University of Nevada

Reno

The Electrowinning of Dilute Zinc Sulfate Solutions in a Fluidized Bed Electrochemical Reactor

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in metallurgical engineering

by

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ABSTRACT

A cylindrical, fluidized bed electrochemical reactor (FBER), was employed to electrowin dilute zinc sulfate solutions containing 2.5 - 15 gr/l zinc. The planar electrodes used in the industrial electrowinning of zinc requires 50 - 65 gr/l zinc. A low acid catholyte solution of 5 gr/l is the maximum concentration necessary for the efficient recovery of zinc. The addition of 60 gr/l of Na₂SO₄ electrolyte improved both the catholyte conductivity and current efficiency.

The optimum current efficiency and current density were obtained using a particle size of +355-500 microns, and a bed width of 1.3 cm. At a zinc concentration of 15 gr/l, the FBER could be operated at current densities and volumetric reaction rates greatly exceeding that of a conventional planar electrowinning cell.
DEDICATION

This work is dedicated to the author's family, for the love and guidance they have provided throughout my life.
ACKNOWLEDGEMENTS

The author wishes to thank his major professor, Dr. Renato G. Bautista, for his help and encouragement during the course of this project. Thanks must also go to Mr. Harvey Jensen of the Ames Laboratory, USDOE, Iowa State University, for his invaluable assistance in constructing the experimental apparatus.

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1. INTRODUCTION

Since their invention in the late 1960's (8,15), there has been much interest in the application of a fluidized bed electrochemical reactor to the electrowinning of metals. Such electrodes have a very large surface area per unit volume and high mass transfer coefficients when compared to conventional planar electrodes. These two factors make the fluidized bed electrochemical reactor (FBER) ideal for metal recovery from dilute solutions.

There are a variety of sources of dilute metal solutions and a number of reasons for their recovery. By far the largest source of dilute metal solutions is from leaching of ores (44). Other sources include mine dump leachings, plating effluents, and industrial waste streams. The metals are recovered for their monetary value or removed so as to conform to environmental laws regulating the disposal of industrial waste.

Being able to handle these dilute solutions directly, without the expensive concentration and purification steps required for conventional electrowinning, makes the FBER economically appealing. Other advantages include capital cost reduction because of the smaller reactor volume, the possibility of continuous metal recovery which allows for steady state operation, and lower labor requirements. In this scheme, the bed is seeded with small metal particles which grow with metal deposition. The large particles
formed settle to the bottom and are periodically removed.

The limiting current density is defined as the current density at which the concentration at the electrode surface of the ionic species being deposited is zero. The transport of ions from the bulk solution, through the diffusional boundary layer, and to the electrode surface, occurs by diffusion due to a concentration gradient, convective transport due to bulk and eddy mixing, and migration due to the forced movement of charged species by an electrical potential. Transport by migration and convection can be neglected because in the presence of an adequate amount of supporting electrolyte, the transport due to migration is small. In the hydrodynamic boundary layer, convective movement of fluid is negligible.

The molar flux of ions transferred to the electrode surface is defined as:

\[ J_i = D_i \left( \frac{dC_i}{dy} \right)_{y=0} \quad \text{Eq. (1)} \]

where \( J_i \) is the molar flux of species \( i \) (mole/cm\(^2\)-sec), \( D_i \) is the diffusivity of species \( i \) (cm\(^2\)/sec), and \( \left( \frac{dC_i}{dy} \right)_{y=0} \) is the molar concentration gradient of species \( i \) at the electrode surface \((y=0)\).

Using Faraday's law, this molar flux can also be written as:

\[ J_i = \frac{I_i}{z_i F} \quad \text{Eq. (2)} \]

where \( I_i \) is the current density supported by the reaction of species \( i \), \( z_i \) is the number of equivalent weights per molecular
weight of species $i$, and $F$ is a constant representing the number of electrons transferred per equivalent weight of $i$.

Under conditions of mass transfer limitations, Eqs. (1) and (2) can be combined to give:

$$I_{\text{lim}}/z_i F = D_i (dC_i/dy)_{y=0}$$  \hspace{1cm} \text{Eq. (3)}

Assuming a constant concentration gradient in the diffusional boundary layer of thickness $T$, integration of Eq. (3) from $C_i$ at $y=0$ to $C_i = C_{b1}$ at $y=t$ gives:

$$I_{\text{lim}} = (z_i D_i F C_{b1})/T$$  \hspace{1cm} \text{Eq. (4)}

Eq. (4) indicates that the limiting current density, $I_{\text{lim}}$, can be enhanced by decreasing the boundary layer thickness, increasing the bulk concentration $C_{b1}$ of species $i$, or increasing the diffusivity. $D_i$ can be increased substantially with higher electrolyte temperatures, but this often results in a nonadherent, poor quality electrodeposits, as well as an increased rate of cell corrosion. $C_{b1}$ is usually increased by employing a concentration or solvent extraction step, but this can be a costly way to increase the limiting current density. The thickness of the diffusional boundary layer, $T$, can be decreased with increased liquid turbulence.

The reason for such a high limiting current density in the FBER is due to the turbulent mixing associated with fluidized particles, which results in a lower value for the boundary layer thickness. This factor, together with a high electrode surface area per unit volume, enables the FBER to
operate at a volumetric reaction rate typically over eight times that of conventional planar electrodes.

In conventional electrochemical cells, air sparging is sometimes used to decrease the boundary layer thickness. However, this technique cannot be used with a FBER because the bubbles have a tendency to adhere to the particles resulting in the bed material being swept out of the cell. Air sparging would also result in a decreased current efficiency due to oxygen reduction on the extended surface(14).

Figure 1 shows the comparison between a conventional planar electrode cell with the two basic types of FBERs(14). The conventional cell shown in Fig. la has a 2-dimensional planar cathode. This cathode has a well defined electrochemically active surface area and a cell current capacity that is limited by the electrolyte surface area. In comparison, the FBER's shown in Figs. 1b and 1c have 3-dimensional particulate cathode electrodes. The electrochemically active surface area and cell current capacity are not well defined and change with the bed expansion and several other operating conditions. The main difference between the two FBERs is that in cell b the electrolyte and current flow perpendicular to each other, whereas in cell c the flows are parallel. Thus cell b is referred to as a side-by-side electrode(SSE), and cell c is known as the plane parallel electrode(PPE). In both the PPE
Figure 1. Comparison of the planar electrode to the PPE and SSE fluidized bed electrodes.
and SSE, the particulate bed is supported by a porous plate located at the bottom of the cell. This plate also distributes the entering electrolyte evenly across the bed to ensure uniform fluidization.

In the PPE design, the anolyte and catholyte are the same solution. For a SSE, careful selection of a diaphragm material allows different anolyte and catholyte solutions to be used.

The maximum bed thickness in the direction of current flow is approximately 2.5 cm. Beyond this value, large regions of the bed become electrochemically inactive(7). Therefore, scale-up of the fluidized bed electrode is limited to the direction perpendicular to the current flow. For this reason, the PPE is not suitable for industrial use.

Typical operating conditions of a planar electrode cell and a FBER are given in table 1.

Table 1. Operating conditions of a planar electrode cell and a FBER.

<table>
<thead>
<tr>
<th>Type of Cell</th>
<th>Planar</th>
<th>FBER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode area/m³</td>
<td>16 m²/m³</td>
<td>3500 m²/m³</td>
</tr>
<tr>
<td>Current intensity</td>
<td>2.5-10 kA/m³</td>
<td>15-50 kA/m³</td>
</tr>
<tr>
<td>Metal concentration</td>
<td>30-150 gr/l</td>
<td>0.001-150 gr/l</td>
</tr>
</tbody>
</table>
The specific cathode area of a FBER is approximately 200x as high as that of a conventional cell. The FBER current intensity, which is a measure of the volumetric reaction rate, is often 5x as high in spite of the low metal concentrations. In the FBER, this concentration range has been extended to as low as 1 mg/l(46).

Finally, it must be pointed out that the operation of a conventional planar electrode cell is essentially a batch process. Plated cathode sheets must be removed periodically and replaced with new starter sheets. For zinc electrowinning, the cathode consists of a large number of aluminum sheets, approximately 3 feet in length and 2 feet in width, which are removed at 24 hour intervals and stripped of their zinc coating. This requires a substantial capital investment as well as additional manual labor. The fluidized bed offers the possibility of continuous operation.

Current efficiency, power consumption rate, and volumetric reaction rate, are important indicators of electrochemical reactor performance. It was the purpose of this research to study the effects of different operating parameters, including the bed width, current density, and particle size, on the operation of a FBER for zinc electrowinning. Previous investigations(26,31) used a bed width of 2.5 cm., zinc coated copper spheres 500-700 microns in diameter, and zinc ion concentrations greater than 20
This investigation employed three bed widths, three size ranges of pure zinc particles, and zinc electrolyte concentrations below 20 gr/l of zinc. The optimum operating conditions were then determined by graphing.

The effect of current density, expressed in terms of both the diaphragm and particulate surface area, was investigated more thoroughly than previous studies. Qualitative predictions from kinetic theory were then correlated with the experimental data.
2. LITERATURE REVIEW

A. Applications

Fluidized bed electrochemical reactors have been shown to be potentially useful for a variety of applications. These include the anodic dissolution of metal and minerals\(^{(4,14,20,41,42)}\), battery systems and fuel cells\(^{(3,6,18,27)}\), inorganic electrosynthesis\(^{(30,33)}\), and organic electrosynthesis\(^{(2,23,34,43,63)}\). Much of the work, however, has been done in the field of extractive metallurgy. There are many reports on the electrowinning of copper using both bench scale\(^{(10,20,21,29,45,55,61)}\), and pilot plant scale FBERs\(^{(24,45,60)}\). Bench scale FBERs have also been used to recover silver\(^{(28,35)}\), cobalt\(^{(10,11,55)}\), nickel\(^{(56)}\), tin\(^{(55)}\), manganese\(^{(55)}\), and zinc\(^{(3,22,26,31)}\).

B. Theoretical Models

Several mathematical models have been developed to describe the different operating aspects of an FBER. One group of models attempts to describe the potential or current distribution throughout a fluidized bed. Newman and Tobias, the pioneers in this field, developed the first model describing the potential distribution in a porous electrode\(^{(58)}\). A more complicated model that applied to a multicomponent electrolyte, but which was still based on the ideas of Newman and Tobias, was proposed by Sabacky and Evans\(^{(51)}\). Fleischmann, in a series of articles, presented a model again based on that of Newman and Tobias, but in
addition used the concept of particle charge sharing (16, 17, 18, 19). Goodridge et al. (22) also proposed a model based on particle charge sharing, and Kreysa (52) proposed a model for describing the current density in a FBER operating under kinetic control.

Another group of models describes metal phase resistance and charge transfer in a FBER. Fleischmann and Oldfield (17) developed a model for calculating the effective resistance of the metal phase assuming partial or complete charge sharing between particles during elastic collisions. Beenackers, van Swaaij, and Welmers (5), derived a model for charge transfer based on the assumption of aggregative fluidization.

Kreysa (36) developed a model for 'a priori' calculation of the metal phase conductivity. The model was based on the assumptions of complete charge sharing during collisions and switch-off behavior during free particle movement. Turner (59) also proposed a model to explain fluidized bed conductance. The model was reported to be very successful for predicting the metal phase conductance in the presence of a low conductivity electrolyte.

C. Models for Design and Operation

Certain operational parameters of a FBER have also been described using mathematical expressions. Pickett (47) arrived at an approximate design relationship by applying established mass transfer correlations to FBERs operating
under mass transfer control. Expressions were derived by Sioda (57) for calculating the electrolysis time to achieve a given degree of conversion using recycle or single pass flow schemes.

The concentration-time behavior of an FBER was modeled by Walker and Wragg (61). Approximate and rigorous plug flow and back-mix flow models were derived. Mustoe and Wragg (46) developed a dispersed plug flow model which predicted the concentration-time behavior of the FBER with only a slight gain in accuracy over the simple plug flow model by Walter and Wragg (61).

Goodridge, King, and Wright (23) have shown that a relatively simple model could be used to predict the energy consumption rate as a function of particle size and cell voltage.

D. Experimental Work

A great deal of experimental work has been done in measuring the bed potential distribution as a function of the operating conditions and the bed geometry. In particular, Backhurst et al. (2) investigated the effect of increasing the fluidized bed width parallel or perpendicular to the direction of current flow. Results indicated that although the total cell current could be increased linearly with scale-up in the direction perpendicular to current flow, scale-up in the direction of current flow was limited to approximately 2.5cm. Any increase above 2.5cm resulted
in little or no increase in the cell current capacity. The
effect of particle size and bed expansion were also studied.

Hutin and Coeuret(29) measured the current-potential
distribution of a plane parallel electrode. Results
indicated a variation in deposition rate with bed position
and dissolution in regions which were not cathodically
protected. Similar results have been reported by
others(21,24,52).

Sabacky and Evans(53) found that conductivity in the
particulate or "matrix" phase is largely independent of the
bed expansion and relatively independent of electrolyte
conductivity and particle size. The mechanism of current
conduction was proposed to be through chains of particles in
momentary contact with each other. Additional experiments
suggested that many FBE reactor operating problems may be due to
extremes in the electrical conductivity of the fluidized
bed.

Turner(59) made measurements of the bed conductivity of
ion exchange resin particles. After experimenting with a
wide range of solution conductivities, he found previous
models did not agree well with the data for low conductivity
electrolytes. Turner then proposed a model for low
conductivity electrolytes which agreed well with the
experimental data.

E. The Zinc Deposition Reaction

Although kinetic rate expressions or reaction
mechanisms could not be applied or studied directly in this work, the knowledge is important for fundamental understanding of the process. A few studies warrant particular mention.

To explain the influence of the pH on the reaction rate, Zvereva and Rotinyan(65,66) proposed different multistep reaction mechanisms for two pH ranges. The ionic species involved in the proposed rate limiting step were assumed to adsorb according to a Langmuir isotherm. Mathematical expressions were then derived to explain the reaction order with respect to the \([\text{Zn}^{2+}]\) and \([\text{H}^+]\) concentration, and the influence of the pH on the partial polarization curves. The derived expressions correlated well with their experimental data. Under the pH conditions of this study, the active ionic species would be a \([\text{Zn}_2\text{H}_2\text{O}^{4+}]\) complex(65), with the following rate determining step:

\[
[\text{Zn}_2\text{H}_2\text{O}^{4+}] + e^- = [\text{Zn}_2\text{H}_2\text{O}^{3+}]
\]

Their experiments and derived rate expressions were done for a zinc sulfate solution in a hydrogen atmosphere; precisely the same conditions of this study. These rate expressions may be used for FBER performance modeling if bed distribution potentials were determined.

Attempting to explain the rates of zinc and hydrogen reduction, Epelboin proposed an autocatalytic step involving the adsorption of three species, including a monovalent zinc
ion(12). Other studies(1,13,32,50,62) have also interpreted the Zn$^{2+}$/Zn reaction as being a multistep mechanism, possibly involving a hexahydrated Zn$^{+1}$ species(1). Work remains to be done in proving which, if any, of the several proposed mechanisms is correct.

F. FBER Electrowinning of Zinc

Few studies have been done on the FBER electrowinning of zinc from acidic solutions. In an attempt to prevent particle deposition on the membrane separator, Goodridge and Vance(26) employed a rectangular FBER inclined 20 degrees from the vertical. The zinc coated copper spheres, 500-700 microns in diameter, would flow in a circular pattern with particles ascending near the membrane, and descending near the cathode feeder. Although little zinc deposition occurred on the membrane or cathode feeder, potential measurements indicated only a small portion of the fluidized bed was active for zinc deposition. The zinc concentration was varied between 20-80 gr/l, with the H$_2$SO$_4$ concentration between 0.2-20 gr/l. Similar electrolyte concentrations were employed by Goodridge(22) in his study using a moving bed electrode.

Perhaps the most thorough and successful work was done very recently by Jiricny and Evans(31). Their rectangular FBER consisted of a dimensional stable anode(DSA) mesh catalytic for water oxidation and a nonsupportive Daramic membrane selective for the passage of hydrogen ions. This
membrane was supported by the adjacent anode mesh. The catholyte consisted of 50-75 gr/l of zinc and 50-100 gr/l of $\text{H}_2\text{SO}_4$. Typical industrial catholyte solutions consist of 60 gr/l and 100 gr/l $\text{H}_2\text{SO}_4$. At 100 gr/l of acid, the FBER was impossible to operate due to excessive zinc corrosion, but at 50 gr/l, the current efficiency and power consumption compared very favorably to the industrial values of 88% and 3-4 kWhr/kg.

They were the first to investigate the effect of trace impurities, such as antimony, arsenic, and cobalt, on the FBER performance for zinc electrowinning. Such impurities proved to be more detrimental to the FBER than to the planar electrode.
3. EXPERIMENTAL PROGRAM

A. Analytical Procedure

An examination of the reactions occurring in the FBER will reveal a very precise analytical method which can be used for determining the current efficiency. Once this value is determined, the recorded amperage and voltage readings allow calculation of the power consumed.

Given in Table 2 are the reactions occurring at the lead anode and particulate cathode.

Table 2. Major reactions pertaining to the FBER electrowinning of zinc.

<table>
<thead>
<tr>
<th>Anode</th>
<th>Cathode</th>
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<tr>
<td>$2\text{H}_2\text{O} = 4\text{H}^+ + \text{O}_2(g) + 4\text{e}^-$ (1)</td>
<td>$\text{Zn}^{2+} + 2\text{e}^- = \text{Zn}$ (2)</td>
</tr>
<tr>
<td></td>
<td>$2\text{H}^+ + 2\text{e}^- = \text{H}_2(g)$ (3)</td>
</tr>
<tr>
<td></td>
<td>$\text{Zn} + 2\text{H}^+ = \text{Zn}^{2+} + \text{H}_2(g)$ (4)</td>
</tr>
<tr>
<td></td>
<td>$\text{O}_2 + 4\text{H}^+ + 2\text{e}^- = 2\text{H}_2\text{O}$ (5)</td>
</tr>
</tbody>
</table>

Reaction 1, water oxidation, is known to consume a great deal of energy due to a high overpotential. Anodes are available which are catalytic for this reaction. These include DSA anodes, which, although energy saving, are very
expensive.

Reaction 2 is zinc reduction, and reactions 3, 4, and 5, are side reactions which lower the current efficiency. Reaction 3 is hydrogen evolution, also termed concentration polarization. Reaction 4 is the redissolution or corrosion of zinc in the presence of acid. This reaction is prevalent in regions of the bed which are not cathodically protected with the current feeder. Reaction 5 is the reduction of oxygen which can dissolve in the catholyte reservoir as the catholyte is mixed in the presence of air. A significant quantity of dissolved oxygen will also be present if the anolyte, nearly saturated with the great quantity of oxygen produced at the anode, is mixed with the catholyte (3). This reaction is known to occur readily to completion in an FBER (10).

In this work, oxygen reduction cannot occur after an initial running period. The oxygen generated at the anode is prevented from entering the catholyte by using separate reservoirs, and by using the Vycor membrane. Also, since the catholyte reservoir is air tight, all oxygen initially present will be reduced or displaced with hydrogen gas. In this state, only reactions 3 and 4 occur, and the measurement of the hydrogen evolved will give an indirect, yet precise value of the current efficiency. The total current is simply a sum of the hydrogen and zinc reduction reactions.
This analytical procedure was checked using atomic absorption spectrophotometry. A small volume of catholyte (1 liter) containing zinc, \( \text{H}_2\text{SO}_4 \), and \( \text{Na}_2\text{SO}_4 \), which was typically added in later runs, was electrowon for 90 minutes. Hydrogen gas measurements were made at 10 minute intervals, and the current efficiency plotted as a function of time. The predicted decrease in zinc concentration, as calculated by graphical integration, agreed closely with the actual decrease as determined by atomic absorption spectrophotometry. Figure 2 is a flow chart including a water filled separatory funnel used for making the hydrogen gas measurements (see D. Procedure and Calculations).

**B. Reactor Design and Construction**

The fluidized bed electrochemical reactor used in this investigation is shown in Fig. 3. The outer cylinder of the FBER was constructed from a clear plexiglass cylinder 14 inches long, with a 3 1/2 inch OD and a 3 inch ID. The cathode chamber was situated in the annular space between the reactor wall and the cylindrical cell diaphragm located in the center of the cell. The particles that comprised the fluidized bed electrode were contained in the cathode chamber. The ends of the reactor were both machined from 4 inch diameter pieces of teflon rod. The catholyte entered through a 1/2 inch hole drilled in the bottom section of the reactor. A distributor plate was positioned directly below the plexiglass cylinder. This 1/8 inch teflon plate both
Figure 2. Schematic diagram of the material flow through the experimental apparatus.

**APPARATUS**
1 - SEPARATORY FUNNEL
2 - CATHOLYTE RESERVOIR
3 - FBER
4 - ANOLYTE RESERVOIR

**STREAM COMPOSITION**
A - H₂ GAS
B - CATHOLYTE + H₂ GAS
C - ANOLYTE
D - ANOLYTE + O₂ GAS
E - WATER
F - CATHOLYTE
Figure 3. Side view of the cylindrical FBER.
supported the cathode bed and ensured uniform electrolyte flow across the cathode chamber.

The anode was located inside the cylindrical diaphragm in the center of the reactor. It was a hollow 5/8 inch diameter lead rod, 7 inches in length, attached to the bottom of an identically shaped copper rod. The hollow center of the connected rods served as the inlet tube for the anolyte. The entire copper rod, and any length of lead anode above the height of the expanded bed, was covered with heat shrinkable polyolefin tubing.

The membrane used to contain the fluidized bed and separate the anolyte and catholyte solutions was a porous Vycor glass, specially ordered as tubes from Corning Glassworks at Corning, New York. As an electrolytic membrane, this porous glass has the properties of being supportive and hydrogen ion selective. This ion selectivity completes the cell circuitry at a relatively low resistance but yet maintains separation of the high acid anolyte and low acid catholyte solutions, which is essential for operation. The permeability, surface area, porosity, and other physical properties of porous Vycor are discussed in an article by Schwertz(54).

As originally designed, the cathode compartment, located between the Vycor membrane and the reactor wall, consisted of six, zinc coated copper bars projecting into the center of the fluidized bed. There were two problems
with this design. First, zinc deposition and particle welding occurred on the side facing the membrane. Second, the production of hydrogen gas was disruptive enough to sweep the zinc particles out of the reactor even when large particles or low catholyte flow rates were used. The hydrogen gas bubbles generated throughout the bed would attach primarily to the zinc particles in the upper bed region. The upward flow of catholyte solution, essential for fluidizing the zinc particles below, would carry these particles and the gas out of the reactor.

To prevent this, the projecting bars were replaced with a circular, zinc-coated copper cathode, located adjacent to the reactor wall. A cross section of the original and redesigned FBER is shown in Figure 4. This design allowed for the positioning of the teflon distributor plate directly above the cathode feeder and the fluidized bed. Disengagement of the hydrogen from the particles could then occur, and the bed would be completely confined regardless of the particle size, flow rate, or hydrogen production rate. To prevent dendrite growth above this distributor plate, the Vycor membrane was covered with acrylic tubing.

For theoretical reasons, it is predicted this design increases the current efficiency. The continuous geometry, a larger cathode surface area, and a better current distribution, are some of the factors which lead to this prediction. An in depth discussion is given by Pletcher in
Figure 4. Cross-sectional view of the original and redesigned FBER.
Previous investigations have employed zinc coated copper spheres 500-700 microns in diameter. In this study, the successful use of an upper distributor plate for bed confinement allowed the testing of pure zinc particles of three sizes, including those of nearly one-half the 700 micron diameter. These irregular shaped particles, purchased from VWR Scientific, were sieved to obtain the size ranges of 355-500, 500-710, and 710-850 microns. The surface area was determined using a Quantasorb surface analyzer. The change in surface area after several experimental runs was determined to be negligible. The irregular shape and small size of the 355-500 micron particles offered a large cathode surface area which was especially useful for electrowinning zinc from dilute solutions.

C. Electrolyte Preparation

A high acid anolyte solution was necessary for minimizing the electrolytic resistance between the lead anode and the inside surface of the Vycor glass. As this distance was increased by using larger diameter Vycor membranes, a high acid anolyte solution became even more essential. Anolyte solutions of 50, 100, 150, and 200 gr/l of sulfuric acid were tested. The change in resistance became progressively smaller with increased acid concentrations. However, the change recorded between 150
and 200 gr/l of acid was still significant, and for this reason, all experiments were performed using 200 gr/l of sulfuric acid for the anolyte. The solutions were prepared one day in advance to allow for cooling to room temperature.

Catholyte solutions were prepared using high purity ZnSO₄(7H₂O) powder and distilled water. This form of zinc readily dissolves in neutral and acidic solutions. The catholyte was periodically replaced between measurements to ensure a steady state zinc and acid concentration.

The catholyte temperature was maintained at 29 ± 1.5°C by immersing the catholyte reservoir in a cold temperature water bath. In cases where the applied voltage and current were high, the anolyte reservoir was also cooled. No stirring was required because the high catholyte flow rate necessary for fluidization was more than sufficient to thoroughly mix the contents of the 4.0 liter reservoir. The space time of the catholyte reservoir was in most cases less than one minute.

D. Procedure and Calculations

After making experimental checks to ensure proper separation of the anode and cathode compartments, the pre-mixed solutions were added and the flow rates adjusted to the proper values. The flow rate necessary for particle fluidization in the acidic solution was determined to be much less than that for a neutral solution. The hydrogen gas evolved in the acid solution was a very effective agent
for both suspending the particles and enhancing the bed turbulence.

The cell was then operated at a given current until a steady state voltage could be recorded. A connection was then made between the catholyte reservoir and the separatory funnel. The hydrogen gas escaping from the FBER would then flow through this connection and begin displacing the water in the separatory funnel. At this time, the water exit valve of the separatory funnel was opened. The time interval necessary to empty the funnel, initially filled with 300 - 600 ml of water, was measured. A larger quantity of water was used when the current efficiency was expected to be low, or when the cell was operated at a large current. The time intervals varied from about one to four minutes. At least two measurements were made at each current value to confirm a steady state condition.

The cell was operated amperostatically by adjusting the voltage. For both safety and accuracy, the current, which ranged from 10 to 100 amps, was measured using John Fluke digital multimeter with a high amperage probe. This device measures the current magnetic field, and could be used over the heavily insulated 4 gauge copper wire.

The current efficiency and power consumption values were determined after the barometric pressure had been recorded. The equations used are given in Table 3.
Table 3. Equations for calculating the current efficiency and power consumption.

Current Efficiency

\[
\text{Coulombs of } H_2 = \frac{273}{273 + T} \times 65.5 \times \frac{V}{76.0} \times 2 \times 96500
\]

Eq. 5

Total Coulombs = (amps) \times (time)  

Eq. 6

Current Efficiency = 100 \times (1 - Eq.5/Eq.6)  

Eq. 7

Power Consumption

\[
\text{Power Consumption (kWhr/kg)} = \frac{0.81974 \times \text{Volts}}{(\text{current efficiency})}
\]

Eq. 8

\[
0.81974 = \frac{(2 \times 96500)}{(65.4 \times 60 \times 60)}
\]

Eq. 9

For these equations, T = room temperature in °C, 65.5 = Reno barometric pressure in cm Hg, and V = ml. of water displaced by hydrogen in the recorded time interval. The molecular weight of zinc is 65.4, and 0.81974 is a combination of several constants.

The volumetric reaction rate and the cell electrowinning capacity, or simply cell capacity, are terms often used to characterize the overall reactor performance. The volumetric reaction rate for the deposition of zinc is defined as the mass of metal deposited per unit reactor volume per unit time. Several definitions are available for cell capacity, but in this study it will denote the total
The current density is also defined in several ways. For the industrial planar electrode, it denotes the total current divided by the cathode surface area. For FBER studies, it represents the total current divided by the surface area of the feeder cathode, the diaphragm, or the fluidized particles. The FBER diaphragm or feeder cathode current density is useful for design work and for comparing the FBER to the planar electrode. The particulate current density is useful for kinetic studies and for FBER performance modeling. Both the diaphragm and particulate current density were used in this work. It should be realized that because of the cylindrical geometry of this FBER, the diaphragm and feeder cathode current densities are different.
4. RESULTS AND DISCUSSION

A. Bed Expansion

The bed expansion is defined as the increase in bed height \( \times 100 / \) static bed height. A bed expansion of less than 20% resulted in zinc deposition on the diaphragm. At values greater than 30 percent, a significant decrease in current efficiency and zinc deposition on the current feeder occurred. This undesirable metal deposition at extreme bed expansions has been observed in other electrowinning studies. A possible explanation has been provided in terms of the sensitivity of the effective bed resistance to the bed expansion (28).

The bed expansion is also known to have a strong effect on the maximum limiting current density (34). Current capacity increases with fluidization because of the increase in available effective surface area compared to static bed. However, at constant voltage, a maximum current capacity is eventually reached because as the degree of fluidization increases, electrical contact between particles decreases. Increased loss of contact eventually outweighs the area increase and results in a sharp loss in current carrying capacity.

These effects were observed in the preliminary experiments used to determine the optimum bed expansion. The optimum value was 20%, and this value was held constant in all additional tests by adjusting the total bed weight.
and the catholyte flow rate.

B. Addition of $\text{Na}_2\text{SO}_4$

As mentioned previously, for a reasonable current efficiency, the acid concentration must be kept in the range of the zinc concentration. For purposes of comparing results using zinc concentrations in the range of 2.5 - 15.0 gr/l, the acid concentration was kept constant at 5.0 gr/l.

With such a low zinc and sulfuric acid concentration, the electrical resistance of the catholyte, and in turn the power consumed, becomes prohibitively large. To alleviate this problem, 60 gr/l of $\text{Na}_2\text{SO}_4$ was added to the catholyte. In a previous study on the fluidized bed electrowinning of nickel, a low acid solution was also critical at low metal ion concentrations, and $\text{Na}_2\text{SO}_4$ was added to improve the electrolyte conductivity (56).

Figure 5 is a graph of the voltage versus amperage with and without the addition of 60 gr/l $\text{Na}_2\text{SO}_4$. The slope of each line is equal to the cell resistance, and this value is much smaller with added $\text{Na}_2\text{SO}_4$. The voltage requirement at 40 amps is decreased from 12.5 to 6.0 volts with the addition of 60 gr/l of $\text{Na}_2\text{SO}_4$.

The voltage requirement was found to be very sensitive to the addition of acid. A small amount of additional acid had the same effect on the voltage as a large quantity of $\text{Na}_2\text{SO}_4$, in agreement with molar conductivity of $\text{H}_2\text{SO}_4$ being 860 cm$^2$/ohm as compared to 260 cm$^2$/ohm for $\text{Na}_2\text{SO}_4$. Thus,
when a greater acid concentration can be tolerated without a
great loss in current efficiency, it should be used.

The linearity of the voltage plots in Figure 5 points
to an ohmic behavior of the cell. Overpotentials, which are
classically nonlinear functions of current, are small
compared to the sum of equilibrium potentials and potential
drops due to resistive cell components. The resistive
components include the anolyte and catholyte, the external
circuitry, and the Vycor membrane.

The effect of Na$_2$SO$_4$ on the current efficiency is shown
in Figure 6. The maximum current efficiency increased from
29% to nearly 37%, and the corresponding particulate current
density increased from 6.0 to 6.6 amps/m$^2$. For industrial
zinc electrowinning, the presence of Na$_2$SO$_4$ has no effect on
the current efficiency, current density, or power
consumption(62).

Since Na$_2$SO$_4$ is unlikely to affect the reaction
mechanisms, it must act to provide a better solution
potential. An evenly distributed potential is essential for
maximum current efficiency and bed activity. This potential
is well distributed for planar electrodes, but varies for
the FBER, especially when the electrolyte conductivity is
low. This is predicted by Turner(59) in his model for FBER
performance using dilute solutions.

The smaller voltage and the increased current
efficiency combined to greatly lower the power consumption,
as shown in Figure 7. The minimum power consumption decreased from 27 kWhr/kg to 13.5 kWhr/kg. For the above reasons, all additional tests were done with 60 gr/l Na₂SO₄ in the catholyte.
Figure 5. Voltage vs. amperage with and without the addition of Na$_2$SO$_4$. 

[Graph showing voltage vs. amperage with and without Na$_2$SO$_4$.]
Figure 6. Current efficiency vs. the particulate current density with and without Na$_2$SO$_4$. 
Figure 7. Power consumption vs. the particulate current density with and without Na$_2$SO$_4$. 

The diagram shows the power consumption (kWhr/kg) on the y-axis and the particulate current density (amps/m$^2$) on the x-axis. The catholyte composition includes 5 gr/l H$_2$SO$_4$ and 5 gr/l Zn, with and without Na$_2$SO$_4$. The bed width is 1.3 cm, and the particle size is +355 - 500 µm.
C. Current Density

The equilibrium potential for zinc in contact with a solution containing zinc ions at unit activity is -0.763 V with respect to the standard hydrogen electrode. Thermodynamics predicts that hydrogen, rather than zinc, would be produced from a solution containing both zinc and hydrogen ions at unit activity. The deposition of zinc from commercial electrolytes, which often contain 100 to 200 gr/l of sulfuric acid, would appear even more unlikely. The fact that zinc is electrowon on an industrial scale from such electrolytes, often with a current efficiency of 90%, is a consequence of the more favorable kinetics for zinc deposition on zinc compared to hydrogen evolution on zinc. Expressed in electrochemical terms, there is a large overpotential for hydrogen deposition on zinc. This overpotential is sensitive to the presence of impurities and to the nature of the zinc electrode surface.

The current efficiency plotted in Figs. 6, 8, 11, and 13, initially shows a steep increase with increasing current density. This is understandable in terms of the kinetics and thermodynamics of two competing reactions: zinc deposition and hydrogen evolution. If operated at a low current density, the fluidized zinc electrode should behave in a manner showing much thermodynamic character. This is a consequence of the large surface area available allowing the heterogeneous electrochemical reactions to approach
equilibrium. Even with the low acid solutions of 5 gr/l of H2SO4, hydrogen production would be greatly favored, and the low current efficiency at low current density is therefore expected. As the current is raised however, hydrogen production becomes kinetically controlled since higher current densities are synonymous with faster electrochemical reactions. Advantage is then taken of the hydrogen overpotential and the current efficiency rises.

In each of the same figures, a peak in current efficiency is seen. This is an indication that at least certain regions of the cathode bed have reached mass transfer limitations of zinc ions to the particles. Any additional current generated in these regions is hydrogen ion reduction.

When compared to other FBER studies, the current density at which the decline in current efficiency occurs is low (15, 18, 22, 34). Also, the decline in current efficiency in Figures 6, 8, 11, and 13 is steep. Both occurrences can be explained if the electroactive surface area is much smaller than the actual surface area. It is the electroactive surface area which determines the point at which mass transfer limitations occur.

The electroactive surface area could be small for two reasons. First, the low electrolyte conductivity may restrict zinc deposition to a region near the diaphragm. Second, hydrogen gas may lower particle-liquid contact; a
problem especially true for a current efficiency below 50%. The upper distributor plate was noted to confine a certain amount of hydrogen when the gas was evolved at a high rate, and this would aggravate the situation further. This would explain the steep decline in current efficiency. As hydrogen is produced in progressively greater quantities beyond the rate limiting current, the electroactive surface area becomes progressively smaller.

The evolution of hydrogen would severely restrict scale-up in the vertical direction. The quantity of gas flowing through the upper bed would be proportional to the extent of scale-up. At some point, the gain in effective surface area with scale up would become very small. Also, the greater flow of gas could easily disrupt the bed. To date, the bed height of 14.5 cm in this experiment has been the tallest attempted for zinc electrowinning.
D. Particle Size

Figure 8 shows the effect of particle size on the current efficiency when using a bed width of 1.3 cm. and a catholyte solution containing 5 gr/l Zn, 5 gr/l H₂SO₄, and 60 gr/l Na₂SO₄. The maximum current efficiency increases as the particle size is decreased. This result is consistent with previous FBER experiments and theoretical models(24,28). Smaller particles generally give better bed potential distributions.

Also increased with small particles is the diaphragm current density at which the maximum current efficiency is obtained. This is understandable in terms of the greater surface area of the small particles. The greater flow rate and turbulence necessary to fluidize the large particles, which increases the mass transfer coefficient, is small when compared to the influence of a large surface area.

When the particle size is increased from 355-500 microns to 500-710 microns, the minimum power consumption, as shown in Figure 9, actually decreases in spite of the lower current efficiency. This occurrence may be explained as follows: the 500-710 micron particles have the highest current efficiency value at a lower applied current, and to achieve this current, a smaller voltage, and hence power supply, is required. In other words, the lower voltage requirement more than offsets the lower current efficiency. For the 710-850 micron particles, this trend is reversed.
Figure 8. Dependence of the current efficiency on the diaphragm current density and particle size.
Dependence of the power consumption on the diaphragm current density and particle size.

Figure 9.
because the lowered current efficiency offsets a slightly lowered voltage requirement.

These results would have direct implications for industrial design. In terms of minimizing the reactor volume, and perhaps capital costs, it would be advantageous to use small particles. The 500-710 micron particles would be ideal for minimizing the power consumption and operating costs. The 710-850 micron particles, however, have a distinct advantage for operating at extended time intervals. The greater turbulence involved minimizes particle welding to the diaphragm and current feeder.

A comparison between the FBER and industrial planar electrode is shown below.

### Table 4. Comparison between the FBER and industrial planar electrode.

<table>
<thead>
<tr>
<th>Type of Electrode</th>
<th>Planar Electrode</th>
<th>FBER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc Concentration</td>
<td>50-60 gr/1</td>
<td>10 gr/1</td>
</tr>
<tr>
<td>Current Efficiency</td>
<td>85-90%</td>
<td>42%</td>
</tr>
<tr>
<td>Current Density</td>
<td>375 amps/m²</td>
<td>3600 amps/m²</td>
</tr>
<tr>
<td>Cell Capacity/m²</td>
<td>330 amps/m²</td>
<td>1500 amps/m²</td>
</tr>
<tr>
<td>Power Consumption</td>
<td>3.4 kWhr/kg</td>
<td>11.3 kWhr/kg</td>
</tr>
</tbody>
</table>

The cell capacity/m² is obtained by multiplying the
diaphragm current density by the corresponding current efficiency. When considering the reactor size requirements, the cell capacity/m² is useful for comparing the FBER to the planar electrode(16). In spite of using a zinc concentration one-fifth of the industrial value, the FBER for this study has a cell capacity/m² over 4 times as large. Due to the resistive cell components and the low current efficiency, the FBER consumes 11.3 kWhr/kg as compared to the industrial planar electrode value of 3.4 kWhr/kg.

Figure 8 changes considerably when the current efficiency is plotted as a function of the particulate current density. This is illustrated in Figure 10. The important data are given in Table 5.

Table 5. Important data from Figure 10.

<table>
<thead>
<tr>
<th>Particle Size Range (miron)</th>
<th>355-500</th>
<th>500-710</th>
<th>710-850</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limiting Current Density (amps/m²)</td>
<td>9.4</td>
<td>8.8</td>
<td>6.4</td>
</tr>
<tr>
<td>Maximum Current Efficiency</td>
<td>42%</td>
<td>38%</td>
<td>29%</td>
</tr>
</tbody>
</table>

As expected after considering the kinetics and thermodynamics of the two competing reactions, a high
limiting current density corresponds to a high current efficiency. The limiting current density increases as the proportion of the total particulate surface area active for zinc deposition increases.
Figure 10 shows that as the bed width is increased by using the larger current density, the maximum current efficiency decreases. This is understandable because smaller bed widths generally allow for more distributed potential gradients. Table 6 summarizes the important experimental results.

![Graph showing current efficiency on current density and particle size]
E. Bed Width

Figure 11 shows that as the bed width is decreased by using the larger diameter Vycor membrane, the maximum current efficiency decreases. This is understandable because smaller bed widths generally maintain evenly distributed potentials\(^{11,27}\). Table 6 summarizes the important experimental results.

Table 6. Experimental results associated with the bed width.

<table>
<thead>
<tr>
<th>Bed Width</th>
<th>1.3 cm</th>
<th>1.7 cm</th>
<th>2.0 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed Weight</td>
<td>700 gr</td>
<td>860 gr</td>
<td>1000 gr</td>
</tr>
<tr>
<td>Total Particle Surface Area</td>
<td>6.5 m(^2)</td>
<td>8.0 m(^2)</td>
<td>9.3 m(^2)</td>
</tr>
<tr>
<td>Cell Current at the Limiting Particulate c.d.</td>
<td>61.8 amps</td>
<td>70.4 amps</td>
<td>74.4 amps</td>
</tr>
<tr>
<td>Limiting Diaphragm c.d.</td>
<td>9.5 amps/m(^2)</td>
<td>8.8 amps/m(^2)</td>
<td>8.0 amps/m(^2)</td>
</tr>
<tr>
<td>Maximum c.e.</td>
<td>42 %</td>
<td>40 %</td>
<td>34 %</td>
</tr>
<tr>
<td>Cell Capacity for Zinc Reduction</td>
<td>30.0 amps</td>
<td>28.2 amps</td>
<td>25.3 amps</td>
</tr>
</tbody>
</table>

Since the bed height and particle size are held constant, a larger bed width offers a larger particulate
Figure 11. Dependence of the current efficiency on the particulate current density and bed width.
surface area. It would then be expected that a bed width of 2.1 cm would have a greater capacity for zinc reduction than a bed width of 1.3 cm. As shown in Table 3, the reverse is true. The zinc reduction capacity decreases from 30 amps for the 1.3 cm bed width to 25.3 amps for the 2.1 cm bed width.

From experiments conducted at extended time intervals, it was found that zinc deposition and particle welding tended to occur in the region on, or near, the Vycor membrane. It can be concluded that the most active region for zinc deposition is adjacent to the diaphragm. With this in mind, the large diameter Vycor, which has a surface area nearly twice as large, would also have a larger bed region which is very active for zinc deposition. Eventually, however, further reductions in the bed width would have little or no effect on the cell capacity. Evidence of this is given in Table 7.

Table 7. Dependence of the cell capacity on the bed width.

<table>
<thead>
<tr>
<th>Bed Width</th>
<th>1.3 cm</th>
<th>1.7 cm</th>
<th>2.0 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell Capacity</td>
<td>30.0 amps</td>
<td>28.2 amps</td>
<td>25.3 amps</td>
</tr>
<tr>
<td>Increase in Cell Capacity</td>
<td>1.8 amps</td>
<td>2.9 amps</td>
<td></td>
</tr>
</tbody>
</table>
The bed width at which the cell capacity begins to decrease, estimated at 1.0 cm, would indicate electrochemical activity in the entire bed. At this point, zinc deposition on the current feeder would begin to occur. Thus, the optimum bed width may be at approximately 1.0 - 1.3 cm. Further testing is required to verify this.

The power consumption values for each bed width are shown in Figure 12. Comparison of the 2.0 cm bed width with the 1.3 cm bed width shows that the power consumption decreases by approximately 10 kWhr/kg.
Figure 12 shows that when the zinc concentration is progressively increased from 2.8 gr/l to 15 gr/l, with all other variables held constant, the limiting current density increased. This is expected for mass transfer control reactions. In certain cases, the increase in the limiting current density was very small due to an increase in current efficiency.

To apply Equation (5), the limiting current density must be multiplied by the corresponding current efficiency.

Figure 12 shows a comparison between the theoretical and experimental dependence of the limiting current density on the zinc concentration. Theoretical results show that if the zinc concentration was doubled, the limiting current density would double. As shown by the curve, experimental results fall short of this prediction.

To explain this result, consideration must be given to the quantity of hydrogen gas evolved, which is shown as the curve in the same figure. As the zinc concentration increases, there is a significant increase in the density of hydrogen gas evolved at the anode, which is due to increased catalytic activity.
F. Zinc Concentration

Figure 13 shows that when the zinc concentration is progressively increased from 2.5 gr/l to 15 gr/l, with all other variables held constant, the limiting particulate current density increases. This is expected for mass transfer controlled reactions. In certain cases, the increase in the limiting particulate current density was very small due to an increase in current efficiency.

To apply Equation (5), the limiting current density must be multiplied by the corresponding current efficiency. This gives the current due to zinc ions transferred to electrode surface. Experimental results did not correlate with Equation (5).

Figure 14 shows a comparison between the theoretical and experimental dependence of the limiting current density on the zinc concentration. Theory predicts that if the zinc concentration were doubled, the limiting current density would double. As shown by the curve, experimental results fall short of this prediction.

To explain this result, consideration must be given to quantity of hydrogen gas evolved, which is shown as a curve in the same figure. As the zinc concentration is increased, there is a significant increase in the quantity of hydrogen gas evolved at the limiting current density. This is true even though the current efficiency increases. From a previous discussion, this excessive hydrogen would lower the
Figure 13. Dependence of the current efficiency on the particulate current density and zinc concentration.
LIMITING PARTICULATE CURRENT DENSITY (amps/m²)

□ - THEORETICAL LIMITING CURRENT DENSITY
○ - EXPERIMENTAL LIMITING CURRENT DENSITY
△ - HYDROGEN PRODUCTION CURRENT DENSITY

Theoretical and experimental dependence of limiting particulate current density on the zinc concentration.

Figure 14.
effective surface area and the limiting current density, which would then account for the deviations from Equation (5).

Figure 15 shows the influence of the zinc concentration on the power consumption. A summary of the experimental results is given below.

Table 8. Influence of the zinc concentration on the power consumption.

<table>
<thead>
<tr>
<th>Zinc Conc.</th>
<th>2.5 gr/l</th>
<th>5.0 gr/l</th>
<th>10.0 gr/l</th>
<th>15.0 gr/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min. Power</td>
<td>17.5</td>
<td>13.5</td>
<td>11.3</td>
<td>10.5</td>
</tr>
<tr>
<td>Cons. (kWhr/kg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The power consumption begins to increase rather rapidly at a zinc concentration below 5.0 gr/l.
Figure 15. Dependence of the power consumption on the particulate current density and zinc concentration.
G. Correlation of Results

Figure 16 illustrates how all the experimental results are correlated. The maximum current efficiency for each experimental condition is plotted on the ordinate, and the corresponding limiting particulate current density is given on the abscissa. As the limiting current density increases, there is an approximate linear increase in current efficiency. The change from 6.0 to 10.7 amps/m² increases the current efficiency 27 percent. Again, this result is understandable in terms of the kinetics and thermodynamics of the two competing reactions; zinc and hydrogen reduction. The means of increasing the total bed activity, and hence the limiting current density, includes the addition of Na₂SO₄, use of smaller particles, decreasing the bed width, and increasing the zinc concentration.
A low acid catholyte solution of 5 gr/l was essential for the efficient recovery of zinc at concentrations below 2%. The addition of 50 gr/l of Am2O3 electrolyte improved both the catholyte conductivity and current efficiency, which resulted in greatly lower the power consumption.

Of the three particle sizes studied, the smallest (75-150 microns) gave the highest current efficiency and volumetric reaction rates. The middle range particles (150-250 microns) gave the lowest power consumption, while the largest particles (+350-500 microns) provided advantages other than the retention of particles floating.

Three trials were carried out by varying the feed stock and rates. The smallest bed width of 1.00 cm gave the maximum results in terms of current efficiency, power consumption, and particulate current density. These findings were confirmed with the appearance of zinc deposition on the anode, indicating a highly active region near the anodic separator.

Figure 16. The maximum current efficiency for each experimental condition is plotted on the ordinate, and the corresponding limiting particulate current density is given on the abscissa.
5. CONCLUSION

A low acid catholyte solution of 5 gr/l was essential for the efficient recovery of zinc at concentrations below 20 gr/l. The addition of 60 gr/l of Na₂SO₄ electrolyte improved both the catholyte conductivity and current efficiency, which combined to greatly lower the power consumption.

Of the three particle sizes studied, the smallest (+355-500 microns) gave the highest current efficiency and volumetric reaction rate. The middle range particles (+500-710 microns) gave the lowest power consumption, while the largest particles (+710-850 microns) had no advantages other than the prevention of particle welding.

Three bed widths were tested by varying the Vycor membrane diameter. The smallest bed width of 1.3 cm gave optimum results in terms of the current efficiency, power consumption, and particulate current density. These factors, together with the appearance of zinc deposition on the Vycor, indicated a highly active region near the membrane separator.

As the zinc concentration was decreased from 15 gr/l to 2.5 gr/l, the current efficiency decreased from 47% to 29%, and the power consumption increased from 11.5 to 17.0 kWhr/kg. These values can be compared to the conventional planar electrowinning cell which has a typical current...
efficiency of 85% and a power consumption of 3-4 kWhr/kg at a zinc concentration of approximately 60 gr/l. The optimum membrane current density of 3700 amps/m² at 15 gr/l of zinc for the FBER compares very favorably to the industrial values of 350-1000 amps/m² at a zinc concentration four times as great. The advantages of the FBER clearly lie in its ability to handle dilute solutions at a volumetric reaction rate exceeding that of conventional cells.

With additional research, the FBER may prove competitive with certain commercial methods of recovering zinc. Applications could include the treatment of plating effluents, the treatment of wastewater from zinc refineries, or the electrowinning of leach solutions from low grade ores. Typical leach solutions from pyrites cinder contain 20 - 30 gr/l of zinc. Several processing steps, including solvent extraction, neutralization, and precipitation, are necessary to obtain a purified and concentrated zinc electrolyte containing 50 - 75 gr/l of zinc. The formation of a neutral or alkaline solution is necessary to precipitate iron impurities, which can then be removed by filtration. In the conventional electrowinning cell, iron lowers the current efficiency because Fe^{2+} is oxidized at the anode and the Fe^{3+} formed is reduced at the cathode. With the separation of the anolyte and catholyte in the FBER, this reaction would not occur. Thus, complete removal of the iron impurities may not be required.
The results of this work can be used in the industry to give an indication of the economic feasibility of using a FBER in zinc electrowinning. The required design characteristics for optimum performance, together with current density and power consumption values, would be of major importance.
6. FUTURE WORK

To a large extent, the performance of a FBER is determined by the solution-matrix potential difference as a function of bed position. For the electrowinning of zinc, optimum performance would be achieved when this potential difference is constant for all bed regions when the limiting current density is applied. Conceivably, by making proper adjustments in the catholyte pH, bed width, bed expansion, particle size, and other factors which can affect this potential distribution, it should be possible to develop a FBER having a current efficiency approaching that of a planar electrode, but which can be operated at over eight times the volumetric reaction rate(24). Thus, the next step in this research would be to make potential measurements as a function of bed position for several operating conditions. A model developed from the experimental data could then be used to predict which combination of operating parameters give the best performance. Although the current efficiency may approach that of a planar electrode, the power consumed will always be greater for the FBER because of the membrane electrical resistance.

A successful study may be done in electrowinning zinc from a hydrochloric acid solution. A major energy problem in the industrial electrowinning of zinc involves the oxidation of water on a lead or lead-silver anode. The utilization of more expensive anodes which are catalytic for
water oxidation(18) does not appreciably lower the very high energy requirement. This problem could be overcome by oxidizing chlorine ions with a ruthenium-coated titanium mesh, which is manufactured by the Diamond Shamrock Company. This mesh, although expensive, lasts for several years and is used extensively in the chloro-alkali process for chlorine and sodium hydroxide production. With the FBER, separation of the anolyte and catholyte solutions would allow for a large production of chlorine gas at the anode, and a small amount of hydrogen gas at the cathode. The anode overpotential would be 5-40 mV as compared to 500 mV for water oxidation, and the cell voltage requirement could be lowered significantly. Also, the valuable product chlorine, rather than oxygen, would be produced. Sodium chloride could be added to improve the electrolyte conductivity and replenish the chlorine. Another possibility is to use an HCl/NaCl mixture for only the anolyte, and acidic zinc sulfate as the catholyte. Conditions would have to be carefully controlled, both for safety and for generating uncontaminated chlorine.

To further lower the energy requirement, the mesh anode could be positioned adjacent to the Vycor diaphragm. This would minimize the anolyte resistance because of the small distance between the anode and the Vycor membrane, and because oxygen would be liberated in a region where no
current passes. An anode material such as a mesh, with its large surface area, would be especially useful for the high current densities employed in a FBER.

Clearly, the FBER offers many possibilities, only a small number of which have been thoroughly investigated.


7. REFERENCES


