during open charge, open circuit, and discharge. The gassing behavior of some cells was tested with a gas chromatograph to determine the gas composition at different points during the charge. The cells were also tested for oxygen recombination by filling the charged cells to 20 psig with pure oxygen and monitoring the pressure decay during a charged open circuit stand.

2.1.3 Test Results

Table IV.2 summarizes the test results for the first group of cells which are listed by design variables, beginning with the separator system. The last two columns of the table each contain two numbers, referring to two cells in each group. Most groups only contained two cells; however since two groups (2C, 2D) contained four cells, the data from the best and poorest cells are reported.

The results for cells with Celgard separator system were scattered. All of the Celgard cells were built twice, first with Celgard 3400 and then with Celgard 3401. The Celgard 3400 cells failed within two cycles and when examined, the separator appeared to be hydrophobic. It was decided that the wetting agent in 3400 had evaporated, so the 3401 material was used. The 3401 has a wetting agent more resistant to evaporation although the results from these tests indicate that a problem with the Celgard still exists.

TAELE IV.2 TEST SUMMARY FOR FIRST SEALED CELL GROUP

SEALED CELL DESIGN VARIABLES					SEALED CELL PERFORMANCE	
SEPARATOR SYSTEM	POSITIVE PLATE TYPE	KOH CONCENT. %	NEGATIVE PLATE ADDITIVE	GROUP NO.	CHARGE INPUT, Ahr	DISCHARGE CAPACITY, Ahr
(+) Pellon/4xCelgard/ Pellon (-)	Sintered	35	1% Tl_2O_3 2% PbO +	IC	>22 / >22	15.8 / 6.8
		25	1% Tl_2O_3 2% PbO +	IA	>22 / >22	14.5 / 0
		30	5% CdO Inert conductive layer	ID	14.9 / 19.4	3 / 3
(+) Nylon/4xCelgard/ Nylon (-)	Rolled	30	1% Tl_2O_3 2% PbO +	2B	16.5 / 15.1	9.5 / 7.2
			5% CdO Inert conductive layer	2A	15.3 / 10.2	9 / 5.8
		35	2.5% HgO	2H	13.7 / 14.1	9.5 / 9.5
(+) Pellon/ERC P-64/ 2xPVA/Pellon (-)	Sintered	35	2% CdO 1% PbO +	IF	14.6 / 15.3	11 / 11.5
	Rolled	35	2% CdO 1% PbO +	2C	11 / 8.5	6.8 / 5.8
(+) Pellon/ERC P-64/ 2xCellophane/Pellon (-)	Sintered	40	2% CdO 1% PbO +	IG	>22 / >22	17.9 / 17.5
	Rolled	40	2% CdO 1% PbO +	2D	11.9 / 9.3	10.5 / 8.5
(+) Pellon/3x ERC cross- linked PVA/Pellon (-)	Sintered	35	2% CdO 1% PbO +	IH	15.5 / 10.5	13.2 / 9
	Rolled	35	2% CdO 1% PbO +	2E	12.8 / 14	10.2 / 9.7

The best of the Celgard groups was IC with 35% KOH and the Tl_2O_3 -PbO binary to the negative. Discharge capacity for Cell IC2 however was poor (6.8 Ahr). Of the cells with rolled positive electrodes, Group 2B containing 30% KOH and the Tl_2O_3 -PbO binary showed the highest capacity output.

Among the other cells, the best designs appeared to be the P-64/cellophane system and the ERC crosslinked PVA system, although the performance of these cells was still not acceptable. The most significant results were obtained with Group IG, which accepted a full charge and delivered just under 18 Ahr capacity. Following preliminary cycling, the cells were put on automatic cycle, charging at C/6 and discharging at C/2.

Table IV.3 gives the data for Group IG on cycle test. Occasionally the pressure in the cells did not decay below the pressure switch cut-off and the cell did not discharge. When this occurred, the cycler switched to charge and the cell would accept a small charge before reaching the pressure cut-off.

Figures IV.5 and IV.7 show the gas production, in terms of partial pressures of hydrogen and oxygen, in the cells during charge No. 23. The cells accepted only 12.4 and 15.4 Ahr charge to the pressure cut-off, which is poorer performance than the initial data.

Cells with crosslinked PVA and P-64/cellophane separator systems were tested to determine the compositions of the gases while on charge. Figures IV.1 through IV.14 and Table IV.4 present the results.

TABLE IV.3
GROUP IG CYCLE TEST RESULTS

CELL NO.	CYCLE NO.	FIRST CHARGE* Ahr/Input	SECOND CHARGE† Ahr/Input	DISCHARGE CAPACITY, Ahr/Out	CHARGE EFFICIENCY, %
IG1	1	20.0		17.5	87.5
	2	19.5	1.26	17.7	85.3
	3	15.5	2.66	16.1	88.6
	4	15.4	1.89	16.9	47.7
	12	15.2		14.1	92.8
	13	14.0		12.9	92.1
	18	17.0		14.4	85.2
	27	12.7		12.1	95.3
IG2	1	14.4		12.3	85.4
	2	13.7	2.36	13.3	82.8
	3	18.1	1.62	17.0	86.2
	4	12.4	2.6	14.8	98.6
	12	15.2		14.1	92.8
	13	14.0	2.2	12.5	82.8
	18	10.2		10.0	98.0
	27	12.3		11.9	96.7

*All charges continue until pressure cut-off of 20 psig is reached.

†A second charge occurs when cells miss the discharge cycle. This occurs when the pressure switch does not open until cell internal pressure falls.

FIGURE IV.1 GAS PRODUCTION FOR CELL 2D1
AT 3A CHARGE RATE

FIGURE IV.2 GAS PRODUCTION FOR CELL 2E1
AT 3A CHARGE RATE

FIGURE IV.3 GAS PRODUCTION FOR CELL 2D1 AT 8A CHARGE RATE

FIGURE IV.4 GAS PRODUCTION FOR CELL 2E1 AT 8A CHARGE RATE

FIGURE IV.5 GAS PRODUCTION FOR CELL IG: AT 3.67A CHARGE RATE

FIGURE IV.6 GAS PRODUCTION FOR CELL IG: AT 3A CHARGE RATE

FIGURE IV.7 GAS PRODUCTION FOR CELL IG2 AT 3.67A CHARGE RATE

FIGURE IV.8 GAS PRODUCTION FOR CELL IG2 AT 3A CHARGE RATE

FIGURE IV.9 GAS PRODUCTION FOR CELL IG1 AT 8A CHARGE RATE

FIGURE IV.10 GAS PRODUCTION FOR CELL IG2 AT 8A CHARGE RATE

FIGURE IV.11 GAS PRODUCTION FOR CELL IH1 AT 3A CHARGE RATE

FIGURE IV.12 GAS PRODUCTION FOR CELL IH-2 AT 3A CHARGE RATE

FIGURE IV.13 GAS PRODUCTION FOR CELL IH1 AT 8A CHARGE

FIGURE IV.14 GAS PRODUCTION FOR CELL IH2 AT 8A CHARGE

TABLE IV.4
CELL TEST RESULTS AT 3A and 8A CHARGE RATES

CELL NO.	CHARGE CURRENT, Amps	CHARGE INPUT TO PRESSURE CUTOFF Ahr	END OF CHARGE VOLTAGE, V	DISCHARGE CAPACITY, Ahr	CHARGE INPUT TO H ₂ EVOLUTION, Ahr	CHARGE INPUT TO O ₂ EVOLUTION, Ahr	Y _{H₂}	Y _{O₂}
2D1	3	11.8	2.52	11.3	4.5 to 11	11	.71	.29
	8	11.9	2.26	10.8	3 to 10	11	.65	.35
2E1	3	11.8	1.94	9.8	0	5	.15	.85
	8	9.3	2.04	6.7	8	0(6)	.69	.31
1G1	3	11.9	1.98	8.7	9	5	.20	.80
	8	13.5	1.93	10.8	0	0(10.5)	.10	.90
1G2	3	13.1	1.94	11.5	0	4 to 9	.23	.77
	8	13.3	1.96	12.0	0	0(10.5)	.17	.83
1H1	3	5.3	2.27	3.0	0(4)	4	.77	.23
	8	6.5	2.39	5.8	0	6	.54	.46
1H2	3	11.6	1.99	10.8	10.2	10.2	.18	.82
	8	13.6	2.06	13.0	0	12	.15	.85

Included in the table are the points during charge when hydrogen and oxygen were initially evolved. When the data is not sufficient for a precise determination, a range is given. If the cell began to produce H_2 or O_2 at the start of the charge, a value of 0 Ahr is reported. In some cases a cell would begin gassing slowly at the beginning of charge and increase to a higher gassing rate later in the charge. In these instances, the point at which the cell gasses at the higher rate is reported in parentheses following the 0 Ahr entry. Also included in this table are the final mole fractions of the gases produced by the cells during charge.

To determine the amount of oxygen recombination in the cells, some cells were tested by filling them to 20 psig with pure oxygen and monitoring the pressure decay. Data for Cell 2B1 and Group 2E are presented in Figures IV.15 through IV.17. Cells 2B1 and 2E1 were refilled with oxygen and tested a second time following the first recombination test. The results indicate a significant recombination capability in the cells. The fact that these second tests showed O_2 recombination comparable to the first test indicates that recombination was limited by oxygen availability and not zinc availability.

2.2 GROUP II SEALED CELLS

2.2.1 Cell Design

Based on the data obtained from Group I cells, the major problems limiting the first group of sealed cells appeared to be: reduced cell capacity in the electrolyte starved condition resulting in gas production rates greater than the cell's recombination

FIGURE IV.15 CHEMICAL RECOMBINATION TESTS FOR CELL 2B1

FIGURE IV.16 CHEMICAL RECOMBINATION TESTS FOR CELL 2E1

FIGURE IV,17 CHEMICAL RECOMBINATION TEST FOR CELL 2E2

capability; and high levels of hydrogen generation in the cell, limiting charge input and making periodic venting necessary. The electrolyte starved condition also accelerated dendrite growth in the cells by creating areas of increased current density in the wetter areas of the cell. Dendritic zinc will not only shorten cell life, but will also generate gas more rapidly than the zinc electrode as it has no additives to raise the hydrogen overvoltage.

The second group of sealed cells was designed to address these problems. Table IV.5 presents a summary of the cell designs. Two cells were made in each group. All of the cells had rolled positive electrodes and a zinc:nickel ratio of 3. The 2R series of cell designs contained recombination electrodes. To increase wetting in the cells, all of the designs had looser packs than Group I. To increase the wetting of the Celgard material, cells were built with alternating layers of Celgard and Pellon absorber. Cells were also built with an experimental filled polymeric separator and thicker, hand-cast crosslinked PVA.

Groups 2L through 2O were built with 2.5% HgO in the negative electrode to determine if reduction in hydrogen evolution was possible with highly amalgamated Zn. Groups 2L and 2M are identical except 2L was built with gold plated nickel exmet positive collectors to determine if the higher oxygen overvoltage on gold will improve nickel electrode efficiency.

Another variable in these designs was the wrapping of the negative electrodes. Previously the negative electrodes were only wrapped in Pellon absorber to maximize gas transport

TABLE IV.5
GROUP II CELL DESIGN SUMMARY

GROUP NUMBER	NEGATIVE PLATE ADDITIVE	SEPARATOR SYSTEM*
2J	2% CdO, 1% PbO, inert conductive layer	(+)NY/CG/P/2xCG/P/CG//P(-)
2K	2% CdO, 1% PbO, inert conductive layer	(+)P/.0018" CLPVA//.0018" CLPVA/P(-)
2L	2.5% HgO	(+)P/3x.0007" CLPVA//P(-)
2M	Same as 2L, but 2L has gold plated Ni Exmet in positive electrodes	
2N	2.5% HgO	(+)P/P-64/2xCG//P(-)
2O	2.5% HgO	(+)P/ P-64C /2xCN//P(-)
2R-1	2% CdO, 1% PbO, inert conductive layer	(+)P/.0007" CLPVA//2x.0007" CLPVA/P(-)
2R-2	2% CdO, 1% PbO, inert conductive layer	(+)P/3x.0007" CLPVA// P(-)
2R-3	2% CdO, 1% PbO, inert conductive layer	(+)P/P-64/CN//P(-)
2R-4	10% Bi ₂ O ₃	(+)NY/2PVA//1PVA/P(-)

*CN - Cellophane
 CG - Celgard
 CLPVA - Crosslinked PVA
 P - Pellon
 NY - Nylon
 P-64 - Polymeric
 P-64C - Polymeric filled

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for oxygen recombination. In these designs, Groups 2R-1 and 2R-2 each have three layers of machine cast crosslinked PVA. In 2R-1, two layers are wrapped on the negative electrode while 2R-2 has all three layers on the positive electrode.

Group 2R-4 combines oxygen recombination electrodes with the separator and negative electrode design which has performed best in the vented cell testing done under the System Engineering Task of this project.

2.2.2 Test Results

During flooded formation cycles, Groups 2L and 2M delivered the same discharge capacity (15 Ahr), but 2L showed a discharge voltage about 30 mV higher than group 2M. This indicates that while the gold plated collectors may have had better electrical contact to the electrode material, ampere-hour efficiency was no greater than with the standard collector.

When tested in the sealed condition, Group 2L accepted only 2 and 6 Ahr charge to 20 psi and showed very high voltages on charge (2L2 was at 5.2V after a 2 Ahr charge). This suggests that the cells had dried out; however vacuum refilling the cells did not improve performance, indicating some other cause for the poor performance.

The testing procedure was altered in groups 2K and 2N during an investigation of alternate formation procedures. Previous cells had shown growth of dendritic zinc during flooded formation cycles, during which time a 25% overcharge based on theoretical nickel capacity was given. In Groups 2K and 2N one cell from each group (2N1 and 2K1) was formed by running two

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manual cycles and charging the cells to 28.8 Ahr (10% overcharge over theoretical capacity) over 16 hours. The other two cells (2N2 and 2K2) were formed by putting the cells on automatic cycle, charging to 22 Ahr over 6 hours and discharging to 1.2V at 10A. The purpose of the investigation was to determine if the reduced charge of the second method would result in less zinc growth.

After nine cycles, Cells 2N2 and 2K2 each delivered 19.6 Ahr to 1.2V (from 22 Ahr charge). When tested, drained and sealed, 2N2 accepted 13 Ahr (to 20 psi) and delivered 10.2 Ahr capacity. Cell 2K2 accepted 14.5 Ahr and delivered 14.2 Ahr capacity.

Cells 2N1 and 2K1 each delivered 14.5 Ahr capacity on the second discharge (from 28.8 Ahr charge). When tested sealed, 2K1 accepted 16.6 Ahr and delivered 12.3 Ahr capacity. Cell 2N1 accepted 16.0 Ahr and delivered 11.3 Ahr. The low capacity indicated that the cells were not fully formed, so they were given 6 automatic cycles. Discharge capacity on cycle No. 6 was 15.0 for 2K1 and 13.9 for 2N1. Tested and sealed again, 2N1 accepted 17.5 Ahr and delivered 10.1 Ahr while 2K1 accepted 15.8 Ahr and delivered 15 Ahr.

In both groups, the No. 1 cell performed better, although more than two cycles were needed to form the cells. This suggests that the reduced charge of the second method offers no improvement in cell performance. The results also suggest that more formation cycles are needed than previously thought.

Data for Groups 2J, 2K, 2M and 2N are presented in Table IV.6. Group 2O, with the experimental polymeric separator, delivered poor flooded capacity and was not tested sealed.

TABLE IV.6 TEST SUMMARY FOR SECOND SEALED CELL GROUP

GROUP NO.	CELL DESIGN VARIABLES		SEALED CELL PERFORMANCE	
	SEPARATOR SYSTEM	NEGATIVE PLATE ADDITIVE	CHARGE INPUT, Ahr	DISCHARGE CAP. Ahr
2J	(+)NY/CG/P/2xCG,P/CG///P(-)	2% CdO + 1% PbO + Inert conductive layer on collector	21 21	15 14.6
2K	(+)P/.0018"CLPVA///.008CLPVA/P(-)	2% CdO + 1% PbO + Inert conductive layer	15.8 14.5	15.0 14.2
2M	(+)P/3x.007"CLPVA//P(-)	2.5% HgO	14.5 10.7	13 9.8
2N	(+)P/P-64/2xCN///P(-)	2.5% HgO	17.5 13	10.1 10.2

CN - Cellophane
 CG - Celgard
 CLPVA - Crosslinked PVA
 P - Pellon
 NY - Nylon

The performance of the groups with 2.5% HgO in the negative electrode showed no improvement over similar designs with other zinc additives. This indicates that the high percentage of hydrogen in the cell gases is not due to mercury substitutes. More likely the high rate of hydrogen production is due to premature zinc polarization in the electrolyte starved condition.

The best group among these designs was Group 2J, with the Celgard/Pellon separator arrangement. The superiority of this group is an indication of the importance of increased electrolyte retention to cell performance. The larger Celgard pores may also be a factor in the superior performance of the cell, allowing improved mass transport for oxygen recombination. After manual sealed formation cycles, the cells were put on automatic cycle with pressure switches set to terminate charge at 20 psi.

With each cycle, the cells generate some hydrogen which is not recombined. The amount of hydrogen eventually accumulates to the pressure cut-off, terminating the cycle test. Group 2J was cycled by evacuating the cells each time the cycle test was terminated.

Figure IV.18 shows the cycle data for Group 2J. The cells showed a decline in performance while on cycle. Two approaches were tried to improve the cells. First the cells were conditioned by discharging the cells to 0.0V to reduce any charge excess that might have existed in the zinc electrode. A slight improvement in performance was observed after this procedure. After the cells were vacuum refilled, drained, and tested again, more significant

* after conditioning to 0 volts
 † after vacuum refilling

CYCLES		
1-16	○	1-12
17-28	□	13-19
29-36	△	20-29
37-45 *	●	30-41 *
46-62 †	■	42-49 †

FIGURE IV.18 GROUP 2J CELL CYCLE RESULTS

improvement was observed indicating that the decline in performance on cycle is due mostly to the drying out of some component in the cell pack.

2.2.3 Cells with Recombination Electrodes

The designs of the four groups of cells with recombination electrodes (2R1 through 2R4) are listed in Table IV.5. The cells were tested in three sealed configurations:

1. flooded
2. electrolyte starved, with recombination electrodes not connected
3. electrolyte starved, with recombination electrodes connected

Test results for these cells are listed in Table IV.7.

One conclusion that can be drawn from this data is that wrapping the zinc electrode is beneficial to sealed cell performance. The two groups which performed best (2R1 and 2R4) had two layers of separator on the negative electrode. Apparently the reduction of zinc growth from the wrapped electrode is more significant than the reduction in recombination capability.

Testing the cells with recombination electrodes connected did not improve performance; however open circuit recombination tests with bottled O_2 showed abnormally high recombination rates with the recombination electrodes both connected and disconnected. This suggests that the recombination electrodes are shorting internally to the negative electrodes.

2.2.4 Single Zinc Electrode Studies

Three designs of zinc electrodes were tested for oxygen recombination. The test consisted of charging a single zinc electrode against exmet and testing its recombination with

TABLE IV.7 PERFORMANCE OF SEALED CELLS WITH RECOMBINATION ELECTRODES

CELL NO.	FORMATION CAPACITY, Ahr	FLOODED Ahi	SEALED Aho	DRAINED WITHOUT RECOMBINATION ELECTRCDE, Ahr		DRAINED WITH RECOMBINATION ELECTRODE, Ahr	
				Ahi	Aho	Ahi	Aho
2R1-1	14.5	17.3	13.8	17.2	10.5	13.2	12.7
2R1-2	17.1	18.5	16.0	19.3	16.3	18.9	15.8
2R2-1	15.3	17.3	14.7	9.3	6.0	8.5	7.2
2R2-2	15.3	17.3	14.7	8.9	6.7	8.4	4.6
2R3-1	12.3	14.1	10.7	12.5	8.8	11.1	9.2
2R3-2	11.7	15.1	9.5	12.7	7.8	10.4	7.8
2R4-1	19.3	-	-	15.3	13.5	15.6	11.8
2R4-2	19.3	-	-	19.1	16.5	17.2	14.7

Ahi = Charge accepted to pressure cut-off

Aho = Discharge capacity

oxygen in a sealed pressure chamber. The electrodes were blotted dry with a towel and shimmed between two pieces of vexar (gas diffusion plastic netting) in the chamber. Table IV.8 shows the test results, given for rates over periods of two minutes and 15 minutes after exposure to 20 psig oxygen. Two electrodes per design were tested and rates are given in terms of pressure decay (psi/min) and equivalent current density (amperes/in²). The electrodes are all close in performance, with the 5% CdO design slightly better than the other two.

2.2.5 Platinum Recombination Studies

To deal with the problem of hydrogen buildup in sealed Ni-Zn cells, work has been done with recombination catalysts consisting of a catalyst-Teflon mixture in a special configuration.

The catalysts were first tested in an electrolytic cell which evolved gas at a rate of 1A. Figure IV.19 presents the data for three catalysts with different quantities of catalyst mix. The sample with 36.6 mg catalyst was cycled in a nickel-zinc cell (see Section 2.2.6) and eventually flooded. To prevent flooding, new configurations of the catalyst are being tested.

Figure IV.20 shows the performance of the catalysts in the electrolytic cell. After being tested individually, a test was run with all four catalysts in the cell together, with the temperature of Type 4 being monitored.

The temperature and pressure data for the individual catalysts are higher than the catalysts tested previously due to the lower amount of catalyst material present. Results indicate the superiority of a multiple catalyst arrangement vs

TABLE IV.8 SINGLE ELECTRODE TEST RESULTS

ELECTRODE COMPOSITION	Pressure Decay $\frac{\Delta P}{\Delta t}$, psi/min		Equiv. Current Density, A/in ²	
	2 min. psi/min	15 min. psi/min	2 min.	15 min.
ZnO, 5% CdO	7.75, 11.7	2.17, 2.20	.159, .250	.044 .045
ZnO, 2% CdO, 1% PbO	5 7	1.64, 1.70	.102, .143	.034, .035
ZnO , 2% CdO, 1% Tl₂O₃	7.5, 7	1.75, 2.00	.154, .143	.036, .041

FIGURE IV. 19 CHARACTERISTICS OF PLATINUM CATALYSTS
IN AN ELECTROLYTIC CELL AT 1A

○ TEMPERATURE
 ■ PRESSURE

FIGURE IV.20. PERFORMANCE OF PLATINUM CATALYSTS IN ELECTROLYTIC CELL AT 1A RATE

a comparable amount of catalyst placed in one larger containment. The catalysts with Telfon film did exhibit lower operating temperature than the control, although the pressure levels were slightly higher. All four catalysts have been sealed in Ni-Zn Cell 2P (described in the next section) and the cell was put on automatic cycle. Without recombination catalysts, the cell stopped cycling after nine cycles. The cell has currently gone 24 cycles with the recombination catalysts and the test is continuing (see Figure IV.21). When the cycle test is terminated, the four catalysts will be tested individually to determine which designs (if any) were more sensitive to flooding.

2.2.6 Cells with Celgard/Pellon Separator System

Because of the superior initial performance of Cell 2J, five cells were made with the Celgard/Pellon separator system and various zinc electrodes. Table IV.9 gives the data for these cells on Cycle No. 5. Figure IV.22 shows the pressure buildup on charge and Figure IV.23 shows the pressure behavior on open circuit immediately following charge cut-off.

The cells were also tested for recombination with pure oxygen on open circuit. Figure IV.24 shows the pressure decay curves. One apparent trend in these results is that cells which accept the most charge input have the slowest rates of recombination on open circuit. There are two possible explanations for this. The poorer cells evolve more hydrogen and have lower partial pressures of oxygen on charge, resulting in less consumption of zinc by recombination and more zinc available for the open circuit test. The poorer cells might also contain more dendritic zinc which will increase gassing during charge

FIGURE IV. 21 PLATINUM CATALYSTS ON CYCLE, CELL 2P

TABLE IV.9 PRESSURE CONTROLLED CHARGE CHARACTERISTICS FOR CELLS WITH
CELGARD-PELLON SEPARATOR SYSTEM (CYCLE #5)

CELL NO.	NEGATIVE ELECTRODE COMPOSITION	CHARGE INPUT TO 20 psi, Ahr	DISCHARGE CAPACITY, Ahr	CHARGE EFFICIENCY, % Aho/Ahi *
2J1	ZnO, 2% CdO, 1% PbO, Inert conductive layer	21.0	15.0	71
2P	ZnO, 2% CdO, 1% PbO	15.7	14.0	89
2Q	ZnO, 2% PbO, 1% Tl_2O_3	13.6	11.0	81
2R	ZnO, 0.5% CdO	15.0	12.2	81
2S	ZnO, 5% PbO	14.0	10.8	77
2T(I)	ZnO, 5% CdO	17.1	14.7	86

*Aho = discharge capacity

Ahi = charge accepted to pressure cut-off

- ZINC ADDITIVES
- 2% CdO + 1% PbO + .004" CdO LAYER (2J1)
 - 5% CdO (2T, I)
 - △ 2% CdO + 1% PbO (2P)
 - ▲ 0.5% CdO (2R)
 - 5% PbO (2S)
 - 2% PbO + 1% Ti₂O₃ (2Q)

FIGURE IV.22 PRESSURE BUILDUP DURING CHARGE IN CELLS WITH CELGARD-PELLON SEPARATOR SYSTEM

- ZINC ADDITIVES
- 2% CdO + 1% PbO + .004" CdO LAYER (2JI)
 - 5% CdO (2T(I))
 - △ 2% CdO + 1% PbO (2P)
 - ▲ 0.5% CdO (2R)
 - 5% PbO (2S)
 - 2% PbO + 1% Ti₂O₃ (2Q)

FIGURE IV. 23 PRESSURE DECAY ON OPEN CIRCUIT (AFTER CHARGE) IN CELLS WITH CELGARD-PELLON SEPARATOR SYSTEM

FIGURE IV. 24 OPEN CIRCUIT RECOMBINATION WITH PURE O_2

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and increase recombination during open circuit (because of the high surface area of the zinc).

Performance on cycle test was limited by hydrogen build-up, as in Group 2J. Table IV.10 lists the data for Cells 2P, 2Q, 2R, and 2S. All cells ran only four cycles except Cell 2P which ran 9 cycles.

To eliminate the problem of hydrogen generation, cells in this group have been tested with the recombination devices described above. Cell 2T(I) was cycled with a catalyst consisting of 36.6 mg of catalyst mixture. Figure IV.25 illustrates that this cell ran for 20 cycles before it stopped accepting charge. The decline in capacity seen in this figure from beginning of test is probably due to redistribution of electrolyte during cycling.

After the cycle test, the cell was given a charge to 25 Ahr in the vented condition to determine the full capacity. On discharge the cell delivered 12.8 Ahr to 1.2V.

Before this discharge, the cell was tested for open circuit oxygen recombination with 20 psig of oxygen. There was a decrease in pressure decay rate following cycling. In terms of recombination rates and equivalent current, results after two and 15 minutes are given in the following table.

Cell 2T(I)	OVER 2 MINUTES		OVER 15 MINUTES	
	$\Delta P/\Delta t$, psi/min.	i, amps	$\Delta P/\Delta t$, psi/min.	i, amps
Before cycling	3.0	2.42	0.65	0.524
Decrease, %	8.3		18.3	

TABLE IV.10 CYCLE DATA FOR SEALED CELLS

CELL 2P				CELL 2Q			CELL 2R			CELL 2S		
Automatic Cycle No.	CHARGE INPUT, Ahr	DISCHARGE CAP. Ahr		CHARGE INPUT, Ahr	DISCHARGE CAP. Ahr		CHARGE INPUT Ahr	DISCHARGE CAP. Ahr		CHARGE INPUT, Ahr	DISCHARGE CAP. Ahr	
		to 0.8V (or EDV*)			to 1.2V	to 0.8V (or EDV)		to 0.8V (or EDV)	to 0.8V (or EDV)			
1	18.7	15.5	EDV: 1.05V	16.3	14.3	19	18.0	15.5	19.0	16.3	14.2	19.5
2	21.3	15.5	1.15V	20.7	16.2	1.15V	19.1	15.0	19.1	20.5	15.5	1.02V
3	20.9	16.5	1.15V	19.5	16.0	1.12V	17.6	12.0	17.5	20.5	16.0	1.02V
4	20.6	16.2	1.17V	17.3	13.7	19.0	9.2	5.0	8.5	20.2	16.0	1.02V
5	20.6	16.0	1.15V	0	--	--	0	--	--	0	--	--
6	20.4	15.8	1.15V									
7	19.8	15.0	1.12V									
8	18.7	13.5	19.0									
9	17.1	11.0	16.8									
10	C	--	--									

*In cases where the cell lasted the entire 20 Ahr Discharge, the end of discharge voltage is listed.

FIGURE IV.25 PLATINUM RECOMBINATION CATALYST ON
AUTOMATIC CYCLE, CELL 2T(I)

After these tests the cell was vacuum refilled and tested flooded. From a 27 in. vacuum, the cell accepted 10.9 Ahr charge to 20 psi (without platinum). At this point the cell was vented and charge was continued to 21 Ahr. On discharge the cell delivered 14.8 Ahr to 1.2V and 20.2 Ahr to 0.8V, which is comparable to the cell's performance after about 6 automatic cycles.

The catalyst that was cycled with 2T(I) was tested in an electrolytic cell after the cycle test. When tested in this cell before being cycled, pressure and temperature reached equilibrium at 22.5 in. mercury and 80°C. When tested after the cycle test, the catalyst failed to catalyze any reaction, and pressure rose at a steady rate. This indicates that the catalyst material had flooded.

3.0 CONCLUSIONS

The first group of cells demonstrated charge acceptance and capacity delivery below what was expected. Several design modifications have been tried in an attempt to improve performance: HgO additive in the zinc electrode, recombination electrodes and new separator systems. None of these modifications significantly improves performance. This suggests that the problems they were meant to address (low zinc electrode charge efficiency, low recombination capability and low mass transport for oxygen recombination) are not the major problems of the system. Both the poor charge acceptance and the high H₂ generation rates are probably due to reduced cell capacity in the starved condition.

Studies performed in this section indicate that the major problem in sealed cell development is electrolyte retention.

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This is most clearly shown by the fact that the most significant improvement in cell performance came from the addition of extra layers of Pellon absorber to the separator system.

Open circuit recombination tests with single electrodes and with cells have demonstrated that a significant recombination capability exists in the cells. However this capability is not enough to allow sustained overcharge in the cells, even with oxygen recombination electrodes. Recombination devices have been developed which can consume gases generated at a rate of at least 1 ampere. These devices would make sustained overcharge in sealed cells possible, once the gases were being generated in stoichiometric proportions.

The results suggest that with proper electrolyte wicking and recombination devices, sealed cells could be designed with capacity and cycle performance at least equivalent to flooded, vented Ni-Zn cells. Work is planned with cells involving other absorber materials and separator materials in conjunction with Pellon absorber. A cell is also being built with a separate chamber for recombination electrode, allowing the cell pack to be run flooded while the recombination electrode is exposed to the cell gases. These efforts are aimed at providing sealed performance which is at least comparable to flooded, vented cell performance. Sealed cell performance achieved to date has been inferior to performance obtained in flooded 20 Ahr cells, which have demonstrated formation capacities as high as 20 Ahr and a cycle life (to 40% of rated capacity) of one hundred cycles. Sealed cell performance (as demonstrated by Group 2J) is limited to 17.5 Ahr initial capacity with poor capacity

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maintenance. These results indicate that the performance differential between flooded and vented Ni-Zn cells is due to electrolyte redistribution in the sealed cells. The problem will have to be solved before the benefits of the sealed cell approach (limited zinc electrode overcharge and reduced cell maintenance) can be realized.

SECTION VI
SYSTEM ENGINEERING - (TASK V)

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1.0 INTRODUCTION

The objectives of this phase of the ANL Ni-Zn program are the design, fabrication and testing of EV type Ni-Zn cells, failure analysis, and development of charging and charge control procedures.

Several 250 Ahr rated EV type cells and 20 Ahr size experimental cells were fabricated to test the design concepts, evaluate the components and update the manufacturing technology. EV type cells were also tested to determine the endurance characteristics at high rates of charge and discharge over a range of temperatures.

The analysis of post failure characteristics consisted of the determination of the negative area reduction due to shape change of the Zn electrode, and charge percentage and graphite loss at the positive electrode.

Constant voltage charging and constant current charging using an auxiliary electrode were also investigated.

2.0 TECHNICAL DISCUSSION

2.1 LIFE CYCLE PERFORMANCE OF EV TYPE CELLS

The baseline design of the EV type Ni-Zn cells consisted of an active pack made up of Teflon-bound NiOOH and Teflon-bound ZnO electrodes (6.25" x 9") in a NorylTM container. PVA was used as the main separator. The cell was vacuum filled with an electrolyte composition of 35% KOH plus 1% LiOH.

Several variations of this design were investigated.

2.1.1 Design A - Framed Positive

The baseline design of the positive was varied by building a frame around the edges of the electrode. Two cells (EV23 and EV24) of 250 Ahr rated capacity (Faradaic capacity of the positive = 310 Ahr) were fabricated. One cell was tested for its life cycle capability and the other was set aside for cell characterization experiments. The cycling regime for Cell EV23 consisted of:

CHARGE: 37.3 Amp for 5.75 hours

DISCHARGE: 85 Amp for 2.25 hours

Figure V.1 shows the cell voltage-capacity relationship obtained for the 70th cycle, when the decline in capacity reached 2.8%. The corresponding decline in watt-hour efficiency is 5.5%, and cell capacity declined by 40% of the rated capacity after 80 cycles.

2.1.2 Design B - Effect of Absorbent Material

The baseline design was modified by incorporating polyamide felt in the main separator sequence. Two cells, EV25 and EV26, were fabricated and life cycle tested in the same manner as in Design A. Figure V.1 shows the discharge curve obtained at Cycle 52. The cell capacity started declining more rapidly beyond 55 cycles.

2.1.3 Design C - Effect of Zigzag Wrap and Electrode Geometry

EV39 was designed with a modified separator (PVA, zigzag wrap) and electrode geometry. This design contains additional electrodes of either polarity in the active core. The cell was life cycle tested. Figure V.1 shows the capacity-cell voltage relationship obtained at Cycle 70. At this cycle the

FIGURE V.1 CELL VOLTAGE-CAPACITY RELATIONSHIPS FOR CELLS EV23, EV25, EV39 AND EV45

ampere-hour capacity had declined by 13.9% of initial capacity (192 Ahr, 75% depth) and the watt-hour efficiency by 17%.

2.1.4 Design D - Effect of Rectangular Electrodes

A vented nickel-zinc cell of 250 Ahr nominal capacity (Cell EVT45) was designed and fabricated with the objective of achieving equalized potential distribution in the electrodes. The dimensions of the core were 23 x 4.5 x 1.50 inches.

The cell, repeatedly charged and discharged at C/6 and C/3 respectively, displayed a life of 45 cycles. After 45 cycles the cell exhibited symptoms of shorting due to dendritic growth. Figure V.1 shows the discharge curve obtained at Cycle 11.

2.1.5 Design E - Au Plated Positive Substrates

The objective of this design was to determine whether the overcharge requirements of the Ni-Zn cell can be reduced by using a Au plated Ni-exmet substrate at the positive electrode. Cell EV82 was fabricated and tested. An identical cell, EV72, was also fabricated with Ni-exmet substrate at the positive. At Cycle 3 the electrochemical utilization (considering the actual weight of $\text{Ni}(\text{OH})_2$) was 58% for EV72 and 62% for EV82; the amount of overcharge was the same in both cells. Cell EV72 exhibited symptoms of dendrite shorting after 10 cycles; Cell EV82 displayed a cycle life of 55 before the capacity declined by 40%. The cell decayed in performance due to dendritic shorting.

From the experimental data it appears that Au plating of the positive electrode current collectors has beneficial effects with regard to low end of charge voltage. Its effect on capacity maintenance with cycling is unclear.

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2.1.6 Design F - Proprietary Current Collector

In the baseline design, a nickel exmet acts as a substrate for the positive and the active material is laminated and pressed onto this collector. A proprietary collector was used as the substrate in this design. Ni-Zn Cell EV83 was fabricated and tested. The Faradaic capacity of the positive electrodes amounted to 340 Ahr. The variation of cell capacity with cycling is as follows:

<u>CELL EV83</u>	
<u>Cycle No.</u>	<u>Capacity, Ahr</u>
2	248
6	192 (limited by depth of discharge)
30	192
55	192
60	170
67	128

2.1.7 Design G - Proprietary Positives

A proprietary treatment procedure was introduced in the manufacturing of the Teflon bound positive electrodes. EV Cell EV92 was fabricated with preformed positives. The experimental capacity of the cell amounted to 297 Ahr in the first and second cycle which corresponds to 100% utilization of the positive active material at C/3 discharge. (Figure V.2 shows a typical performance curve). This represents an improvement in the baseline design. This cell was set apart for high rate and temperature discharge studies.

Life cycle performance of EV type cells is summarized in Table V.1. The life cycle study using various designs has shown that improvements in cycle life may be achieved by:

FIGURE V.2 CELL VOLTAGE-CAPACITY RELATIONSHIP FOR CELL EV92
DESIGN G, EFFECT OF FORMATION

TABLE V.1

SUMMARY OF LIFE CYCLE PERFORMANCE OF EV TYPE CELLS

Design	Cell No.	Design Feature	Theoretical Capacity, Ahr	Rated Capacity, Ahr	Delivered Capacity, Ahr	Maximum Positive Utilization	Life to 60% of Rated Capacity, Cycles
A	EV23	Framed Positive	310	250	240	76%	80
B	EV25	Polyamide absorbent material	310	250	~220	~73%	55
C	EV39	Zigzag wrap, 23 electrodes	300	250	195	65%	66
D	EV Rect.	23 x 4.5" Electrodes	280	250	190	70%	45
E	EV82	Au Plated Positive Substrate	340	250	186	62%	55
F	EV83	Proprietary Positive Substrate	340	250	248	73%	~ 63
G	EV92	Proprietary Positive	297	250	297	100%	

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1) framing the positive electrode and 2) using a proprietary substrate. Preliminary results indicate that the proprietary treatment of the positive increases the electrochemical utilization of the positive.

2.2 ELECTROCHEMICAL CHARACTERIZATION

The EV type cells were characterized for their performance dependency on rate, temperature and depth of discharge.

2.2.1 Charging Curves

The cell voltage-capacity relationship is a function of rate and cycle number for EV type cells. Figure V.3 shows the relationship between cell voltage and state of charge as a function of charge rate. As expected, the relationship is non-linear with increasing polarization of cell voltage with increasing rate. There are no points of inflection in the curves which may be used as a signal to terminate charge.

Figure V.4 shows the same relationship as a function of cycle number. Curve "b" in the figure exhibits an inflection around 80% charged state. The voltage increases to 2.2V in the region which indicates the onset of H₂ evolution on the negative electrode.

2.2.2 Thermal Response

The thermal response of the Ni-Zn cell is a function of geometry, internal configuration and operating conditions. The main source of heat generation in the Ni-Zn cell is caused by individual electrode polarizations. The preferred heat removal mechanism is conduction along the electrodes. Heat is also transferred by gaseous conduction during overcharge. The baseline design of the EV type cell was tested for temperature

FIGURE V.3

CHARGING CURVES
AT DIFFERENT RATES
OF CONSTANT
CURRENT CHARGE
(CELL NO. EVC)

----- = 10.0 Amp
----- = 40.0 Amp
----- = 85.0 Amp

FIGURE V.4
CAPACITY - CELL VOLTAGE
RELATIONSHIP DURING
CONSTANT CURRENT CHARGING
AT C/6

variations during charge and discharge. Figure V.5 shows the temperature rise during constant current charge at C/3. This behavior is typical of alkaline cells. Figure V.6 shows the temperature rise during constant current discharge at C/3. The interrelationship between voltage and temperature during discharge was determined. Figure V.7 shows the variation of cell voltage and temperature during discharge at C/2. From Figures V.5 through V.7 it is evident that more heat is evolved during discharge than charge. Therefore it may be concluded that if precautions are taken to avoid prolonged overcharge, heat evolution during cell discharge becomes the limiting factor. Studies are in progress to develop a thermally compatible design for the EV type cell which lends itself to active cooling. In this regard, our attention is equally divided among developing new and improved electrode and cell designs as well as such heat removal techniques as water and solvent cooling.

2.2.3 Discharge Capacity and Temperature

Temperature dependency of the discharge capacity was investigated for EV type cells. In the first series of experiments, the cell was discharged at various temperatures; the charge preceding each discharge was conducted at 25°C and C/16 for 16 hours. The ampere hour input prior to each discharge was 250 Ahr. Each discharge amounted to an increase in the number of cycles for the cell. The decline in capacity by repeated cycling during this experiment is negligible since previous results show that the discharge capacity is stable at 27°C for Cycles 10 through 25. The variation of cell capacity with temperature is given in Table V.2. As seen, the discharge

FIGURE V.5

VARIATION OF CELL TEMPERATURE DURING CHARGING

FIGURE V.6

VARIATION OF CELL TEMPERATURE DURING DISCHARGE

Cell: EV Type, ERC Ni-Zn
Rate of Discharge: 120A

FIGURE V.7 VARIATION OF CELL TEMPERATURE
AND VOLTAGE DURING DISCHARGE

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capacity is very sensitive to low temperature - at 5°C the decline in capacity amounted to 30%.

TABLE V.2
TEMPERATURE DEPENDENCE OF
THE DISCHARGE CAPACITY

TEMPERATURE, °C	CYCLE NO.	CAPACITY, Ahr
32	12	212.5
40	15	205.4
52	16	192.6
69	17	191.3
15	13	163.0
5	14	147.0
Cell: EV type, Rate of Discharge: 85A		

In another series of experiments, the cell was charged and subsequently discharged at the same temperature. Figure V.8 shows the charge/discharge behavior at 5°C. This experiment demonstrates the low temperature capability of the cell.

2.2.4 Depth of Discharge and Cycle Life

Three EV type cells of identical design (EVT MI-1 through EVT MI-3) were fabricated. EVT MI-1 was repeatedly discharged to 77% depth of the rated capacity. Cell capacity was stable up to 50 cycles, but at the 60th cycle, the capacity declined by 20% of the rated capacity. EVT MI-2 was cycled to 51% depth and cell capacity was stable up to 128 cycles. EVT MI-3 was cycled to 25% depth and the capacity was stable up to 250 cycles.

FIGURE V.8

CELL VOLTAGE - CAPACITY RELATIONSHIP
DURING CHARGE AND DISCHARGE AT 5°C.

Charge-Discharge Current = 40A
Cell = EV Type, Vented

2.3 CHARGE CONTROL

2.3.1 Auxiliary Electrode

It is well known that the nickel hydroxide electrode is poorer in charging efficiency than the zinc electrode. Therefore the nickel-zinc cells are always overcharged to the extent of 10 to 20% to maximize the positive plate capacity. However during overcharge, zinc deposition takes place at a higher over-voltage which promotes dendritic growth. It is possible to limit the overcharge on the zinc electrode by selecting a charge cutoff voltage at which point charging is terminated on the zinc electrode. However the nickel electrode can continue to be charged through an auxiliary electrode incorporated in the active pack.

Three nickel-zinc cells of 20 Ahr nominal capacity were designed and fabricated. Each cell contained an auxiliary electrode composed of unimpregnated sintered nickel. All three cells were tested identically on an automatic cycler. Table V.3 illustrates the capacity maintenance data for these cells. After the 100th cycle, the cells were withdrawn from the cycler since their capacity had declined by 40% of the rated capacity.

2.3.2 Constant Voltage

Constant voltage charging at 1.95V was examined using 3 EV type cells. Cell EV86 was tested in a specially fabricated automatic cycler consisting of power supply, relay, timer, scanner and voltage sensor. The cycling regimen was constant voltage charge for 6 hours and discharge to 75% depth at C/3.

TABLE V.3

CYCLE LIFE DATA OF 20 Ahr CELLS
CONTAINING AN AUXILIARY ELECTRODE

CELL NO.	CAPACITY IN Ahr AT THE			
	25th CYCLE	50th CYCLE	75th CYCLE	100th CYCLE
61	14.4	17.5	15.6	11.9
63	16.9	16.3	17.5	6.9
64	14.4	17.5	16.3	13.9

Cell Type: Vented, Prismatic

Electrodes: 2.875 in. x 3.875 in.

The variation of cell capacity with cycling was:

CELL EV86

<u>Cell No.</u>	<u>Capacity, Ahr</u>
6	192 (limited by depth of discharge)
23	192
30	170
40	106
45	127

Life cycle tests were terminated after 45 cycles.

2.4 POST FAILURE CHARACTERIZATION

A detailed and systematic analysis of the cells after failure and at various stages of their cycle life has been undertaken in support of the component development and system engineering studies. Three parameters have been selected for quantitative evaluation, viz., area reduction due to shape change, charge percentage of the positive, and graphite loss. These parameters play a major role in governing the decline in capacity with cycling.

2.4.1 Zinc Shape Change

Shape change on the Zn electrode can be described as the reduction in the geometric area of the Zn electrode with cycling. On charge and discharge, the deposition and dissolution do not take place in the same location on the Zn electrode; instead the active material is removed from the electrode edges and redeposited toward the plate center. In this process, the edge areas of the current collector are completely denuded of Zn. Area reduction due to shape change is determined using the following procedure. The cell is dissected and negative

electrodes are washed free of most electrolyte then dried. Next, electrodes are traced on a paper. By knowing the original shape of the electrode, the percentage reduction in area can then be calculated.

Twenty nickel-zinc cells of 20 Ahr rated capacity were dissected and the shape change was determined. Table V.4 compares the reduction in area and cycle life for the cells.

Zn electrodes from Cell 62 had an area reduction of 11.4% which is a very low value. However cycle life was 45, which indicates that the reason for cell failure was shorting.

Cells Z43, Z26, and Z53A exhibit high cycle life with low area reduction. These cells differ with regard to the active material composition in the Zn electrode. The additives in these cells were proprietary.

2.4.2 Charge Percentage

The charge-discharge reaction in the nickel electrode can be represented as:

The ratio of NiOOH to total nickel in an electrode determines the charge percentage for a given rate and duration of charge.

The analytical procedure consists of treating the electrode with an excess of ferrous ammonium sulfate in an acetic acid solution. As the trivalent and tetravalent Ni ions are reduced to the divalent Ni, the ferrous ions are oxidized to ferric ions.

TABLE V.4
COMPARISON OF AREA REDUCTION AND CYCLE LIFE

CELL NO.	NO. OF CYCLES	AREA REDUCTION, %
Z42	111	49.1
Z43	191	47.4
Z44A	88	31.2
Z47B	103	43.2
Z38	108	48.5
Z48B	153	53.4
Z51B	109	52.3
61	107	45.4
62	45	11.4
63	106	47.1
X46	66	55.8
X48	65	53.4
X8 (2)	45	21.8
Z26	211	45.9
Z27	167	33.5
Z53A	107	25.9
Z49B	122	37.4
Z56B	138	52.3
X25 (2)	96	49.0
X34 (2)	96	29.2

The excess of ferrous ions can be determined by titration with standard potassium permanganate.

The amount of metal in the charged state is then calculated.

Another portion of the electrode is used to determine total nickel using the dimethyloglyoxime method. The charge percentage is calculated as follows:

$$\% \text{ charge efficiency} = \frac{\text{g charged Ni/g material}}{\text{g total Ni/g material}} \times 100$$

Since in this analysis the nickel grid is discarded after removing all the active materials, the total nickel does not include the metal grid. The experimental values obtained for total nickel compares well with the actual weight of nickel hydroxide used (the design value). Table V.4 illustrates the experimental values for the charge percentages.

Cell Z26 which was cycled 211 times, exhibits a charge efficiency of 95.3%. This indicates that the Teflon bound positive electrodes are quite stable in a rigorous cycling regime.

Charge efficiency values lower than 80% may be due to shorting or due to unbalanced electrical symmetry at the positive due to shape change at the negative.

2.4.3 Graphite Loss

There is a possibility of oxidizing the graphite in the positive as a result of extended cycling at high rates and elevated temperature. The graphite may also disintegrate and form an emulsion in the cell electrolyte. Since the graphite loss at the positive may be minimized by proper choice of cell design parameters, the graphite loss was determined as a function of cell design and cycle life.

The determination of graphite loss consists of dissolving a sample of the positive electrode in 1:1 HCl. Then the insolubles are filtered through a tared Gooch crucible and the crucible is dried in an oven at 90°C, cooled and weighed. (The weight of insolubles consists of TFE and graphite). The amount of graphite loss was then calculated. Table V.5 illustrates the experimental values for graphite loss at the positive electrode withdrawn from Ni-Zn cells of 20 Ahr rated capacity. The percentage of the rated capacity obtained at these cycles was less than 5% for most of the cells.

Cells 61, 62, and 63 were designed with an auxiliary electrode in the active core for charge control purposes. The experimental values for the graphite loss show that this procedure did not aid in lowering the graphite loss for Cells 62 and 63.

Cell Z40-1 (184 cycles), Z48B (153 cycles), Z56B (138 cycles) and Z43 (191 cycles) exhibit high cycle life but the percent of graphite loss is relatively high.

Cell Z53A achieved 107 cycles yet exhibited only 5.4%

TABLE V.5
GRAPHITE LOSS AT THE POSITIVE
AS A FUNCTION OF NUMBER OF CYCLES

CELL NO.	NO. OF CYCLES	GRAPHITE LOSS, %
Z40(1)	184	15.1
Z42	111	6.3
Z43	191	12.8
Z44A	88	10.7
Z47B	103	13.8
Z38	108	18.9
Z48B	153	16.1
Z51B	109	15.1
61	107	4.0
62	45	13.8
63	106	6.0
X46	66	15.6
X48	65	14.7
X8(2)	45	15.0
Z26	211	9.0
Z53A	107	5.4
Z49B	122	13.1
Z56B	138	11.9
X25(2)	96	15.3
X34(2)	96	13.1

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graphite loss. The best performing cell is Z26 with 211 cycles and a graphite loss of approximately 9%. The reason for the lower graphite loss in Z53A and Z26 is not known with certainty. However it may be due to the lower overcharges on the positive on each cycle. This happens because of the cycling regime adopted in which the ampere hour input is constant (22 Ahr) in each cycle regardless of the ampere hour output in the preceding discharge subcycle. Because the cyclor cuts off cells when they reach a discharge voltage of 0.8V, a cell with poor capacity maintenance (due to the deactivation of Zn) is overcharged to a greater extent in the subsequent charge cycle than a cell with good capacity maintenance. This overcharge in combination with the resultant evolution of O₂ may contribute to greater graphite oxidation.

3.0 CONCLUSIONS

Life Cycle Performance:

Life cycle data for various EV type cell designs indicate that marginal improvements in cycle life may be obtained by employing the "framed positive" and proprietary designs. The reproducibility of the results remains to be checked. The proprietary treatment given to the positive electrode prior to cell assembly appears to increase the electrochemical utilization of the positive electrode. The effect of this proprietary treatment on cycle life is not yet known.

Electrochemical Characterization:

The charging characteristics of Ni-Zn are similar to those of Ni-Cd. After the zinc has been fully charged, the charging curve exhibits a plateau at 2.2V corresponding to

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predominant evolutions of H_2 . The plateau occurs at 1.9V in Ni-Cd cells.

The Ni-Zn cell evolves more heat during discharge than on charge, which is typical of alkaline rechargeable cells. On a typical discharge at 120 amps ($\approx C/2$) the cell temperature increased by $16^\circ C$.

When the low temperature performance of the cell was tested at $5^\circ C$, the discharge capacity was lower by 30% as expected. Cycle life increases with decrease in depth of discharge.

Charge Control:

The auxiliary electrode charging procedure showed no improvement in cycle life. A typical 20 Ahr size cell yielded 100 cycles before its capacity declined by 40% of the rated capacity.

The constant voltage charge procedure at 1.95V did not yield any improvements in cycle life. A typical cell (EV86) yielded a cycle life of 40 before the capacity declined by 68% of the rated capacity.

Post Failure Characterization:

Post failure characterization has shown that Zn shape change may be minimized by the proper choice of additives - Cells Z53A, Z43 and Z26 had high cycle life with low values for area reduction.

The charge percentage study not only gives an indication of the state of health of the positive but also possible shorting due to dendrites. Charge efficiency values as high as 90% were obtained after 100 cycles.

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Graphite loss values as low as 6% were obtained after 100 cycles for three of the cells.

In a generally healthy cell the zinc shape change is less, charge percentage is high, and graphite loss is minimal as indicated by the values obtained for Cell Z26.

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