MASTER

COO-4881-13

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

PROGRESS REPORT

For the period August 1, 1979 to October 31, 1979

Robert J. Allen, Walter Juda, and Robert W. Lindstrom

Submitted by
Prototech Company
70 Jaconnet Street
Newton Highlands, Massachusetts 02161

December 12, 1979

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Prepared for
The U. S. DEPARTMENT OF ENERGY
UNDER CONTRACT NO. ET-78-C-02-488.
Modification No. 002

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

CONTENTS

Section	Page
1 ABSTRACT	1
2 INTRODUCTION	2
3 TECHNICAL DISCUSSION	
The Hydrogen Anode for the Electrowinning of Zinc	3
3.1 Technical Considerations	3
3.1.1 Cell Reactions for H_2 Depolarized Anode	3
3.1.2 Cell Design - 2" x 2" Hardware	3
3.1.3 Cell Design - 6" x 6" Hardware	6
3.2 History of Program	9
3.3 Test Data	11
3.3.1 Analysis of Zinc Plant Feed Concentrates	11
3.3.2 Zinc Plating- H_2 Depolarized Anode	11
3.3 Future Experimentation	15

FIGURES

Number	Page
1 Front Cross-Section View : 2" x 2" Zinc Electrowinning Cell	4
2 Side View of 6" x 6" Zinc Electrowinning Cell	7
3 Cross-Section of Zinc Electrowinning Cell 6" x 6"	8

TABLES

Number	Page
1 Analysis of Zinc Plant Feed	12
2 Analysis of Insoluble Residue from Water Dissolution of Zinc Plant Feed Concentrate	13
3 Zinc Plating from Plant Feed H ₂ Depolarized Anode - 2" x 2" Cell	14

SECTION 1ABSTRACT

The Modification No. 002 to DOE Contract No. ET-78-C-02-4881 which has a starting date of August 1, 1979, was signed on September 21, 1979. During August and September 1979, experimentation was interrupted and purchase orders for equipment were delayed until the signing. Instead, emphasis was put (1) on the preparation of the annual report including the analysis and write-up of the data obtained in carrying out the additional July 1979 task which involved the operation of the newly-built 6" x 6" cell; and (2) on interaction with Anaconda staff members for the purpose of planning the pre-pilot plant experimentation called for in the above modification No. 002. Accordingly, experimental investigations commenced in October, 1979.

Initial efforts have been directed toward assembling test hardware and evaluation of a new zinc plant feed. A complete chemical analysis of the feed is reported.

Utilizing the 2" x 2" (active electrode area) hardware and techniques developed under Contract No. ET-78-C-02-4881, 6 hour zinc electrowinning tests have demonstrated a current efficiency of greater than 90% with an energy consumption of 0.54 to 0.55 KWH/lb of zinc. For these tests, 0.1 g/l gelatin was employed as an electrolyte additive and the resultant zinc plates were bright, smooth and compact.

SECTION 2

INTRODUCTION

Substitution of a hydrogen (pure H_2 stream) depolarized anode for the conventional industrial lead electrode has demonstrated an energy savings of over 0.6 KWH/lb of zinc. These data were obtained at $55^{\circ}C$ in 2" x 2" and 6" x 6" (active area) zinc electrowinning cells employing a plant electrolyte containing 155 g/l zinc and 98 g/l sulfuric acid. Zinc plates obtained in six hour tests showed excellent physical characteristics and high purity. The hydrogen depolarized anodes utilized were proprietary Prototech Company carbon cloth based gas diffusion electrodes containing $0.33 \pm 10\% \text{ mg/cm}^2 \text{ Pt}$.¹

Under the current contract, two tasks will be investigated. First, initial performance and durability tests will be run in the 2" x 2" hardware for hydrogen depolarized anodes with platinum content well below the $0.33 \text{ mg/cm}^2 \text{ Pt}$ electrodes previously employed. And second, operating conditions including current density, temperature, acidity, electrode spacing and timing of electrode removal will be optimized in a 6" x 6" electrowinning cell. This data will serve as a basis for a commercial pilot plant. All of the preceeding will employ an actual zinc plant feed.

1. Annual Report #COO-4881, October, 1979, "Energy Savings by means of Fuel Cell Electrodes in Electro-chemical Industries", Section 3.

SECTION 3

TECHNICAL DISCUSSION

The Hydrogen Anode for the Electrowinning of Zinc

3.1 Technical Considerations

3.1.1 Cell Reactions for H₂ Depolarized Anode

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

3.1.2 Cell Design - 2" x 2" Hardware

Figure 1 is a front cross-section view of the 2" x 2" electrowinning cell. It is a modular construction with no metal parts except for the aluminum cathode blank.

1. Oxidation Potentials, Second Edition, Wendell M. Latimer, Prentice Hall, Inc., 1959.

2" x 2"
 FIGURE 1, FRONT CROSS-SECTION VIEW
 Zinc Electro-winning Cell

The electrode assembly consists of the hydrogen anode (with associated hydrogen feed and bleed) and the cathode with a fixed 2.0 inch distance separating the electrodes. The cathode can be easily removed from the assembly for zinc stripping but the construction requires that the anode be removed from the electrolyte at the same time (different from the 6" x 6" cell). The void space between the electrodes is filled with electrolyte when the electrode assembly, which is suspended on PVC holders, is lowered into a battery jar containing the plant electrolyte. The DC current connections and the voltage probes are located at the top of the cell; they are not in contact with the electrolyte. The 15 mil aluminum cathode blank serves as that electrode's current collector as the zinc plate is building up, while a $\frac{1}{4}$ " thick Stackpole Company 20/20 carbon window frame serves as the anode current collector.

The electrolyte temperature in the battery jar is controlled by a mercury switch temperature controller connected to a glass coated heating rod. Stirring is afforded by a Teflon coated magnet rotated with a magnetic stirrer. Auxiliary cell equipment includes a rectified power supply, a 0-2 Amp Amp meter, a digital volt meter and a soap bubble flow meter for monitoring the hydrogen gas flow.

3.1.3 Cell Design - 6" x 6" Hardware

The 6" x 6" hardware described in figure 2 and 3 is quite similar to that previously shown in figure 1 for the 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 is incorporated in the anode gas plenum.

A tank-reservoir system is employed. The main tank, which contains the cell, holds 9 liters of electrolyte and the heating equipment described in section 2.1.2. A reservoir is attached so that feed and bleed conditions can be instituted for longer runs than 6 hours or for continuous operation.

Electrolyte circulation is provided by a pump-flow distributor arrangement. The electrolyte is pumped through a 6" long ($\frac{1}{4}$ " ID) distributor containing 1/16" holes spaced 1/4" apart. Maximum flow is 8 liters per minute with the flow from bottom to top. The system is easily adaptable to other electrolyte flow arrangements.

A Vari-Tech Company Model VT-1176-A Coulometer, with a range of 0.01-20 Amps is incorporated in the electrical circuitry of the 6" x 6" zinc electrowinning cell. Total coulombs of electricity consumed are recorded with this electronic-digital readout instrument.

FIGURE 2, SIDE VIEW OF 6"x6" ZINC ELECTROWINNING CELL

FIGURE 3, CROSS SECTION OF ZINC ELECTROWINNING CELL

3.2 History of Program

The initial experimentation was carried out under DOE Contract No. ET-78-C-02-4881 from August 1, 1978 to July 31, 1979 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 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. An unexpectedly large voltage saving of nearly two volts resulted (ca. 3.5V with the Pb anode; 1.5V with the H_2 -anode). 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. In July, 1979 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).

Energy and cost estimates have been made based on the above summarized experimentation. Taking into account energy losses incurred by producing hydrogen from petroleum coke, an

overall energy saving, at a current density of 30ASF, has been estimated at 40%, compared with conventional zinc electro-winning by means of lead anodes, also at the conventional current density of 30ASF. In terms of purchased electric energy the hydrogen anode process requires of the order of 0.6 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 are predicted for the hydrogen anode process. Finally, due to the absence of lead, major investment savings appear possible by operation at higher temperatures and higher current density with the H₂-anode than is permissible with the lead anode.

3.3 Test Data

3.3.1 Analysis of Zinc Plant Feed Concentrate

The zinc bearing plant feed to be utilized during the current contract was received as a powder prepared by evaporation of a plant liquor. Almost total (>98%) dissolution of the powder was effected when employing water as a solvent. A typical 155 g/l zinc feed was prepared, pH 5.0, and the solution analyzed for major and trace elements.¹ Refer table 1.

The insoluble residue from the water dissolution was also analyzed. This material was essentially all zinc (oxide and/or sulfate) contaminated with the trace metals shown in table 2.

3.3.2 Zinc Plating

H₂ Depolarized Anode

A 150 g/l zinc electrolyte was spiked with 98 g/l sulfuric acid and 0.1 g/l gelatin and zinc plating tests were run in the 2" x 2" hardware at 55°C to obtain preliminary data for this plant feed. For three, six hour tests, in which the sulfuric acid content of the electrolyte was allowed to build up while the zinc content was somewhat depleted, current efficiencies in excess of 90% were achieved and bright, compact zinc plates were obtained. Energy consumption, as shown in table 3 was 0.54 to 0.55 KWH/lb zinc.

1. Analysis through the courtesy of the Anaconda Company, M.R.G. Research Analytical Laboratories.

TABLE 1ANALYSIS OF ZINC PLANT FEEDSOLIDS ANALYSIS

ZINC = 33%

Sulfur = 18.0%

Magnesium = 2.0%

ANALYSIS OF A 155 g/l ZINC SOLUTION (pH 5.0)

<u>Compound Concentration</u>		<u>Element Concentration</u>	
CaO	0.53 g/l	Mn	2.78 g/l
MgO	9.20 g/l	K	0.06 g/l
		Cd	0.004 g/l
		Na	0.19 g/l

SPECTROGRAPHIC ANALYSIS - DETECTED

<u>Element Concentration</u>		<u>Element Concentration</u>	
Al	0.002 g/l	Cu	<0.002 g/l
Ba	<0.002 g/l	Fe	0.002 g/l
Co	0.009 g/l	Si	0.002 g/l

SPECTROGRAPHIC ANALYSIS - NOT DETECTED

Ag	Be	Cr	In	Ni	W
Sb	Bi	Ga	Pb	Su	V
As	B	Ge	Mo	Ti	

TABLE 2

ANALYSIS OF INSOLUBLE RESIDUE
FROM
WATER DISSOLUTION OF ZINC PLANT FEED CONCENTRATE

Semi Quantitative Analysis

Major Component: Zinc

% Weight of Elements

<u>Element</u>	<u>% Weight</u>	<u>Element</u>	<u>% Weight</u>
Al	0.02	Ge	<0.001
Sb	<0.005	In	<0.001
As	<0.005	Fe	0.2
Ba	<0.001	Pd	0.005
Be	0.0001	Mg	0.05
Bi	<0.001	Mn	0.10
B	0.005	Mo	<0.001
Cd	<0.001	Ni	<0.001
Ca	0.5	Si	1.0
Cr	0.001	Sn	0.001
Co	0.003	Ti	0.001
Cu	0.005	W	<0.01
Ga	<0.001	V	0.001

TABLE 3

ZINC PLATING FROM PLANT FEEDH₂ DEPOLARIZED ANODE2" x 2" CellAnode: Standard 0.33 $\pm 10\%$ mg/cm² Pt RA19 Type Electrode

Anode to Cathode Spacing: 2 inches

Stirring: Magnetic Stirrer

14

Test	Feed Composition g/l			Test Hours	Cell Temp °C	Current Density	Coulombs	Grams Plated	Cell Voltage	% Current Efficiency	KWH/lb Zinc
	Zinc	H ₂ SO ₄	Gelatin								
	150.0	98.0	0.1	6	55°C	36ASF	21390	6.89 gms	1.41	95.2	.552
2	146.5	103.3	0.1	6	55°C	36ASF	20957	6.68 gms	1.37	94.0	.542
3	143.2	108.2	0.1	6	55°C	36ASF	21367	6.63 gms	1.34	91.6	.545

Results of these tests are in excellent agreement with data obtained under similar test conditions for the plant feed employed during DOE Contract No. ET-78-C-02-4881. Indeed, energy consumption for these current tests are somewhat better than those reported under the previous contract because the cell voltage obtained in 36ASF with the new feed is lower than with the old feed, and more closely approximates synthetic solutions.¹

3.3 Future Experimentation

Anodes of lower platinum loading ($<.33 \text{ mg/cm}^2$) as well as palladium electrodes have been prepared and they will be screened in the 2" x 2" hardware to determine their effect on cell voltage. Possible effects of lowering the platinum content or changing to another noble metal (Pd) are increased polarization and poisoning, both of which would result in a higher cell voltage.

Experimentation in the 6" x 6" cell has been undertaken and data concerning the effect of changes in cell parameters such as electrolyte flow, composition of the feed and current density on current efficiency and energy consumption are being obtained.

1. Annual Report #COO-4881-12, October, 1979 "Energy Savings by means of Fuel Cell Electrodes in Electro-Chemical Industries", October 31, 1979, page 49.