Energy Savings by Means of Fuel Cell Electrodes
in Electro-Chemical Industries

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SECTION 1ABSTRACT

The objectives of the subject program are (1) to evaluate experimentally, on a laboratory scale, energy and cost savings in electrowinning of zinc by substituting, for the conventional lead anode, a Prototech proprietary hydrogen anode operating on pure and impure feeds; (2) to similarly evaluate experimentally, again on a laboratory scale, voltage, and thus energy savings in chlor-alkali membrane cells by substituting, for the conventional steel cathode, a Prototech proprietary air cathode; (3) to consult with Lockheed and Lawrence Livermore Laboratory (LLL) on the subject of suitable air electrodes for metal/water/air batteries; and (4) prepare cost estimates of all processes investigated based on laboratory results.

SECTION 2SUMMARY

The initial experimentation for zinc electrowinning was carried out in an electrolysis cell having available electrode areas of 2" x 2" and electrode spacing of 2" at a current density of 36 ASF. Using pure hydrogen as fuel and, at first, simulated acid sulfate solutions, it was established that the hydrogen anode functioned well, without significant decrease in zinc-plating current efficiency, in electrolytes of free H_2SO_4 content of up to 120 g/l without an ion exchange membrane. Utilizing pure hydrogen an unexpectedly large voltage saving of nearly two volts resulted (ca. 3.5V with the Pb anode; 1.5V with the H_2 -anode). Impure hydrogen feeds (102 ppm CO) substantially lower this savings. A process has been developed to selectively oxidize CO in the presence of hydrogen in fuel feeds. Subsequent experimentation with actual plant liquors obtained from the Anaconda Company substantially confirmed this data and demonstrated that the usual low level impurities in plant liquors, as well as its calcium sulfate impurity, did not affect the performance of the hydrogen anode. Before the completion of the program, a scaled up (6" x 6" available electrode area) cell was operated reproducing the data within 10% and producing from plant liquor sufficiently large samples of zinc for metallurgical analysis.

Almost lead-free zinc was obtained in the process (any lead traces in the zinc can come only from Pb impurities in the liquor itself). The samples will be examined by the Anaconda Company for potentially new uses of substantially lead-free zinc. Energy and cost estimates have been made based on the above summarized experimentation and have been checked with Anaconda Company staff. Taking into account energy losses incurred by producing hydrogen from petroleum coke, an overall energy saving has been estimated at 40%, compared with conventional zinc electrowinning by means of lead anodes. In terms of purchased electric energy^{*} the hydrogen anode process requires of the order of 0.5 to 0.7 KWH/lb zinc, whereas the conventional lead anode process requires 1.5 KWH/lb zinc. Overall cost savings of between 1½ and 2½ cents/lb zinc appear possible by operation at higher temperature and higher current density with the H₂-anode, than is permissible with the lead anode.

With respect to the air cathode in chlor-alkali cells, extended experimentation, again in a laboratory cell having available electrode areas of 2" x 2", has demonstrated a useful life for Prototech's carbon cloth based electrode of more than 12,000 hours without irreversible deterioration in performance. The performance of the electrode was dependent on the

^{*} Purchased electric energy is termed "power consumption" in Section 3 of this report to distinguish it from the chemical energy consumed in the production of hydrogen from petroleum coke.

Pt loading and was considerably enhanced by the use of specially designed current collectors constructed within the electrode itself. Voltage savings at a current density of 300 ASF (33% CO₂ free air efficiency) and a temperature of 75°C, vs. the conventional steel cathode, amounted to about 0.85 volts on air operation, and to about 0.95 - 1 volt on operation with pure oxygen. The energy savings vs. the steel cathode, when operating on air, is about 20%.

Regarding air cathodes intended for metal air batteries, LLL's and Lockheed's prime interest is the aluminum-air battery. Samples of several different Prototech proprietary air cathodes were submitted to both these institutions for testing therein. Results have been encouraging.

SECTION 3

TECHNICAL DISCUSSION

The Hydrogen Anode in Electrowinning of Zinc

Pure Hydrogen Feed

3.1 TECHNICAL CONSIDERATIONS

3.1.1 Cell Reactions

In the electrowinning of zinc the electrochemical reaction (1) $\text{Zn}^{++} + 2\text{e}^{-} \rightarrow \text{Zn}$ has a negative potential (-0.763 volt at room temperature),¹ with respect to the conventional zero voltage of the reaction (2) $\text{H}_2 \rightarrow 2\text{H}^{+} + 2\text{e}^{-}$. Therefore, zinc cannot be plated from zinc sulfate solution by means of a hydrogen electrode without an external power supply. In the case of zinc, the hydrogen anode contributes a part of the electricity directly through reaction (2) and, in addition, eliminates the oxygen overvoltage associated with the lead alloy anode now used in electrowinning of zinc from slightly acid zinc sulfate solutions.

In view of the fact that the zinc deposition potential is negative with respect to hydrogen, zinc ions cannot be reduced chemically to zinc metal by hydrogen. Thus, there is no apriori need for a membrane to protect the hydrogen anode from contact with zinc ions.

1. Oxidation Potentials, Second Edition, Wendell M. Latimer, p. 182.

Typical zinc plating electrolytes are carefully purified of contaminants and contain about 100 to 150 g/l of zinc as zinc sulfate and up to 100 g/l of free sulfuric acid,* so long as the free acid is kept at or below this level, the current efficiency of conventional electrowinning is 92 to 94%, i.e. small amounts of hydrogen are evolved to account largely for the remaining 6 to 8%. The amount of acid produced anodically in the conventional electrolysis reaction

is the same as that produced by the hydrogen anode electrolysis reaction (4) $\text{Zn}^{++} + \text{SO}_4^{--} + \text{H}_2 \rightarrow \text{Zn} + \text{SO}_4^{--} + 2\text{H}^+$. Therefore, the current efficiency is expected to remain about the same in the latter case, except that there, in contrast to conventional electrolysis, the cathodic by-product hydrogen can be cycled back to the hydrogen anode to approach 100 percent hydrogen utilization.

3.1.2 Parasitic Electrode Reactions

One important question to be resolved is the performance of the electrodes as a function of free acid content in the range of 35 to 60°C. This consideration is important because parasitic anode and cathode reactions are possible in a hydrogen depolarized cell operating at high sulfuric acid concentrations (~ 100 g/l) and temperatures (~ 60°C).

*Private communication, T.P. McNulty, The Anaconda Co.

Parasitic cathode reactions which will lower current efficiency (in both the conventional and the proposed hydrogen depolarized cell) are shown in equations 5 and 6:

Also, a parasitic anode, and indeed detrimental, reaction is possible by generating hydrogen sulfide according to equation 7:

3.1.3 Half Cell Evaluation of Anodes in Sulfuric Acid Electrolytes

With the understanding of the reactions recorded in Sections 3.1.1 and 3.1.2, a series of tests were run in a half cell at 55°C in which the hydrogen depolarization of a standard Prototech Company anode (0.33 mg/cm² Pt) was measured as a function of sulfuric acid concentration. The data, Figure 1, indicate that an acid concentration of at least 50 g/l H₂SO₄ is necessary for acceptable depolarization values.

3.2 EQUIPMENT DESIGN

3.2.1 Zinc electrolysis Cell Design

After consultation with Anaconda Co. and reference to "Electrolysis of Zinc Sulfate Solution", Handbook of Non-Ferrous Metallurgy, Vol. 2, Chapter XIV, a set of initial operation parameters were chosen and a cell designed to evaluate hydrogen depolarized anode performance for the electrowinning of zinc.

Figure 2
Prototech Co. Hydrogen Anode
Half Cell DATA

H₂ Depolarization vs H₂SO₄ Electrolyte Concentration

The cell, Figures 2 and 3 and Photograph 1, is of modular construction and provides 2" x 2" electrode areas. Except for the cathode there are no metal parts in the cell because trace metal contamination is to be avoided to achieve high current efficiency. The assembly consists of distinct anode and cathode sections with a 2.0 inch distance separating the electrodes. The void space between the electrodes is filled with electrolyte when the hardware, which is suspended on PVC holders, is lowered into a battery jar containing the test solution.

Figure 2, which is a top view of the cell depicts the anode and cathode sections of the assembly and clearly shows the Nylon spacers, nuts, bolts and rod used to isolate each section so that when the test is completed the zinc coated cathode can be removed without disturbing the anode compartment.

Figure 3 is a front cross section of the hardware. It displays the hydrogen plenum and anode assembly. As with all Prototech Company cells, a Lucite window is provided to observe the gas side of the electrode under investigation. If it is necessary to employ an ion exchange membrane in the cell, this would be located approximately $\frac{1}{4}$ " in front of the anode, facing the cathode and the 2.0 inch spacing between the electrode would be maintained. The cathode section of the cell is solid, with the aluminum cathode rigidly held in place by Lucite blocks and PVC frames. Current and voltage probes exit the cell at the top and are not in contact with the electrolyte.

FIGURE 2 , TOP VIEW
 ZINC Electrowinning Cell

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FIGURE 3, FRONT CROSS-SECTION VIEW
Zinc Electro-winning Cell

PHOTOGRAPH 1

At the present time a 1/8" thick Stackpole Carbon Company grade 20/20 high density electrical grade graphite window frame current collector is employed in the anode section and a 14 mil aluminum sheet is used as the cathode.

The cell, suspended in the electrolyte in the battery jar, is shown in Photograph 1. It will be noted that the electrolyte temperature is maintained by a mercury switch temperature controller connected to a glass coated heating rod. Also seen is the stirring action of a Teflon coated magnetic stirrer. Auxiliary cell equipment includes a rectified power supply, a 0-2 amp amp-meter, a volt meter and a soap bubble flow meter for monitoring the hydrogen gas flow.

3.2.2 Anode Design

The hydrogen depolarized anodes(Pt) that have been utilized in this program are proprietary gas diffusion electrodes manufactured by Prototech Company. Typical Pt loadings are $0.33 \pm 10\% \text{ mg/cm}^2$ with the preferred catalyst being 15-25 $\text{\AA}^{\circ}$ Pt particles deposited on high surface area carbon (see U.S. Patent No. 4,044,193). The electrodes are normally fabricated on carbon cloth (RA19 type).

3.3 INITIAL TEST DATA

3.3.1 Zinc Electrowinning - Current Efficiency and Power Consumption of Industrial Lead (Ca) Anode vs. Hydrogen Depolarized Anode

Employing the cell described in Section 3.2 and an electrolyte composition of 120 g/l $\text{Zn}^{++}(\text{SO}_4=)$ and 1.0 molar H_2SO_4 (98 g/l H_2SO_4), several tests were run with the conventional Industrial Lead (Calcium) anode and a Prototech Company 0.33 mg/cm² Pt H_2 depolarized anode (RA19 type). The data (Table 1) which were obtained at a current density of 36 amps per square foot, demonstrated the striking energy savings of at least 0.60 KWH per lb of deposited zinc when a hydrogen depolarized anode was employed.¹

For short term tests, (3.5 hours), the energy consumption with a lead anode (1.24 KWH/lb zinc) was at least 2.2 times greater than that required for the hydrogen depolarized anode. The 1.24 KWH/lb figure for the Lead Anode is in rough agreement with today's industrial operations.

1. The measurements and calculations necessary to compute % current efficiency and KWH/lb zinc are as follows:

- a) Cell Voltage: Anode to cathode voltages are obtained with a high resistance digital voltmeter. This value included cell IR and polarizations.
- b) % Current Efficiency: 1 Amp/hour will deposit 1.219 grams of zinc at 100% efficiency. The laboratory model cell with 2" x 2" electrodes operates at this amperage (36ASF) which is approximately equal to the current density of industrial plants. Therefore:

$$\frac{\text{grams deposited} \times 100}{1.219 \times \text{hours}} = \% \text{ current efficiency}$$

- c) KWH/lb zinc: This value is calculated from the measurements obtained in a and b from the equation

$$\frac{\text{amps} \times \text{cell voltage} \times \text{hours} \times 454}{1000 \times \text{grams zinc deposited}}$$

TABLE 1

Electrolysis of ZnSO_4 Solution (Zinc Deposition)Prototech Company H_2 Depolarized Anode and

Commercial Pb(Ca) Anode

Test #	Electrolyte Composition		Test Hours	Type of Anode	Cell Voltage	Current Density ASF	Fuel Efficiency*	Current Efficiency	Cell Temperature	Power Consumption KWH/lb Zinc
	Zn^{++}	H_2SO_4								
1	120 g/l	98 g/l	3.5	Prototech Company H_2 Depolarized Pt anode	1.36 Volts	36ASF	20%	90.3%	55°C	0.560
2 **	119 g/l	100 g/l	23.0	Prototech Company H_2 Depolarized Pt anode	1.30 Volts	36ASF	20%	79.8%	55°C	0.607
3	120 g/l	98 g/l	3.5	Commercial Pb(Ca) Anode	3.15 Volts	36ASF	---	94.1%	55°C	1.250
4	119 g/l	100 g/l	3.5	Commercial Pb(Ca) Anode	3.28 Volts	36ASF	---	98.4%	35°C	1.240
5	117 g/l	102 g/l	3.5	Prototech Company H_2 Depolarized Pt anode	1.36 Volts	36ASF	20%	91.9%	55°C	0.550

* The H_2 fuel efficiency was not optimized.

Heavy treeing on cathode.

3.4 GENERAL OPERATING CONDITIONS AND ANALYSIS

3.4.1 Regeneration of Depleted Zinc-Sulfuric Acid Electrolytes

The original zinc and sulfuric acid concentrations of a spent electrowinning electrolyte can be regenerated by the simple addition of ZnO. The original cell and regeneration reactions are as follows:

Therefore, the overall reaction is:

In actual practice, water is evaporated from the hot electrolyte (55°C) and the mole of water formed as a reaction product is not sufficient to maintain a specific electrolyte concentration. Therefore, regeneration of a spent electrolyte is accomplished by the dissolution of ZnO and the addition of water.

3.4.2 Analytical Procedures

Since the deposited zinc is easily stripped from the aluminum cathode it is a simple procedure to weigh the zinc and calculate the quantity of ZnO necessary to be added to the electrolyte to regenerate the original zinc concentration. It therefore only remains to titrate the sulfuric acid content of the electrolyte to determine if the original acid concentration was being maintained.¹ (Table 2)

1. Tritration to pH 4.2 with 1.0N NaOH (Slow addition of titrant).

TABLE 2

Calculated vs. Analytically Determined H_2SO_4 Concentration
in a Zinc Electrowinning Bath

Original Electrolyte

Calculated H_2SO_4	Titrated H_2SO_4
98.0 g/l	97.1 g/l

After 4 hours of Electrolyte at 92.3% Efficiency*

Calculated H_2SO_4	Titrated H_2SO_4
101.0 g/l	100.8 g/l

After Electrolyte Regeneration

Calculated H_2SO_4	Titrated H_2SO_4
98.0 g/l	98.1 g/l

*Electrolysis carried out at a constant current of 1 Amp.
Deposited Zinc = 4.50 grams. 1 amp-hour theoretically
deposits 1.219 grams Zinc.

3.4.3 Appropriate Running Time Necessary to Obtain Representative Data

Utilizing the present hardware it has been found advantageous (within the scope of the current contract) to limit runs to 4 hours for the following reasons:

- (1) Running at 36ASF provides 4-5 grams of deposited zinc which quantity is easy to strip from the aluminum collector and can be weighed accurately.
- (2) Current, voltage, gas flows and other operating parameters can be monitored by laboratory personnel at close intervals and the need for recording equipment and constant current apparatus is avoided.
- (3) Comparison tests run for 4 and 24 hours yielded power consumptions of 0.54 and 0.58 KWH/lb of zinc respectively as compared to 1.25 and 1.30 KWH/lb of zinc for the commercial Pb(CA) anode. This decreased efficiency for the longer tests has been documented and reported on page 422 of "Electrolysis of Zinc Sulfate Solution", Handbook of Non-ferrous Metallurgy, Vol. 2, Chapter XIV that

The period of deposition affects ampere efficiency: As the period of deposition increases the effect of any impurity becomes more pronounced. With absolutely pure solutions, high ampere efficiency can be obtained with 48, 72, 96 hours or even longer periods of deposition. In plant operation it is frequently found advisable to decrease the period to 24 hours or less.

- (4) For tests run above 4 hours, "treeing" (dendrites built up along the edges of the cathodes) becomes noticeable. It is not the intent of this program to solve the treeing problem for experimental hardware as industry successfully limits this effect.
- (5) At 55°C, evaporation of water from the electrolyte pool becomes an important consideration as the length of a test is increased above 4 hours.

3.5 CELL PARAMETERS THAT EFFECT CELL VOLTAGE AND CURRENT EFFICIENCY

3.5.1 Introduction

Cell parameters that affect cell voltage and current efficiency are:

- a) Cell Temperature
- b) Electrolyte Acid Concentration
- c) Current Density
- d) Electrolyte Zinc to Acid Ratio
- e) Current Collection
- f) Electrolyte Impurities
- g) Duration of Plating

With respect to cell voltage, items a through e predominate while items f and g are the main parameters affecting current efficiency. Other variables such as electrode spacing, stirring rate etc. are also of importance but are not of major concern

in this study as long as they are held constant for all cells tested.

The subject program has been undertaken to demonstrate the magnitude of energy savings (KWH/lb zinc) that results when a hydrogen depolarized anode is substituted for the conventional (industrial) lead anode. Thus, in studying any of the parameters listed above it is necessary to obtain power consumption data which involve both cell voltage and current efficiency. While an arbitrary separation of variables has been offered it is well known that it is difficult to change some operating parameters without affecting both voltage and current efficiency.

3.5.2 Cell Voltage as a Function of Cell Temperature

Figure 4 is a plot of cell voltage vs. cell temperature over a range of 22 to 80°C employing a 120 g/l zinc and 98 g/l H_2SO_4 electrolyte. This curve shows that the major decrease in cell voltage is afforded as the temperature is initially raised above room temperature and then starts to level off at cell temperatures around 55°C.

Figure 5 shows the current efficiency and power consumption curves for hydrogen depolarized zinc electrowinning cells operating between 55-80°C. The desired cell reactions still predominate at 80°C but a significantly reduced ampere efficiency and rapidly increasing power consumption is demonstrated above 70°C, thus, the normal cell temperature of 55°C is well under any value that will lead to a noticeable increase in KWH/lb zinc.

Figure 4

Cell Voltage vs Cell Temperature
9P 9/L H_2SO_4 AND 120 g/L Zinc
.36 AGF

1.50

1.40

1.30

1.20

1.10

Cell Voltage - Anode to Cathode

Electrolyte Temperature, $^{\circ}C$

10

20

30

40

50

60

70

80

Figure 5.
Effect of Electrolyte Temperature
ON
Current Efficiency and Power Consumption
55 - 80°C

3.5.3 Cell Voltage as a Function of Sulfuric Acid Concentration in the Electrolyte

The specific conductance of sulfuric acid solutions increases very rapidly over the range of 49 to 147 g/l. The effect of this acid range on cell voltage, current efficiency and power consumption was studied with a 120 g/l zinc electrolyte at 55°C.

Cell voltage, Figure 6, decreased initially as the acid concentration was increased but approached a limiting value above 100 g/l H_2SO_4 . Since the curve (Figure 6) includes all polarizations and resistances it is concluded that any voltage gain resulting from an increase in specific conductance of the electrolyte is being overshadowed by other voltage losses.

Several observations can be made:

- 1) Increased sulfuric acid resulted in an erratic but steady decrease in current efficiency.
- 2) Calculated power consumption (KWH/lb zinc) plotted out to be a rather smooth curve with maximum values at the lower and higher sulfuric acid concentrations and a large minimum portion between 70 and 120 g/l H_2SO_4 .
- 3) Inspection of Figures 6 and 7 indicate that unless some unexpected benefit surfaces, electrolyte acid concentration should be at least 49 g/l to decrease cell resistance and help anode polarization but optimum limits should be determined in the light of effect of impurities.

Figure 6

Cell Voltage vs. Sulfuric Concentration

55°C - 36 ASF

120 g/l Zinc

Figure 7
Effect of Sulfuric Acid Concentration
ON
Current Efficiency and Power Consumption

3.5.4 Effect of Current Density on Cell Voltage, Ampere Efficiency and Power Consumption

3.5.4.1 Preliminary Considerations

It has been found that the slope of the discharge curves (9 to 72 ASF) of a Pb(Ca) and hydrogen depolarized anode in a zinc electrowinning cell containing a synthetic electrolyte (120 g/l zinc and 98 g/l H_2SO_4 at $55^{\circ}C$) are essentially identical. Refer to Figure 8. The effect of hydrogen depolarization is to decrease the cell voltage by approximately 1.85 volts at all current densities.

Ampere efficiency, as calculated by equation 1, is independent of cell voltage:

$$(1) \quad \frac{\text{grams zinc deposited} \times 100}{1.219 \times \text{amps} \times \text{hours}} = \% \text{ ampere efficiency}$$

but cell voltage, is a most important consideration when calculating the power consumption for zinc deposition by equation 2,

$$(2) \quad \frac{\text{amps} \times \text{cell voltage} \times \text{hours} \times 454}{1000 \times \text{grams zinc deposited}} = \text{KWH/lb zinc.}$$

With an assumed 90% current efficiency (see Figure 8), these data can be translated into KWH/lb zinc vs. current density, as shown in Figure 9. To confirm these calculated values, tests were run at varied current densities.

Figure 8.
Current Density - Voltage Curves

FIGURE 9

Power Consumption (KWH/lb Zinc)

Pb(Ca) Anode vs H₂ Depolarized Anode

Assuming 90% Current Efficiency

1.40

1.50

1.40

1.30

1.20

1.10

1.00

.90

.80

.70

.60

.50

.40

.30

.20

.10

KWH/lb ZINC

Pb(Ca) Anode

Cell Temperature

55°

H₂SO₄ Concentration

98 g/l

ZINC Concentration

120 g/l

H₂ Depolarized Anode

CURRENT DENSITY, ASF

9

18

27

36

45

54

63

72

81

3.5.4.2 Experimental Data-Current Density vs. Power Consumption

Data obtained for a hydrogen depolarized anode operating at varied current densities in zinc electrowinning cells are shown in Figure 10. These data indicate that the ampere efficiency increases with current density and consequently since these values rise above 90%, the power consumption is somewhat lower than the calculated values presented in Figure 9 .

3.5.5 Current Efficiency and Power Consumption as Effected by Decreasing Zinc and Increasing Acid Concentration

According to the cell reaction $\text{ZnSO}_4 + \text{H}_2 \rightarrow \text{Zn}^0 + \text{H}_2\text{SO}_4$ 1 mole of zinc metal is deposited while 2 moles H^+ ions are generated. When 1.0 gram of zinc is deposited, 1.5 grams of additional H_2SO_4 is produced. Employing a synthetic solution containing initially 120 g/l zinc and 98 g/l H_2SO_4 , the stoichiometric effect is to increase the acid concentration at a faster rate ($\times 1.5$) than the depletion of zinc. This situation is increasingly in favor of lower current efficiencies according to Figure 7. However, the increased acid concentration is favorable for lower cell voltage (Figure 6).

A series of tests have been conducted in which the % current efficiency and power consumption were computed for deposition times of 4-6 hours for a standard synthetic electrolyte. Data obtained, table 3 indicate that as the zinc concentration is depleted and acid concentration is increased, the

- 1) cell voltage is decreased
- 2) the percent current efficiency decreases
- 3) The power consumption slowly rises.

Figure 10.
Effect of Current Density
ON

Current Efficiency and Power Consumption

TABLE 3

Effect of Decreasing Zinc and Increasing H₂SO₄ Concentrations
on Current Efficiency and Power Consumption

Test	Electrolyte Composition		Test	Cell	Current	Cell	%Current	Energy
	Zinc	H ₂ SO ₄	Hours	Temp °C	Density	Voltage	Efficiency	Consumption
								KWH/lb Zinc
1	120 g/l	98 g/l	4	55°C	36ASF	1.35	93.5%	.538
2	117.7 g/l	101.4 g/l	5	55°C	36ASF	1.30	91.7%	.528
3	115.0 g/l	105.4 g/l	6	55°C	36ASF	1.29	88.0%	.542
4	111.6 g/l	110.5 g/l	6	55°C	36ASF	1.28	87.0%	.548

3.5.6 Effect of Anode Current Collector Assembly on Cell Voltage (A-C)

Since the zinc electrowinning cell operates at a low current density (36ASF) it has not been felt that the conductivity of the cloth substrate (anode) was a significant limitation in attaining a low cell voltage. However, to establish the effect, if any, a 4 square inch (active area) cloth anode was assembled incorporating a current collector and data obtained in typical hardware with normal synthetic electrolyte at 36ASF and at a cell temperature of 55°C.

Data obtained with a current collector assembly are tabulated vs. a non-current collector electrode in Table 4. It is observed that the cell anode to cathode voltage is nearly identical for the two electrodes in question. Therefore, for a 4 square inch (active area) anode, a current collector is without significant benefit.

3.5.7 Effect of Impurities on Current Efficiency

3.5.7.1 Introduction

It is stated on page 423 of "Electrolysis of Zinc Sulfate Solution", Handbook of Non-Ferrous Metallurgy, Vol. 2, Chapter XIV that "Cathodic impurities have the greatest effect upon the efficiency of zinc deposition, and their control is one of the major problems in electrowinning". If any impurity which lowers the hydrogen overvoltage on zinc to the point where hydrogen can be evolved, comes into contact with a zinc surface during electrolysis, hydrogen will be evolved on the surface of the impurity and zinc will be dissolved.

TABLE 4
Effect of Current Collector Assembly
on Performance of
H₂ Depolarized Zinc Electrowinning Anode

Electrolyte Composition: 120 g/l zinc and 98 g/l H₂SO₄

Cell Temperature: 55°C

H₂ face flow: 3 times stoichiometric

CELL VOLTAGE

<u>ASF</u>	<u>No Current Collector</u>	<u>6cc Current Collector</u>
9	.94	.94
18	1.08	1.07
27	1.20	1.19
36	1.32	1.32
45	1.45	1.44
54	1.57	1.56
63	1.69	1.68
72	1.83	1.81

Those metals whose hydrogen overvoltage is below that of zinc but whose decomposition voltage is above that of sulfuric acid, including iron, nickel and cobalt, are injurious to electrolysis but do not ordinarily contaminate the deposited zinc. They are soluble and consume power by being alternately deposited on the zinc surface and redissolved in the acid electrolyte. They are particularly detrimental to electrolysis when present with certain other impurities.

Metals such as copper, arsenic, germanium and antimony are deposited with zinc and form points of low hydrogen overvoltage where hydrogen is evolved at the expense of zinc. Another metal which falls into this class is platinum. Platinum is particularly deleterious to zinc plating because hydrogen overvoltage is so low on this metal that if present in sufficient concentration, no zinc is plated at all.

In order to establish the utility of the hydrogen depolarized anode, tests were run with known impurity levels in the electrolyte. These data are reported in the following sections.

3.5.7.2 60ppm Fe⁺⁺ Impurity

Current efficiency data obtained for a hydrogen depolarized and a Pb (Ca) anode in the presence of 60 ppm of Fe⁺⁺ ions are tabulated in Table 5. While each cell shows effects from this level of iron impurity, the hydrogen anode cell is much more tolerant than the currently utilized industrial

TABLE 5

Effect of Iron Impurity
on
Current Efficiency and Power Consumption
H₂ Depolarized vs. Industrial Pb(Ca) Anode

<u>H₂ Depolarized Anode</u>					
Test	ppm Fe ⁺⁺ Impurity	g/l H ₂ SO ₄	Cell Voltage	% Current Efficiency	Power Consumption KwH/lb Zinc
1	-----	98	1.23	92.3	.500
2	60 ppm	101	1.23	87.6	.523
3	60 ppm	105	1.22	85.3	.530
4	60 ppm	108	1.23	83.7	.550
5	60 ppm	111	1.21	81.5	.550

<u>Pb(Ca) Anode</u>					
Test	ppm Fe ⁺⁺ Impurity	g/l H ₂ SO ₄	Cell Voltage	% Current Efficiency	Power Consumption KwH/lb Zinc
1	-----	98	3.11	90.0	1.30
2	60 ppm	101	3.10	86.8	1.33
3	60 ppm	105	3.10	77.5	1.49
4	60 ppm	108	3.10	60.3	1.91
5	60 ppm	111	3.10	54.6	2.10

cell as the acid concentration is increased above 1 molar H_2SO_4 .¹

3.5.7.3 10ppm Co^{++} Impurity

Current efficiency data obtained for a hydrogen depolarized and a lead (calcium) anode in the presence of 10ppm of Co^{++} ions are tabulated in Table 6. The impurity effect was essentially equal for both anodes at 55°C. However, as the temperature of the electrode was lowered, the current efficiency of the Pb anode cell improved at a somewhat faster rate than the hydrogen depolarized cell.

3.5.7.4 1ppm Cu^{++} Impurity

The presence of 1 ppm Cu^{++} impurity in the electrolyte had little effect on ampere efficiency for either a Pb (Ca) or a hydrogen depolarized anode. Data are presented in Table 7.

3.5.7.5 Ge^{++++} Impurity

Germanium is by far the most troublesome impurity tested to date. This ion lowers the hydrogen overvoltage on zinc to such an extent that the presence of 1 ppm in the electrolyte (55°C) is sufficient to prevent the deposition of a continuous zinc plate. The cathode product is essentially H_2 gas. This effect is independent of the anode employed.

-
1. The hydrogen depolarized anode eliminates the anodic oxidation of Fe^{++} to Fe^{+++} thus, ampere efficiency is not lowered by iron being alternately reduced at the cathode and re-oxidized at the anode.

TABLE 6
EFFECT OF COBALT IMPURITY
ON
CURRENT EFFICIENCY AND POWER CONSUMPTION
H₂ Depolarized vs. Industrial Pb(Ca) Anode

H₂ Depolarized Anode

Test	ppm Cobalt Impurity	Cell Temperature	Cell Voltage	% Current Efficiency	Power Consumption KwH/lb Zinc
1	10 ppm	35°C	1.38	91.5	0.562
2	10 ppm	45°C	1.30	89.5	0.545
3	10 ppm	50°C	1.26	86.8	0.542
4	10 ppm	55°C	1.27	85.7	0.552

Pb(Ca) Anode

Test	ppm Cobalt Impurity	Cell Temperature	Cell Voltage	% Current Efficiency	Power Consumption KwH/lb Zinc
1	10 ppm	35°C	3.22	94.1%	1.27
2	10 ppm	45°C	3.12	92.5%	1.25
3	10 ppm	50°C	3.07	92.5%	1.24
4	10 ppm	55°C	3.03	84.5%	1.33

TABLE 7

Effect of Copper Impurity
on
Current Efficiency and Power Consumption
H₂ Depolarized vs. Industrial Pb(Ca) Anode

<u>H₂ Depolarized Anode</u>					
Test	ppm Cu ⁺⁺ Impurity	g/l H ₂ SO ₄	Cell Voltage	% Current Efficiency	Power Consumption KwH/lb Zinc
1	1 ppm	98.0	1.24	93.1	.50
2	1 ppm	101.4	1.25	92.5	.51
3	1 ppm	104.7	1.25	90.0	.52

<u>Pb(Ca) Anode</u>					
Test	ppm Cu ⁺⁺ Impurity	g/l H ₂ SO ₄	Cell Voltage	% Current Efficiency	Power Consumption KwH/lb Zinc
1	1 ppm	98.0	3.11	93.1	1.24
2	1 ppm	101.4	3.10	91.1	1.26
3	1 ppm	104.7	3.11	92.2	1.25

In order to determine a tolerable Ge^{++++} concentration range (current efficiency > 85%), the impurity level was decreased by orders of magnitude until substantially typical zinc plating was achieved. These data, which are presented in Table 8 show that it is necessary to avoid germanium concentration above 0.05 ppm in the zinc electrowinning solution in order to maintain good ampere efficiency.

Studies indicate that the effect of similar levels of Ge^{++++} in a Pb anode cell are equal to or worse than that described above for the hydrogen depolarized anode.

3.5.7.6 Platinum Impurity

It has recently been reported that the presence of traces of dissolved platinum in a sulfuric acid electrolyte causes the rapid dissolution of zinc metal.¹ Since the hydrogen depolarized anode currently being investigated by Prototech Company contains a highly dispersed (surface area 120-170 m²/gram) platinum catalyst it is extremely important to establish that such an electrode does not introduce a highly injurious impurity into the system.

Employing the standard synthetic electrolyte (120 g/l zinc and 98 g/l H_2SO_4) a series of tests were run to establish a tolerable level of platinum impurity. These data, Table 9, show the following:

-
1. Dr. Anthony F. Sammells, Institute of Gas Technology and Dr. John Appleby, Electric Power Research Institute, during presentations and discussions at the Metal-Air Battery Project Meeting held in Washington, D.C. on April 10-11, 1979 and sponsored by DOE.

TABLE 8
EFFECT OF GERMANIUM IMPURITY
ON
CURRENT EFFICIENCY AND POWER CONSUMPTION
OF
HYDROGEN DEPOLARIZED ANODE

55°C Cell Temperature

33% H₂ Efficiency

Test	g/l H ₂ SO ₄	g/l Zinc	ppm Ge ⁺⁺⁺⁺	Cell Voltage	% Current Efficiency	Power Consumption KwH/lb Zinc
1	98	120	0.000	1.24	93.0%	0.500
2	98	120	0.001	1.24	91.0%	0.510
3	98	120	0.010	1.25	87.0%	0.535
4	98	120	0.050	1.24	87.1%	0.530
5	98	120	0.100	1.25	79.4%	0.587
6	98	120	1.000	1.26	00.0%	0.000

TABLE 9

Zinc Electrowinning

Effect of Platinum Impurity on Current Efficiency and Power Consumption

H₂ Depolarized Anode

Test	ppm Platinum Impurity	Cell Temperature	Current Density	Cell Voltage	% Current Efficiency	Power Consumption KWH/lb zinc
1*	5.0 ppm	55°C	36 ASF	<<1.00	-----	-----
2	1.0 ppm	55°C	36 ASF	1.25	83.1%	0.61
3	1.0 ppm	55°C	36 ASF	1.27	83.0%	0.57
4.	0.1 ppm	55°C	36 ASF	1.26	82.7%	0.57
5.	0.1 ppm	55°C	36 ASF	1.25	86.0%	0.54
6	0.1 ppm	55°C	36 ASF	1.25	86.1%	0.54
7	0.1 ppm	55°C	45 ASF	1.38	85.2%	0.60
8	0.1 ppm	55°C	54 ASF	1.51	86.4%	0.64

*Sufficient Platinum solution at start up to render the cathode comparable to a Pt Electrode.

- a) For the system under study, a dissolved platinum impurity level of 0.1 ppm appears to be a safe maximum. At this level, the ampere efficiency and power consumption (KWH/lb zinc average 85% and 0.55 respectively.
- b) Ampere efficiency at 0.1 ppm platinum impurity, is independent of current density over the range of 36 to 54 ASF.
- c) Excessively high levels of dissolved platinum (5 ppm) result in a hydrogen concentration cell (H_2 depolarized anode and H_2 evolved at platinized cathode) as the cell voltage at 36 ASF is well below the decomposition potential of zinc.

About the only conceivable way that platinum could be introduced into the electrolyte (0.1 ppm) of a zinc electro-winning cell from a hydrogen depolarized electrode is if erosion results in fragmentation of the catalytic layer. An attempt was made to create such a situation by abrading the electrolyte surface of electrodes so that small catalytic particles were free to drop off the anode when it was placed in the electrolyte. Several tests were run with abraded anodes and results, as described in Table 10 indicate that such treatment had no effect on zinc plating, indicating that the platinum particles were insoluble in the electrolyte.

TABLE 10

Current Efficiency and Power Consumption Data

New H₂ Depolarized Anodes

Surface Abraded

Test	Cell Temperature	Current Density	Cell Voltage	% Current Efficiency	Power Consumption KWH/lb zinc
1	55°C	36 ASF	1.25	91.0%	0.51
2	55°C	36 ASF	1.24	92.5%	0.50
3	55°C	36 ASF	1.32	94.3%	0.52

3.5.8 Long Term Zinc Electrowinning Tests

Utilizing the data obtained in section 3.5.3, two long term tests (20-24 hours) were run. The first test was run with a starting acid concentration of 49 g/l and the second with 98 g/l H_2SO_4 while the zinc concentration in both tests was 120 g/l.

Data, Table 11, obtained at 55°C was excellent for both initial acid concentrations. With a starting concentration of 49 g/l H_2SO_4 , the average cell voltage for a 25 hour run was 1.40 volts and the % current efficiency was 99%. When the initial acid concentration was raised to 98 g/l the average cell voltage was 1.26 volts and the % current efficiency was 91%. The power consumption was 0.52 KWH/lb zinc for both acid concentrations.

3.5.9 Calculated Values-Power Consumption vs. Cell Voltage and Current Efficiency

During the course of this investigation sufficient data has been obtained to estimate the cell voltage that will result from changes in cell temperature and acid concentration. Data presented in previous sections of this report indicate that a cell voltage of between 1.20 to 1.40 volts are a realistic operating level. Using this voltage range and assumed current efficiencies of between 75 and 100%, it is possible to calculate power consumptions (KWH/lb zinc) for a series of voltages and ampere efficiencies. These calculated data are presented in Figure 11. Thus, for any combination of conditions

TABLE II

Long Term Zinc Electrowinning Runs22 - 24 Hour Tests

Test	Electrolyte Composition				Test Hours	Cell Temp °C	Current Density	Present Current Efficiency	Power Consumption KWH/lb Zinc
	<u>Initial</u>		<u>Final</u>						
	<u>Zinc</u>	<u>H₂SO₄</u>	<u>Zinc</u>	<u>H₂SO₄</u>					
1	120g/l	49g/l	105g/l	72g/l	25	55°C	36ASF	99%	0.52 for average voltage cell of 1.40
2	120g/l	98g/l	108g/l	116g/l	21.5	55°C	36ASF	91%	0.52 for average voltage cell of 1.26

Figure 11

Calculated Power Consumption (KWH/1b Zinc) vs Cell Voltage and % Current Efficiency

Calculated Values

that yield cell voltages between 1.20 and 1.40 volts there is a minimum current efficiency that is necessary to maintain the power consumption below 0.60 KWH/lb zinc. In practice, it has been found that those conditions which lower cell voltage, also lower ampere efficiency and vice versa. With this in mind it is obvious that power consumption should be able to be maintained at $0.55 \pm 10\%$ KWH/lb of zinc because it will take a dramatic change in cell voltage or ampere efficiency to alter this value.

3.6 ZINC ELECTROWINNING - ANACONDA PLANT LIQUOR

3.6.1 Background

A 55 gallon drum of zinc electrowinning plant liquor was received by Prototech Company from Anaconda Company. The complete chemical analysis was provided (refer Table 12) and tests run to determine if data obtained for a hydrogen depolarized anode with a synthetic electrolyte could be duplicated with a plant feed liquor.

3.6.2 Effect of Cell Temperature on Cell Voltage (Plant Liquor)

The plant liquor contains 155 g/l zinc at a pH of 5.0. It also contains a small quantity of precipitate. When the acid concentration was adjusted to 98 g/l H_2SO_4 no further precipitation occurred.

TABLE 12Analysis of Zinc Electrowinning Plant LiquorGeneral Data

Solution pH = 5.0

Sp. G = 1.392Chemical Analysis

<u>Element</u>	<u>Concentration</u>	
Zinc	155	g/l
Calcium	0.69	g/l (as CaO)
Magnesium	10.8	g/l (as MgO)
Sodium	1.58	g/l
Manganese	3.52	g/l
Potassium	0.11	g/l
Aluminum	.005	g/l
Barium	.005	g/l
Chromium	.005	g/l
Cobalt	.02	g/l
Copper	.02	g/l
Iron	.004	g/l
Nickel	.004	g/l
Silicon	1.20	g/l

Not detected by Spectrographic Analysis

Silver	Beryllium	Gallium	Lead	Tungsten
Antimony	Bismuth	Germanium	Molybdenum	Tin
Arsenic	Cadmium	Indium	Titanium	Vanadium

Preliminary tests with this electrolyte (98 g/l H_2SO_4) provided a cell (anode to cathode) voltage that was higher than that observed with synthetic electrolytes. This higher voltage was confirmed over a wide range of cell temperatures with both the lead (Ca) and the hydrogen depolarized anodes at 36 ASF. Compare Table 13 to Figure 4, Section 3.5.3. The increased voltage is undoubtedly due to a difference in conductivity between the electrolytes.

In addition, these tests provided the following information:

- a) Above 40°C , the precipitate dissolved and did not reappear until the tank was cooled below this temperature.
- b) The liquor contains 3.52 g/l of manganese and has a distinctly pink color. With a hydrogen depolarized anode, the electrolyte color (valence state of manganese plus two) remained unchanged. With the oxygen evolving lead (Ca) anode some manganese was plated as MnO_2 on the anode and indeed permanganate was detected in the electrolyte.^{1,2}

-
1. "Electrolysis of Zinc Sulfate Solution" Handbook of Non-Ferrous Metallurgy, Vol. 2, Chapter XIV, page 419.
 2. Treatise on Inorganic Chemistry by H. Remy, Elsevier Publishing Company, 1956, Vol. 3, page 217.

TABLE 13ZINC ELECTROWINNING - ANACONDA PLANT LIQUOREFFECT OF ELECTROLYTE TEMPERATURE ON CELL VOLTAGEPROTOTECH CO. H₂ DEPOLARIZED ANODE VS INDUSTRIAL LEAD (Ca) ANODE

Electrolyte zinc concentration = 155 g/l

Electrolyte H₂SO₄ concentration = 98 g/l

Current Density = 36 ASF

Cell Voltage Anode to Cathode

<u>Electrolyte Temperature</u>	<u>Pb (Ca) Anode</u>	<u>H₂ Depolarized</u>
30°C	3.54	1.70
35°C	3.47	1.63
40°C	3.41	1.57
45°C	3.35	1.51
50°C	3.31	1.47
55°C	3.27	1.44
60°C	3.22	1.41
65°C	3.18	1.37
70°C	3.15	1.34

3.6.3 Zinc Electrowinning - Plant Liquor Power Consumption and Current Efficiency

3.6.3.1 Electrolyte Temperature Variation 155 g/l Zinc - 98 g/l H₂SO₄

It was found that the current efficiency of zinc plating from the Anaconda plant liquor (155 g/l zinc) which was spiked with 98 g/l H₂SO₄, decreased as the temperature of the electrolyte was increased. Indeed, at 55°C, no continuous plates were obtained for four hour tests. This effect was independent of the anode employed. These data are summarized in Table 14.

At 55°C, a situation existed where plating commenced at a high efficiency (very low H₂ evolution at cathode) for several hours but a reaction threshold was reached shortly after this time period which resulted in the predominance of parasitic reactions resulting in the rapid dissolution of the plated zinc.

3.6.3.2 Adjusted Running Conditions for High Current Efficiency at 55°C with Anaconda Plant Feed

The efficiency of zinc plating is dependent on the following factors and combinations thereof:

1. Purity of Electrolyte
2. Cell Temperature
3. Hydrogen ion concentration
4. Duration of Plating
5. Current Density

TABLE 14

ZINC ELECTROWINNING - ANACONDA COMPANY PLANT LIQUORPOWER CONSUMPTION OF PROTOTECH COMPANY H₂ DEPOLARIZED ANODE VS. INDUSTRIAL LEAD (Ca) ANODEELECTROLYTE TEMPERATURE VARIATION

Electrolyte Zinc Concentration = 155 g/l
 Electrolyte H₂SO₄ Concentration = 98 g/l

Electrolyte Additives = None

Test	Anode	Test Hours	Cell Temperature	Cell Voltage	Current Density	% Current Efficiency	Power Consumption KWH/lb Zinc
1	Prototech	4	35°C	1.59	36ASF	94.1%	0.630
2	Industrial	4	35°C	3.53	36ASF	94.5%	1.39
3	Prototech	4	45°C	1.50	36ASF	92.3%	0.605
4	Industrial	4	45°C	3.40	36ASF	91.9%	1.38
5	Prototech	4	55°C	1.46	36ASF	≈ 0.00%	----
6	Industrial	4	55°C	3.30	36ASF	≈ 0.00%	----

Since it has already been shown that synthetic electrolytes containing 98 g/l H_2SO_4 could be run at a current efficiency in excess of 90% for four hour plating tests at 36 ASF and 55°C , the problem obviously centered around the impurity content of the plant feed.

Tests have been run under conditions which diminish the harmful effects of electrolyte impurities. These new conditions are typical industrial process changes that allow the presence of some low level impurities in plant feeds.¹ Data obtained with known electrolyte additives demonstrate the operability of the H_2 -anode process at 55°C , in contrast to operation without additives (Table 14).

It has been and continues to be the aim of the zinc electrowinning program to develop a process which yields the highest energy savings possible. Therefore, those cell parameters which provided the lowest cell voltage, consistent with high (greater than 90%) current efficiency, will be the cell conditions of choice. Based on the data provided in Table 15, test 5 and 6, gelatin will routinely be added to the Anaconda plant feed for the 9-fold (6" x 6" active area) scale-up tests described in Section 3.7.

1. Electrochemistry by Giulio Milazzo, Elsevier Publishing Company, 1963, Chapter 9, Section 10.

TABLE 15

ADJUSTED RUNNING CONDITIONS FOR HIGH CURRENT EFFICIENCYANACONDA PLANT FEED (155 g/l ZINC)Prototech Company H₂ Depolarized Anode

Test	Test Hours	Cell Temperature	Electrolyte Acid Concentration	Electrolyte Additive	Current Density	Cell Volatge	% Current Efficiency	Power Consumption KWH/lb Zinc	54
1	6	55°C	49 g/l	None	36ASF	1.66 V	95.3%	0.652	
2	4	55°C	98 g/l	None	54ASF	1.69 V	88.9%	0.708	
3	4	55°C	98 g/l	B Napthol 0.05 g/l	36ASF	1.42 V	93.3%	0.567	
4	4	55°C	98 g/l	Gelatin 0.1 g/l	36ASF	1.47 V	94.4%	0.580	
<u>Lead (Ca) Industrial Anode</u>									
5	4	55°C	98 g/l	0.05 g/l B Napthol	36ASF	3.30 V	92.3	1.32	
6	4	55°C	98 g/l	Gelatin 0.1 g/l	36ASF	3.29 V	93.0	1.31	

3.7 SCALE-UP - 6" x 6" ZINC ELECTROWINNING CELL

3.7.1 Introduction

In view of the spectacular "purchased electric energy" savings demonstrated in the 2" x 2" cell, the additional task of designing, building and operating a 6" x 6" cell was authorized for the last month of the contract. This scaled-up zinc electrowinning cell was to be run on Anaconda Company plant feed and provide the following information.

- A. Substantiate the energy saving obtained with the 2" x 2" hardware.
- B. Generate sufficient zinc (0.1 to 0.5 lbs) to obtain chemical as well as physical analysis.
- C. Provide insight into any scale-up problem prior to engaging in pre-pilot plant research.

3.7.2 Design of Equipment

3.7.2.1 Electrode Design

The RA19 type carbon cloth-based hydrogen diffusion anodes employed during the initial stages of DOE Contract No. ET-78-C-02-4881 proved to be excellent electrodes and no changes were made in electrode fabrication throughout the program. Some anodes were run for more than fifty (50) cycles of testing and accumulated more than 200 hours of running time. No anode failures were noted and, indeed, no anode showed any deterioration with time. This occurred irrespective of whether a synthetic or plant feed was employed as the electrolyte. Thus,

the electrodes selected for the 6" x 6" (active area) zinc electrowinning was proprietary Prototech Company RA19 type anode having a platinum loading of $0.33 \pm 10\% \text{ mg/cm}^2$.

3.7.2 Hardware Design

The 6" x 6" hardware described in Figures 12 and 13 is quite similar to the previously employed 2" x 2" cell except that the cathode can be withdrawn from the electrolyte for zinc removal without removing the anode; and a simple hydrogen gas distributor was incorporated in the anode gas plenum. With respect to tank design and electrolyte construction, instead of using a standard battery jar, a tank-reservoir system was utilized which held approximately 20 liters of solution. This volume was sufficiently large so that, irrespective of running times of 4 to 24 hours, the electrolyte did not drastically change in zinc and sulfuric acid concentration. Electrolyte circulation was afforded by continuously pumping the liquor between the electrodes, from side to side, at a flow rate of 1 to 2 liters per minute.

FIGURE 12, SIDE VIEW OF 6"x6" ZINC ELECTROWINNING CELL

FIGURE 13, CROSS SECTION OF ZINC ELECTROWINNING CELL

3.7.3 Technical Data - 6" x 6" (Active Area) Zinc Electro-winning Cell: Anaconda Plant Feed Liquor

3.7.3.1 Preliminary Tests

Utilizing the hydrogen depolarized anode and hardware previously described (Section 3.72) and Anaconda Company plant feed spiked with 98 g/l H_2SO_4 and 0.1 g/l gelatin, successive four hour tests were run. Data for power consumption (KWH/lb zinc), Table 16, was reproducible and was within 10% of that obtained in the 2" x 2" cell for the same feed and under the same conditions. (See Tables 16 and 15).

Comparison of current density-voltage curves for the 2" x 2" and 6" x 6" cells are shown in Figure 14. At 36 ASF, (9 amps) the normal operating amperage of the zinc electrowinning cell, the 6" x 6" anode has reached a point where a current collector needs to be incorporated into or attached to the anode.

3.7.3.1.1 Chemical Analysis of Zinc Plate

A 43.3 gram piece of zinc plated from Anaconda Company plant feed (refer Section 3.6 for the analysis of the feed) runs submitted for trace chemical analysis. The analysis, Table 17, demonstrate the extremely pure form of zinc metal that is produced by the hydrogen depolarized anode process.

TABLE 16

Zinc Electrowinning - Anaconda Plant Liquor6" x 6" (Active Area) AnodePreliminary Tests

Test	g/l Zinc	Feed Composition g/l H ₂ SO ₄	g/l Gelatin	Test Hours	Cell Temp °C	Current Density	Cell Voltage	% Current Efficiency	Power Consumption KWH/lb Zinc
1	155	98.0	0.1	4	55°C	36 ASF	1.62	98.7	.611
2	155	98.0	0.1	4	55°C	36 ASF	1.66	98.8	.626

Figure 19

Zinc Electroplating
Discharge Curves
ANA GENCO PLANT LIGHT
25.0 cm² VS 232.3 cm² Electrodes

ZINC CONCENTRATION 155 g/l
H₂SO₄ CONCENTRATION 98 g/l
Gelatin CONCENTRATION 0.1 g/l
Cell Temperature 55°C

TABLE 17

Preparation and Analysis of Zinc Plate - Anaconda Company Plant Liquor

Prototech Company Hydrogen Depolarization Process

6" x 6" (Active Area) Electrowinning Cell

Part A - Zinc Electrowinning Data

<u>Date</u>	<u>Hrs. Run</u>	<u>Feed Composition</u>			<u>Cell Temp.</u>	<u>Current Density</u>	<u>Cell Voltage</u>	<u>Grams Zinc</u>	<u>Current Efficiency</u>	<u>Power Consumption Kwh/lb zinc</u>
		<u>g/l zinc</u>	<u>g/l H₂SO₄</u>	<u>g/l Gelatin</u>						
7/26/79	4	155	98	0.1	55°C	36ASF	1.62	43.3	98.7%	0.611

Part B - Zinc Plate Analysis*

<u>Element</u>	<u>% of Element in Plate (Spectrographic Analysis)</u>	<u>Element</u>	<u>% of Element in Plate (Spectrographic Analysis)</u>	<u>g</u>
Iron	<0.001	Arsenic	<0.001	
Cadmium	>0.01	Nickel	0.003	
Copper	0.005	Cobalt	0.001	
Lead	<0.001	Chromium	<0.001	
Antimony	Not detected	Bismuth	Not detected	
Tellurium	<0.001			

* Analysis through the courtesy of the Metallurgical Research Department, Anaconda Company.

3.7.3.2 Power Consumption as a Function of Increasing Acid and Decreasing Zinc Concentration

A series of 4 to 5 hour runs were made (same feed) in which the acid level of the electrolyte rose as the zinc was depleted. The data, Table 18, are similar to that obtained in the 2" x 2" hardware with synthetic electrolytes (Section 3.5.5, Table 3). Between increasing acid concentrations of 80 to 110 g/l H_2SO_4 and decreasing zinc concentrations of 150 to 130 g/l, a consistent power consumption of 0.64-0.65 KWH/lb zinc has been demonstrated.

3.7.3.3 Current Efficiency as Determined with an Electronic Coulometer

A Vari-Tech Company Model VT-1176-A Coulometer, with a range of 0.01-20 Amps was incorporated in the electrical circuitry of the 6" x 6" zinc electrowinning cell. Current efficiency data obtained using this electronic-digital readout instrument confirmed previous calculations within 1-2%.

Five to six hour tests, at 55°C, were initiated which provided a reproducible current efficiency of 95-96% and a power consumption of 0.63-0.64 KWH/lb zinc. (Table 19). Finally a 22.5 hour run was made in which 209 grams of zinc metal plated.

For the 22.5 hour test, run 5, Table 19, the feed was 155 g/l zinc, 78 g/l H_2SO_4 and 0.2 g/l gelatin at zero time. By calculation the final concentrations of the 20 liter tank and reservoir were 144.5 g/l zinc and 93.7 g/l H_2SO_4 . An approximate average voltage of 1.63 volts was determined. The zinc plate

TABLE 18
Zinc Electrowinning - Anaconda Plant Liquor
Pure Hydrogen Fuel - 6" x 6" (Active Area) Anode
Power Consumption and Current Efficiency as a Function of
Increasing Acid and Decreasing Zinc Concentration

Test	g/l Zinc	Feed Composition		Test Hours	Cell Temp °C	Current Density	Cell Voltage	% Current Efficiency	Power Consumption KWH/lb Zinc
		g/l H ₂ SO ₄	g/l Gelatin						
1	155	49	0.1	4	55°C	36 ASF	1.90	99%	.706
2	152	54	0.1	4	55°C	36 ASF	1.88	99%	.698
3*	150	86	0.1	4	55°C	36 ASF	1.68	96.2%	.650
4	146	90	0.1	4	55°C	36 ASF	1.71	95.7%	.665
5	144	94	0.1	4	55°C	36 ASF	1.63	93.4%	.658
6	141	98	0.1	4	55°C	36 ASF	1.62	94.6%	.638
7	138	102	0.1	4	55°C	36 ASF	1.65	94.0%	.652
8	135	106	0.1	5.5	55°C	36 ASF	1.58	90.3%	.652
9	132	111	0.1	4.5	55°C	36 ASF	1.57	92.2%	.634

* Spiked in H₂SO₄ to bring acid level in line with typical operating conditions.

TABLE 19

Zinc Electrowinning - Anaconda Plant Liquor
Pure Hydrogen Fuel - 6" x 6" (Active Area) Anode

% Current Efficiency as Determined with an Electronic Coulometer *

Test	Initial Feed Composition			Test Hours	Cell Temp °C	Current Density	Cell Voltage	Grams Zinc Plated	% Current Efficiency	Power Consumption KWH/lb Zinc
	g/l Zinc	g/l H ₂ SO ₄	g/l Gelatin							
1	150	105	0.1	5.0	55°C	36 ASF	1.65	52.3	96.6%	0.630
2	147	109	0.1	5.5	55°C	36 ASF	1.64	53.4	95.4%	0.640
3	150	97	0.1	6.0	55°C	36 ASF	1.65	62.1	96.3%	0.639
4	147	102	0.1	6.25	55°C	36 ASF	1.63	64.0	95.7%	0.634
5	155	78	0.2	22.5	55°C	36 ASF	1.63	209.0	85.3%	0.711

* Vari-tech Company Model Vt-1176-A Coulometer

was dull gray with many dendrites, especially along the edges of the plate. Some dendrites were fragile enough to break off during the last few hours of the run and fall to the bottom of the tank, which fact probably accounts for the 85.3% current efficiency.

3.7.3.4 Effect of Type of Electrolyte Flow on Physical appearance of the plated zinc

Data presented in Table 20 serves to illustrate the effect of electrolyte flow on the physical appearance of the plated zinc. It was possible to produce plates that were dull gray and rough to plates that were bright, shiny light gray and almost perfectly smooth. While these tests were not extensive enough to draw any firm conclusions, it would appear that the side-to-side flow was slightly more efficient than the bottom-to-top runs, showing that flow design is significant.

3.7.3.5 6" x 6" Zinc Electrowinning Cell - Summary

- A. A nine fold scale-up in hardware has been successful.
- B. Hydrogen-depolarized zinc electrowinning in a 6" x 6" (active area) cell has demonstrated a short term saving, employing plant feed, of 0.6 KWH/lb zinc which amounts to about one half of the power consumption of today's conventional electrowinning with lead anodes.
- C. Zinc plates obtained from plant feeds in about 6-Hour runs show excellent physical characteristic and high purity.

TABLE 20

Zinc Electrowinning - Anaconda Plant Liquor6" x 6" (Active Area) AnodeEffect of Type of Electrolyte Flow on Physical Appearance of Zinc Plate

Cell Temperature = 55°C

Current Density = 36 ASF

Test	Initial Feed Composition			Test	Cell	Grams	Type of	Physical	% Current *	Power
	g/l Zinc	g/l H ₂ SO ₄	g/l Gelatin	Hours	Voltage	Zinc Plated	Electrolyte Flow	Appearance of Zinc	Efficiency	Consumption KWH/lb Zinc
1	155	98	0.1	6.25	1.63	64.0	Side to side Fast	Compact and gray, very rough surface.	95.7%	.634
2	145	92	0.1	5.33	1.62	54.3	Side to side Medium	Compact-Shiny gray smooth surface but many streaks and pockmarks.	94.3%	.639
3	142	98	0.1	6.5	1.62	64.7	Bottom to top Medium	Compact-bright shiny gray, some outline of flow pattern.	93.5%	.644
4	138	103	0.1	5.5	1.63	54.5	Bottom to top Slow	Compact-bright shiny gray, only few pockmarks.	92.2%	.658

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* As determined with Vari-Tech Company, Model Vt-1176-A Coulometer.

SECTION 4

TECHNICAL DISCUSSION

Zinc Electrowinning with Impure Fuels and Selective Combustion of Carbon Monoxide in Impure Hydrogen Streams

4.1 BACKGROUND INFORMATION

4.1.1 Preparation of Impure Fuels

Nearly all commercial hydrogen is produced utilizing a catalytic reaction of steam and a hydrocarbon. Generally, a nickel catalyst is used, and since the reaction is endothermic, a high temperature favors the reaction (750° - 850° C). The desired reaction is (1):

Unfortunately, a second reaction (2) also occurs. This reaction produces $CO + H_2$ rather than the preferred $CO_2 + H_2$.

The formation of CO by (2) is undesirable. The H_2 yield is reduced, and the toxic CO is an unwanted product. A normal product from the steam reformation of a hydrocarbon contains almost as much CO as CO_2 .

In order to mitigate the problems introduced by (2), a second catalytic reaction (3), is utilized following reformation, the water-shift process.

Reaction (3) is exothermic, and is favored by the lowest temperature consistent with favorable reaction kinetics, $350^{\circ} - 400^{\circ}\text{C}$. Even so, the final product contains 0.4-1.0% CO.

For the production of pure H_2 , CO_2 and CO must be removed. Present commercial practice is to pass the impure gas mixture through a molecular sieve column. The CO and CO_2 impurities are strongly adsorbed, whereas H_2 passes readily through the bed. The product is quite pure, but considerable energy is required to regenerate the sieve. Most of this energy is spent desorbing CO_2 , by far. It has been estimated that about 20% of the available energy present in the hydrocarbon is needed for the purification step.

For a platinum catalyzed H_2 anode, CO is a poison, whereas CO_2 is merely an innocuous diluent. For a H_2 anode operating at $160^{\circ}\text{C} - 190^{\circ}\text{C}$, some CO is tolerable. However, for aqueous electrolytes, wherein the maximum feasible temperature is below 100°C , CO tolerance is negligible. This being the case, the most energy conservative system involves the removal only of CO, leaving the CO_2 intact. To effect such a purification is the object of research now in progress.

The role of CO as an H_2 -Pt anode poison is quite straightforward. Platinum adsorbs H_2 quite weakly, and this in part accounts for the fact that the H_2 -Pt anode is nearly perfectly reversible. On the other hand, CO is strongly adsorbed, even in the presence of an enormous excess of H_2 . Hence, as the anode reaction proceeds, the platinum bearing anode sequesters

CO, and as CO saturation is approached, anode polarization increases until it is inoperative, or nearly so.

The acceptable level of CO that will permit prolonged, effective anode performance is a function of cell temperature, current density, H₂ utilization, platinum loading, and platinum dispersion. High temperature, high H₂ utilization, high platinum loading and dispersion, and a low current density all prolong anode performance at a given CO concentration in the fuel. At cell temperatures less than 100°C, it is safe to say that CO adsorption is very nearly quantitative, and that at nearly any CO concentration, from time to time, the anode must be purged of adsorbed CO. There is, of course, always an equilibrium between adsorbed H₂ and adsorbed CO, so that total CO adsorption need not take place, but since the equilibrium favors CO adsorption so strongly at moderate temperatures, one would expect CO adsorption to be almost totally dominant. One would like to hope that reaction (4) would mitigate the problem. Unfortunately, this reaction

will not proceed at a helpful rate until the anode is already polarized to an unacceptable degree.

In short, it is not possible to predict what CO concentration is tolerable, other than it must be very low. This problem can be mitigated to a degree if the anode is purified at appropriate intervals during the process. Since the

restoration of the anode should conform to process cycles, (i.e. periodic cathode removals) the longer the cycle, the less the acceptable concentration of CO in hydrogen.

4.2 EXPERIMENTAL DATA

4.2.1 Operation of Zinc Electrowinning Cell on Impure Hydrogen

To evaluate the role of CO, relative to the supposition made above, a zinc plating cell, operating at 55°C, was subjected to fuel feeds containing various levels of CO. The electrolyte was 120 g/l zinc - 98 g/l H₂SO₄, and cell temperature was maintained at 55°C. Fuel was fed to the anode, active area 25.8 cm². Platinum loading on the anode was 0.3 mg Pt/cm². Three separate experiments were conducted with H₂ containing 25 ppm, 50 ppm, and 100 ppm CO contamination. The current flow was 1 Amp (36 ASF) and fuel flow, 50 ml/min. For 1 Amp current flow, this fuel input is about 6 times the stoichiometric requirement. The reason for the high flow of fuel was to hasten the onset of CO poisoning, if it were to occur. During each test, periodic measurements of the CO content of the effluent fuel were made.

The results of these tests, in terms of increased cell voltage required to maintain 1 Amp are plotted in Figure 15 as a function of operating time. As can be seen from the data, all levels studied were detrimental to cell performance, and the times required to produce a given level of performance

Figure 15
Zinc Cell Performance Loss
As a function of
Carbon Monoxide Concentration in H_2 Fuel

Cell Temperature = 55°C
 Electrolyte conc. = 120 g/l Zn
 = 98 g/l H_2SO_4
 Fuel Efficiency = 15%

○ = 162.7 ppm CO
 × = 54.3 ppm CO
 □ = 25.6 ppm CO

Cell Temperature = 55°C
 Current Density = 36 ASF
 Electrolyte conc. = 120 g/l Zn
 98 g/l H_2SO_4

loss are roughly in the ratio of 1:1.5:3.0.

For all three runs, CO concentration in the effluent fuel were measured. Initially, at all three levels of CO contaminant, the effluent CO concentration was 2-3 ppm. This CO concentration slowly increased with time, but even for times wherein the cell was largely inoperative, CO out was only about 30-40% of CO in. Hence, with a badly polarized electrode, there is evidence that some CO was being consumed as fuel. Unfortunately, at these levels of cell polarizations, about 0.5 volt, a current of 1 Amp could not be maintained, and the cell pulsed, showing a buildup of current and then a decrease in current of 0.5 Amp around the desired level of 1 Amp. Performance losses, and cell instability were unacceptable at all three levels. Lower levels of CO and reduced flow rates of input fuel to attain 60-70% fuel utilization will be studied. In addition, selective air oxidation of CO in the presence of H_2 will be studied to determine how much the concentration of CO can be reduced from an input of 7000 ppm in a 80% H_2 -20% CO_2 gas mixture.

4.3 SELECTIVE COMBUSTION OF CARBON MONOXIDE IN AN IMPURE HYDROGEN STREAM

4.3.1 Background Information

A platinum anode cannot tolerate even traces of carbon monoxide (CO) at zinc electrowinning temperatures, i.e. 35-55°C. A steam reformed hydrocarbon will normally contain 0.5-1.0% CO, 79-80% H₂, and the balance CO₂. The CO₂, other than being a H₂ diluent, is harmless to the anode. Therefore, in order to prepare a fuel acceptable to the H₂ anode, only the CO need be removed. However, in conventional H₂ purification processes, such as adsorption of CO on a molecular sieve, the CO₂ must be removed before the CO. This, of course, is an energy penalty for a fuel anode that is tolerant of CO₂.

Prototech has developed a proprietary platinum catalyst that permits the selective oxidation of CO in H₂ streams. The characteristic of a platinum catalyst that possesses this selectivity are summarized below:

(1) The platinum should have the highest possible dispersion. This is best attained by depositing the platinum on alumina. The reason a high surface area platinum deposit is required is that, as the surface area decreases, the catalyst activity declines. This, in turn, demands a higher oxidation temperature, which in turn, lowers the selectivity of the catalyst. Above about 200°C, regardless of the activity of the catalyst, selectivity of the catalyst for CO oxidation largely disappears.

(2) There is a thermal window for the reaction that dictates that, even for the most active catalyst, a temperature rise across the catalyst bed of more than 60°C will seriously impair the catalyst selectivity. This is our acknowledgement of the fact that the easier it is to combust CO, the easier it is to combust H_2 . Obviously, the higher the CO content of the fuel, the greater will be the ΔT across the bed, if the reaction is conducted under adiabatic conditions. The advantage of a highly active catalyst is that combustion requires little or no input heat, and that operation at isothermal conditions can be obtained by using water as a coolant.

(3) Between the limits of 0.1% Pt-1.0% Pt deposited on the alumina substrate, the temperature for the combustion of CO declines as the platinum content of the catalyst increases. However, as has been already pointed out, the thermal window still exists, regardless of how low is the temperature of CO combustion, and this ΔT must be maintained at less than 60°C . Ideally, combustion should commence at ambient temperatures, and the bed condition be largely isothermal through use of a coolant. This, of course, means that the thermal value of the CO content and any H_2 burnup is lost. Hence, the lower the CO content of the fuel to be purified, the more a fuel conservative system is obtained. Thus, the CO reduction level of the $\text{CO-H}_2\text{O}$ shift reaction is an important economic factor.

(4) Aluminum is the favored construction material for the reactor because stainless steel, steel, and other transition metal alloys catalyze the burnup of hydrogen.

(5) Other noble metals, present as impurities in the platinum, are detrimental. In this respect, palladium is particularly bad.

(6) Hydrogen sulfide and other sulfur compounds are totally unacceptable, even at the 1 ppm level of concentration.

4.3.2 Experimental Parameters and Hardware

The selective oxidation of CO in the presence of H_2 has been studied under varying conditions. The fuel input consisted of 80% H_2 , 0.7% CO, and 19.3% CO_2 . The variables considered were:

- a) Platinum content of the catalyst
- b) Air flow relative to the stoichiometric amount required to oxidize the CO
- c) Space velocity and pellets vs. monolith structures as well as alumina coated aluminum tubes
- d) Steam content of the reformat.

For the experiments, the reactor consisted of an aluminum cylinder, 3/8" in diameter and 6" deep. The platform for the catalyst consisted of a perforated aluminum disk. Inlet and outlet fittings were standard nipple hardware. A

heated line connected to a heated water saturator provided for maintaining various partial pressures of steam. Thermocouples were provided at the bed inlet, one inch deep into the bed, and an adjustable thermocouple that could be set so as to be exactly at the top of the catalyst bed.

Gas flow rates were measured using precision Fischer and Porter flow meters. Gas analyses were made using a Perkin and Elmer Sigma 1 gas chromatograph. Using a six foot molecular sieve column, and a five ml sample provided by an automatic flow through valve connected to the outlet of the reactor, as little as 1 ppm of CO could be detected. The computer program was set so that clear separations were obtained for H_2 , N_2 , O_2 , CO, and CO_2 . The program was set using a previous gas standard containing the above normal gases. The N_2 value was used as a standard in order to verify the fact that the air introduced to combust the CO conformed to the values predicted from the flowmeter chart.

4.3.2.1 Platinum Content of the Catalyst

Two substrates were considered, $\frac{1}{4}$ " gamma alumina pellets and gamma alumina coated Torvex honeycomb ceramic. With both substrates, the effective temperatures decreased as the platinum levels of the catalyst increased. The results obtained for several platinum loadings are presented below.

Air levels were maintained at 50% excess over the amount needed for total CO oxidation.

<u>Pt %</u>	<u>Effective Temperature °C</u>
0.1	175°C
0.2	115°C
0.5	85°C
1.0	50°C

At the optimum temperature, for all catalyst loadings, CO levels were less than 10 ppm. For the two higher loadings, CO levels were less than 1 ppm.

4.3.2.2 Effect of Air Flow

Air flow rates relative to input CO levels were studied for effect on CO conversion. For this study, stoichiometric 20% and 50% excess air were evaluated. For all catalysts, 50% excess air was all that was needed and for the two higher levels, only 20% excess air was needed to reduce the CO level to less than 10 ppm.

4.3.2.3 Space Velocity and Catalyst Structure

Space velocity is a critical variable. The two important variables involved are, reaction kinetics and the rate of heat absorption. With respect to these variables, pellets are the most sensitive, especially with respect to heat loss. With a pellet bed, a space velocity of $8,000 \text{ hr}^{-1}$ is about

the maximum permissible if one desires a CO reduction to 1 ppm or less. With Torvex, a honeycomb ceramic coated with alumina and platinum catalyzed, space velocities as high as 14,000 hr^{-1} can be used and still yield the necessary CO reduction. By far the best system, but one which has to be improved so as to have the necessary mechanical properties for prolonged usage is an aluminum tube coated on the inside with platinized alumina. Very high space velocities are possible, as high as 30,000 hr^{-1} with very good performance. The reason for this very good performance at a high space velocity is the ability of the aluminum tube to conduct heat away from the reaction sites.

4.3.2.4 Steam Content of the Reformate

Water vapor does not affect the efficiency of the catalyst. Water vapor concentrations up to the 50°C dewpoint (100 mm Hg) were found to be without effect and possibly helpful in that the pressure of the water increases the heat capacity of the gas.

4.3.2.5 Summary

To summarize, it is possible to take impure H_2 containing as much as 0.7% CO, and reduce the CO content to 1 ppm or less using at the most, 50% excess of air required for the oxidation of the CO. Higher Pt content of the catalyst

reduces the temperature necessary for CO burnup. Because of the thermal window with respect to selectivity between CO and H₂ burnup, the reactor should be maintained at a isothermal condition and not operated under adiabatic conditions.

Section 5

TECHNICAL DISCUSSION

Air Cathodes in Caustic Half Cells

5.1 DESIGN OF EXPERIMENTAL CAUSTIC HALF CELLS

5.1.1 Cell Reactions

The evaluation of air breathing cathodes, as an energy saving device for the caustic chlorine industry, can be expedited by utilizing half cell apparatus rather than the more complex ion exchange membrane - DSA Anode - Chlorine producing hardware. In a half cell apparatus, the overall effect is to consume oxygen (from air) at the cathode and generate oxygen at the anode, while the caustic electrolyte remains unchanged. The anode and cathode reactions are as follows.

The cathode can also be operated on oxygen or nitrogen. In the case of oxygen, Equation 2 describes the reaction. When employing nitrogen, hydrogen is liberated at the cathode according to the following reaction:

If equation 3 is operative, the electrolyte is not invariant but increases in caustic concentration because of the consumption of water in the electrolysis reaction.

5.1.2 Baseline Cell

The caustic half cell hardware described in Figures 16, 17, 18 and 19 has been developed over several years. It provides electrode areas of 2" x 2" (25.8 cm²) separated by a distance of approximately 1½". The caustic is continuously pumped from a reservoir through the electrolyte cavity which is somewhat larger in dimension than the working area of the electrodes so that gas bubbles rising to the top of the cavity do not reduce available electrode area. Both the gas and electrolyte exit from the top of the plenum, with the electrolyte returning to the reservoir and the gas vented to the atmosphere.

Figure 16, which is a top view of the cell, depicts the modular construction of the cell and the arrangement of inlet and outlet lines. Also shown is the position of the thermocouple well and electrolyte back pressure tube.

Figure 17 and 18 are the right side (anode side) and left side views (cathode side) of the hardware. A small heater pad mounted on the graphite end plate (right side) provides the means for operating the cell at temperatures between 50 and 100°C. The left side view outlines the 6 mil nickel foil window frame cathode current collector. This frame has a 2" x 2" opening and together with a gasket and thin Lucite plate of similar dimensions defines the cathode working area.

FIGURE 1b TOP VIEW
CAUSTIC HALF CELL

FIGURE 17 , RIGHT SIDE VIEW
CAUSTIC HALF CELL

FIGURE 18, LEFT SIDE VIEW
CAUSTIC HALF CELL

When the bolts are tightened during cell assembly, the foil current collector and cathode are pressed together to provide a reproducible means of distributing current to the electrode.

The front cross section, as shown in Figure 19, displays the air plenum and electrolyte cavity. A Lucite window allows observation of the entire air chamber and gas side of the cathode. Visual inspection of the gas side of the cathode is highly desirable because gas diffusion electrodes tend to "weep", especially when utilized as air cathodes in caustic electrolytes and the effectiveness of means to prevent or minimize this phenomenon is most readily ascertained visually. It will be observed that the air plenum is void of any gas distribution system. To this point in our investigation no attempt has been made to optimize this variable; such optimization is likely to become necessary when the cells are scaled-up. This cell design, especially the electrolyte cavity has several desirable features. Because of the modular construction, an ion exchange membrane can easily be placed between the anode and cathode and sufficient space is available to insert a Luggin capillary against the cathode and connect a reference electrode into the circuit.

While Figure 19 clearly shows the gas space above the working area of the electrodes, it does not show the electrolyte and gas vent which is located in the rear of the cell, directly behind the electrolyte back pressure tube.

CAUSTIC HALF CELL
(front cross-section)

Figure 19

5.2 AIR-CATHODE DEVELOPMENT

5.2.1 Background

Prototech Company had been involved in an internally sponsored research project directed at adapting its proprietary air depolarized cathode to typical caustic-chlorine cell conditions for about two years prior to the start of DOE Contract No. ET-78-C-02-4881. When this project was initiated, proprietary processes in the fields of Pt catalysis and electrode fabrication had already been developed at Prototech during several preceeding years. These developments had produced low loaded carbon supported Pt air cathodes which have now been proven to be efficient and stable in a caustic half cell application for the production of hydroxyl ions. The electrodes were also evaluated, for short term performance, in caustic chlorine hardware containing an ion exchange membrane (Nafion) and found to provide a saving of from 0.9 to 1.0 volts over the traditional iron grid cathodes employed in today's industrial processes.

5.2.2 Methods of Evaluating Electrodes

5.2.2.1 Δ Voltage Method

The performance of an air depolarized cathode in a caustic half cell was initially evaluated as follows:

- a) Difference in Voltage ($\Delta V_{N_2 - \text{Air: Cathodic } H_2 \text{ Evolution vs. Cathodic Air Operation}}$)

When the cell operates in the absence of air, hydrogen is evolved at the cathode during electrolysis.

As the cathode is platinized, the hydrogen overvoltage is low and increases slightly with increasing

current density. Thus, introducing pure nitrogen to the cathode yields a hydrogen-evolving cathode which is, in effect, merely a reference electrode requiring a correction for the hydrogen overvoltage. This overvoltage is estimated to be of the order of 50-100 mv at 200-300 ASF. When the gas feed to the cathode is switched from nitrogen to air, air cathode operation sets in, and the drop in cell voltage ($\Delta V_{N_2 - \text{air}}$) is then a measure of the air cathode performance, with only the H_2 overvoltage being a relatively minor correction. At least every 168 hours of running (1 week) a discharge curve is taken over the range of 50 to at least 300 ASF on air and nitrogen. The difference in cell voltage values between air and nitrogen at 300 ASF have been arbitrarily used as criteria of cathode performance. This difference ranges from 0.78 to 0.82 volts for acceptable initial performance, and progression to a lower level has been viewed as some sign of cathode weakening.¹

b) $\Delta \text{Voltage } O_2 - \text{Air}$

Similar to a), comparison of voltage difference

1. The hydrogen overvoltage on platinized carbon is at least 0.2 volts lower than on an iron grid. Thus, the overall voltage reduction for air depolarization of an air diffusion cathode is the Δ value of the air and nitrogen readings plus at least 0.2 volts minus the hydrogen overvoltage correction.

between cathode operation on air and oxygen, under electrolysis at various current densities, provides data on diffusion, flooding and catalyst poisoning problems. In theory $\Delta V_{O_2 - \text{air}}$ should be merely the Nernst difference estimated at 27 mv at 33% air utilization. Invariably, $\Delta V_{O_2 - \text{air}}$ is larger than a Nernst loss and as the $\Delta V_{\text{air-nitrogen}}$ decreases the $\Delta V_{O_2 - \text{air}}$ increases. Typical values between air and oxygen at 300 ASF and 33% efficiency are 0.10 to 0.13 volts, demonstrating losses other than Nernst losses. These losses are attributed to diffusion losses perhaps resulting from electrode structure involving accessibility of platinum particles.

5.2.3 Hg/HgO Reference Electrode Method

The mercury/mercuric oxide electrode was chosen for use with the air-depolarized cathode cells because of its reported reproducibility and stability in hot alkaline solutions. The mercury/mercuric oxide cell can be made with various concentrations of NaOH, thus allowing the reference cell NaOH concentration to be matched with the NaOH concentration of the catholyte within the air-depolarized cathode cell.

Reference electrodes were constructed as shown in Figure 20. A small quantity of distilled mercury was placed in the bottom of the test tube completely covering the

FIGURE 20, SCHEMATIC OF THE MERCURY/
MERCURIC OXIDE ELECTRODE.

platinum connection. Red mercuric oxide of certified grade was placed over the mercury. Electrical contact was made through a platinum connection, sheathed in a glass tubing and electrolyte path to the face of the working cathode was provided by utilizing a fine bore (20 mils) polypropylene Luggin capillary.

5.3 LIFE TEST CATHODE

5.3.1 Background

Early in December 1977, Prototech Company started a life test on an RA19 type air breathing cathode with a platinum loading of 0.43 mg/cm^2 , the platinum being supported on a high surface area carbon and the electrode fabricated on a carbon cloth substrate. (See U.S. Patent No. 4,044,193). This electrode is still operational and has surpassed 12,500 hours of service in four segments. Segments 1 and 2 were completed prior to the initiation of DOE Contract No. ET-78-C-02-4881 and segments 3 and 4 were run during the contract period.

The life test was conducted in the hardware described in Section 5.1.2. Cell temperature was 75°C and the electrolyte was 23% NaOH. This electrode, as well as all others run at Prototech Company, was evaluated at 33% (CO_2 free) air efficiency. Compressed air was provided by an on site compressor and soda lime was employed to scrub out carbon dioxide. The electrode was run with an air overpressure of 15 inches of water.

5.3.2 Performance Data

5.3.2.1 Life Test Cathode - Evaluation of Δ Voltage Method Segments 1 and 2

As previously stated, testing segments 1 and 2 were completed prior to the starting date of the subject contract. During the first segment of testing, cathode performance was stable for the initial 1600 hours of operation before performance decay was noted. Decay was attributed to air diffusion and/or poisoning problems as performance on oxygen was excellent. The run was terminated after 3850 hours of continuous operation. (Figure 21)

The electrode was removed from the hardware and subjected to a simple washing and drying procedure. Operation was resumed, segment 2, in the same hardware and with the electrode oriented in its original alignment.

Initial performance of segment 2 was excellent being within 40 mv of the zero time data obtained in segment 1. (Refer Figure 21). These data demonstrate that at least some form(s) of electrode decay is reversible. However, as is shown in Figure 21, the restored performance was not maintained and a decaying performance mode was established in less than one week of operation. Segment 2 was terminated after 2370 hours. The electrode had logged 5220 hours of life testing during these periods.

Figure 21

Life Test

ProtoTech Co. RA19 Type Cathode

5.3.2.2 Life Test Cathode - Evaluated by Δ Voltage Method Segment 3

Simultaneous with the start of DOE Contract No. ET-78-C-02-4881, a third segment of testing was initiated. The electrode had been washed by the procedure established between segments 1 and 2 and the same hardware continued to be used. However, two modifications, one in hardware and one in procedure were then initiated:

- a) Since the neoprene rubber employed in the hardware showed signs of deterioration, Hypalon gaskets were substituted.
- b) For long term tests, that is greater than one week, the 23% NaOH electrolyte was thrown away every week and new solution inserted in the circuit.

This third segment of testing reached 5280 hours of continuous operation (total of 10,500 hours of operation for the RA19 type electrode under study) before the test was voluntarily stopped to insert a Hg/HgO reference electrode in the circuit (Figure 22).

Important milestones achieved during this third segment of testing are as follows:

- a) Cathode evaluation by the Δ volts-Air vs. N_2 method showed only 20 to 30 mv of decay over the 5280 hour time period demonstrating that restored performance could be maintained.

Figure 22

Life Test
ProtoTech Co. RA 19 Type Cathode
Segment 3
5280 Hours

Air vs N_2 (Anode to Cathode)

90

80

70

60

50

5000

5800

6600

7400

8200

9000

9800

10600

Cell Temperature = 75°F
Electrolyte Concentration = 23% NaOH
Air (CO_2 free) Efficiency = 98%
Current Density = 300 ASE
Electrode Area = 4.5 sq inches

initial

at one year life on element 11019

at half year continuous operation 11019

when finally terminated 11019

- b) The electrode surpassed one year of operation (non-continuous) and continues to operate at 300 ASF and 33% air efficiency in excellent fashion. (23% NaOH electrolyte and 75°C cell temperature).
- c) Over one-half year of continuous operation had been logged on this air depolarized cathode and no evidence of catalyst failure and/or deterioration of electrode structure was evident.

5.3.2.3 Life Test Cathode - Evaluated by Hg/HgO Reference Electrode Segment 4

The cathode was washed again and the life test resumed in the same piece of hardware with a Hg/HgO reference electrode in the circuit. After the electrode achieved steady state (one day of operation) a discharge curve was taken and the data compared to a new RA19 type electrode. The curves, Figure 23, show that the performance of the 10,500 hour old cathode was only 50 mv inferior, at 300 ASF (33% CO₂ free air efficiency), to a new cathode whose life time of operation was one hour. The fourth segment of testing had to be terminated after 2036 hours of continuous operation because the reference was slipping away from the normal fixed position.

Figure 24 shows the performance vs. reference at 300 ASF for the fourth segment of testing. Total accumulated hours of operation on the life test cathode has now reached 12,536 hours (1.43 years).

CURRENT DENSITY DATA
NEW ELECTRODE VS. 10,500 HOUR OLD ELECTRODE
0.33 mg/cm² Pt

Figure 23

Figure 29

Performance vs Time
RA19 Type Cathode - Life Test Electrode
Segment 4
HALVED Reference Data
2036 Hours

5.3.3 Summary - Life Test Cathode

Prototech Company's life test cathode has been run in a caustic half cell for over 12,500 hours. During this time period the electrode has decayed to unacceptable performance (twice) and has been restored to its original zero time performance level by a simple washing process. The use of Hypalon gaskets in the hardware and weekly changes of the electrolyte have resulted in stable running periods of over one-half year. Reference data measurements have confirmed the level and stability of performance that was documented by the Δ Voltage method.

With respect to the electrode itself the following conclusions have been made:

1. The proprietary catalyst (refer U.S. Patent No. 4,044,193) used to fabricate this 0.43 mg/cm^2 Pt air cathode has demonstrated long term stability.
2. The thin porous conducting substrate (Standard 9-11 mil, SPWB-3 carbon cloth) on which the catalyst layer was deposited has demonstrated the physical integrity necessary to withstand the environment and air/electrolyte pressures that are present in small caustic hardware.
3. The electrode structure is capable of preventing flooding for long periods of time and "weeping" is non-existent.

4. The flowing electrolyte, approximately 7 cc/min., has not eroded the catalyst layer from the conducting substrate.
5. The periodic measurements (weekly) taken on the hardware, which involve the substitution of nitrogen and oxygen gas for air and a variation of current density from 50 to 350 ASF, are without effect on the steady state operation of the cathode.
6. The use of Hypalon gaskets for sealing purposes and soda-lime for carbon dioxide scrubbing are acceptable materials. -

5.4 EFFECT OF HALF CELL PARAMETERS ON THE PERFORMANCE OF RA19 TYPE AIR CATHODES ($0.33 \pm 10\%$ mg/cm² Pt)

5.4.1 Introduction

It has been found that the performance of RA19 type air cathodes is extremely reproducible when the electrodes are run at 75°C with 23% NaOH electrolyte and at an air efficiency of 33%, which are the operating conditions of the air depolarized cathode life test discussed in Section 5.3. There are, however, many cell parameters which can affect this performance:

1. Current density
2. Air efficiency
3. Cell temperature
4. Electrolyte concentration (NaOH concentration)

These variables have been studied and the data are presented in the following section.

5.4.2.1 Preliminary Data

Several tests were run at current densities (340-350 ASF) above the customary 300 ASF. At 33% air efficiency it was found that stable performance was easily achieved but that the Δ air-N₂ voltage had decreased by 20-40 mv.

The normally utilized hardware was ruled unacceptable for studying current densities higher than 350 ASF due to the increased evolution of O₂ at the anode (half cell reaction) which interfered with the normal exit of gas and flowing electrolyte from the cell.

5.4.2.2 Limiting Current Density of RA19 Type Cathode as Determined in a 1" x 1" (Active Area) Cell

By decreasing the active cathode area to 1 square inch it has been possible to obtain air depolarized cathode data up to 1000 amps per square foot. These data, Figure 25, were obtained at an air efficiency of 20% for all of the current densities tested and it was found that an RA19 type cathode does not attain a limiting current density out to 1000 ASF.

When these data, which include IR, were plotted, Figure 26, using ΔO_2-N_2 , $\Delta air-N_2$ and ΔO_2-air voltages several striking features were observed. First, the air data has a pronounced break at around 500 ASF. (Not readily seen in Figure 25). For both $\Delta air-N_2$ and ΔO_2-air points, the curves show two straight line segments with a dramatic change in slope occurring approximately at the 500 ASF point. One possible explanation for the phenomenon is that hydrogen evolution commences on the air depolarized cathode around 500 ASF and the change in slope reflects competition between two reactions. Second, the ΔO_2-N_2 curve shows that the hydrogen overvoltage on the cathode increases with current density. And third, the RA19 type cathode performs extremely well on oxygen over the current density range of zero to 1000 ASF.

Figure 25

Limiting Current Density

at

Petro Tech Co. RB-19 Type Air Cathode

FIGURE 26

Δ Voltages

1 Square Inch Electrode Area

C = 1000 Amps/Square foot C.D.

5.4.3 Cathode Performance vs. Air Efficiency (CO_2 free)

5.4.3.1 Air Efficiency of Standard Cathode in Standard Hardware

Figure 27 is a plot of the average 300 ASF Δ air- N_2 values obtained from three cells over an air efficiency range of 16 to 74.7%. This plot is considered to be the present state of the art for standard 2" x 2" electrodes run in the hardware described in Section 5.1.2 and it will be used to evaluate other substrates, low loaded air cathodes, and cathodes with current collectors.

5.4.3.2 Air Efficiency Comparison of Standard Cathode in 1" x 1" and 2" x 2" Hardware

No attempt has been made to optimize air distribution on the gas side of the cathode in the standard half cell. Since the construction of the air plenum for the 1" x 1" and 2" x 2" cells is similar except that the standard cell has a void volume four times that of the 1" x 1" experimental cell, air efficiency data was obtained in this piece of hardware to more closely identify the diffusion characteristics of the RA19 cathode.

Data obtained at 288 ASF and air efficiencies of from 16 to 80% are plotted Figure 28. Less than 0.10 volts were lost in electrode performance over this range of air efficiencies. These data were obtained fairly rapidly so the possibility existed that the electrode had not reached equilibrium after each increase in air efficiency. This theory was tested by running the cell at approximately 80% air efficiency for 24 hours.

Figure 27

Δ Air-H₂ Voltage vs % Air Efficiency
Average Data for RA-14 Type Cathodes

Figure 23

EFFECT OF AIR EFFICIENCY ON

Δ Voltage Air + N_2

1 Square Inch Electrode Area

CURRENT DENSITY = 288 AMPS/FT²

During this period no detectable decrease in cathode performance was observed. Thus, for at least this period of time, the cathode is capable of stable performance at a very high air efficiency: A fact which is not negligible since one has to remove CO_2 from the air.

The air efficiency data obtained at 288 ASF in the 1" x 1" cell was compared with that obtained at 300 ASF in the standard 2" x 2" hardware. A plot of these data, Figure 29, clearly demonstrates the superiority of the data collected in the smaller cell. Undoubtedly, air distribution is an important consideration even in cells having only a 2" x 2" electrode area, but other factors, such as current distribution, may well play a significant role also.

5.4.3.3 Air Efficiency of Standard Cathode as Determined with a Reference Electrode

Air efficiency data, at 300 ASF, was obtained for a standard cathode-hardware assembly with a reference electrode. It was found, Figure 30, that the curves of the "reference" ($\Delta\text{Air-N}_2$) voltages and "cell" ($\Delta\text{Air-N}_2$) voltages vs. air efficiency were not parallel, the reference voltage plot showing a smoother and less pronounced detrimental effect as the air efficiency was increased. The reference curve more closely resembles that presented in Figure 11 for a 1" x 1" working area. Since the reference measures the potential of a point within the working area of the electrode, it is quite possible that these data are indicative of the current distribution phenomenon, which effect was somewhat negated when a smaller electrode was employed.

Figure 29

EFFECT OF Electrode Size - Air Plenum Design

Δ Voltage Air - N₂ vs % Air Efficiency

Figure 30

Δ Air - N_2 Voltage vs % Air Efficiency
Anode to Cathode and Reference to Cathode Plots

5.4.4 Cathode Potential (vs. Reference) at 300 ASF vs. Cell Temperature

5.4.4.1 Tests at 65°C - 75°C - 85°C

One of the cell variables under investigation during the current contract is cathode air depolarization as a function of cell temperature.

Employing air cathodes containing 0.33 mg/cm² Pt, half cells were run at 65°C, 75°C and 85°C. These temperature levels are sufficiently different to provide data regarding short term effect of temperature on air cathode performance.

Data presented in Figure 31 show that, at least on a short term basis, cell temperatures within the above range have little effect on the potential (vs. a reference) of Prototech Company air cathodes at 33% air efficiency and at a current density of 300 ASF.

5.4.5 Effect Electrolyte Concentration (NaOH) on Cell Voltage and Air Depolarized Cathode Performance at 75°C

5.4.5.1 Caustic Half Cell Voltage (anode to cathode) vs. NaOH on Cell Voltage and Air Depolarized Cathode Performance at 75°C

The anode to cathode voltage, including all IR and polarization losses, of a caustic half cell was measured over the electrolyte range of 8 to 32% NaOH. The data, Figure 32 yielded a smooth curve which has a cell voltage minimum between 19 to 23% NaOH. Concentration levels above and below 19 to 23% provided higher cell voltage. These data are in close agreement

Figure 31

Cell Performance vs Time

Standard Prototech Co. 0.33 m²/cm² Pt Electrodes

Cell Temperature 65°C - 75°C - 85°C

with bulk conductivity data presented in the literature for room temperature measurements.¹

While the data presented in Figure 32 could be interpreted to mean that the cell voltage varied proportionally to the change in electrolyte resistance and no polarization effects were encountered, it is pointed out that the reference in footnote 1 also lists some meager conductivity values at 75°C (cell temperature) which show that the temperature effect on conductivity is sufficient to distort the room temperature curve.

5.4.5.2 Cathode Potential (vs. Reference) in 14%-23%-30% NaOH Electrolytes

Reference data has been obtained for air cathodes run in 14, 23, and 30% NaOH electrolytes for extended periods of time. These data are plotted in Figure 33.

Electrodes run in 14 and 23% electrolyte yielded good performance and stability. The cathode run in 30% electrolyte showed acceptable initial performance but deteriorated somewhat with time and stabilized performance was not achieved over 450 hours of testing. Inspection of the air and oxygen data showed that the electrode was not flooded. No explanation can be afforded at this time for the poor stability obtained.

1. Handbook of Fuel Cell Technology, Prentice Hall, Inc., 1968 pp 48-49, Figures 11 and 13.

Figure 32
Caustic Half Cell Voltage
vs
Electrolyte NaOH Concentration

3.20

3.00

2.80

2.60

2.40

2.20

Cell Voltage Anode to Cathode

2

4

6

8

10

12

14

16

18

20

22

24

26

28

30

32

% NaOH Electrolyte

Figure 33
Cathode Performance VS Time
Standard ProtonTech Co. 0.33 mg/cm² Pt Electrodes
NaOH Electrolyte Variation

5.5 VARIATION OF CATHODE PLATINUM LOADING

5.5.1 Preparation of Catalyst and Electrodes

Catalysts ranging from 1-15% Pt were prepared on a high surface area carbon support according to Prototech Company's U.S. Patent No. 3,044,193. By maintaining the same weight and thickness of the catalyst layer, the electrode loading was varied in direct proportion to the %Pt catalyst employed.

Since carbon itself is catalytic for air reduction in a caustic media, electrodes were also fabricated without platinum.

5.5.2 Cathode Polarization (Reference) and Stability as a Function of Platinum Loading - 0.00 to 0.55 mg/cm² Pt

5.5.2.1 Initial Cathode Potential (Reference) vs. Platinum Loading

Figure 34 shows the performance on air and oxygen depolarization and H₂ evolution of electrodes whose Pt content has been varied from 0.00 to 0.55 mg/cm² and run in standard hardware at standard conditions. Since performance on air depolarization is the criteria of evaluation of air cathodes, Figure 35 has been plotted on an expanded scale for this mode of cathode operation. It will be observed that as the Pt content of the electrode is raised from 0.00 to approximately 0.20 mg/cm², the gain in performance (vs. a Hg/HgO Reference) is in the order of 0.20 volts. Above 0.3 mg/cm² only a slight effect is noted.

Figure 34

Cathode Depolarization on N_2 -Air- O_2

Cathode Pt loading

VOLTS VS Hg/HgO
VS
CATHODE PLATINUM LOADING
ZERO TIME DATA

Figure 35

CELL TEMPERATURE = 75°C
 ELECTROLYTE CONCENTRATION = 23% NaOH
 AIR (CO₂ FREE) EFFICIENCY = 33%
 CURRENT DENSITY = 390 ASF
 ELECTRODE AREA = 4 SQ IN

5.5.2.2 Performance vs. Time Curves (Reference) 0 to 300 Hours Variation of Platinum Cathode Loading

The performance vs. time curves, obtained over several hundred hours of operation for a variety of electrode Pt loadings are shown on Figure 36. The profile of the curves indicate that the initial performance loss (vs. a reference) is independent of Pt loading. Over the short time period in which the various cathodes were tested, good performance stability was displayed by all of the electrodes irrespective of Pt loading. Substantially longer runs (> 1000 hours) would be required to document electrode stability characteristics as a function of Pt loading.

5.5.2.3 Summary

The following is a summary of the Pt loading tests run in half cells at 75°C with a 23% NaOH electrolyte.

1. Cathode potential vs. a Hg/HgO reference electrode becomes more positive as the platinum loading is increased in the electrode. The effect is pronounced as the loading is increased from 0.00 to 0.20 mg/cm².
2. Initial electrode decay appears to be independent of Pt loading.
3. Cathode performance stability up to 300 hours is independent of Pt loading.
4. Elimination of platinum and utilization of the catalytic activity of the carbon itself for the reduction of air in a caustic half cell results in a voltage loss of over 0.20 volts vs. a standard 0.33 mg/cm² Pt electrode.

Figure 34

Variation of Platinum Cathode Loading
Performance vs Time

5.6 CATHODE PERFORMANCE AS A FUNCTION OF THIN, POROUS CONDUCTING SHEET

5.6.1 Background

The thin, porous, conducting substrate that holds the catalyst layer is extremely important if an efficiently operating air cathode is to be produced. Over the past several years Prototech Company has examined some of the options that are available with respect to substrates and has selected a carbon cloth as the material of choice.^{1,2} This cloth, which will be referred to as the standard cloth or SPWB-3 substrate (RA19 type cathode) has proven to be stable in the caustic half cell environment and provides excellent utilization of the catalyst bearing layer.

There are, however, many types of carbon and graphite cloths available and the question of whether a superior material is available is of prime importance.

In evaluating substrates, the ultimate criteria of acceptability is the performance of electrodes fabricated on that material and more specifically an electrode fabricated on that substrate containing less than 0.50 mg/cm^2 Pt must yield good air depolarized performance in a caustic half cell.

-
1. Carbon (graphite) cloth was selected for many reasons but paramount were the weight, cost, corrosion properties and ease by which electrodes could be manufactured with large areas and in large volume. Except for electrode resistance, which problem can be overcome, this substrate should be equal to or better than other materials.
 2. Prototech Company also fabricates electrodes on metal substrates. These substrates may or may not be noble metal coated depending on the application.

Some factors which cause deviation from acceptable performance are:

- A. Air diffusion problems
- B. Electrolyte weeping
- C. Electrode flooding
- D. Excessive percolation of air through the electrode

5.6.2 Evaluation of Carbon (Graphite) Cloths as Substrates

5.6.2.1 Electrodes Fabricated by the Standard Process

Six substrates, obtained from three different companies have been tested in the standard caustic half cell. These data are summarized in Table 21. Of these, the CLTCM material could not be evaluated in a half cell as it was not compatible with the electrode fabrication process currently being utilized. Only two substrates, SKFB and SPW6, were considered worthy of further testing (Table 21) and cells employing cathodes fabricated on these substrates were allowed to run for at least one week during which time decay data, discharge curves, (Table 22) and air diffusion data were obtained.

Figure 37 is a plot of the air diffusion characteristics of the two substrates which yielded performance data that was deemed acceptable for further consideration. Included in the figure is the diffusion curve for the standard cloth. It can be seen that at least up to 50% air efficiency, the SKFB material is quite close to the standard but tails off

Table 21

Evaluation of Electrode Substrates

Cell Temp°C = 75

Electrolyte Concentration = 23% NaOH

Substrate Identification	Electrode Thickness	Pt Loading mg/cm ²	Air Efficiency	Performance Data ΔAir-N ₂ Voltage at 300 ASF	Current Density at which cathode performance is equal to standard
UCWCA	20 mils	0.35	16%	0.41 volts	---
UCWCA	20 mils	0.36	16%	0.38 volts	100 ASF or less
			33%	0.32 volts	
SKFB*	36 mils	0.53	33%	0.78 volts	All values tested
SKFB*	36 mils	0.45	33%	0.80 volts	All values tested
SSWB8	20 mils	0.34	16%	0.63	200 ASF or less
			33%	0.48	
SPWB6	17 mils	0.34	16%	0.77	250 ASF or less
			33%	0.72	200 ASF or less
CLTGM	22 mils	0.33	16%	0.68	200 ASF or less
			33%	0.53	
CLTCM	14 mils	COULD NOT FABRICATE ELECTRODE - SUBSTRATE NOT COMPATIBLE WITH PROCESS			

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*Low bubble pressure at 15" H₂O ΔP

Table 22

Discharge Curve Data
for
SKFB and SPWB6 Substrates

Cell Temp^oC = 75

Electrolyte Concentration = 23% NaOH

Standard Substrate
Cathode
Pt Loading = 0.33

SKFB Substrate
Cathode
Pt Loading = 0.45

SPWB6 Substrate
Cathode
Pt Loading = 0.34

ASF Δ Air-N₂ Volts

50 .88

100 .88

150 .87

200 .86

250 .85

300 .81

350 .77

ASF Δ Air-N₂ Volts

50 .86

100 .86

150 .87

200 .86

250 .84

300 .80

350 .75

ASF Δ Air-N₂ Volts

50 .88

100 .89

150 .87

200 .85

250 .81

300 .72

350 .61

Figure 37
Air Diffusion Characteristics
of
SKFB AND SPW36 Substrates

rapidly beyond this point. The SPWB6 does not have a flat portion to its curve and is deviating rapidly from the standard as the air efficiency increases.

5.6.2.2 Electrodes Fabricated by An Alternative Process

New electrodes were fabricated on the carbon cloths under study by an alternative proprietary process which involved a catalyst deposition technique developed by Prototech Company in 1977.

Data, Table 23, demonstrate that electrochemical performance levels were increased for all substrates but that another problem, specifically, gas percolation through the electrode was created. In the one case, Test 3 of Table 23, for UCWCA cloth where the percolation was low, the performance, while improved over the standard catalyzation process was still far below accepted values.

To this point in the investigation electrodes fabricated by the standard method on SPWB-3 cloth (RA19 type - Life test and those employed for other parameter variations) are the most promising.

5.6.3 Evaluation of Stiffened Carbon (Graphite) Cloths as Substrates

5.6.3.1 Electrodes Fabricated by Standard and Alternative Processes

Samples received, varied somewhat in degree of stiffness while essentially maintaining the thickness range (10-12 mils) and texture of the standard cloth.

TABLE 23

Evaluation of Carbon Cloth SubstratesByAlternative Fabrication Method

Test	Substrate	Electrode Thickness	Electrode Loading	Gas Percolation	Electrode Weeping	Peak Electrode Performance at 300ASF	
						Δ Air-N ₂ Volts	Δ O ₂ -N ₂ Volts
1	SPWB-3	10 mils	0.30 mg/cm ²	Moderate	Normal	.81	.91
2	SPWB-6	17 mils	0.32 mg/cm ²	Moderate	Normal	.80	.93
3	UCUCA	20 mils	0.30 mg/cm ²	Low	Normal	.69	.95
4	CLTGM	22 mils	0.31 mg/cm ²	Heavy	Problem: Air side of electrode would not stay clear for more than a few hours.	.81	.97
5	SKFB	36 mils	0.42 mg/cm ²	Massive	Too much percolation to obtain data.		

The initial tests with cathodes fabricated by the standard process on three samples of stiffened cloth yielded some very interesting data.

Air depolarization was below acceptable levels but the cathode could withstand at least 30" of water overpressure on the gas side without excessive percolation of gas through the electrode. This value is significantly above the typical range of 15-20" for the standard cloth. Also, the added stiffness was sufficient to substantially reduce the degree of bowing of the cathode toward the anode while under overpressure.

Air depolarization data obtained with "stiff" cathodes fabricated by the alternative process were superior to the original data and essentially equal to the routine performance of RA19 type cathodes. These data, which are tabulated in Table 24 for electrodes fabricated by both methods, offer evidence of the importance of the electrode fabrication process in obtaining maximum performance from an air depolarized cathode. Also presented, Figure 38, is air efficiency data for both fabrication methods at 15" and 30" of water overpressure. This figure demonstrates the improvement obtained in both performance and air efficiency as the overpressure was raised. The effect was independent of the mode of electrode catalyzation.

TABLE 24

EVALUATION OF STIFFENED CLOTH SUBSTRATE

Stiffened Cloth #	Test	Electrode Fabrication Method	Pt Loading on Cathode	Gas Overpressure on Cathode	Electrode Performance at 300ASF	
					Δ Air-N ₂ Volts	Δ O ₂ -N ₂ Volts
034-71-B-22	1	Standard Process	0.35 mg/cm ²	15" H ₂ O	.73	.91
	2	Standard Process	0.32 mg/cm ²	15" H ₂ O	.60	.93
	3	Alternative Process	0.31 mg/cm ²	15" H ₂ O	.80	.95
	4	Alternative Process	0.29 mg/cm ²	15" H ₂ O	.80	.91
				30" H ₂ O	.81	.92
034-71-C-6	1	Standard Process	0.36 mg/cm ²	15" H ₂ O	.77	.97
				30" H ₂ O	.79	.99
	2	Standard Process	0.33 mg/cm ²	15" H ₂ O	.66	.93
				30" H ₂ O	.70	.90
	3	Alternative Process	0.33 mg/cm ²	15" H ₂ O	.82	.94
				30" H ₂ O	.83	.94
	4	Alternative Process	0.32 mg/cm ²	15" H ₂ O	.81	.94
034-71-D-24	1	Standard Process	0.37 mg/cm ²	15" H ₂ O	.63	.91
	2	Standard Process	0.33 mg/cm ²	15" H ₂ O	.58	.92
	3	Alternative Process	0.33 mg/cm ²	15" H ₂ O	.81	.94
				30" H ₂ O	.83	.94
	4	Alternative Process	0.33 mg/cm ²	15" H ₂ O	.76	.91
				30" H ₂ O	.80	.92

Figure 39
OVER pressure Performance Curves
Electrodes Prepared by Standard and Alternative Process Methods
Stiffened Carbon Cloth Substrate

5.6.4 Evaluation of Carbon Paper

5.6.4.1 Electrodes Fabricated by the Standard and Alternative Process

A carbon paper material was evaluated by both catalyzation techniques. This material is fragile and has a much lower porosity than cloth. Interest in this substrate was generated by the fact that it would easily lend itself to the alternative catalyzation process.

Table 25 lists the half cell performance data obtained with electrodes fabricated on 11 mil carbon paper. This paper has proven to be inferior to carbon cloths irrespective of catalyzation method.

5.7 CURRENT COLLECTION - CARBON CLOTH ELECTRODE ASSEMBLY

5.7.1 Preliminary Data - Cloth Cathodes Incorporating a Current Collector

When a series of current collectors were incorporated into the cathode assembly, the cell voltage of caustic half cells decreased, illustrating the effect of this parameter. Refer Table 26 and Figure 39. These initial data were obtained without the use of a reference electrode, but all subsequent data obtained in this study utilized the Hg/HgO reference as a measure of cathode performance.

To determine the effectiveness of one type of carbon cloth current collector assembly, comparative tests were run

TABLE 25

Evaluation of Kureha CVD Carbon Paper Substrate

Test	Electrode Fabrication Method	Electrode Thickness	Pt Loading on Cathode	Gas Percolation	Electrode Weeping	Electrode Performance at 300 ASF	
						Δ Air-N ₂ Volts	Δ O ₂ -N ₂ Volts
1	Standard Process	11 mils	0.34 mg/cm ²	OK	OK	0.60	0.90
2	Alternative Process	11 mils	0.31 mg/cm ²	OK	Excessive	Electrode flooded very rapidly. Electrode air data extremely poor. O ₂ data ~ 0.90.	

TABLE 26

EFFECT OF CATHODE CURRENT COLLECTIONONCELL VOLTAGE (AC)

Cell Temperature = 75°C
 Cathode = 0.33 mg/cm² Pt

Electrolyte Concentration = 23% NaOH

Test	Current Collector	Current Collector Identification	Anode to Cathode Cell Voltage						
			350 ASF	300 ASF	250 ASF	200 ASF	150 ASF	100 ASF	50 ASF
1	No	None	2.80	2.51	2.23	1.97	1.69	1.41	1.09
2	Yes	R-1	2.63	2.37	2.12	1.88	1.65	1.38	1.10
3	Yes	R-2	2.61	2.35	2.10	1.87	1.63	1.36	1.10
4	Yes	R-4	2.54	2.30	2.07	1.84	1.61	1.36	1.09
5	Yes	R-6	2.54	2.30	2.07	1.85	1.62	1.38	1.09
6	Yes	R-10	2.52	2.28	2.04	1.82	1.61	1.36	1.09

Figure 39Effect of Cathode Current CollectorORCell Voltage (A-C)

on this electrode and others fabricated on raw cloth and on a 100 mesh gold plated tantalum metal screen. This latter rather expensive electrode obviously possesses efficient current collecting capabilities.

Results, as shown in Figure 40, for essentially zero time data, demonstrates the major performance improvements of a carbon cloth electrode when a current collector is incorporated into the cathode assembly. With the particular current collector under test, this improvement fell short of equalizing the cloth to the above 100 mesh metal screen electrode.

5.7.2 Air Cathode Performance vs. Time (Reference)

Carbon Cloth, Carbon Cloth/Current Collector Assembly and Silver Plated Nickel Screen

Performance data obtained as a function of time on stream are plotted in Figure 41 for cathodes fabricated on carbon cloth, carbon cloth/current collector assembly and a 100 mesh silver plated nickel screen. Performance vs a Hg/HgO reference decreased over the initial 7 to 10 days of operation but then assumed at a steady state mode of operation for the remainder of the tests (> 1000 hours). The decrease in performance of the cloth/current collector assembly was somewhat greater on air than on oxygen (Figure 42). Figure 43 is a plot of the discharge curves obtained at approximately 1 and 720 hours of operation. It is of interest to note that the performance below 100 ASF actually improved during this time period.

CURRENT DENSITY DATA
0.33 mg/cm² PT ELECTRODES
EFFECT OF CONDUCTIVITY OF SUBSTRATE
STANDARD CELL CONDITIONS

Figure 90

ENDURANCE

Performance at 300 amps per square foot

FIGURE 41

Figure 92

Cathode Performance vs Time

0.33 Ang/cm² Pt Electrode with R-6 Current Collector

STANDARD CELL CONDITIONS

Figure 92

Discharge Curves As a function
of Time on Stream

0.33 mg/cm² Pt Cathode with Au Ra Current Collector

VOLTS VS. AMP/CM²

Cell Temperature = 75°C
Electrolyte concentration = 23% NaOH
Air Efficiency (Coul) = 33.9%
Electrode Area = 450 cm²

For comparative purposes, an electrode fabricated on a silver plated nickel screen was allowed to run for 1700 hours. The performance vs. time curve is also shown in Figure 41. The only distinct difference between the cloth-current collector and screen data is that the performance loss of the metal screen electrode was greater than that of the cloth electrodes over the initial 7 to 10 days of operation. Beyond this point, the performance of all electrodes was steady for more than 1200 hours.

5.7.3 Tests with Carbon Cloth/Current Collector Electrodes

5.7.3.1 Cathode-Current Collector Potential at 300 ASF and 75°C vs. %CO₂ Free Air Efficiency

One criterion used to evaluate air cathodes is the ability of that electrode to operate at high air efficiencies. Data (reference) obtained for a standard cloth cathode current collector assembly in a cell that had reached steady state vs. %CO₂ free air efficiency are presented in Figure 44. Refer to Section 5.4.3 for data without a current collector.

It was found that air efficiencies of up to 50% had relatively little effect on cathode performance. Above this value, increasing polarization losses are observed. It is mentioned that these values were obtained without the use of an effective gas distribution system. Thus, this performance is subject to improvement.

VOLTS vs. Hg/HgO
VS.
CATHODE AIR EFFECENCY
0.33 mg/cm² PE ELECTRODE

Figure 99

5.7.3.2 Cathode-Current Collector Potential at 300 ASF vs. Cell Temperature

Cathode (with current collector) to reference voltages at 300 ASF are plotted in Figure 45 for a cell in which the cell temperature was raised from approximately 40 to 90°C.

It will be observed that cathode performance (vs. reference) improved with increasing temperature. The effect is pronounced from 40 to 60°C but is rather negligible as the temperature is raised above 75°C. Refer to Section 4.5.5 for data without a current collector.

5.7.3.3 Effect of CO₂ on Air Cathode Performance

If an air cathode possessed tolerance to CO₂ (caustic electrolyte) that property would be of great importance in reducing systems costs as well as providing increased utility. Tests run at Prototech Company, prior to the start of DOE contract No. ET-78-C-02-4881 have indicated that the standard RA19 type electrode did possess some CO₂ tolerance but significant data were never attained.

An electrode/current collector assembly that had been run for over 700 hours on CO₂ free air at 33% efficiency was subjected to ambient air (.03 to .04% CO₂) as oxidant and the cathode performance vs. a reference was monitored for another 300 hours.

It can be seen from the discharge curves plotted in Figure 46 that performance decreased 40 mv at 300 ASF and less

Figure 95

Volts vs H_2/H_2O

vs

Cell Temperature $^{\circ}C$

0.33 mol/cm^2 PLATINUM

Data obtained with a
Cathode - Current Collector Assembly

Cell Temperature = AS SHOWN
Electrolyte Concentration = 23% NaOH
Air (CO_2 free) Efficiency = 83.9%
Current Density = 300 ASF
Electrode Area = 4.50 IN.

Volts vs H_2/H_2O
-E

Cell Temperature $^{\circ}C$

Figure 7b

Effect of CO_2 on Air Cathode Performance
with Current Collector
Cathode to $\text{Hg}/\text{H}_2\text{O}$ Reference Voltage

CURVE A - STANDARD FOR SCRUBBED AIR (CO_2 free)
CURVE B - after 174 HOURS ON AMBIENT AIR (0.038 = 0.04% CO_2)
CURVE C - after 208 HOURS ON AMBIENT AIR (0.03 = 0.04% CO_2)

at lower current densities over the first 144 hours of operation on ambient air (.03 to .04% CO₂). Performance loss over the next 144 hours was lower than the initial time period, being only 20 mv at 300 ASF. Thus, for a total of 288 continuous hours of operation on ambient air a stabilized cathode lost 60 mv in performance at 300 ASF.

5.7.3.4 Stiffened Cloth Electrodes - With Collector Assembly

Performance of cathodes fabricated on stiffened cloth substrates were reported in Section 5.6. Electrodes fabricated by the standard method were inferior to the normal cloth electrodes but use of an alternative proprietary process for electrode preparation eliminated the suspected flooding problems and performance was equalized to the RA19 type cathodes.

A substantial supply of #03494 stiffened cloth substrate had been obtained and this material was evaluated by the standard and alternate fabrication methods and with a current collector assembly.

Performance data are presented in Figure 47. These data show

- a) the alternate fabrication process continues to be necessary if this substrate is to provide acceptable performance, and
- b) as was the case with SPWB-3 cloth, the use of a current collector assembly markedly improved cathode performance.

Figure 97

0.33 m²/cm² Pt Electrodes

03494 Stiffened Cloth

Effect of Method of Fabrication - With and Without Current Collector

5.8 ENERGY SAVINGS-AIR DEPOLARIZED CATHODE VS. INDUSTRIAL STEEL GRID

5.8.1 Background Information

Industrial chlor-alkali cells produce caustic at a steel grid cathode by the following reaction:

When an oxygen depolarized cathode is substituted for the steel grid, the reaction is as follows:

Thus, the potential savings in cell voltage from an oxygen depolarized cathode applied to a chlor-alkali cell from theoretical thermodynamics is 1.229 volts. However, hydrogen overvoltage on the steel grid, the peroxide mechanism of the oxygen electrode, the use of air (not O_2) and polarization losses in an operating cell (100 to 300 ASF) result in an experimental voltage saving in the range of 0.80-1.00 volts.

5.8.2 Half Cell Data - Air Depolarized vs. Steel Grid Cathode

Utilizing the standard half cell hardware, discharge curves have been obtained in a 23% NaOH electrolyte at 75°C for an industrial steel grid cathode and a Prototech Company RA19 type air cathode/current collector assembly. These data, Figure 48, demonstrate a voltage saving of 0.83-0.85 volts over the current density range of 50 to 350 ASF when the air cathode was operated on CO_2 free air at 33% efficiency.

Figure 48

Discharge Data

Air Depolarized Cathode vs Steel Grid Cathode

Caustic Half Cell

5.9 CHLOR-ALKALI MEMBRANE CELL

5.9.1 Design of Hardware

The standard half cell (Section 5.1.2) was expanded to accomodate a Nafion 316 membrane, an inert anode, and an internal electrolyte heater. These additions resulted in an anode to cathode spacing of 2.5 inches. The anolyte and catholyte chambers were separated by the membrane. A Luggin capillary was placed in the catholyte chamber and data were obtained vs. a Hg/HgO reference electrolyte. Figure 49 is a front cross section view of the cell.

5.9.2 Operating Conditions

The Chlor-Alkali membrane cell was only run for short term tests, (<1 day) and a product material balance was not obtained. The catholyte chamber was fed with 20% NaOH at a flow rate of 10cc/minute and exited through an overflow into a reservoir. Saturated brine was the anolyte feed, again a feed rate of 10cc/minute. The depleted brine and chlorine gas were captured after exiting the cell and passed through a NaOH- Na_2SO_3 scrubber. The cell was run at 75°C and the electrodes operated at an air (CO_2 free) efficiency of 33% with an overpressure of 15" of water.

FIGURE 49, CHLOR-ALKALI MEMBRANE CELL CROSS SECTION

5.9.3 Experimental Data, Chlor-Alkali Membrane Cell

5.9.3.1 Performance Data - New One Year Stored and 12,500 Hour Old Carbon Cloth Based Electrodes - Non Current Collection Assemblies

A newly fabricated, an electrode fabricated a year before and stored under ambient room conditions, and the 12,500 hour old life test electrode were evaluated in the Chlor-Alkali membrane cell. These electrodes were void of current collector assemblies, except for the customary 6 mil nickel window frame collector. Data were generated to document the utility of Prototech Company's carbon cloth based air electrode in the subject hardware.

The data, Figure 50, demonstrate the reproducibility, shelf life and stability of this type of gas diffusion cathode. Over the current density range of 50 to 200 ASF little variation is noted in discharge curves for the electrodes tested.¹ Above 250 ASF, the electrode previously run for 12,500 hours in a caustic half cell proved to be somewhat superior.

The significance of the data presented in Figure 50 is

A. Half cell data has been reproduced in a chlor-alkali

1. All tests were run in the same hardware and with the same Luggin capillary securely positioned in front of the cathode. Because unsupported 2" x 2" cloth electrodes tend to bow slightly under 15" of water overpressure, it is difficult to position the tip of the capillary exactly the same distance from the electrode when building new hardware. However, reference data is very reproducible for a series tests run in the same hardware.

ENDURANCE OF CARBON-CLOTH CATHODE

Performance in Chlor-Alkali Membrane Cell

Figure 50

membrane cell for the carbon cloth based RA19 type air diffusion cathodes.

- B. Over the current density range of 50 to 250 ASF, initial performance data is essentially identical for a newly fabricated, a one year stored and an electrode previously run for 12,500 hours in a caustic half cell.
- C. Shelf life of the carbon cloth based electrode has been established.
- D. Reproducibility of the fabrication procedure is illustrated.
- E. Endurance of the life test electrode demonstrates the stability of the platinum catalyst employed.

5.9.3.2 Energy Savings - Air Depolarized Cathodes vs. Industrial Steel Grid Electrodes

The energy savings attainable by replacing a steel grid cathode with an air depolarized electrode in a chlor-alkali membrane cell is shown in Figure 51 for a carbon cloth cathode, a carbon cloth/current collector assembly and a silver plated 100 mesh nickel screen based electrode. An energy savings of 0.85 to 0.88 volts can be obtained for operation on air if adequate current collection is provided. Operation on oxygen would raise this savings to 0.92 - 0.98 volts.

Figure 51
Energy Savings
Steel Grid vs Air Depolarized Electrodes

SECTION 6TECHNICAL DISCUSSIONMetal - Water - Air Batteries

6.1 ALUMINUM - AIR BATTERIES

6.1.1 Air Cathode Half Cell Data-Sodium Aluminate Electrolyte

A series of tests were conducted with a half cell to obtain performance of a representative Prototech Company air cathode in the typical alumina-NaOH electrolyte of an aluminum-air battery. The cell, which was run with a flowing electrolyte and at a temperature of 75°C, showed no signs of performance decay at 100 ASF (33% air efficiency) for the 140 hours of the test.

A discharge curve obtained during the course of the run is shown in Figure 52. The slopes of the curves for cathode operation on air, nitrogen and oxygen are similar to those obtained with the same type electrode in a 23% NaOH electrolyte.

In addition to operation at 100 ASF, the cell was run for several days at 300 ASF. Again, performance was quite stable.

Figure 52
 Discharge Curve
 Prototech Cell Air Cathode - $\text{NaOH}/\text{NaAlO}_2$ Electrolyte

6.1.2 Evaluation of Prototech Company Air Cathodes in an Aluminum - Air Battery

Samples of Prototech carbon cloth based (CC) electrodes (Pt loading of $0.33 \pm 10\%$ mg/cm²) without special current collectors have been supplied to Lockheed, and samples with and without a current collector (same Pt loading) have been supplied to LLL. Figure 53 has been presented by Dr. Littauer of Lockheed at the Metal-Air Project meeting in Washington, April 10-11, 1979; the Prototech "CC" RA19 cathode has performed in accordance with the goals set for the battery up to a current density of about 300 ma/cm² at 60°C. Figure 54 has been presented by Dr. Cooper of LLL at the same meeting. Here he has used the Prototech "CC" electrode with the special current collector showing performance of the Prototech electrode of about -0.78 V (vs. Hg/HgO reference) at 17.5 amps at 60°C.

Figure 53

LOCKHEED

EFFECT OF TEMPERATURE ON POLARIZATION
OF PROTOTECH RA-19 CATHODE WITH REYNOLDS 45210 ANODE

SOURCE: Lockheed

POLARIZATION CHARACTERISTICS OF ALUMINUM-AIR CELLS

SOURCE: Lawrence Livermore Laboratory

Figure 54

SECTION 7Energy and Cost Estimates7.1 ELECTROWINNING OF ZINC: HYDROGEN VS. LEAD ANODE7.1.1 Cost of Hydrogen

On March 1, 1979, a meeting involving only non-confidential information, was held at the Research Laboratories of Tosco Corporation, 18200 W. Highway 72, Golden, Colorado, attended by Dr. B. Shulman, Director of Research of Tosco, Messrs. T. McNulty and W. Stern of Anaconda Company, Dr. H. Shalit of Atlantic-Richfield Company and Dr. W. Juda of Proton-tech Company. The subject of the meeting was Tosco's petroleum coke gasification process for pure hydrogen. The process involves catalytic steam reforming-partial oxidation of the coke, followed by the shift reaction and final methanation (to eliminate residual CO). With respect to economics, Shulman stated that the original figures (see Appendix I) may have been too low because they were based on gasifying 250-1000 T coke/day producing 17.5-70 million cu ft H₂/day, whereas a zinc electrowinning plant, depending on size, would require only some 2-5 million cu ft/day. But, in view of the fact that the Tosco process can be carried out in ordinary steel equipment, there should not be too serious a cost penalty. A reasonable figure to be used for the zinc project

at this time should be 0.2¢/SCF H₂ with coke at \$20/ton, and 0.23¢/SCF H₂ with coke at \$40/ton. The H₂ produced has ca. 70% of the BTU content of the coke. It was generally agreed that petroleum coke is likely to remain a readily available source of hydrogen in contrast to natural gas.

Dr. Shulman then gave us a conducted tour of the Tosco pilot plant which gasifies routinely ½-2 tons/day of coke to H₂-CO mixture (the 1st step of the process). Tosco plans to scale-up to a level of about 20 T/day in the near future. (The eventual large scale production of H₂--up to 70 million cu ft/day--is intended for Tosco's Avon refinery). Should Tosco's process turn out to be the most economical, Tosco would consider selling hydrogen over the fence or licensing the technology for use in a zinc electrowinning plant.

Further information on hydrogen is summarized in Appendix I. Consideration of using crude hydrogen has been excluded for the present for the reasons indicated in Appendix I-B.

7.1.2 Comparative Energy and Cost Estimates

The estimates presented in Tables 27-30 are based on laboratory results and have been examined and approved by Mr. W. Stern and other staff members of the Anaconda Company.

Table 27 compares the energy requirements of the H₂-anode and lead anode processes and indicates an estimated

TABLE 27 COMPARISON OF ENERGY REQUIREMENTS FOR ELECTROWINNING OF ZINC:
HYDROGEN ANODE VS. LEAD ANODE

Basis: Anaconda Liquor Fuel: Petroleum Coke; operating current density: 30ASF, 90% C.E. 35°C

System	Energy used for conversion to hydrogen or electric energy	Hydrogen and/or electric energy	Energy per lb zinc
A. <u>H₂ - anode</u>	≈430 Btu/SCF H ₂ * (≈70% efficiency)	6.2SCF/lb (ca. 97% H ₂ utilization)	≈ 2,700 Btu
<u>H₂ requirement</u>			
<u>Electric energy requirement</u>	10,000-11,400 Btu/KWH (≈34-30% efficiency)	≈0.65 KWH/lb (Includes rectifier efficiency of 93%)	≈ 6,500-7,400 Btu 9,200-10,100 Btu
B. <u>Lead Anode</u>	10,000-11,400 Btu/KWH (≈34-30% efficiency)	≈1.5 KWH/lb (Includes rectifier efficiency of 93%)	15,000-17,100 Btu

Conclusion: Overall energy saving due to H₂ process (including estimated energy inefficiency due to H₂ from petroleum coke) ca. 40%

* Tosco process: 70,000 SCF H₂/ton petroleum coke. H₂ heat content: ≈300 Btu/SCF. Petroleum coke heat content: ≈30 x 10⁶ Btu/ton. Heat content of H₂ produced/ton coke: 21 x 10⁶ Btu.

energy saving of about 40% when the H_2 -anode replaces the conventional lead anode. Note that the estimate includes the energy inefficiency of producing hydrogen from petroleum coke.

Table 28 compares the respective energy costs and indicates an estimated savings of 1.3-2¢/lb Zn by the H_2 -anode process.

Table 29 estimates capital costs for the two processes, operated at a current density of 30 ASF and 35°C and producing 100 T/day of zinc, at \$20 million for the conventional lead anode process and \$19 million for the H_2 -anode process, resulting in amortization costs of 2.74¢/lb Zn and 2.6¢/lb Zn respectively. However, as shown in Table 30, the H_2 -anode process which has been shown in the laboratory studies to be operable at 50 ASF and at temperatures in the 40-60°C range (in contrast to the lead anode process) has an estimated capital cost for a 100 T/day plant, of only \$13.3 million with a corresponding amortization cost of 1.8¢/lb.

In summary, the combined amortization-plus-energy cost saving due to the H_2 -anode process (at 50 ASF, 40-60°C) is estimated at 1.9-2.54¢/lb Zn and the corresponding energy saving at 40%.

TABLE 26 COMPARISON OF H₂ AND/OR ELECTRIC ENERGY COSTS FOR ELECTROWINNING OF ZINC:

HYDROGEN ANODE VS. LEAD ANODE ***

Basis: Anaconda Liquor Fuel: Petroleum Coke; operating current density: 30ASF, 90% C.E. 35°C
Temperature: °C

System	H ₂ Cost ¢/SCF	Electric Energy Cost ¢/KWH	SCF H ₂ /lb Zinc	KWH/lb Zinc	Total Cost/lb Zn ¢/lb
A. <u>H₂ Anode</u>	0.2* - 0.23**	3* - 4**	6.2	0.65	3.2*- 4.0**
B. <u>Lead Anode</u>		3* - 4**	---	1.50	4.5*- 6.0**
Projected Saving: (a) in 1979 dollars					1.3 - 2.0
					1.3
(b) when commercialized					2.0

* In 1979 dollars

** In anticipated cost increases due to inflation

*** Anode replacement costs assumed equal for Pb-anode and H₂-anode

TABLE 29 COMPARATIVE CAPITAL COST ESTIMATES;

H₂-Anode vs. Pb-AnodeBasis: Anaconda Liquor Fuel: Petroleum Coke; operating current density: 30ASF, 90% C.E, 35^c

Production Rate: 100 ton/day; 365 d/yr

	<u>Pb-Anode</u>	<u>H₂-Anode</u>
A. Investment (excluding power plant or H ₂ plant)	\$ 20,000,000*	\$17,000,000 (arrived at by subtracting (a), (b), (½c) and (d) from \$20,000,000)
Includes:		
(a) H ₂ SO ₄ -mist ventilation	(\$ 1,000,000*)	
(b) cooling	(500,000*)	
(c) rectifier	(600,000)	
(d) anodes	(1,200,000*)	\$ 2,000,000**
Total	\$ 20,000,000	\$19,000,000

*Private communication, W. Stern

**H₂ anode at \$15/sq ft, or with 86% area utilized → \$18.75/sq ft x 115,000 sq ft → \$2.156 x 10⁶Notes:

- (1) At 30ASF, 90% CE: 635 lb Zn/sq ft-year = 0.3175 ton Zn/sq ft-year.
- (2) Pb-anode: 14 sq ft (immersed) price: \$150/anode.
- (3) Anode Requirement: 36,500 tons/yr at 0.3175 ton/sq ft-yr = 115,000 sq ft @ ≈\$10.71(sq ft for Pb: \$1.232 x 10⁶).
- (4) Rectification: 3.5V x 30ASF x 115,000 = 12,075 KW @ \$50/KW → \$603,750; approximately ½ saved by H₂-anode.

Amortized cost 10 years (excluding interest on capital) - 36,500 ton/yr.
Pb-anode: 2.74¢/lb Zn H₂: 2.60¢/lb Zn

TABLE 30. ANTICIPATED COST LOWERING
WITH H₂-ANODE OPERATING AT HIGH CURRENT DENSITY

Basis: Current density 50ASF.

Temperature in 40-60°C range.

90% C.E.

- Assumptions: (1) Operation is permissible due to production of Pb-free zinc.
- (2) 75% of H₂-Anode investment is inversely proportional to current density.
- (3) Electric energy requirement becomes 0.76 KWH/lb zinc.
- (4) H₂ requirement is unchanged.

Investment Fixed: \$ 4,750,000
 C.D. dependent : 14,250,000 at 30 ASF
 8,550,000 at 50 ASF
 Total at 50 ASF: 13,300,000

Amortized Cost: 10 years (excluding interest on capital)
 36,500 ton/yr: 1.8¢/lb Zn

Energy Requirements

H₂ 1.24* - 1.4¢**/lb Zn
 Electricity 2.3* - 3.0¢**/lb Zn
 Total 3.54* - 4.4¢**/lb Zn

H₂-Anode at 50 ASF: Amortization + energy cost: 5.34* - 6.2¢**/lb Zn

Pb-Anode at 30 ASF: Amortization + energy cost: 7.24* - 8.74¢**/lb Zn

Saving due to H₂-Anode at 50 ASF: 1.9* - 2.54¢**/lb Zn

[Saving due to H₂-Anode at 30 ASF: 1.44* - 2.14¢/lb Zn]

* In 1979 dollars

** In anticipated cost increases due to inflation

7.2 COST CONSIDERATIONS

Air/oxygen Cathode for Caustic Chlorine Production

Reference is made to "ENERGY COST CALCULATIONS:

1. OPTIMIZATION OF ELECTROCHEMICAL PROCESSES TO ACHIEVE MINIMUM PRODUCT COST AND THE IMPACT ON ENERGY CONSUMPTION" by Rudolf Keller, Report ANL/OEPM-78-2, prepared for the U.S. Department of Energy under contract W-31-109-Eng-38. Keller's chapters VII D and E (p. 29-33) entitled "Membrane-Type Chlorine Cell with Oxygen Electtode" is reproduced in Appendix II in its entirety as it applies substantially to the laboratory data and results of the present study and places the oxygen cathode in the context of the other caustic-chlorine cell processes. The voltage saving in the laboratory experimentation was about 0.85 with air and about .95 V with oxygen. The figure of \$10/ft²-year for the Prototech air cathode with current collector is a reasonable estimate, as the cathode performed for 12,500 hours, or about 1.4 years, at which time the endurance test was terminated arbitrarily and not because of cathode failure. Prototech's cathode cost, in large scale production, has been estimated in the range of \$10-\$20/sq ft justifying the figure of \$10/sq ft-year of the Keller reference.

7.3 COST CONSIDERATIONS

Air Cathodes in Aluminum - Air Batteries

Cost Considerations. Some data leading to indications of permissible air cathode costs have been published by Cooper and Littauer (Reference 1) and by Cooper and Behrin (Reference 2).

In Reference 1, Table 2, p. 5, fifty cells, each having an anode area (equal to the cathode area) of 0.2 m^2 are projected to have a "nominal, net power output" of 12.7 KW, requiring a total of 10 m^2 (ca. 108 ft^2) of cathode. The corresponding cost of raw materials for this quantity of cathodes, shown in Table 5, p. 6 of Reference 1, is estimated at $\$14/\text{m}^2$ and the anticipated life expectancy of the cathodes is 500 hours of operation. Similarly, Reference 2, p. 44, calls for a galvanic unit of fifty cells, each containing two 0.90 m^2 anode plates (with same size cathodes), or a total of 9 m^2 (ca. 97 sq ft) of cathode per unit producing 12.5 KW.

The goal of $\$1.30/\text{sq ft}$ ($\$14/\text{m}^2$), in 1979 dollars, of cathode raw materials is at present far out of reach,

1. Reference 1. "Mechanically Rechargeable Metal-Air Batteries for Automotive Propulsion", prepared for submission to the 13th Intersociety Energy Conversion Engineering Conference, Aug. 20-25, 1978, San Diego, California.
2. Reference 2. Proposal for the Development of the Aluminum-Air Power Cell for Automotive Propulsion, prepared for the Division of Energy Storage Systems, U.S. Dept. of Energy, Aug., 1978.

whereas the projected 500 hours operating life would appear to be excessively low, by about one order of magnitude, in view of the durability test described in Section 5.3.2 of this report. In 1979 dollars, the raw material cost of Prototech's "CC" RA19 air electrode is about \$7/sq ft, including four dollars worth of platinum, i.e. about five times the goal, but this is compensated by its at least ten times longer expected life.

APPENDIX I

I. Dr. Shalit of Atlantic-Richfield Co. thought it possible that his patented process involving one-step production of pure hydrogen by reacting steam with carbon (a carbonaceous fuel including petroleum coke) in the presence of molten caustic may be lower in cost than the Tosco process, when developed. He would initiate cost calculations based on his laboratory experiments and the known recycle step of liming the sodium carbonate produced and evaporating water from the aqueous caustic to re-produce molten caustic.

II. On October 24, 1978 a meeting was held at Prototech attended by Dr. B. Shulman, Director of Research of Tosco Corporation and W. Juda and H.G. Petrow of Prototech. The purpose of the meeting was to obtain costs of pure and crude (i.e. CO-containing) hydrogen produced from fuels available at Tosco, using Tosco's gasification technology. (The October meeting was a follow-up of a September, 1978 visit by W. Juda to the Tosco Laboratories in Golden, Colorado during which the hydrogen cost inquiry was made, but could not be answered in Dr. Shulman's absence).

Dr. Shulman presented the following information. Petroleum coke is likely to become a reliable source of fuel for low cost hydrogen as coke is easier to keep at "depressed" price levels than natural gas, SNG or other hydrocarbons. Using a present cost of \$20/ton of coke, pure hydrogen would be priced at 0.162¢ per SCF when produced by Tosco's catalytic gasification process. The process requires a pilot plant demonstration program over a period of 6-12 months. According to Shulman, commercial hydrogen could become available at that price at the end of two years.

With regard to crude hydrogen, presumably coming off the reformer-shift units and containing between 0.5-1% CO in addition to mostly CO₂ and water, Shulman stated that its cost is expected to be 0.132¢ per SCF contained hydrogen, i.e. a saving of 18.5% vs. the cost of pure hydrogen.

These figures, in conjunction with exploratory zinc electrowinning laboratory tests (Prototech Progress Report for the Period August 1, 1978 to October 31, 1978 issued in December, 1978 for the U.S. Department of Energy under contract No. ET-78-C-02-4881, p. 52-59) lead to the following preliminary estimates of the energy and operating cost savings due to the use of hydrogen anodes in lieu of lead anodes in electrowinning zinc.

A. PURE HYDROGEN

Prototech's exploratory tests have demonstrated the feasibility of electrowinning of Zinc with Hydrogen anodes without the use of an anion exchange membrane, thereby

increasing the voltage saving to almost 2V from the 1.0-1.5 V estimated in Prototech's Proposal, Part 1, Addendum dated July 21, 1976.

The corresponding energy consumption, using pure hydrogen is only 0.55-0.607 KWH/lb Zn in the laboratory experiments.

With pure hydrogen it is easy to visualize practically quantitative hydrogen utilization in a feed-and-bleed system in which hydrogen is recycled to the cathode and in which the hydrogen consumed ("bled") in the cell is made up in the recycling stream by "feeding" into it pure hydrogen from its source and from that evolved at the cathode as current inefficiency. Hence, here a hydrogen efficiency figure of 95-98% is plausible. Stoichiometrically, six SCF of hydrogen are required to produce one pound of zinc. Hence, at 95-98% efficiency, the corresponding 6.12-6.32 SCF H₂ would cost 0.99-1.02¢/lb Zn, i.e. just about one cent per pound.

Energy consumption, in laboratory experiments at the commercially practiced temperature of 35°C was 1.24 KWH/lb Zn, using the conventional Pb(Ca) anode. This figure is lower than the range of 1.29-1.42 KWH derived from the data given in the Chapter entitled "Electrolysis of Zinc Sulphate Solution", p. 420 of the Handbook of Nonferrous Metallurgy, which figure, in turn, is lower than the 1.5 KWH (D.C.)/lb figure stated in the appended letter dated July 12, 1976 by Anaconda's T. McNulty.

Thus, the data indicate that at least about .65 KWH/lb Zn and perhaps as much as 0.9 KWH/lb can be saved when the hydrogen anode replaces the standard lead (Ca) anode. A reasonably recent electrical utility sales figure to industrial consumers is 2.33¢/KWH, according to "Report of the Electrolytic Industries for the Year 1977, J. of the Electrochemical Society, Vol. 125, No. 11 (1978), page 464C. Hence, an energy saving of between 1.5¢ and 2.1¢/lb Zn, at the expense of about 1¢/lb worth of hydrogen, is achievable, yielding a net operating cost saving in the range of 0.5-1.1¢/lb Zn. Obviously, these figures need to be refined in subsequent experimentation, on a laboratory as well as pilot plant scale.

The potential electric energy saving resulting from the use of the hydrogen anode is, similarly, much larger than had been anticipated in the above Anaconda letter, namely 50-60%, instead of 33%, which, on the basis of an annual production of 750,000 tons zinc, amounts to 1200-1450 MM KWH annually.

B. CRUDE HYDROGEN

It is evidently more difficult to achieve near quantitative hydrogen utilization with crude hydrogen as the impurities (mostly CO_2 and water) could build up rapidly in a recycle scheme, even if the CO anode poison is catalytically removed. Some recycle would appear to be feasible, provided

that the water is condensed out prior to feeding the hydrogen to the anode. In any event, the above cost figures indicate that the crude hydrogen utilization efficiency must be at least 80% to break even, on a cost basis, with pure hydrogen.

In view of the hydrogen utilization problem and the need for the additional step of CO removal from crude hydrogen, the use of crude hydrogen is not contemplated at this time.

A P P E N D I X I ID. Membrane-Type Chlorine Cell with Oxygen Electrode

If an oxygen electrode is used in a membrane cell, the evolution of hydrogen at the cathode is replaced by the electrolytic reduction of oxygen according to the equation $\frac{1}{2}O_2 + H_2O + 2e = 2OH^-$.

* According to some industrial optimization data for diaphragm-type cells⁸, the relationship between optimum current density and energy price is $i_{op} = \text{const.} \times b^{-0.374}$, rather than $i_{op} = \text{const.} \times b^{-0.50}$ as would correspond to the model. The reasons for this deviation and its significance will be the subject of further studies.

Fig. 20. Cost (electrolysis only) vs. Current Density for a Membrane-Type and a Diaphragm-Type Chlorine Cell

The main benefit in the use of an oxygen electrode is a cell voltage at zero current about 1 V lower than that for a membrane-type cell¹¹; this is somewhat less than the theoretical 1.23 V decrease in decomposition voltage because of higher electrode polarization. For the membrane cell with an oxygen electrode, the voltage was estimated to be 1.5 V at zero current, with the voltage increasing with increasing current density as in the diaphragm- and membrane-type cells.

A cost of \$150/m² has been projected for the oxygen consuming cathode by Yeager.¹¹ With a lifetime of 10⁴ hr, a cost of \$130/m²-yr would result. For the present calculations, a future cost of \$10/ft²-yr is assumed to be realistic. Adding the oxygen electrode cost to the investment cost of a membrane-type cell results in a cost factor of \$0.0625/m²-hr.

The resulting cost vs. current density plot for a membrane-type cell with an oxygen cathode is shown in Fig. 21. A diaphragm-type cell and a membrane-type cell are presented for comparison purposes. For the membrane-type cell with oxygen electrodes, the optimum cell voltage is 3.08 V and the optimum current density is 0.40 A/cm²; the corresponding energy consumption is 2.45 kW-hr/kg Cl₂ (as compared with 3.09 kW-hr/kg Cl₂ for a conventional membrane-type cell).

Fig. 21. Cost (electrolysis only) vs. Current Density Diagram for a Chlorine Cell with Membranes and Oxygen Electrodes.

E. Discussion

The total current-density-dependent cost (*i.e.*, $K_E + K_I$) is shown in Fig. 22 for chlorine electrolysis employing cells of the mercury-type, the diaphragm-type, and the membrane-type (without and with an oxygen cathode). The energy cost (K_E) which is representative of the electric energy consumption is also indicated. The assumptions used for these calculations were described above. The optimum operating conditions and the corresponding energy consumption for these cells are listed in Table 6.

The diaphragm-type cell has the lowest current-density-dependent operating cost ($K_E + K_I$). However, the electrolysis process for this type of cell has to be combined with an additional process step to concentrate the alkali in caustic evaporators. Consequently, additional investment and energy are required. Beck¹² estimated that 2.66 kW-hr/kg Cl_2 (9.06×10^6 Btu/ton Cl_2) is the enthalpy change in the evaporator-dissolver. (Inefficiency in electric power production should be considered in a comparison with electric energy requirements of the electrolysis.)

Fig. 22. Cost vs. Current Density for Various Chlorine Cells (only electrolytic process step considered)

The production of chlorine using membrane-type cells is, under certain conditions, economically competitive with chlorine production employing diaphragm-type cells. The additional step in the latter process is of greater significance for smaller plants because costs (per kg Cl₂) resulting from this step are dependent on plant size. In comparison with the diaphragm cell, the membrane-type cell has a higher optimum current density and a higher specific energy consumption, actually 11% higher. If the investment costs could be reduced by decreasing the cost of the membrane, the specific energy consumption would be reduced. For example, if the membrane cost could be halved, the optimum current density of a membrane cell would shift so that the energy consumption would consequently be reduced by 4.5%.

With respect to $K_I + K_E$ and energy consumption, membrane cells with oxygen electrodes look attractive. With this type of cell, energy consumption is expected to be 11% lower than that of the diaphragm cell (no credit for the hydrogen produced). If operation above a current density of

Table 6. Optimum Conditions for Various Chlor-Alkali Cells
According to Model Calculations

Cell Type	Optimum Current Density, A/cm ²	Optimum Cell Voltage, V	Energy Consumption, ^a kW-hr/kg Cl ₂
Mercury	0.84	4.8	3.32
Diaphragm	0.25	3.48	2.77
Membrane	0.35	3.88	3.09
Membrane with reduced cost	0.31	3.70	2.95
Membrane with oxygen cathode	0.40	3.08	2.45

^aElectrolysis only considered.

0.30 A/cm² is impossible, even less energy would be consumed, but investments would be correspondingly larger, and total current-density-dependent costs would be increased.

Mercury-type cells appear the least competitive of the cells listed in Table 6. The figures given in the table for these cells may be somewhat high, but are in accordance with the trend to replace them more and more.