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FLUIDIZED BED ELECTROWINNING
OF ZINC FROM CHLORIDE ELECTROLYTES

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ABSTRACT

The fluidized bed electrowinning of zinc from chloride electrolytes has been studied in a laboratory cell. The cell has been operated at superficial current densities in the range 1,200 - 7,500 A/m² with catholytes containing up to 62 kg/m³ Zn and up to 28 kg/m³ HCl. Anolytes examined contained 58 kg/m³ NaCl and up to 100 kg/m³ HCl and, in some instances, had the same composition as the catholyte. Both "pure" catholytes and ones with deliberate additions of impurities (Ni, Co and Sb) were used. Pure solutions yielded current efficiencies and power consumptions comparable to or better than those of cells with conventional electrodes. Antimony (particularly in combination with Ni and Co) has a detrimental effect on cell performance; this detrimental effect was largely alleviated by simultaneous additions of glue.

INTRODUCTION

In recently published work¹⁻⁴, the electrowinning of zinc from aqueous chloride systems has been considered from the points of view of both direct competition with conventional electrowinning from sulphate solutions¹ and for systems where the zinc ore is not readily amenable to the conventional extraction processes²⁻⁴. To date, the investigators have considered conventional electrochemical cell technology. However, the necessity of new plants for a chloride system gives scope for new electrochemical cell technology to be incorporated from the onset. The fluidized bed electrode is one alternative possibility for the metal-winning cathode.

The electrolysis of zinc from aqueous zinc chloride systems offers several possible advantages. Although the decomposition voltage of zinc chloride is marginally greater than that of zinc sulphate (standard cell potential of 2.121 volts, versus 1.992 volts), the overpotentials of the chlorine evolution reactions on suitable anode materials is less than for the equivalent oxygen evolution in sulphate systems. At higher current densities the voltage, and thus the energy expended in the electrochemical anode reactions, will tend to be lower in the chloride system. This is of great importance to fluidized bed cathode systems where the anode is a planar or mesh type electrode and must necessarily run at very high current densities. Aqueous zinc chloride systems offer another advantage for zinc electrowinning voltage reductions through the solubility and conductivity of the zinc chloride solutions. Zinc chloride is extremely soluble in water³⁻⁵ (to levels similar to molten

salts), allowing solutions to be produced with concentrations and conductivities several times greater than sulphate systems. This can help in reducing the energy consumption due to IR drops in the cell. Of less significance to fluidized bed electrodes (which operate at lower actual surface current densities), the higher zinc concentrations allow higher current densities to be sustained before concentration polarization becomes significant^{3,4}. Also Fray⁴ determined that addition of 10 wt% ammonium chloride to a 30 wt% ZnCl₂ solution increased the conductivity by a factor of three.

The evolution of chlorine at the anode results in several cell design problems. Since chlorine is a toxic gas, it must be removed as a gas, or if the temperature is kept below 9.6°C the chlorine forms a hydrate^{3,4} (Cl₂·xH₂O) and can be removed as a slurry. If chlorine is evolved as a gas, a membrane separating the anode and cathode compartments is necessary both to prevent back reaction of zinc at the cathode and to facilitate effective gas collection. This criterion is again beneficial to fluidized bed electrode technology where the required membrane would represent no additional complication. The collected chlorine may be considered as a saleable by-product or, more likely, it will be required in the extraction process (e.g. dry chlorination or leaching of ores) to complete the chlorine balance.

Published research suggest that the FBE can be used satisfactorily for the electrowinning of copper⁶⁻⁸, silver⁹, cobalt¹⁰, nickel¹¹ and, more recently, zinc from zinc sulphate systems¹². No studies of the fluidized bed electrowinning of

zinc from chloride systems have been reported in the literature. Jiricny¹² has examined the fluidized bed electrowinning of zinc from sulphate systems. The results indicate zinc could be electrodeposited from solutions similar to those used industrially with current efficiencies of 60-70% at superficial current densities of 4-6 kA/m². The power consumptions are higher than those of conventional electrowinning (3-4 kWh/kg Zn). Fluidized bed electrodes were found to be more sensitive to impurities than planar electrode systems. The work of Goodridge and Vance¹³ on the electrowinning of zinc from sulphate systems in a circulating bed indicated zinc electrowinning was only feasible in such a cell at relatively low acid concentrations (<20g/l H₂SO₄).

Nogueira et al.¹ and MacKinnon et al.² have determined that high (80-90%) current efficiencies of zinc deposition can be obtained from chloride systems in planar electrode diaphragm cells at zinc concentrations as low as 15 g/l at current densities of 300-400 A/m². Fray^{3,4} found that at 15-35 wt% ZnCl₂, zinc could be electrowon at 90% current efficiency at 2200-2500 A/m² provided sufficient gas sparging and periodic current reversal was employed. These investigations determined that the power consumptions for zinc electrowinning from chloride systems were comparable with that of conventional (sulphate system) zinc electrowinning. For all these studies, the addition of ionic species was found beneficial to the power consumption by way of increased conductivity. The addition of hydrogen ions is not particularly desirable in the catholyte because this enhances

the evolution of hydrogen at the cathode, reducing current efficiencies. Levels of $0.12M^2$ and $0.19M^1$ HCl were, however, found tolerable for these specific systems. These researchers^{1,2} also added up to 2M NaCl to enhance the conductivity without significantly affecting the current efficiencies of zinc electrowinning. Fray^{3,4} added 7 wt% NH_4Cl to substantially increase the electrolyte conductivity. If a membrane cell is used the anolyte can, in theory, be radically different from the catholyte and can be optimized for chlorine evolution. The material balances of the species within the system seldom, however, allow a completely free selection of the anolyte composition. Mackinnon, et al.² appear to circulate the feed through the anolyte compartment. Nogueira, et al.¹ used the catholyte which had been depleted of zinc (by a solvent extraction step) as the anolyte, such that the anolyte composition is about 1M NaCl and $0.1M$ HCl. In this case a brine solution is a waste product.

The detrimental effects of impurities on the electrowinning of zinc from sulphate systems has been examined by several authors¹⁴⁻²⁴ and less extensively for chloride systems^{1-4,25}. The chloride studies suggest there is some similarity between the impurity effects in sulphate and chloride systems. However, as the maximum permissible levels and effects depend on process parameters and the electrolyte composition, it is difficult to quantify the results. The chloride investigations were conducted at considerably lower acid concentrations ($0.1M$) than the sulphate investigations based on industrial solutions (2-3M);

thus because of the strong acid dependence of impurity effects^{1,2} more tolerance to impurities in the chloride system may be expected.

The negative effects of impurities can loosely be divided into three groups: 1. loss of current efficiency, 2. co-deposition, and 3. deposit morphology. Antimony^{1,2,25} which acts as a cathode depolarizer was found to affect the current efficiency of zinc electrowinning in chloride systems. Germanium² was also found to have a negative affect on the current efficiency. There is disagreement between the reported effects of Ni, Cu and Fe^{1,2,25}. Lead, copper and cadmium have been found to codeposit with zinc^{1,2}. Cobalt was found to have relatively little effect on zinc electrowinning. Synergistic effects of impurities have also been observed². Deposit morphology is not such a serious problem in fluidized bed cathode electrowinning as it is on planar electrodes.

Addition agents have been found to positively effect the deposit quality (on planar electrodes) and also to increase the current efficiency of electrowinning by reducing the detrimental effects of certain impurities (eg. Sb) in chloride systems¹⁻⁴. Glues were found to be the most effective additives²⁻⁴; however it is reported² that they tend to hydrolyze. Tetrabutyl ammonium chloride and associated species were also found to be effective additives²⁻⁴.

In the present study, the current efficiency, voltage and power consumption of fluidized bed cathode electrowinning of zinc was examined for varying zinc ($20-62 \text{ kg/m}^3$) and hydrochloric acid

(0-28 kg/m³) concentrations in electrolytes containing 2M sodium chloride. The effects of various anolyte compositions and impurity (Sb, Co, Ni) and glue (Swift IV) additions and their combinations were also examined.

The aim of the study was not to optimize the fluidized bed cathode electrowinning of zinc from chloride systems but rather to examine the feasibility of such electrowinning for a range of zinc and acid concentrations. The absence of industrial zinc chloride electrowinning systems makes the study of impurity effects rather a theoretical exercise and thus the impurity studies are presented here as a contrast to the sulphate studies of an earlier paper¹².

EXPERIMENTAL APPARATUS AND PROCEDURE

The "50 amp" cell used in this investigation was similar to that used in previous investigations (Jiricny^{9,12}, Fig. 1). The cell employs a cathode consisting of a bed of fluidized zinc coated copper particles 400-600 μm in diameter. The zinc coating is produced by prior deposition from sulfate solutions and is non-porous; such zinc coated particles should therefore behave like pure zinc particles that would be used in a commercial plant. When expanded, the bed measured approximately 70mm x 23mm x 125mm high. 25% bed expansion was used in all runs; from previous investigations¹² this was found the optimum to minimize zinc deposition on the current feeder and diaphragm. A 4mm thick graphite plate was used as a current feeder. The anode was of the DSA mesh type (titanium mesh with proprietary coating which is catalytic for chlorine evolution, Eltech Corporation). The

anode and cathode compartments were separated by a flexible porous plastic diaphragm ("Daramic", W. R. Grace Corporation) which enables the use of different compositions of catholyte and anolyte because of its very low permeability. In all the experiments the active area of the diaphragm was $4 \times 10^{-3} \text{m}^2$; the rest of the diaphragm was masked by glue. The ratio of the non-active area of the diaphragm to active area in the fluidized bed was 1.2:1.

The catholyte was maintained at a temperature of $17 \pm 1^\circ \text{C}$. Electrolytes were pumped to the cell compartments from the catholyte and anolyte storage tanks. The catholyte flow rate determined the bed expansion. The spent liquor from each compartment was returned to the appropriate tank.

Current efficiency for zinc deposition was determined by an indirect method; this consisted of measuring the volume of hydrogen evolved during the electrowinning of zinc. The hydrogen burette was connected in an airtight fashion with the catholyte compartment and storage tank. Chlorine gas was removed from the anolyte compartment by a negative pressure air sparging system with suction provided by a water flow ejector pump (see Fig. 2). The chlorine was absorbed from the outlet stream in a sodium hydroxide scrubbing system.

The cell was electrically connected to a Hewlett-Packard 6260B DC power supply operated amperostatically. The current and cell voltage were continuously monitored on a standard strip chart recorder.

The anolyte and catholyte were prepared from AR grade

reagents (A.R. Mallinckrodt, Inc.). Stock solutions containing 1 kg/m³ of cobalt or nickel were prepared by dissolving cobalt (II) chloride or nickel (II) chloride in distilled water. Antimony solution was prepared by dissolving antimony potassium tartarate in distilled water to a level of 10⁻² kg/m³. The stock solution concentrations were checked using atomic absorption spectrophotometry. Stock solutions of glue (Swift IV) with concentration of 1 kg/m³ were prepared as required by dissolving the organic in distilled water and storing under refrigeration to minimize degradation. 5 litre volumes of anolyte and catholyte were prepared for each experiment. Zinc concentrations were determined by complexometric titration using EDTA.

The experimental procedure consisted of filling each storage tank with the appropriate volume of desired anolyte and a neutral catholyte. The particles were added to the cathode compartment and pumps were turned on. The catholyte flow rate was then adjusted to bring the bed expansion to the desired level. The power supply was turned on and electrolysis commenced. The desired quantity of acid was then added slowly to the catholyte. The cathode compartment was sealed and the hydrogen evolution was measured indirectly by measuring the volume of water which was displaced from the hydrogen burette. After reaching steady state, measurements of hydrogen evolution were made. The cell current was then adjusted to the next level. For the impurity and glue experiments the desired quantity of addition was added just prior to measurement. Circulation of catholyte from the tank to the pump and directly back to the tank (see Fig. 2) was

roughly four times the flow to the cell, and therefore the impurities were rapidly mixed into the catholyte volume.

EXPERIMENTAL RESULTS AND DISCUSSION

The preliminary experiments were carried out with catholyte and anolyte compositions similar to those used in the "Zinchlor Process" pilot plant experiments¹. The catholyte composition was 20-30 kg/m³ zinc, 116 kg/m³ NaCl and 7 kg/m³ HCl and the anolyte composition was 3 kg/m³ HCl and 58 kg/m³ NaCl. The investigation then examined catholytes with up to 28 kg/m³ HCl and 62 kg/m³ zinc.

The Effects of Zinc and Hydrochloric Acid Concentration

The results of measurements at zinc concentrations of 20, 24 and 29 kg/m³ at an acidity of 7 kg/m³ HCl for current densities from 1250 - 7500 A/m² are shown in Figure 3a-c. Further results of measurements at hydrochloric acid concentrations from 0 to 28 kg/m³ and zinc concentrations between 20 and 62 kg/m³ over a similar range of current densities are given in Figures 4a-c.

Increasing the zinc concentration results in a gradual increase in the current efficiency of zinc electrowinning (Fig. 3a). Conversely, increasing the acid concentration results in an increasingly large decline in the current efficiency (Fig. 4a). For the case of no added acid the current efficiency for zinc electrowinning from a 20 kg/m³ zinc solution was effectively 100% for the whole range of current densities examined. For all the other measurements at various acid and zinc concentrations the current efficiency-current density curves are of a similar shape. The current efficiencies of zinc electrowinning decline at low

current densities. At higher current densities a region of approximately constant current efficiency exists and another decline in current efficiency at the highest current densities examined was observed. The effects of zinc and acidity appear to be opposite in nature. Increasing the catholyte zinc concentration increases current efficiencies and decreases the decline of current efficiency at lower current densities. Conversely increasing the acid concentration reduces the maximum current efficiency of zinc electrowinning, and increases the decline of current efficiency which occurs at lower current densities. The current density of maximum current efficiency is also shifted to higher current densities with increasing acid concentration. Increasing the zinc concentration (at $7 \text{ kg/m}^3 \text{ HCl}$) from 20 to 24 to 29 kg/m^3 results in an increase in the maximum current efficiency from 81 to 88 to 94% , respectively at 5000 A/m^2 (Fig. 3a). Increasing the hydrochloric acid concentration (at 20 or 29 kg/m^3 zinc) from 0 to 7 to 14 to 21 to 28 results in a decline in maximum current efficiency from 100% to 94% to 87% to 73% to bulk dissolution of the electrodeposited zinc respectively. Up to $21 \text{ kg/m}^3 \text{ HCl}$ the current density at which the maximum current efficiency occurs rises from 5000 to 6250 A/m^2 . At 62 kg/m^3 zinc, zinc can be electrowon at $28 \text{ kg/m}^3 \text{ HCl}$ with current efficiencies of greater than 80% for current densities above 5000 Am^2 .

The results of Figs. 3b and 4b suggest that increasing the zinc concentration of the catholyte ($7 \text{ kg/m}^3 \text{ HCl}$, $116 \text{ kg/m}^3 \text{ NaCl}$) up to 30 kg/m^3 results in a slight decline in overall cell

voltage. Increasing the zinc concentration of the catholyte from 20 to 29 kg/m³ results in a decline in cell voltage from 7.2V to 6.6V @ 7500 A/m² (Fig. 3b). Above this level, increasing the zinc or acid concentration of the catholyte (Fig. 4b) has no significant effect on the cell voltage. The minimum power consumption increases (and occurs at increasingly high current density) for decreasing catholyte zinc concentration and increasing catholyte acidity. Only for high zinc concentration and low acidity catholytes at relatively low current densities, are the power consumptions comparable to those of conventional sulphate zinc electrowinning (3-4 kWh/kg Zn). The current efficiency plots presented in Figs. 3 and 4 are understandable in terms of the thermodynamics and kinetics of the two competing reactions (zinc deposition and hydrogen evolution). If operated at low current, a fluidized zinc electrode should behave in a manner showing much thermodynamic character. This is a consequence of the large particulate surface area available for reaction so that the heterogeneous electrochemical reactions are close to equilibrium. Thermodynamically, hydrogen should be evolved, rather than zinc deposited, and the low current efficiency at low current density is therefore to be expected. As the current is raised the behavior takes on a more kinetic character since higher currents are synonymous with faster electrochemical reactions. Kinetically the deposition of zinc is favored and the current efficiency rises as seen in Figs. 3a and 4a.

It is to be expected that the rate of zinc deposition would

reach a maximum value (determined by mass transfer) on further increasing the current density, and that increasing the current density beyond this point could only result in more hydrogen evolution and a decline in current efficiency. Current efficiency should therefore pass through a maximum on increasing current density, and the existence of this maximum may be discerned in most of the curves of Figs. 3a and 4a.

The effect of acid and zinc concentration observed in the experiments is as expected. For both thermodynamic and kinetic reasons an increase of acid concentration or a decrease in zinc concentration favors the evolution of hydrogen and reduction of current efficiency.

The linearity of the cell voltage plots in Figs. 3b and 4b points to an ohmic behavior of the cell, i.e., overpotentials (which are characteristically non-linear functions of current) are small compared to the sum of equilibrium potentials and potential drops due to resistive cell components. The last are reduced by increases in electrolyte conductivity, e.g. by increases in acid concentration, hence the slight reduction in cell voltage evident in these Figs. on increasing the acid in the catholyte.

The shapes of the curves in Figs. 3c and 4c is a consequence of the interaction of the effects already discussed. On increasing the current density from low values the cell voltage increases slightly (i.e. there is a slight increase in electrical energy consumed per unit of charge passed), but the current efficiency increases sharply (i.e. there is a sharp increase in

the zinc deposited per unit of charge passed). The ratio of energy consumed to zinc deposited therefore diminishes, particularly at higher acid concentrations where the greatest increases in current efficiency occur. At higher current densities the voltage continues to increase, but now the rate of increase in current efficiency declines or is even zero or less. Consequently the ratio of energy consumed to zinc produced shows an increase with increasing current density.

The experimental measurements for a catholyte of varying acid concentrations (7 to 28 kg/m³ HCl) with a zinc concentration of 53 kg/m³ and 116 kg/m³ NaCl and an anolyte of 100 kg/m³ HCl, 58 kg/m³ NaCl are presented in Figs. 5a to c. The results are a continuation of the previous experiment presented in Figs. 3 and 4. Despite the different anolytes the current efficiencies are directly comparable because of the limited hydrogen ion migration across the diaphragm. The results of Fig. 5a fit the general patterns observed previously. The region of high current efficiency at 7 and 17.5 kg/m³ HCl extends to low current densities. The maximum current efficiency at 53 kg/m³ zinc and 7 kg/m³ HCl (Fig. 5a) is about the same (90-95%) as observed for 30 kg/m³ zinc and 7 kg/m³ HCl (Fig. 3a). This suggests that at low acid concentrations little benefit is achieved by increasing the catholyte zinc concentration above 30 kg/m³. The measured cell voltage is slightly higher than predicted from Figs. 6 and 7 (see below). This may be due to poor bed fluidization observed at the higher zinc concentration. The increased zinc concentration of the catholyte also makes the system more prone to zinc deposition on the diaphragm and current feeder especially at low acid concentrations. At low current densities the

increase in current efficiencies are mainly responsible for the reduction in power consumption for this system (Fig. 5c). The reduction in power consumption at high current densities are, however, primarily due to decreases in anolyte compartment voltage drop resulting from the high acid level in the anolyte compared to the runs of Figs. 3 and 4.

The effect of anolyte composition

The effect on cell voltage and power consumption that results from switching from a relatively low conductivity anolyte (Figs. 3 and 4) to one of higher conductivity (Fig. 5) is a consequence of the high current densities at the anode. Increased anolyte chloride concentration and ionic conductivity should reduce any mass transfer component of the anodic overpotential as well as ohmic resistances in the anode compartment.

The effects of increased hydrochloric acid concentration in the anolyte on the cell voltage-current density relationship for a 30 kg/m^3 zinc, 7 kg/m^3 HCl and 116 kg/m^3 NaCl catholyte are given in Figs. 6 and 7.

The results indicate that increased hydrochloric acid concentration in the anolyte greatly reduces the overall cell voltage, and consequently the energy consumption for zinc production, the reduction being greater at higher current densities.* The relative decreases, however, become smaller with

*For relatively short experiments (1 hour) the current efficiency of the cathode reaction was unaltered; however, after some time hydrogen ion migration from the anolyte to the catholyte raised the catholyte acidity such that the current efficiencies began to fall.

increasing concentration. At a current density of 7500 Am^2 , increasing the anolyte acid concentration from 3 to 50 kg/m^3 HCl results in a 20% reduction in cell voltage (from 6.8 to 5.5V); however, further increasing the acid concentration to 100 kg/m^3 HCl results in only a further 14% reduction in cell voltage (from 5.5 to 4.5V).

The feasibility of using a strong hydrochloric anolyte in industrial practice is doubtful. Hydrochloric acid would be consumed in the process requiring the purchase of hydrochloric acid and possible neutralization of hydrogen ions migrating into the catholyte.

Use of feed as both anolyte and catholyte

The use of the cell feed solution as both the anolyte and catholyte offers a possible alternative method of reducing the voltage drop in the anode chamber. The relatively high conductivity of the catholyte is utilized. If zinc and chlorine are electrowon at high efficiencies and the chlorine is recycled to the leaching process the chlorine balance will be maintained.

The measurements for results of experiments conducted with similar anolyte and catholyte compositions are given in Figs. 8a to c. The compositions are similar to the catholytes used in the earlier experiments (Figs. 3 and 4) and for comparable catholytes the current efficiencies are in good agreement. For low acid experiments the agreement is within 5% over the whole range of current densities. At higher acid concentrations the variation is greater but still acceptable.

For anolyte and catholyte of 7 kg/m^3 HCl, 30 kg/m^3 zinc and

116 kg/m³ NaCl the cell voltage was 5.05 V @ 7500 a/m³ (Fig. 8b). This results in a 29% reduction in energy consumption from the similar experiment (Fig. 3a-c) using an anolyte of 58 kg/m³ NaCl and 3 kg/m³ HCl.

Increasing the acid concentration to 14 and 21 kg/m³ HCl results in relatively small decreases in cell voltage. These reductions in cell voltage do not offset the accompanying reductions in the current efficiency of zinc electrowinning (Fig. 8a) such that the overall power consumption increases with increasing acid concentration. The results also indicate that sodium chloride additions play an important role in minimizing the overall cell voltage.

The use of a neutral catholyte results in a considerable energy saving by virtue of increased current efficiencies and negligible increase in cell voltage. Again it should be stressed that there is a greater tendency for zinc to deposit on the current feeder and diaphragm from neutral solutions.

For systems where the electrolyte was 30 kg/m³ zinc, 116 kg/m³ NaCl and 7 kg/m³ HCl (or less in the catholyte) the power consumptions achieved are comparable to or lower than for conventional sulphate zinc electrowinning (3-4 kwh/kgZn). Even at 7500 A/m², power consumptions of 4 - 4.3 kwh/kg zinc were achieved (Fig. 8c).

THE EFFECTS OF IMPURITIES

The experiments examining the effects of impurities on zinc electrowinning were carried out in anolyte and catholyte of 7 kg/m³ HCl, 30 kg/m³ zinc and 116 kg/m³ NaCl. The choice of a

slightly acidic solution was to accentuate the deleterious effects of impurity additions which are reported¹² to be strongly acid dependent (in the sulphate system, at least).

The effects of cobalt, nickel, antimony and glue (Swift IV) individually and as combinations on fluidized bed cathode electrowinning of zinc from chloride solutions have been examined (Figs. 9, 10, 11 a-c). It was not the intention to establish the permissible impurity levels, but to compare the results with those of Jiricny and Evans¹² obtained from a sulphate system. The effects of cobalt, nickel and antimony individually

Nickel and cobalt (singly) at levels up to 10ppm (Fig. 9a) had relatively little effect on the current efficiency of zinc electrowinning. At low current densities, the effect of both impurities was similar. An 8% decline in current efficiency from additive free solutions was observed at a current density of 3750 A/m² - a trend which may be expected to worsen at even lower current densities.

For planar electrodes, Nogueira et al.¹ observed a similar decline (6% from 95% to 85% @ 400A/m²) of current efficiency for 10ppm levels of nickel. (However, it is not clear if pearl glue additions were present during the experiments). Jiricny and Evans¹² reported considerable loss of current efficiency for nickel and cobalt additions to the sulphate system even at levels of 3 ppm. Nickel was observed to result in considerably greater reduction of current efficiencies than for cobalt.

The variations in overall cell voltage with the addition of nickel and cobalt (Fig. 9b) is not readily explainable.

Antimony additions up 50 ppb result in a marked decline in the current efficiency of zinc electrowinning. The decline in current efficiency with increasing antimony concentrations is worse at lower current densities (at 50 ppb antimony the current efficiency at 5000 A/m^2 was 43% and at 7500 A/m^2 it was 63%).

Nogueira et al.¹ observed a similar effect of antimony on electrowinning of zinc (onto planar electrodes) from chloride solutions at 400 A/m^2 (however, it is not clear whether pearl glue additives are present). For the fluidized bed cathode, Jiricny and Evans¹² found that for the sulphate system, 8 ppb antimony gave declines in current efficiencies similar to the declines observed with 50 ppb antimony in the present experiments.

A slight increase in the overall cell voltage (Fig. 10) was observed with increasing antimony concentration; a fact probably attributable to increased gas volume in the bed.

The power consumption is increased significantly by a decline in current efficiency of zinc electrowinning. Consequently the presence of nickel and cobalt at concentrations up to 10 ppm has relatively little effect on power consumption, whereas the presence of antimony even at concentrations of a few ppb results in considerable increases in the power consumption for zinc electrowinning. The experiments with impurities demonstrate that fluidized bed electrowinning of zinc from chloride systems is considerably less sensitive to impurities than for fluidized bed electrowinning of zinc from sulphate systems. It is believed that it is the differences in acid

concentration between the sulphate¹² ($100 \text{ kg/m}^3 \text{ H}_2\text{SO}_4$) and chloride ($7 \text{ kg/m}^3 \text{ HCl}$) systems which is the overwhelming cause of the difference in the fluidized bed electrowinning behavior of the two systems and their relative sensitivities to impurities. For the chloride case, there is some indication that the effect of impurities on zinc electrowinning is similar for both the case of fluidized bed and planar electrodes.

The effect of impurity combinations

The effect of 10 ppm nickel plus 10 ppm cobalt on current efficiency is seen in Figure 9a. The 10 to 20% decline in the actual current efficiency from the pure solution case is considerably worse than for the individual species at levels of 10 ppm.

The current efficiencies observed for antimony, nickel and cobalt additions (in combinations) of (1) 10 ppb, 10 ppm and 10 ppm; and (2) 50 ppb, 1 ppm and 1 ppm, respectively, are given in Figures 9a and 11a. When compared with the results of antimony alone (Figure 10a), it is apparent that nickel and cobalt additions are synergistic with antimony in their effect on the current efficiency of zinc electrowinning. At 50 ppb antimony, 1 ppm nickel and 1 ppm cobalt the current efficiency is about 10% lower than for antimony alone for the range of current densities ($5,000$ to $7,500 \text{ A/m}^2$) examined (Figures 10a and 11a). At 10 ppb antimony, 10 ppm nickel and 10 ppm cobalt the current efficiency at high current densities ($6,000$ - $7,500 \text{ A/m}^2$) is 15% below that of the added losses of current efficiency for 10 ppb antimony singly and 10 ppm nickel and 10 ppm cobalt together. At current

densities of less than $5,000 \text{ A/m}^2$ there is a catastrophic decline in current efficiency for this mixture which is not observed in the added losses of the constituents. (The mixture results in a current efficiency [22%] which is 66% below that of the pure solution [88%] and 40% lower than obtained by adding the losses for 10 ppb antimony individually [9%] and for 10 ppm nickel and cobalt combined [18%]).

The minimum power consumptions from (1) 10 ppb antimony, 10 ppm nickel and 120 ppm cobalt and (2) 50 ppb antimony, 1 ppm nickel and 1 ppm cobalt are 6 kWh/kgZn @ $6,000 \text{ A/m}^2$ and 8.8 kWh/kgZn @ $7,500 \text{ A/m}^2$, respectively.

The effects of glue

The effects of Swift IV glue alone on the current efficiency of zinc electrowinning is shown in Figure 11.

The addition of 5 ppm glue resulted in a 5 to 10% increase in current efficiency. The current efficiency was relatively constant for all the current densities examined. Further increases in the glue concentration resulted in a gradual decline in the current efficiency such that at 50 ppm glue the current efficiency was lower than that for addition-free solutions.

The addition of glue in general caused an increase in cell voltage of up to 0.6V; however the bed fluidization characteristics were greatly improved by the addition of glue. The small variations of both current efficiencies and cell voltages with glue additions resulted in a spread of power consumptions rather than a general trend. For all cases power

consumptions were between 3.4 and 3.7kwh/kgZn @ 3,750 A/m² and increased to between 4.5 and 5 kwhr/kgZn at current densities of 7,500 A/m².

The increase in current efficiencies resulting from small additions of glue are in agreement with the results of zinc electrowinning on planar electrodes in chloride systems¹⁻⁴ and opposite to the case of sulphate systems where the addition of glue alone is reported¹² to result in small decreases in current efficiency. It has been reported³ that for planar electrodes the increase in current efficiency with glue additions is due to morphological changes at the electrodeposition surface. This seems improbable for a fluidized bed system where particle collision and dissolution (in inactive regions of the bed), would tend to be a large factor in determining the deposit morphology.

At 50 ppb antimony, 1 ppm nickel, 1 ppm cobalt and 50 ppm glue the current efficiency of zinc electrowinning was 80 to 82% for current densities between 3750 and 7500 A/m² (see Figure 11a). The power consumption over the same range of current densities was 3.9 to 5.4 kwhr/kg Zn. This can be compared with the current efficiencies and power consumption for the same impurity levels without glue additions of 34 to 46% and 10 to 8.8 kwhr/kgZn, respectively.**

** A caution is necessary: the experiments with both glue and metal impurities were carried out by adding the latter to the catholyte tank immediately after experiments in which the effects of glue alone had been measured. The results may not therefore be the same as for an experiment in which glue and metal impurities are simultaneously introduced into the electrolyte.

In agreement with investigators of chloride systems¹⁻⁴ and sulphate systems^{12,14-16,19-21} the experiments showed a strongly beneficial effect of glue on current efficiency in interaction with certain impurities (e.g. antimony). No attempt was made to optimize the glue-impurity interaction. The ratio of glue to antimony used (weight:weight) was 1000:1. (Workers with sulphate systems¹⁴ determined the optimum glue to antimony ratio for that case was 375:1).

CONCLUSIONS

Experiments in which zinc has been deposited from chloride solutions using a fluidized bed electrode have been carried out. The effect of a range of zinc and acid concentrations on the current efficiencies, cell voltages and power consumption of zinc electrowinning for a wide range of current densities (1250 to 7500 A/m²) were examined. Preliminary experiments into the effects of some impurities (cobalt, nickel, antimony and Swift IV glue) singly and as combinations were also conducted.

It was found that for chloride systems:

1. For neutral catholytes the current efficiency of zinc electrowinning was 100% for the whole range of current densities examined.
2. The acid concentration of the catholyte has a strong influence on the current efficiency and power consumption, the current efficiency falling rapidly with increasing acid content.
3. Increasing the zinc content in the catholyte opposes the effects of increasing the catholyte acid content.

4. Use of the same electrolyte for anolyte and catholyte (30 kg/m^3 zinc, $0-7 \text{ kg/m}^3$ HCl and 116 kg/m^3 NaCl) resulted in relatively low overall cell voltages.
5. For "impurity free" solutions power consumptions better than or comparable to the case of conventional zinc sulphate electrowinning was possible.
6. Nickel and cobalt additions up to 10 ppm had very little effect on the current efficiency of zinc electrowinning.
7. Antimony was detrimental to the current efficiencies of zinc electrowinning. At 50 ppb Sb the current efficiency was reduced to 62% at $7,500 \text{ A/m}^2$.
8. Cobalt, nickel and antimony additions together produce synergistic declines in current efficiency.
9. Glue additions of 50 ppm Swift IV produced a great increase in the current efficiency of zinc electrowinning in solutions containing 50 ppb Sb, 1 ppm Ni and 1 ppm Co. Power consumptions similarly declined from $10-8.8$ to 4 to 5.5 kwh/kgZn .

This preliminary experimental study indicates that, even with considerable impurity levels, fluidized bed zinc electrowinning from chloride solutions has energy consumptions comparable to conventional zinc sulphate electrowinning. The fluidized bed electrode performs better in the chloride system than the sulphate system probably because of the much lower acidity of the former. The fluidized bed in the chloride system is at least a factor of ten less sensitive to the impurities examined in these experiments at acid levels appropriate for each electrolyte.

With its possible savings in capital and labor costs (and comparable energy consumption), the fluidized bed electrowinning of zinc from chloride systems appears competitive with conventional zinc sulphate electrowinning. The adoption of a zinc chloride process by the industry requires new technology and thus would be an opportunity to incorporate fluidized bed electrowinning from the onset. A thorough investigation of the feasibility of fluidized bed electrowinning for the precise composition of the envisioned industrial solution would, however, be a prerequisite to such an undertaking.

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FIGURE CAPTIONS

1 Laboratory scale cell with fluidized cathode used in this investigation.

2 Experimental system including the cell, electrolyte reservoirs, devices for absorbing chlorine from the anode chamber and measuring hydrogen from the cathode chamber, power supply and voltage/current recorder.

3 Effect of superficial current density (current per unit area of cell diaphragm) and zinc concentration in the catholyte on (a) current efficiency (b) cell voltage (c) power consumption for electrolytes containing low levels of HCl.

4 Effect of superficial current density and catholyte composition for experiments with anolytes containing low levels of HCl.

5 Effect of superficial current density and catholyte composition for experiments with anolytes containing high levels of HCl.

6 Effect of anolyte acid content on cell voltage at a fixed catholyte composition.

7 Effect of anolyte acid content on cell voltage at $7,500 \text{ A/m}^2$ for catholyte composition of Fig. 6.

8 Effect of using anolyte and catholyte of the same (or similar) composition.

9 Effect of Ni and Co impurities added (singly, in combination, or in combination with Sb) to the catholyte.

10 Effect of antimony additions to the catholyte.

11 Effect of Swift IV glue additions to the catholyte, either singly or in combination with impurities that otherwise impair cell performance.

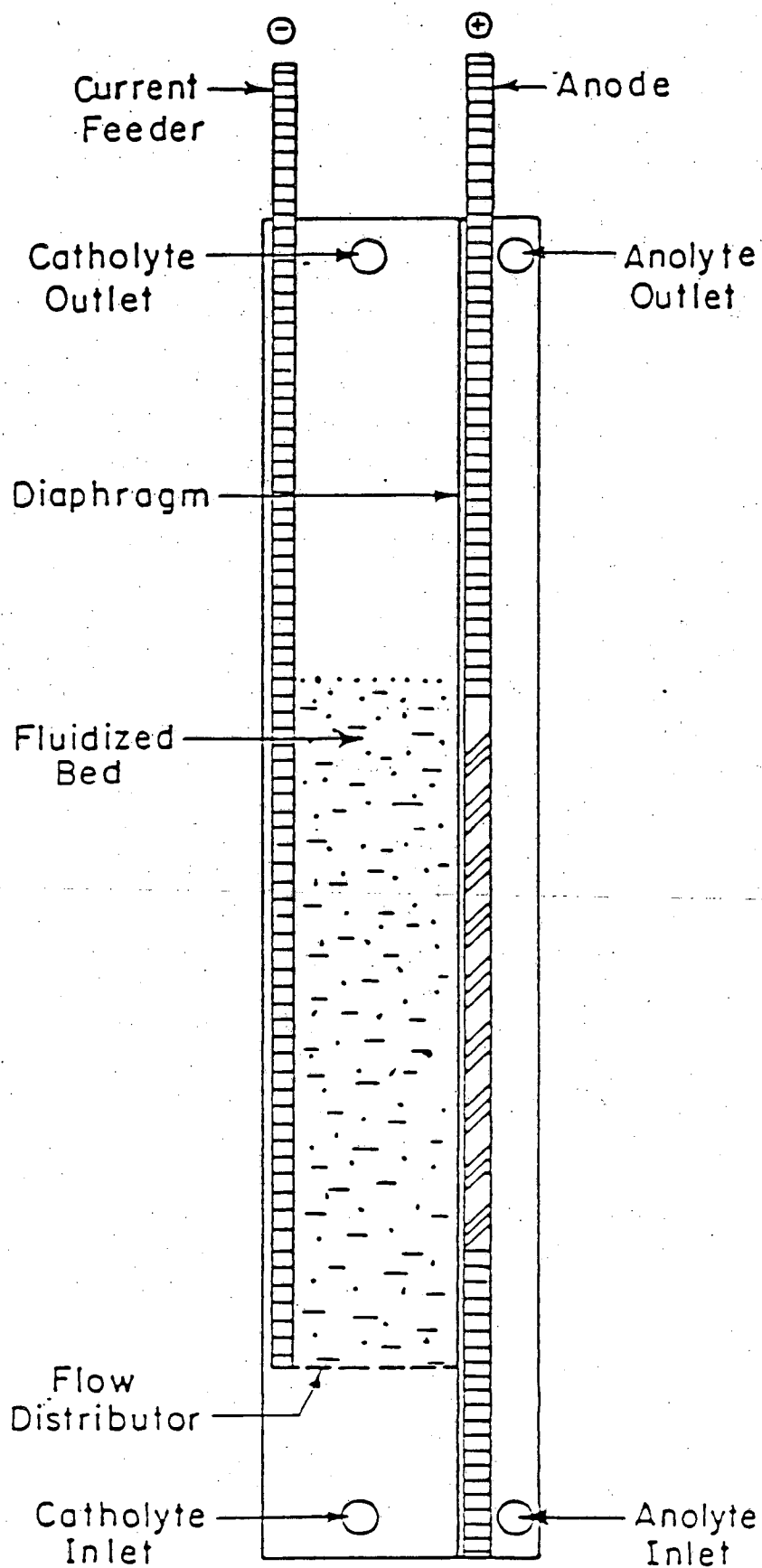
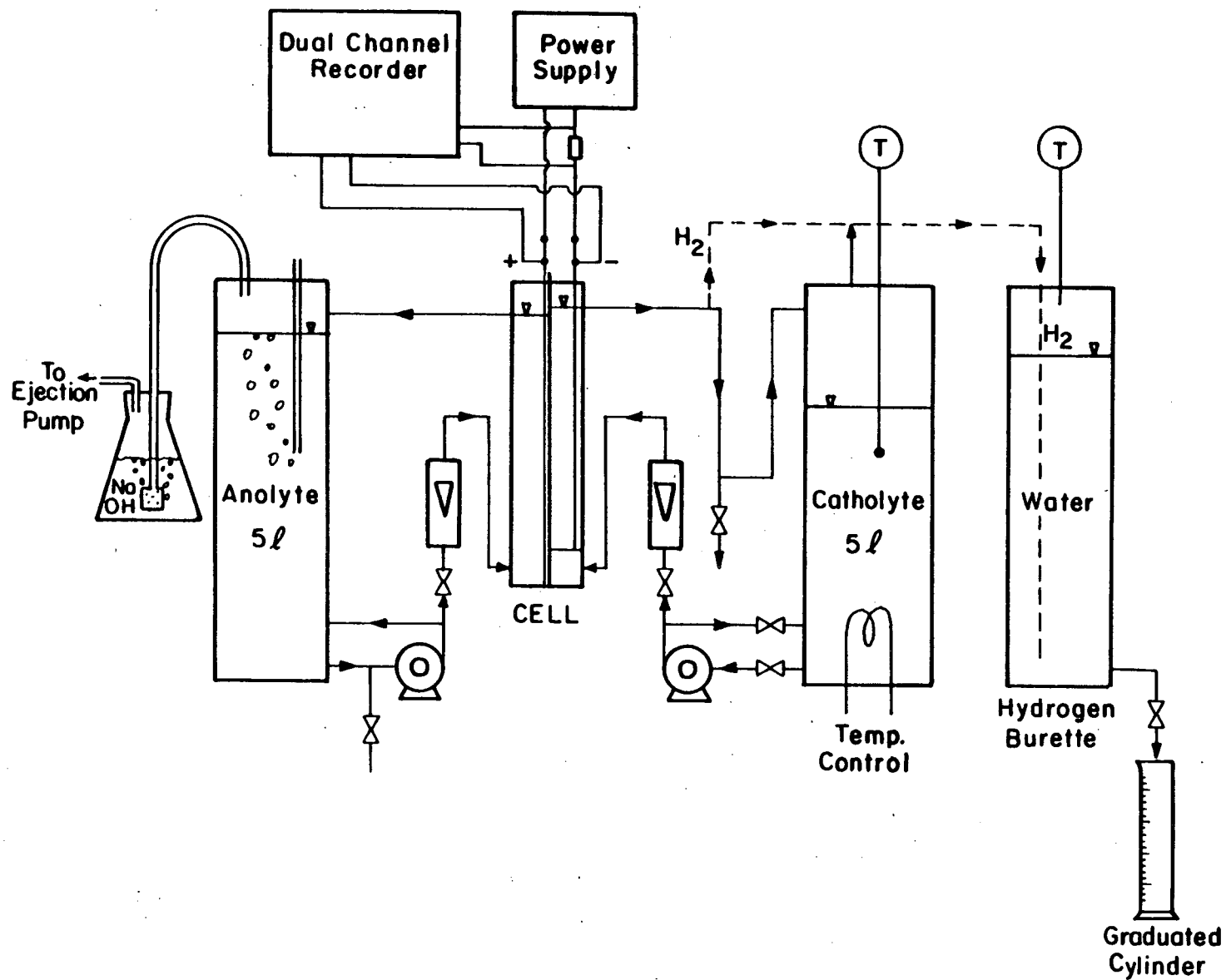
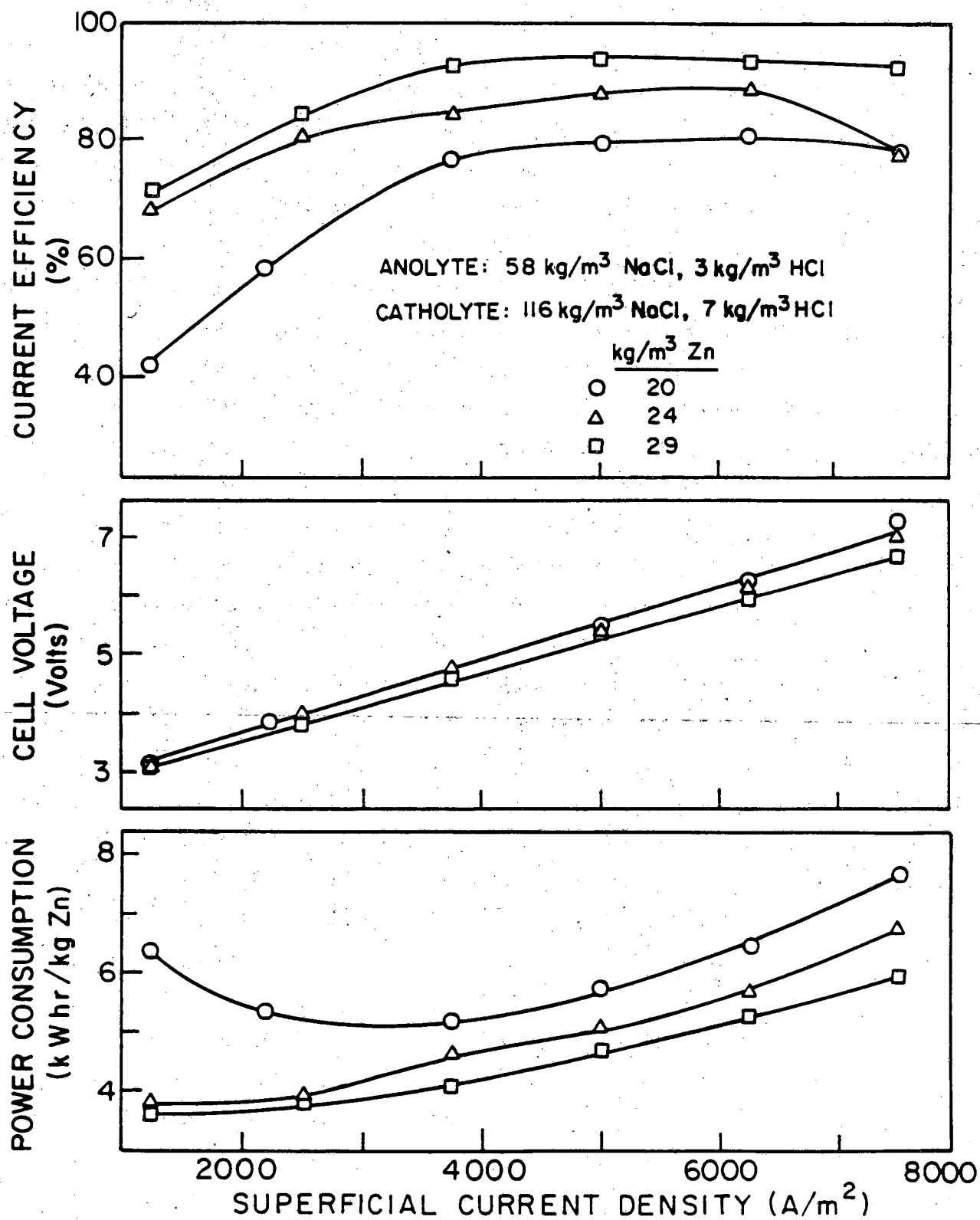
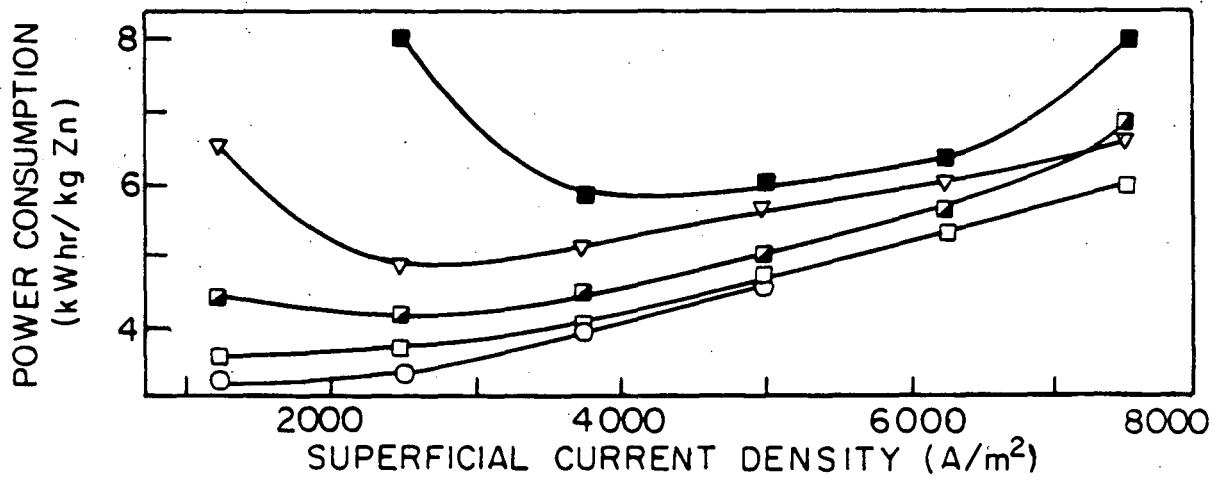
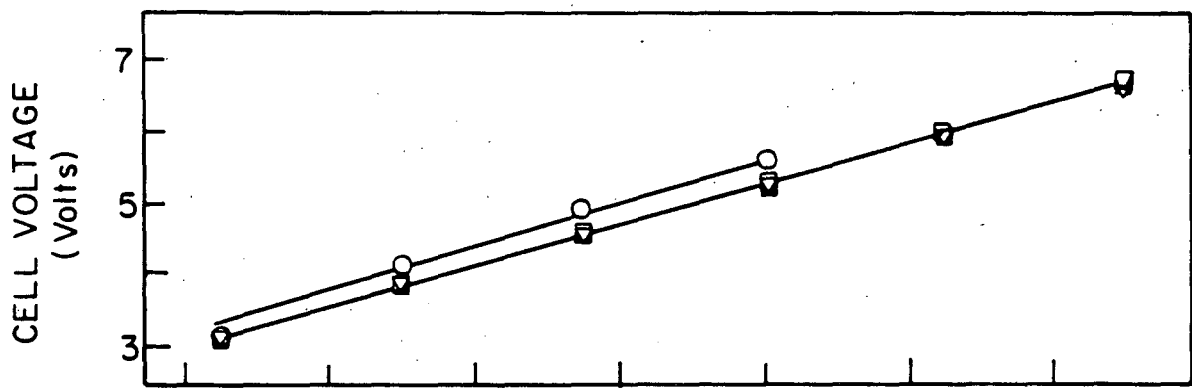
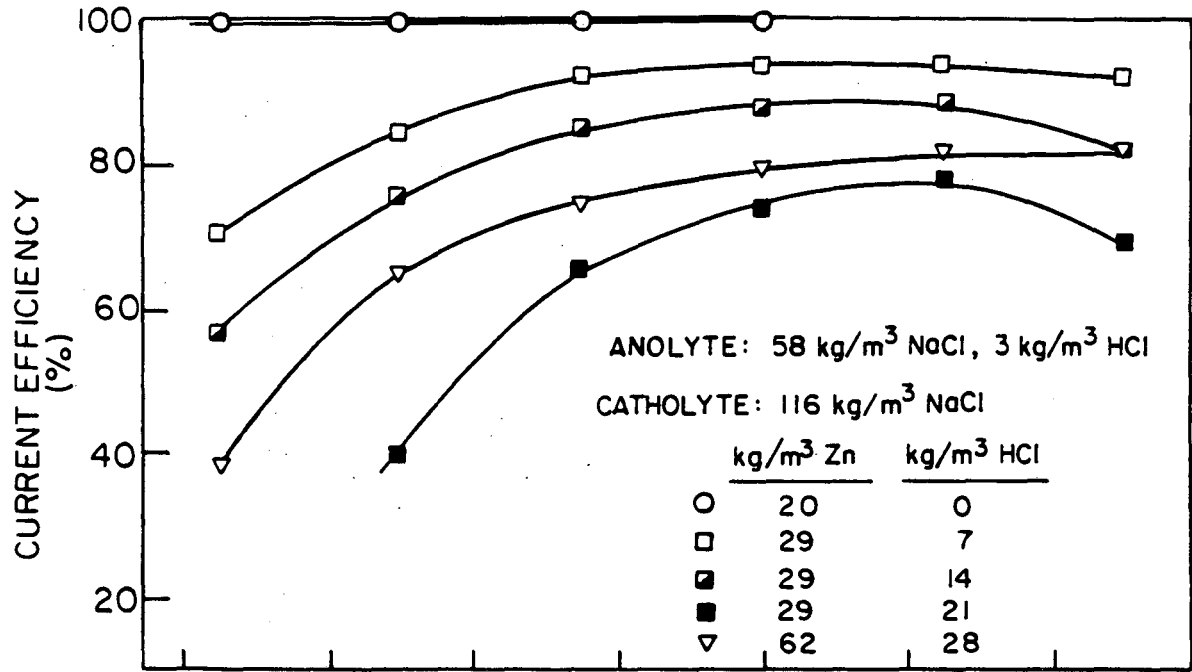


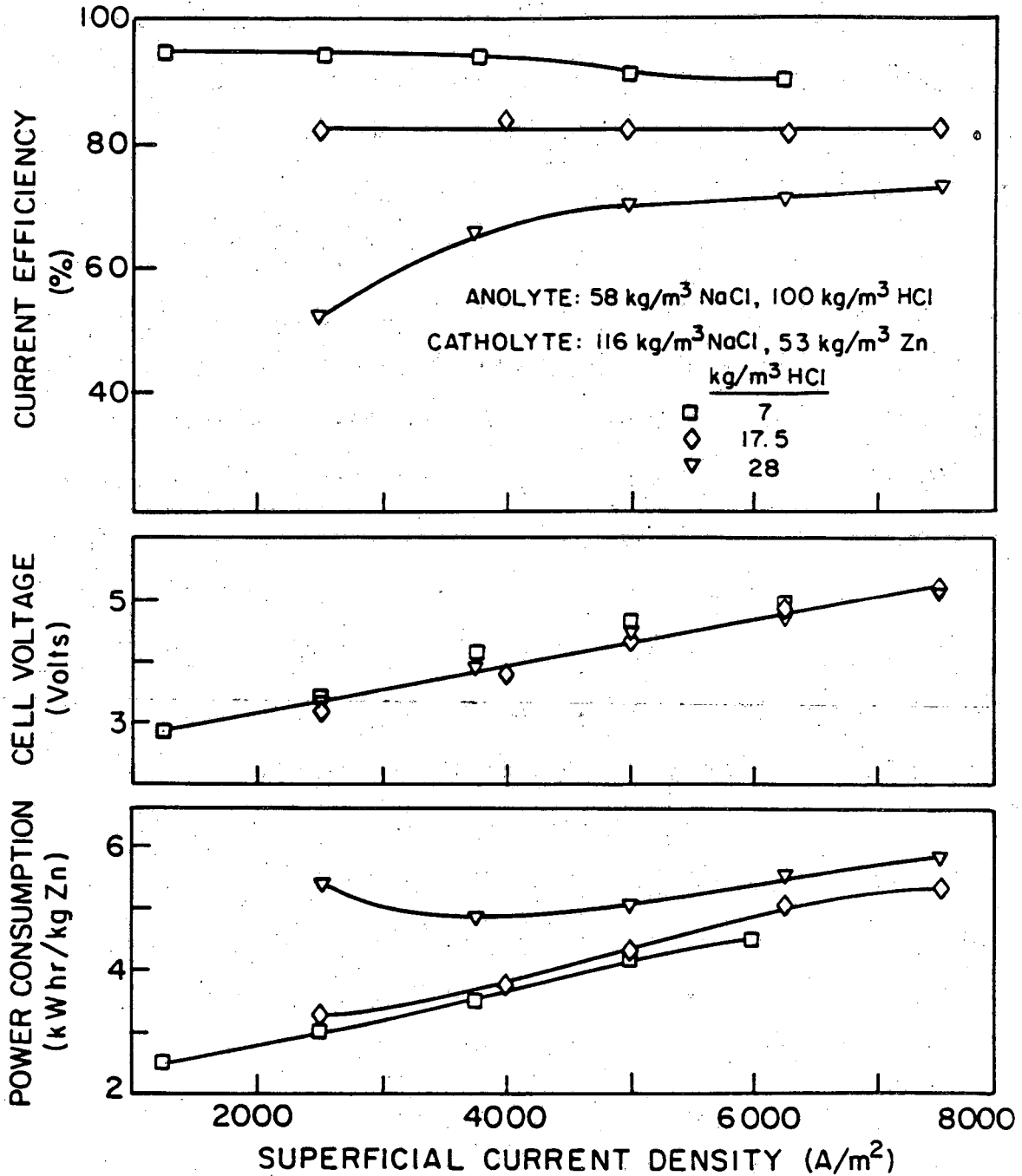
Fig. 1: Laboratory scale cell with fluidized cathode used in this investigation.

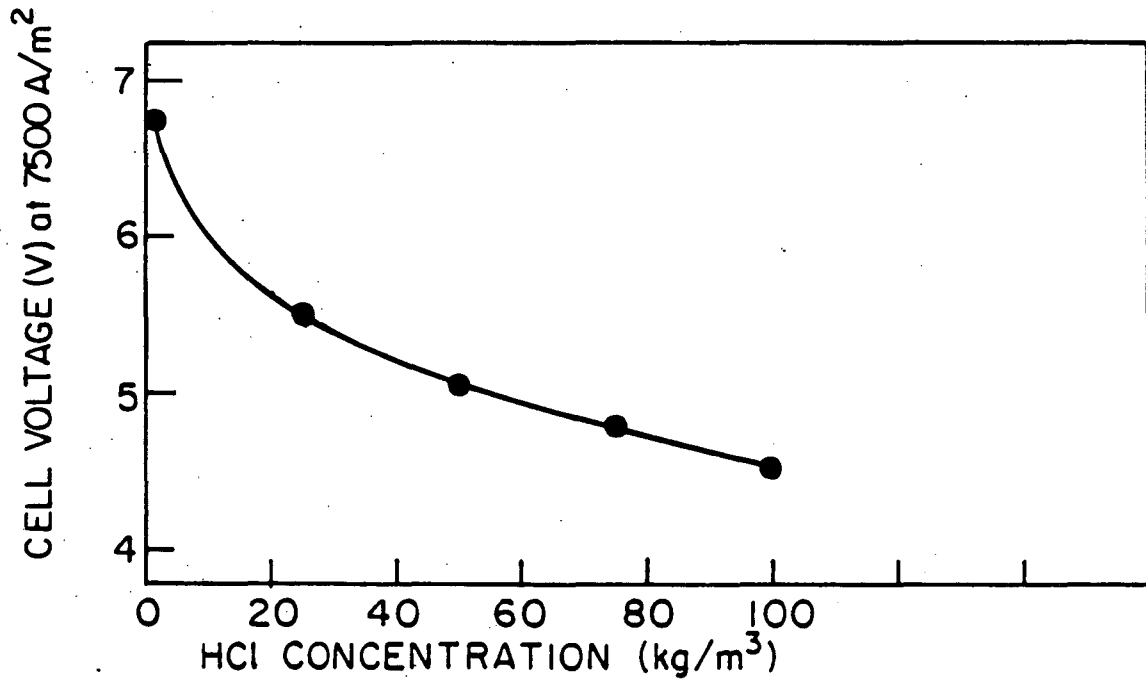
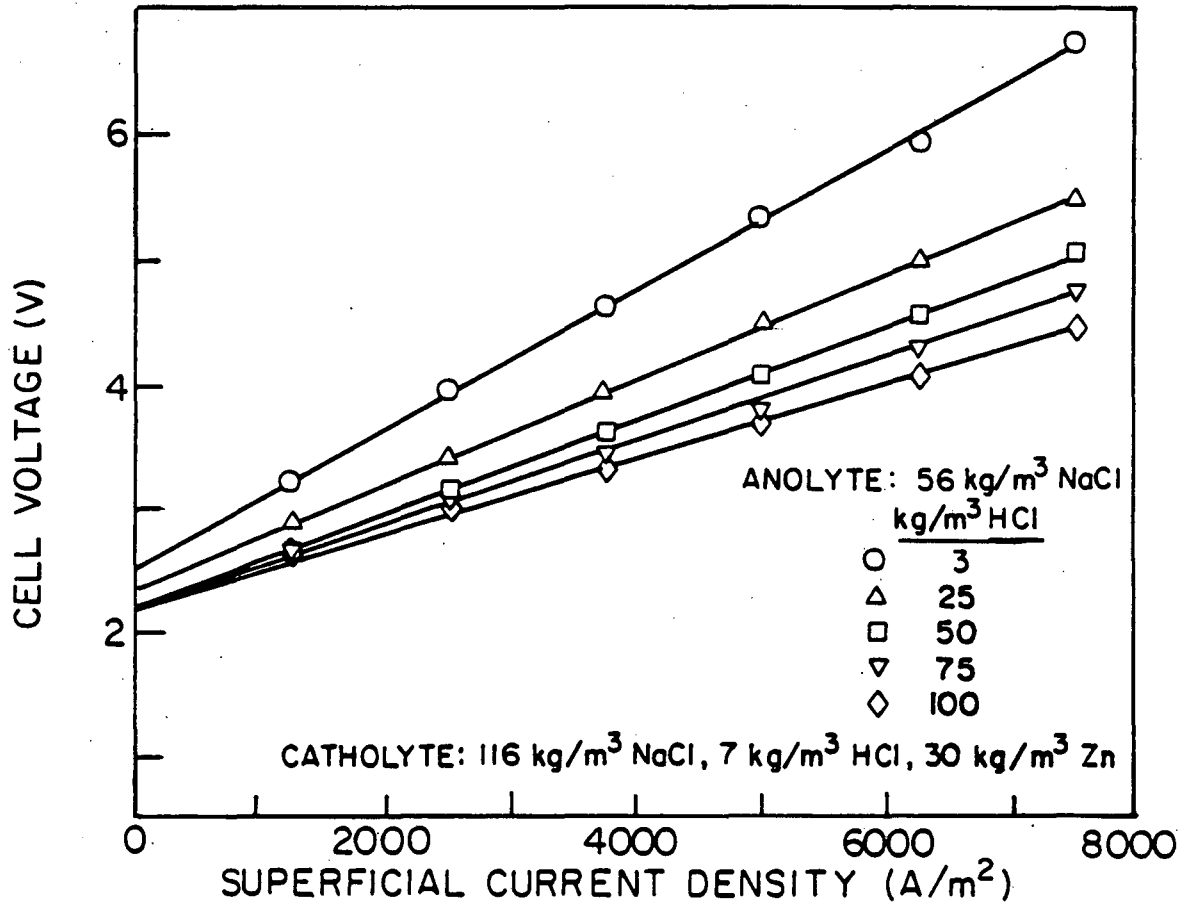


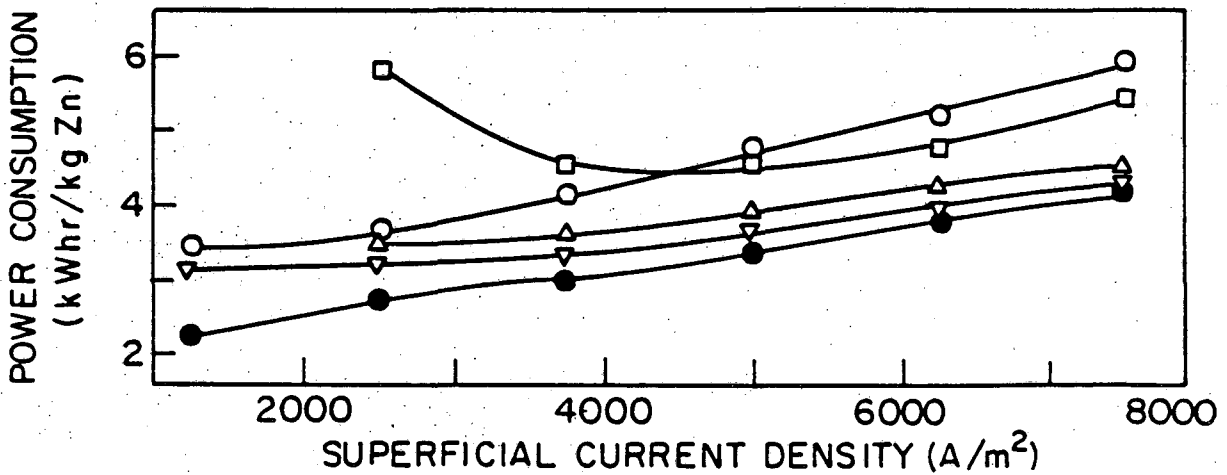
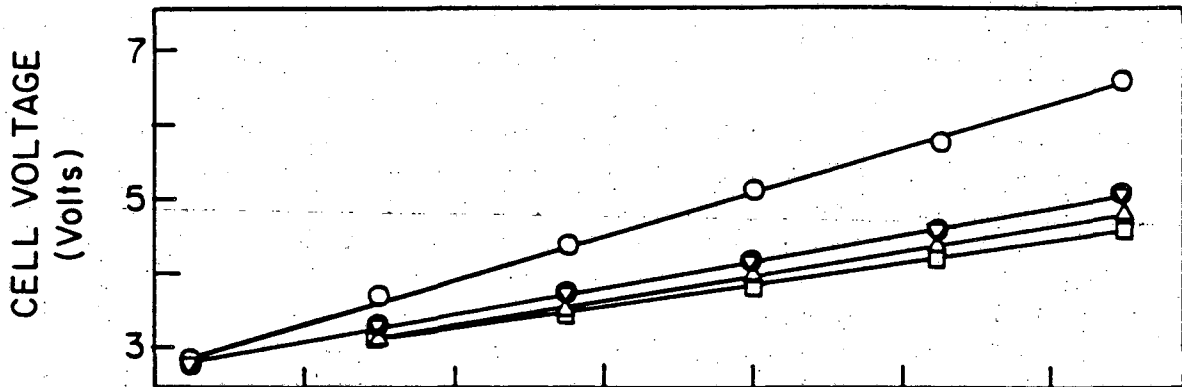
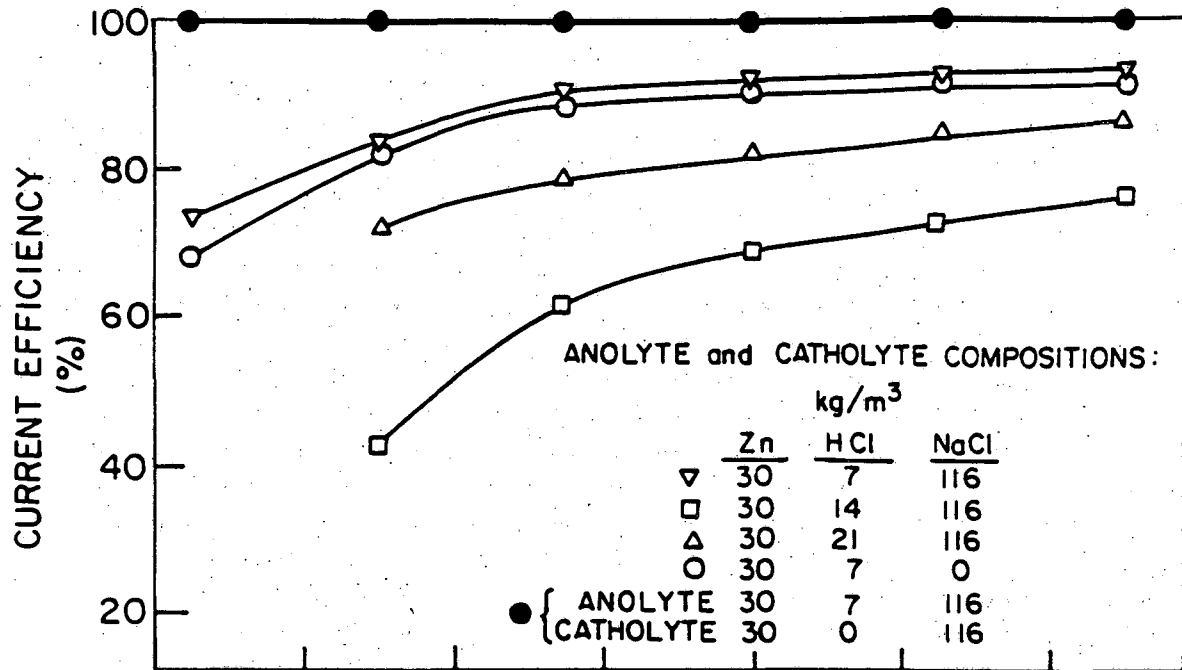
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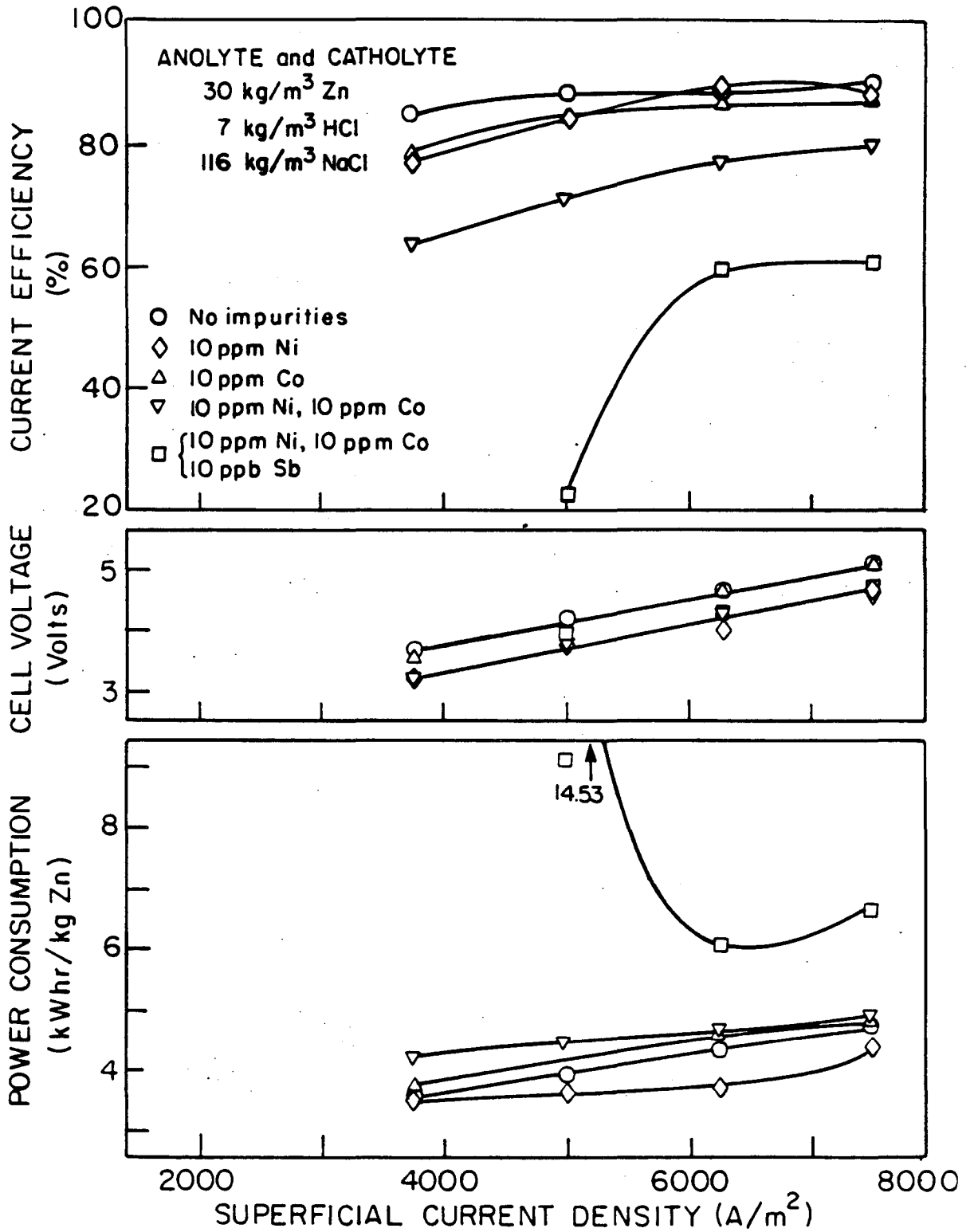


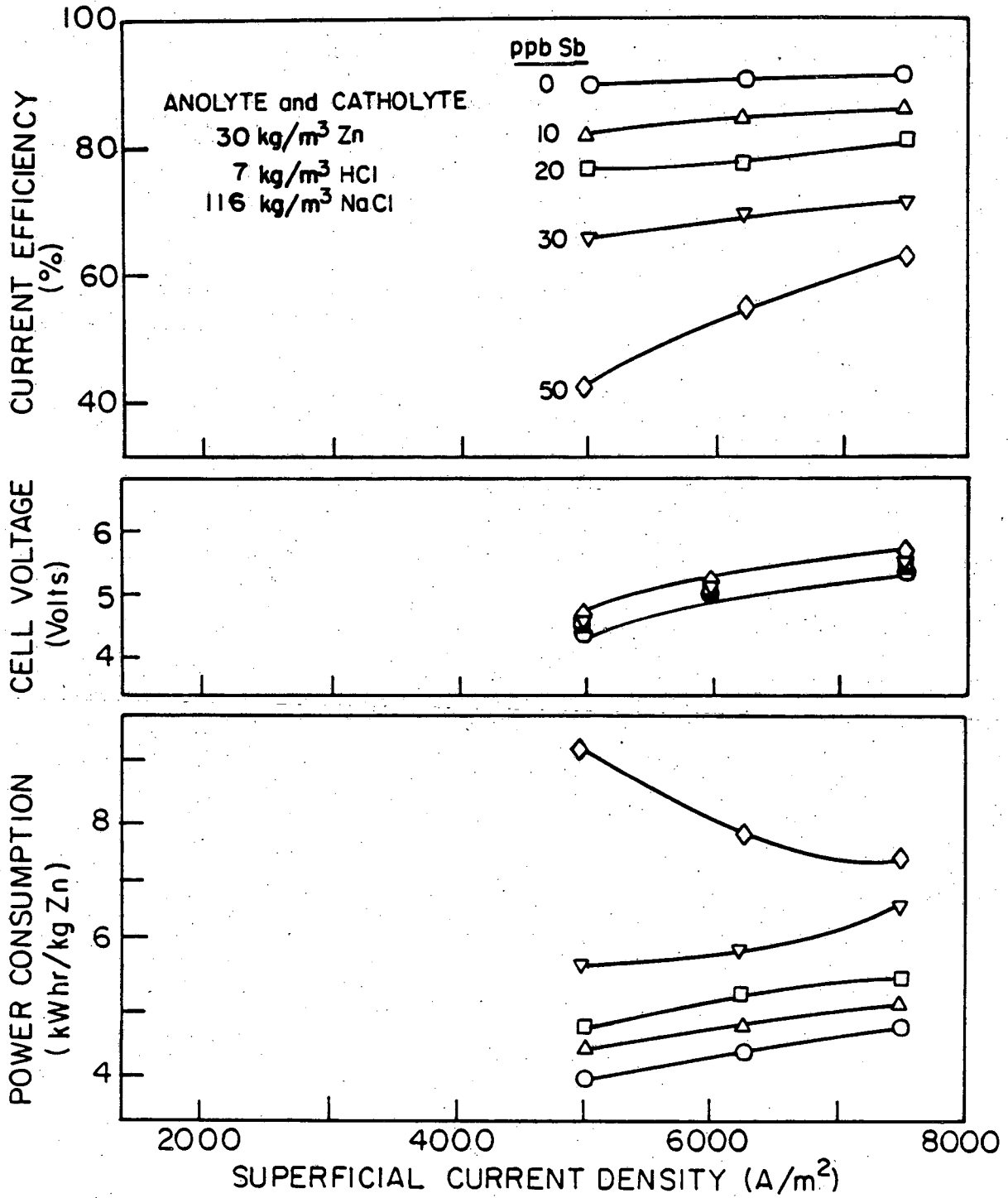


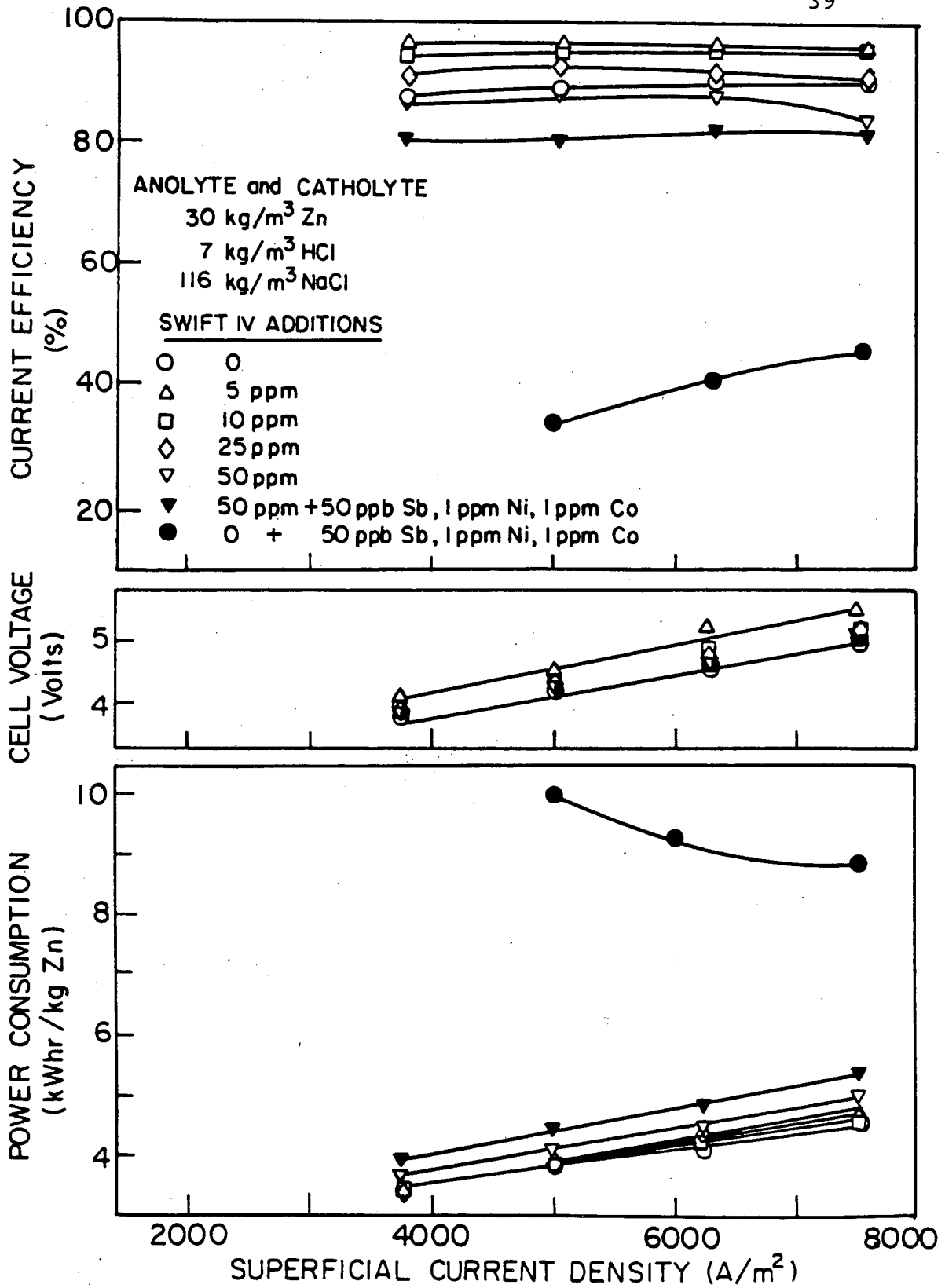












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