ENERGY SAVINGS BY MEANS OF FUEL CELL ELECTRODES
IN ELECTRO-CHEMICAL INDUSTRIES

PROGRESS REPORT

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SECTION 1ABSTRACT

Zinc electrowinning data, obtained with hydrogen depolarized anodes operating in a plant feed electrolyte at 55°C, are presented in this quarterly report for investigations involving the following:

- a) Performance of an anode containing a low platinum loading, i.e. 0.09 mg/cm² instead of the typical 0.33 mg/cm², and an anode catalyzed with palladium instead of platinum.
- b) Establishment of a feed and bleed system to maintain a constant electrolyte composition.
- c) Exploratory experiments on the effect of the rate and mode of electrolyte flow on the quality of the zinc plate at high current densities.
- d) Performance of the anode with feeds of varying degrees of purification pre-treatment, and containing either 50 or 150 g/l Zn⁺⁺.
- e) The effect upon cell voltage of decreasing the hydrogen flowrate to the anode by dilution of the feed gas with nitrogen.
- f) The effect upon cell voltage of increasing the back pressure of the hydrogen gas fed to the anode.
- g) The effect upon energy consumption and current efficiency of varying the current density and the Zn⁺⁺ concentration.

- h) Trace elemental analysis of a cathodic zinc plate of commercial-size thickness, as produced using the catalytic H_2 anode.
- i) Further comparison of the effects of feed solution purification.
- j) Performance of four different Prototech Pt anodes.

SECTION 2
INTRODUCTION

Preliminary testing of a low loaded (0.09 mg/cm^2) Pt hydrogen diffusion anode for the electrowinning of zinc has been extremely encouraging. Reduction of the platinum content by a factor of over three did not increase anode polarization (as compared to a 0.33 mg/cm^2 electrode) over the current density range of 9 to 72 ASF. Indeed, performance of the 0.09 mg/cm^2 anode was slightly better than the standard above 27 ASF.

In an exploratory experiment, substitution of palladium for platinum as the hydrogen catalyst in the anode resulted in a 50 mv increase in cell voltage at all current densities. This increase is quite small in comparison to the large voltage savings demonstrated by replacing the industrial lead anode with a hydrogen depolarized electrode. Also, the possibility of replacing platinum with a cheaper catalyst is obviously of great interest.

In zinc electrowinning plants, the zinc and sulfuric acid concentrations are kept constant at steady state conditions. This is accomplished by employing a feed and bleed system. Such a system has been developed for experimental cells (2" x 2" and 6" x 6"). Analytical data for both zinc and sulfuric acid concentrations confirm constant steady state levels.

In order to maintain a smooth, dense cathodic zinc plate at high current densities (>36 ASF), it has been found necessary to change the mode and rate of electrolyte stirring. Increasing the current density required a proportional increase in the rate of agitation.

Experiments were undertaken to re-establish the suitability of the hydrogen depolarized catalytic platinum anode for the handling of plant feed solutions, and to examine the dependence, if at all, of cell performance upon feed purification pre-treatment. Steady-state (i.e., continuous liquid electrolyte feed and bleed) operation of a 2" x 2" cell has indeed confirmed the low cell voltage requirement for handling a typical Anaconda plant feed.

Furthermore, current efficiency and power consumption have been found to be insensitive to the degree of purification pre-treatment of the feed, at liquid electrolyte concentrations of 100 g/l H_2SO_4 and both 50 and 150 g/l Zn^{++} . However, as noted previously, both current efficiency and power consumption depend on the ratio of the acid and Zn^{++} concentrations.

Additional experiments have been performed to determine the effect upon cell voltage of decreasing the feed of hydrogen gas to the catalytic anode of a 6" x 6" cell, from values rather in excess of to values below the exact amount theoretically required to maintain the current. It was found that, when the current density was fixed, the cell voltage

and consumption of hydrogen remained remarkably constant, the latter at the theoretical minimum, until the H_2 feed rate was decreased below the theoretical minimum. At that point the cell voltage began to increase, indicating the production of molecular oxygen at the anode.

Another series of experiments was conducted with a 6" x 6" cell in which the pressure of pure hydrogen gas fed to the catalytic anode was increased stepwise to a value of 32 cm H_2O above atmospheric. This effected a decrease in cell voltage from 1.68v to 1.51v.

In a 6" a 6" (active electrode area) cell, the current density was varied between 36 and 90 ASF, at Zn^{++} concentrations of 50, 80 and 90 g/l. The current efficiency was observed to increase modestly with current density, except at the lowest Zn^{++} concentration, at which the current efficiency was insensitive to current density. Power consumption (in KWH/lb zinc) increased consistently with current density and Zn^{++} concentration.

A trace element analysis of the zinc plate deposited at the cathode demonstrated high purity and, as reflected by a very low sulfur content, the solidity and non-porosity of its surface.

A comparison of the performance of the catalytic Pt anode using feed electrolyte solutions of four different methods of pre-treatment revealed a remarkable insensitivity to feed purification approach.

Finally, discharge curves were obtained for four Prototech Pt anodes of widely varying times in service, but essentially equal Pt loading. The performances of the four anodes were nearly indistinguishable.

SECTION 3

TECHNICAL DISCUSSION

Zinc Electrowinning

Pure Hydrogen Fuel

3.1 Performance of Low Loaded Platinum and Typically Loaded Palladium Anodes

3.1.1 Background and Experimental

During the previous contract period, zinc electro-winning experiments were conducted with hydrogen anodes having a Pt catalyst loading of about 0.3 mg/cm^2 . Preliminary experiments with electrodes containing approximately one third of the regular Pt loading, i.e. 0.090 mg Pt/cm^2 , or 0.3 mg/cm^2 Pd instead of Pt have been carried out during this contract period with encouraging results.

A comparison of the discharge curves of the various types of anodes is shown in Figure 1. The data were obtained in a 2" x 2" cell. Studies with low loaded Pt anodes as well as Pd anodes will be continued, and studies of anodes with low loaded Pt-Pd mixtures will be initiated.

3.1.2 Discussion

The three discharge curves shown in Figure 1 are linear. The 0.3 mg/cm^2 Pd curve is parallel to that of the 0.3 mg/cm^2 standard Pt curve but is higher by about 0.05 volts. The low loaded Pt anode curve is also linear, and

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while not quite parallel to the above two curves it is very close to the standard 0.3 mg/cm^2 Pt data. It remains for life tests to show the stability of the performance of low loaded Pt and typically loaded Pd electrodes. Until now, 0.3 mg/cm^2 Pt anodes have been tested for hundreds of hours in zinc electrowinning hardware without signs of performance deterioration, and they are considered to be the standard for comparison. In view of the known ability of palladium to act as a hydrogen "sponge" as well as a catalyst, low catalyst loadings consisting of Pd-Pt mixtures will be investigated.

3.2 Feed and Bleed Experiments at 50 and 150 g/l Zinc and 100 g/l H_2SO_4

3.2.1 Background and Experimental

Industrial Zn electrowinning is carried out under feed-and-bleed conditions in which constant, steady-state Zn^{++} and free H_2SO_4 acid concentrations in the bulk electrolyte are maintained. Under these conditions a near neutral solution containing a high concentration of Zn^{++} is fed into the cell and a low Zn^{++} , but high acid, solution is bled from the cell with the bleed used as a leach of zinc concentrate to prepare a new near neutral feed.

These conditions were approximated in a series of experiments conducted in the 2" x 2" cell, in which the steady state Zn^{++} concentration was 50 or 150 g/l while the acid was held constant at 100 g/l. A comparison of typical discharge curves at steady state concentrations is shown in Figure 2.

In another series of experiments utilizing an electrolyte of ca. 50 g/l Zn^{++} and 100 g/l H_2SO_4 , plating was carried out at current densities between 36 ASF and 144 ASF, the duration of the runs chosen so as to produce comparable weights of Zn deposit at each current density. Table 1 shows the steady state analytical data for both Zn^{++} and H_2SO_4 concentrations of the bulk electrolyte, while Table 2 shows the results of the effect of increased current densities on current efficiency and power consumption at the above steady state concentrations.

Utilizing the steady state concentrations of zinc and acid during four of the electrowinning runs at 55°C , listed in Table 1, we found unexpectedly (see Table 2) a substantially constant current efficiency of 86%-87%, substantially independent of current density in the range of 36-144 ASF.

When the cell was operated at 100 g/l Zn and above, with the same acidity, the current efficiency ranged from 90% to ca. 94% with increasing current density. The fact that the current efficiency is lower at the 50 g/l Zn^{++} than at the 100 g/l Zn^{++} concentration (both electrolytes containing about 100 g/l of free acid) is clearly attributable to the lower free acid-to-zinc ratio of the latter.

Figure 2 shows the comparison of discharge curves obtained at high and low Zn^{++} concentrations. The two curves

TABLE 1

Zn^{++} and H_2SO_4 concentrations during an
electrowinning test under feed and bleed
(steady state) conditions

Elapsed Time (Hours)	Zn^{++} g/l	H_2SO_4 g/l
0	49.72	100.54
1	49.41	100.69
2	49.34	100.25
3	49.87	101.45
4	49.65	100.59
5	49.82	100.71

TABLE 2

Effect of current density on current efficiency
and power consumption and 100 g/l
 H_2SO_4 (steady state concentrations) at $55^\circ C$

Current Density (ASF)	Duration of run (Hours)	Current Efficiency (%)	Power Consumption KWH/lbs Zn
36	8	87.1	0.59
45	7	89.4	0.64
72	4	87.4	0.70
90	3	86.6	0.80
120	3	86.1	0.97
144	3	86.1	1.09

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are linear but not parallel. Here, the 50 g/l Zn^{++} electrolyte has a higher conductivity than that of 150 g/l Zn^{++} , at a fixed acid level (100 g/l). The difference is about 4.6×10^{-3} Ω -sq ft. Thus, a concentration will be determined experimentally that balances the benefit of higher conductivity at lower concentration with that of higher current efficiency at higher concentration.

3.3 The Effect of the Mode and Rate of Electrolyte Stirring on the Quality of Cathodic Zinc Plate

In a series of experiments conducted at fixed Zn^{++} and H_2SO_4 concentrations and at various current densities, it has been found that both the mode and rate of mixing of the electrolyte affect the quality of cathodic zinc deposited. As the current density is varied, the rate of electrolyte agitation must be changed in order to maintain a smooth and dense zinc cathodic plate. It has been found that at any current density the absence of agitation caused H_2 bubbles to adhere to the zinc cathode, which resulted in the development of irregular depressions from the bottom to the top of the plate. On the other hand, if agitation was too fast, vertical stripes appeared in the deposited zinc. In most cases, when a slow flow of electrolyte between the electrodes was maintained, i.e. when turbulence was avoided, the physical quality of the zinc plate was superior.

SECTION 3 CONTINUED

TECHNICAL DISCUSSION

The Hydrogen Anode for Electrowinning of Zinc

3.4 Comparison of Performance Using Filtered Plant Feed Solution and Unfiltered and Filtered Purified Zinc Sulfate (B & W) Solutions

3.4.1 Background and Experimental

During the previous contract period, it was demonstrated that the Prototech hydrogen depolarized anode may be successfully used in the electrowinning of zinc from Anaconda plant feed solution at 55°C, and that the required power consumption in KWH/lb zinc was less than half that of a conventional lead anode based cell. The results were obtained in a batch operation, during which the Zn^{++} concentration decreased continuously while the acid concentration increased.

The performance of a 2" x 2" (active electrode area) Prototech anode based cell, using solutions of identical 100 g/l sulfuric acid concentrations, either 50 or 150 g/l Zn^{++} , and with 3 varieties of purification pre-treatment, has now been examined under steady-state (feed and bleed) conditions, and is reported in Tables 3 and 4.

3.4.2 Discussion

For a filtered plant feed and both unfiltered and pH 5 filtered, purified ZnSO_4 (B & W) solutions, all of which were maintained at a constant Zn^{++} concentration of 50 g/l (Table 3),

TABLE 3

Comparison of Performance using Filtered Plant Feed
Zn Solution, Unfiltered Purified ZnSO_4 Solution and
pH-5 Filtered ZnSO_4 Solution

Experimental Conditions:

Current Density: 90 ASF

Cell Size: 2" x 2"

Pt Anode Loading: 0.33 mg Pt/cm²

Temperature: 55°C

Electrolyte: 50 g/l Zn^{++}

100 g/l H_2SO_4

0.1 g/l animal glue

Steady State feed and bleed.

Source of Zinc	Current Efficiency	Energy Consumption (KWH/lbs Zinc)
Plant feed filtered Solution	87.1%	0.81
Unfiltered purified ZnSO_4 (B & W) Solution	86.6%	0.80
pH-5 filtered purified ZnSO_4 (B & W) Solution	85.0%	0.82

TABLE 4

Comparison of Performance using 50 g/l Zn^{++}
and 150 g/l Zn^{++} at fixed acid Concentration

Experimental Conditions:

Current Density: 90 ASF

Cell Size: 2" x 2"

Pt Anode Loading: 0.33 mg Pt/cm²

Temperature: 55°C

Electrolyte: 100 g/l H_2SO_4

0.1 g/l Animal glue

Steady State feed and bleed.

Zn^{++} Concentration and Source	Current Efficiency	Energy Consumption (KWH/lbs Zinc)
<u>Plant feed filtered</u>		
Solution		
50 g/l	87.1%	0.81
150 g/l	94.2%	0.94
<u>Unfiltered, purified</u>		
$ZnSO_4$ (B&W) Solution		
50 g/l	86.6%	0.80
150 g/l	95.3%	0.93
<u>pH 5 filtered, purified</u>		
50 g/l	87.3%	0.80
150 g/l	94.8%	0.93

there are negligible differences in current efficiency (range 85-87%) and power consumption (range 0.80-0.83 KWH/lb zinc).

Additional runs (Table 4) in which the steady-state Zn^{++} concentration was raised to 150 g/l confirm the observation made in section 3.2 of this report, that both the current efficiency and power consumption increase as the ratio of acid to Zn^{++} concentrations decreases. These results further confirm that performance--in terms of both current efficiency and power consumption--is independent of further purification pre-treatment of either the Anaconda plant or B & W feed solutions.

3.5 The Effect of Feed Gas Hydrogen Concentration upon The Cell Voltage at Constant Total Gas Feed Rate and Current Density

3.5.1 Experimental Design

In the scaled-up 6" x 6" (active electrode area) cell, the hydrogen flowrate through to the catalytic platinum anode was reduced, at a constant total gas flow of $193 \text{ cm}^3/\text{minute}$, by mixing the hydrogen with varying proportions of nitrogen. The electrical current was maintained at 9 amps (36 ASF), and the consumption of hydrogen was monitored.

For a theoretical consumption of 1 mole of hydrogen for every 2 equivalents of electricity passed through the cell, the H_2 requirement is $7.5 \text{ cm}^3 \text{ (STP)/minute per amp}$, or $67.5 \text{ cm}^3 \text{ (STP)/minute}$ at 9 amps. Thus, when the H_2 feed rate is lowered

to the range of $67.5 \text{ cm}^3 (\text{STP})/\text{minute}$ or below, alternative electrode reactions are necessary to sustain a 9 amp current. The prevalence of such reactions will engender a change in overall cell voltage.

The results obtained at 55°C with 130 g/l Zn^{++} and 100 g/l H_2SO_4 are reported in Table 5 and Figure 3.

3.5.2 Discussion

The anode functions remarkably efficiently up to the point of 100% H_2 utilization. At H_2 feed rates above that required by stoichiometry there is residual, unconsumed hydrogen which can be recirculated to the anode.

In the absence of sufficient hydrogen to sustain the reaction, $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$, molecular oxygen is apparently produced as well at the catalytic anode, as in conventional zinc electrowinning cells, and the cell voltage increases correspondingly, since then a mixture of two electrowinning reactions takes place:

3.6 The Effect of Hydrogen Gas Back Pressure upon the Cell Voltage at Constant Current Density

3.6.1 Experimental Design

Experiments were conducted to examine the effect of changing the pressure of a pure hydrogen feed upon catalytic

TABLE 5

Effect of Feed Hydrogen Gas Concentration upon
the Catalytic Pt Anode Performance

Experimental Conditions:

Current Density: 36 ASF

Cell Size: 6" x 6"

Temperature: 55°C

Electrolyte: 100 g/l H₂SO₄
 0.1 g/l Animal glue

<u>H₂ Gas Flow Rate* (cm³/minute)</u>	<u>Cell Voltage (Volts)</u>
193	1.60
150	1.60
125	1.60
90	1.60
75	1.60
68.8	1.61
67.5	1.64
64.3	1.64
57.7	1.72
50.0	1.74

*Total feed gas flow rate (H₂ + N₂) was 193 cm³/minute while varying H₂/N₂ ratio. H₂ consumption as consumed by the catalytic Pt anode was essentially constant at 67.5 cm³/minute until the H₂ feed rate went below that value, after which all the H₂ was consumed.

Figure 3
Effect of H_2 Feed Rate on Cell Voltage

Pt anode performance, as measured by the full cell voltage. The pressure was adjusted by varying the depth of submersion in water of a tube connected to the H_2 exit stream. The overall voltage drop was measured in a 6" x 6" cell operating at 36 ASF, 55°C , and a hydrogen feed rate 50% in excess of the minimum. Results are presented in Table 6 and Figure 4.

3.6.2 Discussion

Increasing the hydrogen back pressure from zero to 32 cm H_2O (gauge; 1 atm $\approx$ 1033 cm H_2O) results in a maximum 0.15 volt improvement in cell performance. This corresponds to a power consumption decrease from 0.674 to 0.614 KWH/lb zinc, i.e., a saving of 0.06 KWH/lb zinc. The cell voltage initially drops sharply with increasing H_2 back pressure and then decreases more slowly beyond a pressure of 10 cm H_2O .

Enhancing the hydrogen back pressure thus promotes the efficient functioning of the Pt electrode. This is due, at least in part, to the prevention of the liquid electrolyte's flooding the cloth electrode surface, and to the promotion of gaseous hydrogen diffusion into the catalytic surface.

It is conceivable that above a certain level of back pressure, one not reached in the experiments, there will either be damage to the electrode surface, or the liquid electrolyte will be prevented from penetrating the electrode surface. In the latter case, contact between hydrogen gas,

TABLE 6

Effect of Hydrogen Gas Backpressure upon
the Catalytic Pt Anode Performance

Experimental Conditions:

Current Density: 36 ASF

Cell Size: 6" x 6"

Electrolyte: 130 g/l Zn^{++} 100 g/l H_2SO_4

0.1 g/l Animal Glue

Temperature: 55°C

 H_2 Excess: 50%

<u>H_2 Gas Backpressure (cm H_2O)</u>	<u>Cell Voltage (Volts)</u>
0	1.68
1.0	1.66
2.0	1.65
5.0	1.63
9.5	1.60
12.0	1.59
14.0	1.58
16.5	1.57
20.0	1.56
24.0	1.55
28.0	1.54
32.0	1.53

Figure 4

Effect of Hydrogen Gas Backpressure
ON
CELL VOLTAGE

H^+ -containing liquid electrolyte and solid catalytic electrode will be sub-optimal, and the cell voltage will again rise; i.e., there will be a minimum in the curve of cell voltage vs. H_2 back pressure. The optimal back pressure would have to be determined in a pilot plant size cell, with electrode construction material and cell assembly analogous to those of the ultimate industrial unit.

3.7 The Effect of Current Density upon Energy Consumption and Current Efficiency at Various Zn^{++} Concentrations

3.7.1 Introduction

In Section 3.4 the Zn^{++} concentration was shown to affect both current efficiency and energy consumption, at a constant current density and acid concentration. In this section we report the effects of varying current density and Zn^{++} concentration upon energy consumption and current efficiency. Results obtained at $55^\circ C$ with a 6" x 6" cell are presented in Table 7 and Figure 5. These results complement those presented in Section 3.2.

3.7.2 Discussion

It is generally accepted in the zinc electrowinning literature¹ that, all else being equal, current efficiency increases somewhat with the applied current density and that the energy consumption (in KWH/lb zinc) is directly related to the current density.

1. I.W. Wark, "The Electrodeposition of Zinc from Acidified Zinc Solution," J. Appl. Electrochem. 9, 721 (1979).

TABLE 7

The Effect of Current Density upon Energy
Consumption and Current Efficiency at
Various Zn^{++} Concentrations

Experimental Conditions:

Cell: 6" x 6"

Anode Loading: 0.30 mg Pt/cm²

Temp: 55°C

H₂SO₄: 100 g/l

Animal Glue: 0.1 g/l

Steady State feed and bleed

pH-5 filtered (B & W) ZnSO₄

Experiment Number	Zn ⁺⁺ (g/l)	Current Density (ASF)	Duration of Run* (Hours)	Current Efficiency	Energy Consumption (KWH/lb Zinc)
1	50	36	8.0	87.7%	0.59
2	50	45	6.4	87.4%	0.65
3	50	54	5.3	86.9%	0.68
4	50	72	4.0	87.5%	0.78
5	50	90	3.2	87.3%	0.80
6	50	90	8.0**	85.1%	0.91
7	80	36	8.0	89.2%	0.61
8	80	54	5.3	91.4%	0.71
9	80	90	3.2	94.3%	0.98
10	80	90	8.0**	93.0%	0.99
11	90	36	8.0	91.0%	0.63
12	90	54	5.3	93.6%	0.76
13	90	90	3.2	94.7%	1.00
14	90	90	8.0**	93.3%	1.00

* Run duration was selected to equalize the deposits at each current density.

** At each zinc concentration a longer (8 hours) run was conducted to yield an approximately commercial size thickness of zinc plate.

% Current
Efficiency

FIGURE 2

The Effect of Current Density upon Current Efficiency at Various Zn^{++} Concentrations

The current efficiency-current density relationship holds only partially. At a relatively high acid to Zn^{++} concentration ratio (100:50 in gm/l), the current efficiency values are all below 90% and appear to be effectively independent of current density over a wide range of current densities (36-90 ASF). Additional results (Table 2) show that at current densities as high as 144 ASF, and under the same experimental conditions, the current efficiency does not exceed 88%. However, as the ratio of the dissolved acid to Zn^{++} concentration decreases from a value of 100:50, the current efficiency becomes dependent upon current density as expected.

At the constant acid concentration of 100 g/l H_2SO_4 , the energy consumed per lb of zinc deposited increases with both the current density and the Zn^{++} concentration. Its increase with the current density (which is offset by increasing rates of zinc deposition) is related to energy losses associated mostly with heat generation. The increase in energy consumption with Zn^{++} concentration, at fixed current density and acid concentration, is related to the corresponding decrease in electrolyte conductivity (see Figure 2).

3.8 Trace Analysis of a Commercial-Size Thickness Cathodic Zinc Plate Produced Using the Catalytic H_2 Electrode

3.8.1 Introduction

The cathodic zinc plate produced under the conditions of experiment 14 in Table 7 was submitted for a trace element

analysis. The results are summarized in Table 8, where they are compared with the trace analysis of the feed solution from which the zinc plate was deposited.

3.8.2 Discussion

Impurity metals having a redox potential more negative than zinc (in the reaction: $\text{Zn} \rightarrow \text{Zn}^{++} + 2\text{e}^-$) tend to deposit along with the zinc at the cathode plate. These metals include Cd, Cu, Ag and Pb.

In light of literature data ¹ and in the opinion of Anaconda's zinc experts, the analysis of the feed solution indicates a typical and acceptable impurity content of plant feed. The amount of impurities found in the cathodic zinc plate is also typical of industrial zinc electrodeposition plates and, in Anaconda's judgment, indicates very good quality cathodic zinc.

Table 8 shows that Cd in particular tends to be depleted preferentially at the zinc cathode. The analysis also shows that Mn^{++} ion, present in fairly large amounts in the feed solution, does not contaminate the cathode-deposited zinc plate.

The sulfur content of the cathodic plate is usually taken as an indicator of the plate's porosity. The more porous the plate, the more H_2SO_4 solution is trapped in the pores, and thus the higher the sulfur content. In Anaconda's judgment, the observed sulfur content (<10 ppm) signifies a desirably solid, nonporous cathodic plate.

1. AIME World Symposium on Mining and Metallurgy of Lead and Zinc, Vol. II, The Am. Inst. of Mining, Metallurgy and Petroleum, Eng. Inc., NYC, 1970.

TABLE 8

Trace Analysis of a Cathodic Zn plate Produced by
the H₂ Catalytic Pt Anode

Impurity	<u>Concentration(Parts per million parts zinc)*</u>	
	<u>In Electrolyte Feed</u> <u>Solution</u>	<u>In Cathodic-formed</u> <u>Zn Plate</u>
Pb	2.57	20
Fe	12.9	6
Cd	26.3	70
Cu	15.4	10
Ag	N.D.	<1
Sn	0.5	<10
Mn	17986.	<5
S	873.333	<10

* The analyses were performed by the analytical laboratories of the Anaconda Company.

3.9 Further Comparison of the Effects of Feed Solution Purification Procedures

3.9.1 Introduction

In Section 3.4 we reported the results of experiments conducted in the 2" x 2" cell, in which the performance using plant feed solution (1) has been compared with that using purified non-filtered ZnSO_4 (B & W) solution (2) and pH-5 filtered solution (3). Additional purification procedures have been investigated: (4) Air stream dissolution and oxidation of the feed solution at pH-5, followed by filtration of all solids at the same pH; (5) Air stream dissolution and oxidation at pH-5, followed by filtration, zinc dust treatment (zinc dust added to the extent of 10% of the total zinc content in the feed solution) and refiltration. Table 9 summarizes the results obtained with the 6" x 6" cell the variously purified solutions, under varying experimental conditions.

3.9.2 Discussion

From the results presented in Table 9 it may be concluded that there is essentially no effect of method of feed purification (1)-(5) upon cell performance, as measured by current efficiency and power consumption. This agrees with data for the 2" x 2" cell as reported in Section 3.4.

At a given Zn^{++} concentration there is a very slight increase in current efficiency, with practically no change in the energy consumption, in going from purification methods

TABLE 9

The Effect of Various Purification Procedures and Zinc Concentrations upon Cell Performance

Experimental Conditions:

H₂SO₄: 100 g/l

Animal Glue: 0.1 g/l

Temp: 55°C

Steady State feed and bleed

Experiment Number	Zn ⁺⁺ Concentration (g/l) and method of feed purification		Current Density	Duration of Run (Hours)	Current Efficiency	Energy Consumption (KWH/lbs zinc)
	<u>Concentration</u>	<u>Method</u>				
1	90	(4)	90	3.2	94.8%	0.99
2	90	(5)	90	3.2	94.9%	0.99
3	90	(3)	90	3.2	94.2%	1.00
4	90	(2)	90	3.2	94.1%	1.00
5	100	(4)	90	3.2	94.5%	1.02
6	100	(5)	90	3.2	94.7%	1.02
7	100	(2)	90	3.2	93.5%	1.03
8	85	(4)	90	3.2	93.0%	0.98
9	85	(5)	90	3.2	93.2%	0.98
10	85	(5)	54	5.3	91.6%	0.74
11	85	(5)	36	8.0	90.1%	0.62

(2) and (3) to (4) and (5) (compare experiments 1 and 2 with 3 and 4, and compare 5 and 6 with 7).

In addition, experiments 9, 10 and 11 confirm the effects of current density upon current efficiency and power consumption, as discussed in Section 3.5. Similarly, comparison of experiments 2, 6 and 9 reveals again the effects of Zn^{++} concentration upon current efficiency and power consumption, as also discussed in Section 3.7.

It can generally be concluded that i) the various purifications methods so far attempted have essentially no influence upon cell performance, and ii) the performance at a given set of conditions (i.e., acid concentration, temperature, current density, and duration of run) is determined mostly by the acid to Zn^{++} concentration ratio.

It is conceivable, however, that extended purification following the industrial methods step by step could further improve the current efficiencies with solutions of high acid to zinc ratio.

3.10 Comparison of Performance of Four Different 6" x 6" Platinum Anodes Produced by the Prototech Company

3.10.1 Introduction

Four different 6" x 6" anodes produced by the Prototech Company were tested in the 6" x 6" zinc deposition cell under identical experimental conditions. The Pt loading of each anode is listed in Table 10, while a comparison of anode performance is made in Table 11. See also the discharge curves (cell voltage vs. current density) of Figure 6.

TABLE 10Comparison of Platinum Loadings of Four
Prototech Company Catalytic Anodes

<u>Anode Number</u>	<u>Pt Loading (mg Pt/cm²)</u>
1	0.33
2	0.30
3	0.30
4	0.29
<hr/>	<hr/>

TABLE 11

Comparison of Performance of Four
Prototech Company Catalytic Pt Anodes

Experimental Conditions:100 g/l Zn^{++} H_2SO_4 : 100 g/l

Temp: 55°C

Animal Glue: 0.1 g/l

Steady State feed and bleed

Current Density (ASF)	<u>Cell Voltage (volts)</u>			
	<u>Anode Number</u>			
	1	2	3	4
0	0.74	0.75	0.75	0.76
9	0.98	1.03	1.00	0.99
10	1.16	1.20	1.18	1.17
27	1.36	1.37	1.36	1.35
36	1.52	1.56	1.53	1.53
45	1.68	1.71	1.70	1.71
54	1.85	1.89	1.88	1.89
63	2.01	2.06	2.05	2.08
72	2.19	2.26	2.23	2.26
81	2.36	2.42	2.40	2.44
90	2.55	2.59	2.58	2.63

3.10.2 Discussion

The data of Table 10 indicate little difference among the four 6" x 6" Pt anodes, and suggest that they should be nearly equally effective. It should also be noted that anode #1 had been used in the Zn^{++} cell for several hundred hours, anode #2 for ca. 200 hours, and anodes #3 and #4 for a few tenths of an hour. No significant difference in performance is indicated with any of the above four anodes.

Figure 6 shows a typical discharge curve for anode #3 (the curves for the four anodes practically overlap, and therefore only one has been drawn). Since the discharge curve remains linear up to 90 ASF (22.5 Amps applied current) there is no apparent significant change in anode polarization or IR drop at that current density. Furthermore, we have ample reason to believe that even higher current densities are feasible using the Prototech Pt hydrogen anode.