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ABATEMENT OF HEAVY METALS IN INDUSTRIAL EFFLUENTS BY A CATALYZED, ELECTROCHEMICAL REMOVAL SCHEME

by

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DISCLAIMER STATEMENT

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ABSTRACT

The evaluation of lead and copper deposited on a reticulated vitreous carbon surface as a catalytic agent for the electrodeposition of Cu(II), Ni(II), Pb(II), and Zn(II) from dilute solutions (10 mg/l) was performed using a flow-through porous electrode reactor. The lead was not found to catalyze the deposition of Zn(II); it did, however, show an inhibition to H_2 side reaction at the highest loading level of 50 ug/cm^2. The copper, on the other hand, showed a very strong catalytic activity for Zn(II) and Ni(II) electrodeposition at loadings from 20 to 50 ug/cm^2.

The presence of 10 to 100 ppm of Cu(II) in solution acted as a catalyst for CN^- electrooxidation. Copper coated RVC was not evaluated as a catalyst for CN^- oxidation because the anodic polarization required for CN^- oxidation would cause its dissolution.

The removal efficiency of Cu(II) from a 100 mg/l solution circulated from a reservoir to a porous, flow-by, uncatalyzed electrode and back to the reservoir was examined. A current efficiency of 87 percent was measured as the concentration of Cu(II) was lowered from 95.6 ppm to 0.05 ppm. An electrical operating cost of 11 cents per lb. of copper recovered can be estimated from the results. This should be compared to the cost of chemicals required if precipitation is used of 65.3 cents per lb. of copper removed. In addition, the volume of waste generated is

considerably lower in the electrolytic route in comparison to precipitation; the volume of precipitation-generated sludge composed of 4 per cent solids is 4.45 gal per lb. of copper as compared to .0279 gal per lb. copper (50 per cent of void volume in RVC filled by copper) electrochemically generated.

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SUMMARY AND CONCLUSIONS

This report presents the work performed in the first year of a two year project. Consequently, some of the results are preliminary; further data and interpretation will be given in the final, second year report.

Lead and copper coated on a carbon surface have been evaluated as catalysts for the electrodeposition of Cu(II), Ni(II), Pb(II), and Zn(II). Lead coated onto the carbon electrode was not found to enhance Zn(II) deposition, although at the highest loading (50 ug/cm^2) it showed an inhibition to the evolution of hydrogen. Metallic copper at loadings of 5, 20 and 50 ug/cm^2 on the carbon surface was also evaluated as a catalyst. The voltage-current relationship obtained for Zn(II) and Ni(II) deposition on the copper-coated electrode exhibited complex behavior which may be explained by the adsorption of H^+ and eventual H_2 evolution that occurr simultaneously with the metal deposition. At a current of 1.0 mA and a copper loading of 50 ug/cm^2, a decrease in overvoltage of 180 mV and 300 mV was observed for Zn(II) and Ni(II) deposition, respectively, in comparison to the uncoated electrode. Evaluation of the catalytic effect of metallic copper on Pb(II) and Cd(II) deposition is currently under investigation. A catalyst consisting of codeposited copper and lead (such as that evaluated by NASA for the REDOX battery system) might offer an optimal surface by

exploiting the catalytic effect of copper on the metal deposition reaction and the inhibition effect of lead on the hydrogen side reaction.

The presence of Cu(II) ions, at concentrations of 10 and 100 ppm appeared to catalyze the electrooxidation of CN^- at low currents, but the enhancement of the reaction diminished as the current was increased. This may be due to the relative predominance of the O_2 generation reaction at the higher currents.

A 400 ml solution of 95.6 ppm Cu(II) was processed in the flow-by reactor with an uncatalyzed carbon electrode at a flowrate of 60 ml/min and a current of 15.7 mA in a recirculation flow mode. The reactor performance was exceptional with an 87 per cent current efficiency. At this current efficiency and a cell voltage of 5 volts, and 5.8 cents per kilowatt-hour, the cost of electricity for removing copper from a waste stream would be 11 cents per lb. of copper removed. In addition, once the copper is deposited, it may easily be removed by chemical stripping or anodic dissolution to form a concentrated solution for reuse or recovered from the RVC and sold for scrap metal. The high cost of replacing a RVC electrode, about 30 cents per cubic inch, makes the anodic recovery and reuse necessary. A conservative estimate of the cost of anodic recovery of copper is 10 cents per lb. recovered copper which corresponds to a total electrical operating cost of 21 cents per lb. copper removed. This compares favorably to the operating and disposal

cost of $ 1.10 per lb. copper removed by precipitation of the hydroxide salt. This cost includes $ .226 per lb. copper for caustic to neutralize the waste, $ .189 per lb. copper for caustic to precipitate the metal ions, $ .238 per lb. copper for polyelectrolyte required for flocculation, and $ .446 per lb. copper for disposal of a sludge consisting of 4 per cent solids. Electrochemical removal of heavy metals provides a direct method for treating wastes without requiring the additional costly chemicals.

Future experiments in the flow-by reactor to remove Zn(II), Ni(II), Pb(II), and Cd(II) will provide the information needed to assess the expected improvements in current efficiency and power consumption for the catalyzed electrochemical removal scheme.

INTRODUCTION

The electroplating industry generates a significant amount of heavy metal-containing discharge water in its daily operation. Heavy metals are toxic to living organisms and tend to accumulate in the environment over a period of time. A recent study (1) of the Haw and New Hope rivers revealed a significant accumulation of heavy metals in the river sediment and in suspension. Within North Carolina there are approximately 150 independent plating shops operating today (2). This number does not include nonmembers of the American Electroplater's Society nor the plating operations which are only a processing step in a larger manufacturing scheme. The growth of the microelectronics industry in North Carolina will increase the number of shops since plating is an integral part of circuit board preparation. The largest volume of waste water is generated in the rinsing operation which is applied to every workpiece to remove residual plating bath solution. Because of the large volume of rinsewater used in comparison to the residual solution, the metal ions are low in concentration. Effluent standards for heavy metal-containing discharge waters have been proposed by the Environmental Protection Agency for the metal finishing industry and are given in Table 1. Along with the metal cations, the associated anions, possibly cyanide, chloride, or sulfate, are also present.

Table 1. Proposed maximum effluent standards for metal-finishing plants with effluent of 10,000 gpd or more.*

Species	Concentration mg/l
CN^-,total	1.9
Cu	4.5
Ni	4.1
Cr	7.0
Zn	4.2
Pb	0.6
Cd	1.2

*Federal Register, Vol. 46, No. 18, pp. 9462-9473, Jan. 28, 1981.

Various standard technologies exist to remove these pollutants (3). Among others, chemical oxidation and reduction, ion exchange, electrodialysis, activated-carbon adsorption and reverse osmosis have been utilized for heavy metal and cyanide removal. Probably the most used for heavy metal removal is a precipitation reaction which generates metallic hydroxides or sulfides. A solid sludge results which in turn must be dealt with. Precipitation requires ancillary equipment such as mixing tanks, clarifiers, filters and an inventory of chemicals (e.g., caustic). Since the precipitates are usually colloidal, coagulating

agents must be added in order to assure effective solids removal. Cyanide must be removed in a separate operation which treats the water before the precipitation. Typically, the cyanide is chemically oxidized with hydrogen peroxide, chlorine, or hypochlorite to produce cyanate, nitrogen, and carbon dioxide.

An alternative technology to treat rinse water on site is the electrodeposition of the metals along with concurrent electrooxidation of the cyanide. The primary product of cyanide electrooxidation is believed to be cyanogen ($(CN)_2$) which reacts with water to form cyanate, oxamide, oxalic acid, and/or ammonia depending upon the pH of the solution (26). This technology has not been widely utilized because of the slow rate of the electrochemical cation deposition and cyanide oxidation at the low concentrations found in rinse waters. Recent advances in electrocatalysis are proposed to circumvent these problems. It is suggested that a significant increase in the metal reaction can be obtained by the addition of a simple catalyst, submonolayer metallic copper, on the reactor surface. In addition, it is believed that the addition of metallic lead codeposited with copper on the reactor surface will increase the coulombic efficiency of the metal deposition since lead acts as a hydrogen evolution inhibitor. Furthermore, the presence of metal ions such as Cu(I) and Cu(II) in solution should serve as a catalyst for the oxidation of cyanide ion (26).

The electrochemical reactor as envisioned offers advantages over the alternate technologies: No sludge is generated, instead, a compact deposit of the metals on the reactor surface is the end product. The economic value of the metals may be reclaimed by dissolution of the deposit which is an enticing aspect of this separation. Even if recovery is not attempted, the weight and volume of the deposited metals are much less than that of a hydroxide or sulfide precipitate and there is no need for the ancillary precipitation equipment. No large inventory of chemicals is required. The cyanide and metals are removed in a single operation reducing the complexity of the water purification scheme. The plating operators are familiar with electric power supplies which is to be the motive force driving the separation.

Such a simple, one step treatment procedure will, presumably, enable plating operations to reduce significantly the heavy metal content in their discharge streams, to below that required by the EPA. Therefore, the recycling of treated rinse water will become possible, reducing the effluent volume.

The electrochemical removal technology described here is not limited to plating operations but can be applied to any stream containing heavy metals; for example, the discharge of cooling tower blowdown contains hexavalent chromium which can be reduced in the electrochemical reactor to the less noxious trivalent species or further to metallic chromium

deposited on the surface of the reactor.

In the following presentation, a review of the pertinent water resources and electrochemical literature is presented, wherein the scientific basis for this scheme is given. Following the literature review, the experimental procedure is given along with illustrations of the apparatus used. Next, the results and a discussion of the results are presented. The evaluation of lead and copper as catalysts for Pb(II), Cu(II), Zn(II), and Ni(II) deposition is given and the performance of the flow-by reactor in treating a 94 ppm Cu(II) waste is presented.

ELECTROCHEMICAL REMOVAL SCHEME

Before a review of the literature is presented, a brief discussion of the thermodynamics and kinetics of electrochemical reactions is given.

Thermodynamic considerations

The standard redox potentials for a few half-cell reactions are presented in Table 2.

Table 2. Selected Standard Reduction Potentials

Reaction	E^o, Volts
$Cr_2O_7^{-2} + 14H^+ + 6e^- = 2Cr^{+3} + 7H_2O$	1.33
$1/2O_2 + 2H^+ + 2e^- = H_2O$	1.23
$Cu^{+2} + 2e^- = Cu$	0.337
$2H^+ + 2e^- = H_2$	0
$Pb^{+2} + 2e^- = Pb$	-0.126
$Ni^{+2} + 2e^- = Ni$	-0.246
$Cd^{+2} + 2e^- = Cd$	-0.403
$Cr^{+3} + e^- = Cr^{+2}$	-0.41
$Zn^{+2} + 2e^- = Zn$	-0.676
$Cr^{+2} + 2e^- = Cr$	-0.91
$CNO^- + H_2O + 2e^- = CN^- + 2OH^-$	-0.97

The ions are assumed to be in their standard state of 1 molar ideal solution at a solution pH=0. The Nernst equation,

$$E = E^{o} + \frac{RT}{nF} \ln(C_{Ox}/C_{Red})$$

can be applied to calculate the potentials at nonstandard conditions where C_{Ox} is the concentration of the oxidized species and C_{Red} is the concentration of the reduced species. The reactions are written as reductions in Table 2; the less positive the redox potential, the less energetically favorable is the reduction. Conversely, the less positive the redox potential, the easier becomes the oxidation reaction. Thus, the reduction of Cu^{+2} is more energetically favorable than that of H^{+}, but the reduction of H^{+} is more energetically favorable than that of Zn^{+2}. The oxidation of CN^{-} is the most favorable oxidation of all half-cell reactions listed on the table. As the metal cation concentration is lowered, the more negative (cathodic) becomes the open circuit potential, hence the more difficult becomes the reduction.

Because of the exponential relationship between concentration and potential, the Nernst equation shows that a modest polarization of an electrode below its open-circuit value can cause a dramatic decrease in the equilibrium concentration of a dissolved metal. The equilibrium concentration can never be obtained in any real device because of mass-transfer and intrinsic kinetic limitations. These thermodynamic calculations permit, however, a lower bound on effluent concentrations to

be calculated a priori and are useful for estimating ultimate performance limits of an electrochemical removal scheme. Table 3 shows the calculated wall concentrations (concentration of a species directly adjacent to the electrode surface) at the exit of an uncatalyzed electrochemical reactor for various dissolved metals under a given polarization measured with a calomel reference electrode in the exit stream (4).

Table 3. Experimentally measured metal ion concentrations and predicted minimum wall concentration for various systems (4).

System	Feed Concentration (mg/l)	Observed Effluent Concentration (mg/l)	Electrode Potential (V)	Calculated Wall Concentration (mg/l)
Copper	667	0.06	-0.25	4.7×10^{-5}
Silver	1000	42	-0.46	23
Lead	4.32	0.55	-0.56	0.028
Mercury	4.12	<0.005	-0.46	1.36×10^{-14}
Antimony	100	5	-0.3828	1.62×10^{-13}

The calculated wall concentrations should be compared to the concentration actually observed exiting the reactor. It is clearly evident the performance of these electrochemical reactors could be greatly improved by increasing the rate of the deposition reactions.

Kinetic considerations

From a thermodynamic viewpoint, electronegative ions such as Pb(II), Zn(II), Cr(III), Cd(II), and Ni(II) should not be deposited from an aqueous solution before hydrogen gas is evolved. However, consideration only of thermodynamics can be misleading since the intrinsic kinetics of a reaction determines its actual progress. Electrochemical rate constants are conventionally reported as, so-called, exchange current densities, i_o. The rate for many simple electrochemical reactions may be written as:

$$i = i_o[\exp(a_A N) - \exp(-a_C N)]$$

where i is the current density of the reaction (A/cm^2); N is the overpotential, the electrical driving force, and is the electrode's displacement from the equilibrium potential; a_A is the anodic transfer coefficient; and a_C is the cathodic transfer coefficient. The exchange current density of a few sample reactions are reported in Table 4.

Table 4. Order of magnitude of the exchange current density for selected reactions

Reaction	Electrode	$i_o(A/cm^2)$
$H^+ + e^- = 1/2H_2$	Pb(1)	10^{-13}
	Hg(1)	10^{-12}
	Cd(1)	10^{-8}
	Ni(1)	10^{-6}
	Pt(1)	10^{-4}
	C(2)	10^{-7}
$Cu^{+2} + 2e^- = Cu$ $[Cu^{+2}] = 1$ M	Cu(3)	10^{-2}
$Zn^{+2} + 2e^- = Zn$ $[Zn^{+2}] = 1$ M	Zn(3)	10^{-3}
$Cd^{+2} + 2e^- = Cd$ $[Cd^{+2}] = 1$ M	Cd(3)	10^{-1}

1) B. E. Conway, Theory and Principles of Electrode Processes, 132 (1965).
2) Reference 23.
3) J. A. Harrison, Proceedings Electrode Processes, Electrochemical Society, 246 (1979).

The data clearly indicate a large variation in intrinsic electrochemical reaction rates. The effect of substrate on the rate of the hydrogen evolution reaction is remarkable. Lead and mercury are particularly ineffective surfaces on which to evolve hydrogen. If an attempt is made to remove a cation by discharging it on an electrode, hydrogen evolution

should be minimized for safety reasons and to keep current efficiency high. It could be inferred metallic lead is a good candidate for such an electrode.

In 1979, Giner and Cahill (5) discovered that the addition of a few ug Pb/cm^2 on a graphite fiber electrode greatly decreased hydrogen evolution when a Cr(III) solution was reduced to Cr(II). The chromium reduction is highly electronegative (E^o = -.40 volt) and a substantial thermodynamic driving force exists for the H^+ deposition. This simple electrocatalyst has enabled the development of the soluble REDOX battery system (6). Lead is at a submonolayer coverage at this loading and the electrocatalyst effect cannot be simply attributed to the carbon electrode acting as if it were a lead electrode. Adzic (7) has reported that submonolayer metallic lead can catalyze electropositive metal deposition reactions. Presumably the lead acts as a nucleation site for the deposition and lowers the crystallization overvoltage. Trace amounts of heavy metals, usually lead, are commonly added in gold deposition baths because they are found to give smoother metal deposits. The lead is not "covered over" by the depositing metal, but rather is found to "float" upon the deposit as it grows (7).

Lead has been found to act not only as a cathodic electrocatalyst but is an effective electrooxidation catalyst for simple organic reactions. Two recent studies have been published (7,8) which

demonstrate a marked increase in the oxidation rates of CO, HCOOH, CH_3OH and $(CH_2OH)_2$ in the presence of metallic lead on the electrode surface. At the anodic potentials at which these oxidations occur, the lead is thermodynamically unstable in the bulk form, but exists as a stable submonolayer in the so called "under potential deposited" (UPD) form. Metallic lead can exist in the UPD form hundreds of millivolts anodic to its dissolution potential. The study of the electrocatalytic properties of UPD metals is a developing area of electrochemical research and has recently been reviewed (9). The principles by which these catalysts function are not clearly understood. It is postulated that they increase the adsorption of reactant by offering more energetically favorable adsorption sites than the bare electrode, but at the same time they inhibit the adsorption of reaction intermediates which tend to poison the surface. These catalysts, regardless of their functional mechanism, are now exploitable for the development of new technologies, specifically for electrochemical pollution abatement schemes.

Electrochemical reactors

Because of the low pollutant concentration in the plating plant rinse waters, a low reaction rate is to be expected. Consequently, in order to obtain significant metal removal rates, a large surface area for the reactor will be required. Porous flow electrodes provide a large surface area per unit volume of the reactor and have been utilized for the removal of pollutants. The reaction rates are spatially nonuniform

in porous electrodes and care must be taken in their design and scaleup. The theory of porous electrode design has been presented by Newman and Tiedemann (10) and design aspects for mass-transfer limited reactors have been discussed by Fedkiw (11). The distinction between flow-through and flow-by electrodes are explained in these citations.

Some work has been reported in the literature using electrochemical procedures to reduce pollutant levels. Most of this work has been exploratory in nature, and little attempt was made to examine the procedures for realistic concentration levels and mixture contents.

Entwistle (12) compared various CN^- removal schemes for concentrated plating bath solutions. He studied incineration, biological oxidation, combustion of HCN liberated from acidic solutions, chlorination at high pH and electrooxidation. He concluded that electrooxidation was the most cost effective for concentrated waste streams.

Bennion and Newman (13) removed Cu(II) in a porous flow-through electrode of graphite particles. They found the procedure to be very effective in removing the Cu^{+2} to levels near .02 mg/l but only at very low flowrates. The cell's performance was limited by the evolution of hydrogen gas at the most cathodic potentials. Van Zee and Newman (14) examined the electrochemical recovery of Ag(I) from thiosulfate-photographic-fixing bath solutions. They also used a porous

graphite electrode. Even though the silver cation is a highly electropositive ion, they observed large hydrogen evolution rates with resulting low current efficiencies for the metal deposition. This result was explained by the complexation of Ag(I) ions with thiosulfate which makes it more stable in the solution and hence less electropositive. Adams et al (15) have shown that a porous graphite electrode can be used to reduce the concentration of ferric ions found in mine waste drainage by reduction to the less noxious ferrous species.

In a series of publications (16, 17, 18) Jansson and coworkers demonstrated that a trickle-tower electrode can simultaneously remove Pb(II), Cd(II), or Cu(II) and the associated CN^- anion from an aqueous stream. The trickle tower consists of a series of conductive particles with each layer of particles separated by an insulating mesh. The fluid trickles down from one particle layer to the next below and the two current collectors are placed at the top and bottom of such a stack. This arrangement, unfortunately, results in large power requirements and does not seem to be industrially promising. The electrodes were made of graphite and were uncatalyzed. Consequently, a long time was required in their recycle reactor to substantially reduce the metal ion concentration. This work is important because it demonstrates the ability to deal simultaneously with both the cation and anion in a single cell.

Yaniv and Ariel (19) have demonstrated Cu(II), Pb(II) and Cd(II) may be simultaneously removed from a Cl^- solution on an uncatalyzed graphite cloth electrode. Not surprisingly, they found that the more electropositive metal was preferentially removed.

Electroflotation of concentrated Cd(II) and CN^- wastes has been demonstrated (20). A NaCl solution was electrolyzed in this cell and not the pollutants.

The EPA has recently recognized the utility of electrochemical procedures for heavy metal ion removal. They have jointly sponsored a demonstration (21) of an electrochemical reactor for Zn(II) removal from the drag-out line water (pre-rinse bath) of a barrel plating line. A Canadian company, H.S.A. Reactors Limited, has developed a proprietary reactor which is being used in the demonstration. Details of the reactor system are unavailable but it is known that the electrodes are uncatalyzed.

EXPERIMENTAL

Electrode material

The literature review has shown that graphite has been the preferred electrode material usually in the form of flakes, powder, or cloth. These particulate electrodes are inconvenient to use because of the necessity to restrain mechanically the packing within the bed. Interparticle contact resistance can become significant which causes a large ohmic voltage drop unless the bed is tightly compressed which subsequently adds to the pressure loss and operating costs. Cloth electrodes avoid these problems; however, it is inconvenient to construct a flow-by cloth electrode.

A new form of porous carbon, Reticulated Vitreous Carbon (RVC), has become commercially available (22) and was used as the electrode in this work. This is a glassy carbon material with a hydrogen exchange current density the same as that of ordinary graphite (23). The RVC is a highly porous, contiguous material with a low electrical resistivity. It is machinable, has a high abrasion resistance, and a large surface area per unit volume. RVC has proven to be a useful electrode material for electroanalytical work (24).

Catalyst loading

The metallic catalyst was loaded onto the RVC by electrodeposition. A 9 mm diameter and 4.7 mm long RVC plug was placed in the flow-through reactor shown in Figure 1. The internal surface area of the RVC was approximately 50 cm^2/cm^3. The lead coatings were obtained by recirculating a 1 mM $PbCl_2$ in a 10^{-2} M HCl solution through the RVC. A cathodic current of 100 uA was applied causing the Pb(II) ions to electrodeposit. The loading was varied by varying the time the current was applied and assuming a 100 per cent current efficiency; for example, for a lead loading of 10 ug/cm^2, the current was applied for 1,397 seconds.

The loading procedure for lead was found to be unacceptable for copper. An extremely nonuniform deposit of copper was obtained: a large amount was deposited on the face nearest the counterelectrode and very little, on the other face. The nonuniformity in the copper coating indicated a strong influence of reaction kinetics on the deposit. Consequently, an improved loading procedure was developed to minimize these effects. Electrolyte (10^{-2} M $HCl_{(aq)}$) was recirculated from a well stirred reservoir through the RVC in the flow-through reactor and returned to the reservoir. The total volume of electrolyte recirculated was 400 ml. The chloride salt of the metal ($CuCl_2$ for copper or $PbCl_2$ for lead) was then added to the electrolyte. A small amount was added

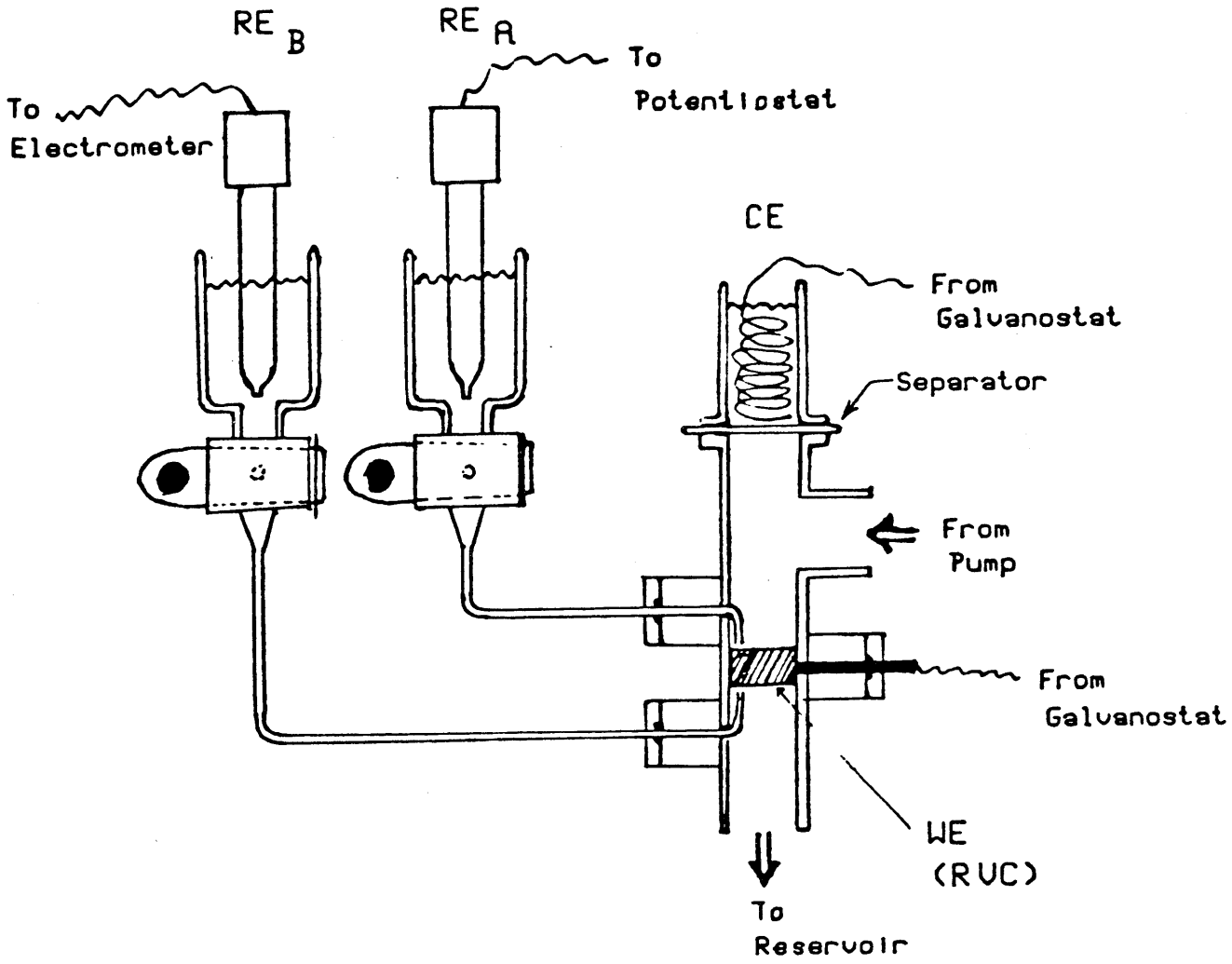

Figure 1. Schematic diagram of the flow-through electrode used to evaluate the effectiveness of the RVC electrode for metal ion removal.

incrementally to keep the metal ion concentration in solution below .5 ppm Cu(II) which gave a more uniform deposit. For copper, a single addition of 2.28 ml of 1.035 x 10^{-3} M $CuCl_2$ was added for a copper loading of 10 ug/cm^2. A cathodic current was applied to the RVC electrode causing the metal ions in solution to deposit on the surface of the RVC. The current was applied until the electrodeposition was completed as evidenced by the sharp rise in overvoltage. The rise in voltage of the RVC vs saturated calomel electrode (SCE) indicated that the metal ion had been depleted from solution and that the reduction of H^+ to H_2 had become the dominating reaction. The catalyst loaded RVC plug was washed and stored in deionized water until needed. The catalyst loading was changed by varying the amount of the chloride salt added to the electrolyte; for example, for a copper loading of 20 ug/cm^2, a second addition of 2.28 ml of 1.035 x 10^{-3} M $CuCl_2$ was made to the solution after the deposition of the first addition had been completed as indicated by the rapid voltage rise.

Catalyst evaluation

The catalyst effectiveness was evaluated from the current-voltage relationship obtained on the RVC plugs. The catalyzed or uncatalyzed RVC electrode was placed in the flow-through reactor (Figure 1). The RVC served as the working electrode (cathode) on which the metal ions were deposited. A platinum wire upstream of the RVC was the counterelectrode (anode). A DuPont Nafion membrane was used as a separator which allowed

the passage of current from the counterelectrode to the working electrode but prevented O_2 from entering into the catholyte. The catholyte and anolyte consisted of 10^{-2} $\underline{M}$ $HCl_{(aq)}$ containing 10 ppm of the dissolved metal. The catholyte was recirculated (to minimize mass-transfer effects) from a well stirred reservoir through the flow-through reactor (Figure 1) and back to the reservoir at a flowrate of 60 ml/min. The anolyte was not recirculated. The resulting voltage of the RVC relative to a SCE at the inlet and outlet when a current was applied to the RVC was measured. The current was varied either by staircasing the current at .01, .1, .4, 1.0, and 2.5 mA and measuring the voltage transients over 500 sec at each current, or by continuously ramping the current at a rate of 2 uA/sec from 0 to 2 mA and simultaneously recording the inlet and outlet voltages. The voltage of the RVC relative to the SCE at the inlet is used in the voltage-current relationships graphically presented in this report.

The effectiveness of the catalyst on metal deposition was characterized by the current passed at a given voltage: the smaller the cathodic voltage at a given current level, the better was the catalyst.

Continuously ramping the current at 2 uA/sec from 0 to 2 mA was applied to the CN^- oxidation study; however, due to the problem of dissolution of the metallic catalysts at the anodic overvoltages required for CN^- oxidation, the CN^- oxidation is performed on bare RVC. The

catalytic effect of the presence of Cu(II) ions in solution on CN^- oxidation was examined.

Flow-by electrode

The reactor system consists of a flow-by RVC porous electrode (Figure 2a and 2b) and a reservoir , the contents of which are continually recycled through the reactor. This arrangement has been chosen since it will closely reproduce the system envisioned at an actual site where the reactor is used to clean the contents of a rinse tank. A once-through system is not anticipated to be feasible because of the high conversion which would be required in a single fluid pass.

The anolyte and catholyte are separately pumped through the Lucite reactor. The uncatalyzed RVC is thin (5 mm) and rectangular in shape. The anode and cathode RVC electrodes are separated by a DuPont Nafion membrane which permits the passage of H^+ ions only. This prevents the mixing of anolyte and catholyte which could result in a drop in current efficiency due to the reduction of anode-generated O_2 at the cathode or the oxidation of cathode-generated H_2 at the anode. In studying the removal of individual metal ions, a separate reservoir for the catholyte and anolyte is used. The catholyte consists of 100 ppm of the metal ion and electrolyte (10^{-2} $\underline{M}$ $HCl_{(aq)}$); the anolyte consists of electrolyte only.

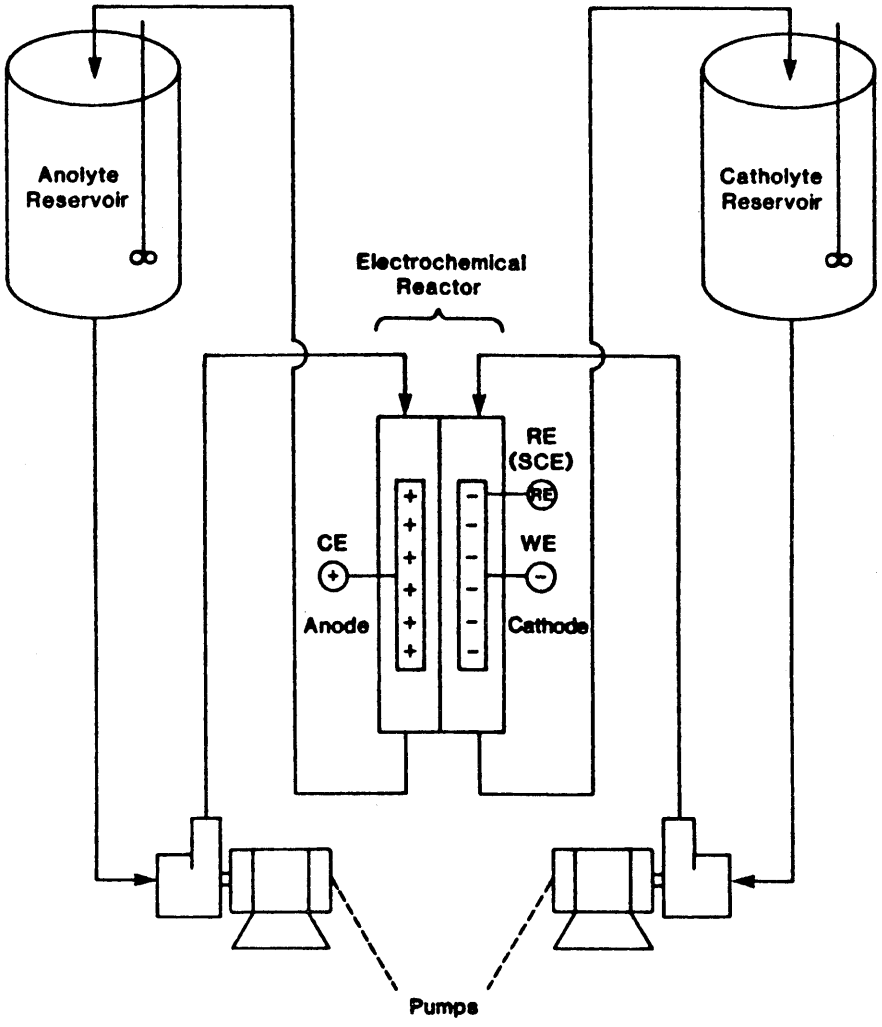

Figure 2a. Schematic diagram of the flow-by reactor and recirculation scheme employed for the removal of heavy metal ions.

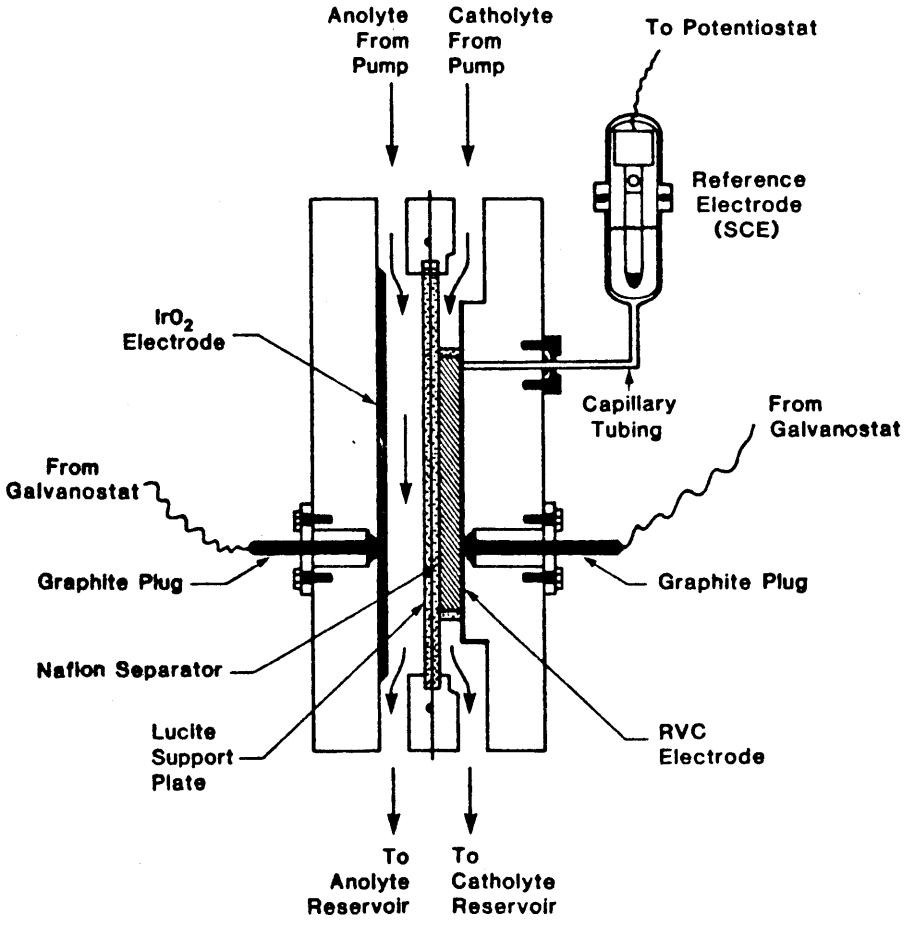

Figure 2b. Detailed schematic diagram of the flow-by reactor cell.

A simulated waste consisting of 94 ppm Cu(II) and pH of 2 (10^{-2} M $HCl_{(aq)}$) was treated in the flow-by reactor. The flow-by reactor was operated at a constant current of 15.7 mA. This corresponded to a current of 1 mA in the smaller flow-through reactor for small mass-transfer effects on a cross-sectional area basis. The current and voltage of the RVC vs the SCE were measured during the experiment. Samples of the fluid in the reservoir (1 ml) were periodically withdrawn and analyzed for metal content by atomic absorption spectrophotometry. The current efficiencies were calculated by a mass balance.

RESULTS

Figures 3 and 4 illustrate typical potential responses measured between the RVC and the upstream reference electrode at two currents, 0.1 and 1.0 mA, respectively. In our initial work the current was varied three orders of magnitude (.01 to 10 mA) by controlling the current at .01, .10 , .40, 1.0 and 2.5 mA and measuring the voltage transients at each current for 500 seconds. The resulting voltage after 50 seconds at each current level is shown on Figures 5, 6, 7, and 8 for a solution with no metal ion, Cu(II) , Pb(II), and Zn(II), respectively. Data collected from different RVC plugs is shown to illustrate the reproducibility of the measurements. All voltages are reported relative to the upstream calomel reference electrode.

Figure 9 shows the current-voltage relationship for Zn(II) deposition from a 10 mg/l solution on a RVC plug coated with lead at four loadings: 0, 1, 10, and 50 ug/cm^2. Figure 10 illustrates the current-voltage relationship on the lead coated RVC measured with no metal ion in the solution. Figure 11 shows the current-voltage relationship for Zn(II) deposition from a 10 mg/l solution on a RVC plug coated with Cu at loadings of 0 and 30 ug/cm^2.

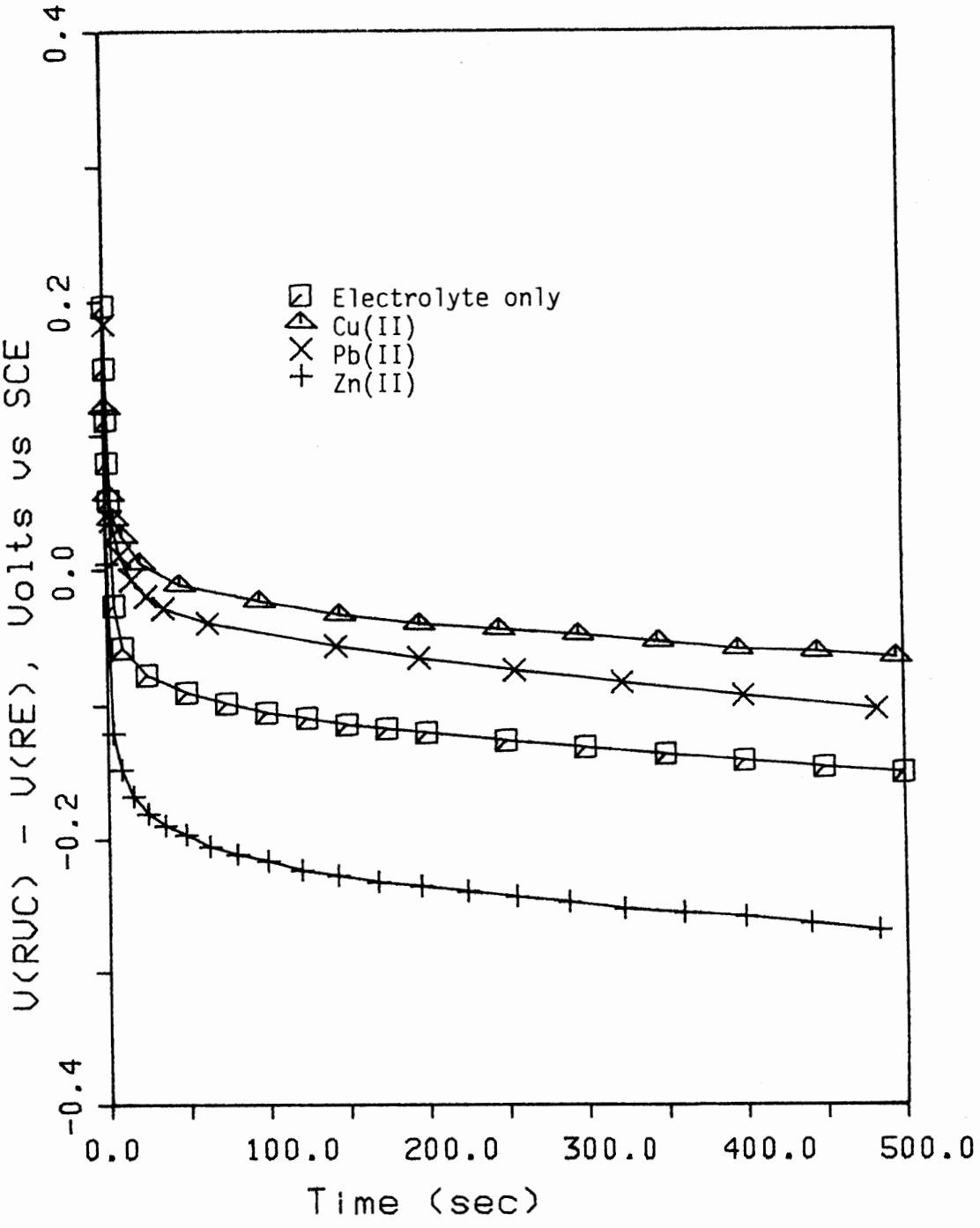

Figure 3. Response of the potential difference between the RVC flow-through electrode and the upstream calomel reference electrode to a 0.1 mA current for the indicated metal ions. All solutions were 10 mg/l of the chloride salt at pH=2.

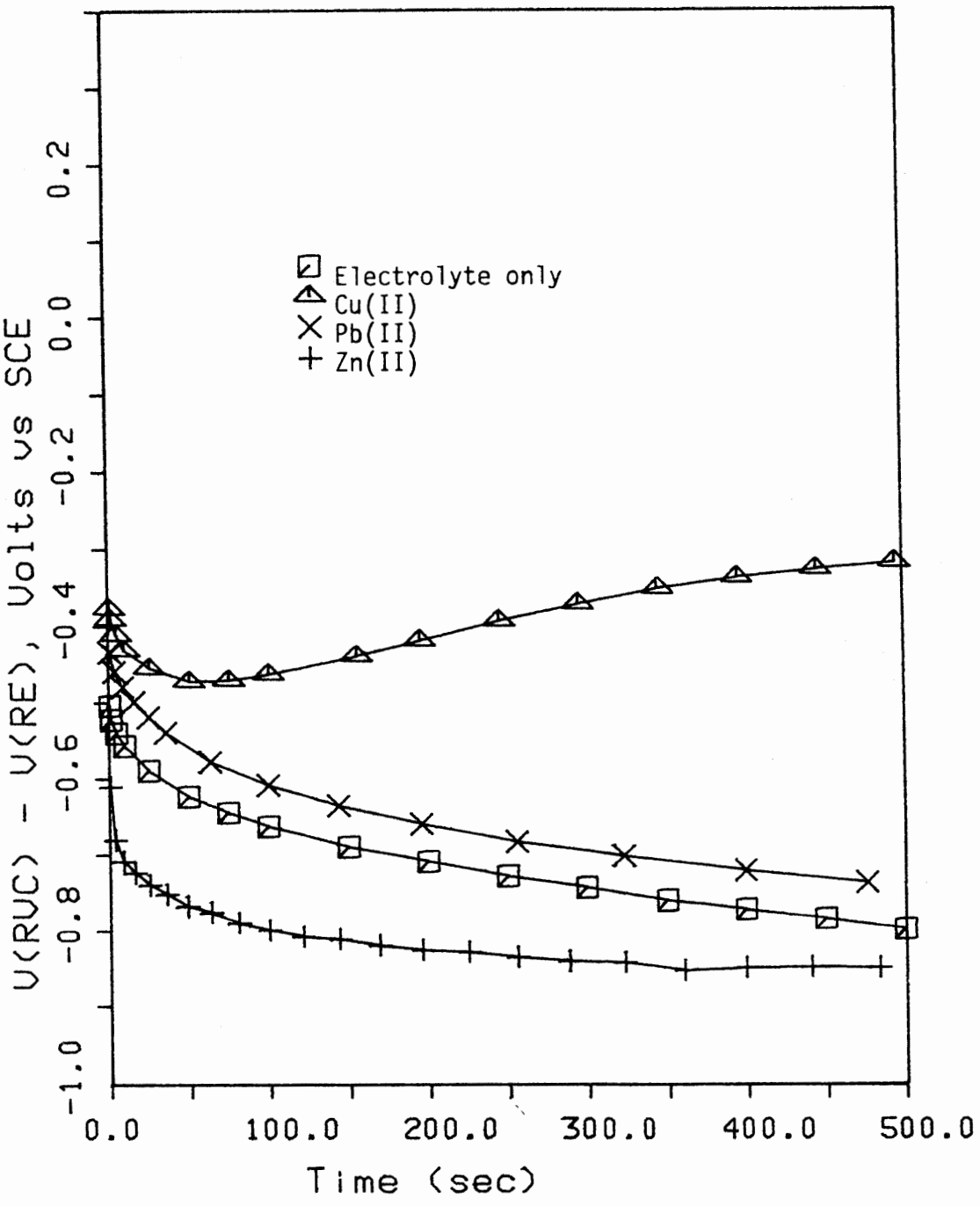

Figure 4. Response of the potential difference between the RVC flow-through electrode and the upstream calomel reference electrode to a 1.0 mA current for the indicated metal ions. All solutions were 10 mg/l of the chloride salt at pH=2.

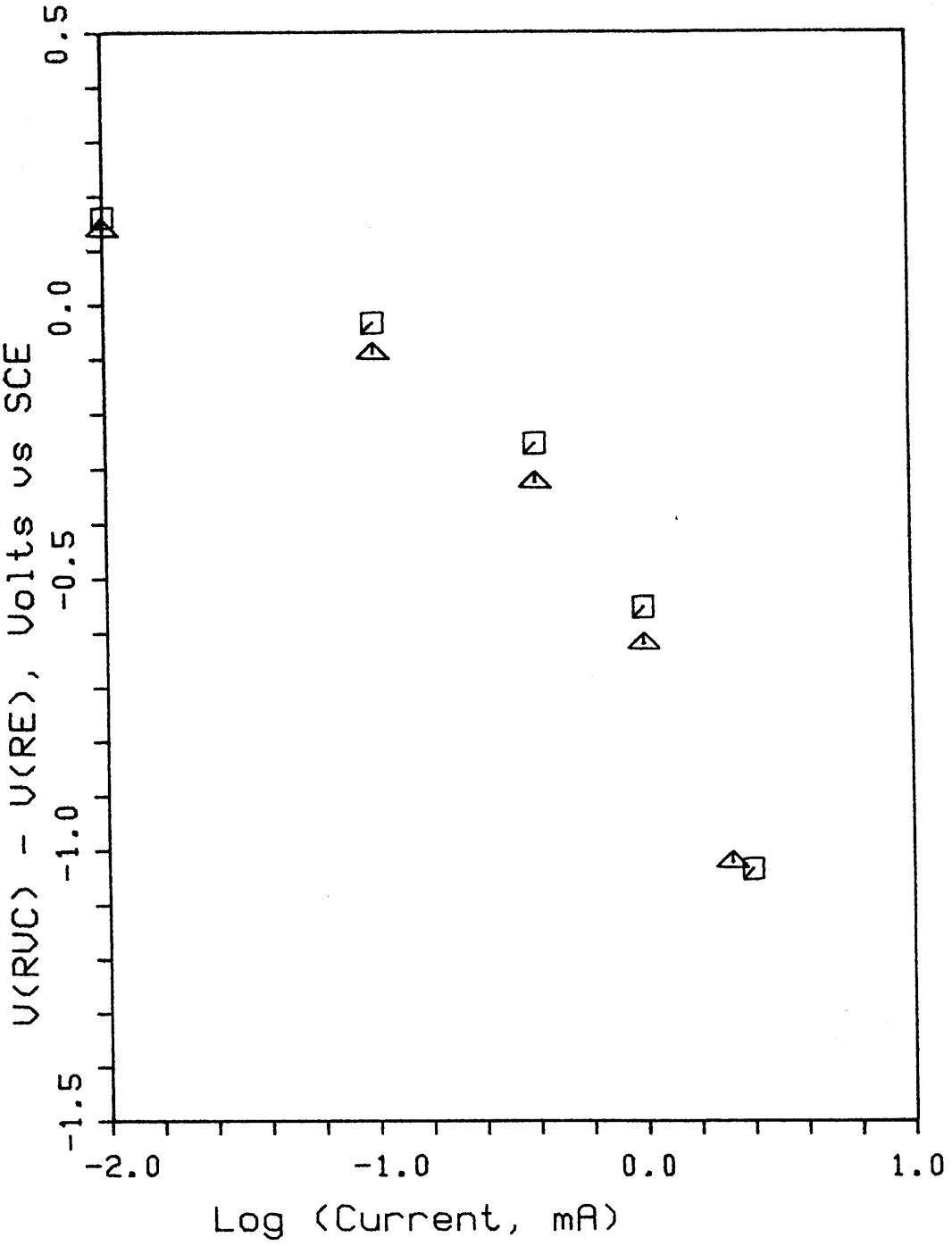

Figure 5. Tafel plot for the uncoated RVC electrode in the absence of metal ions in the electrolyte at pH=2.

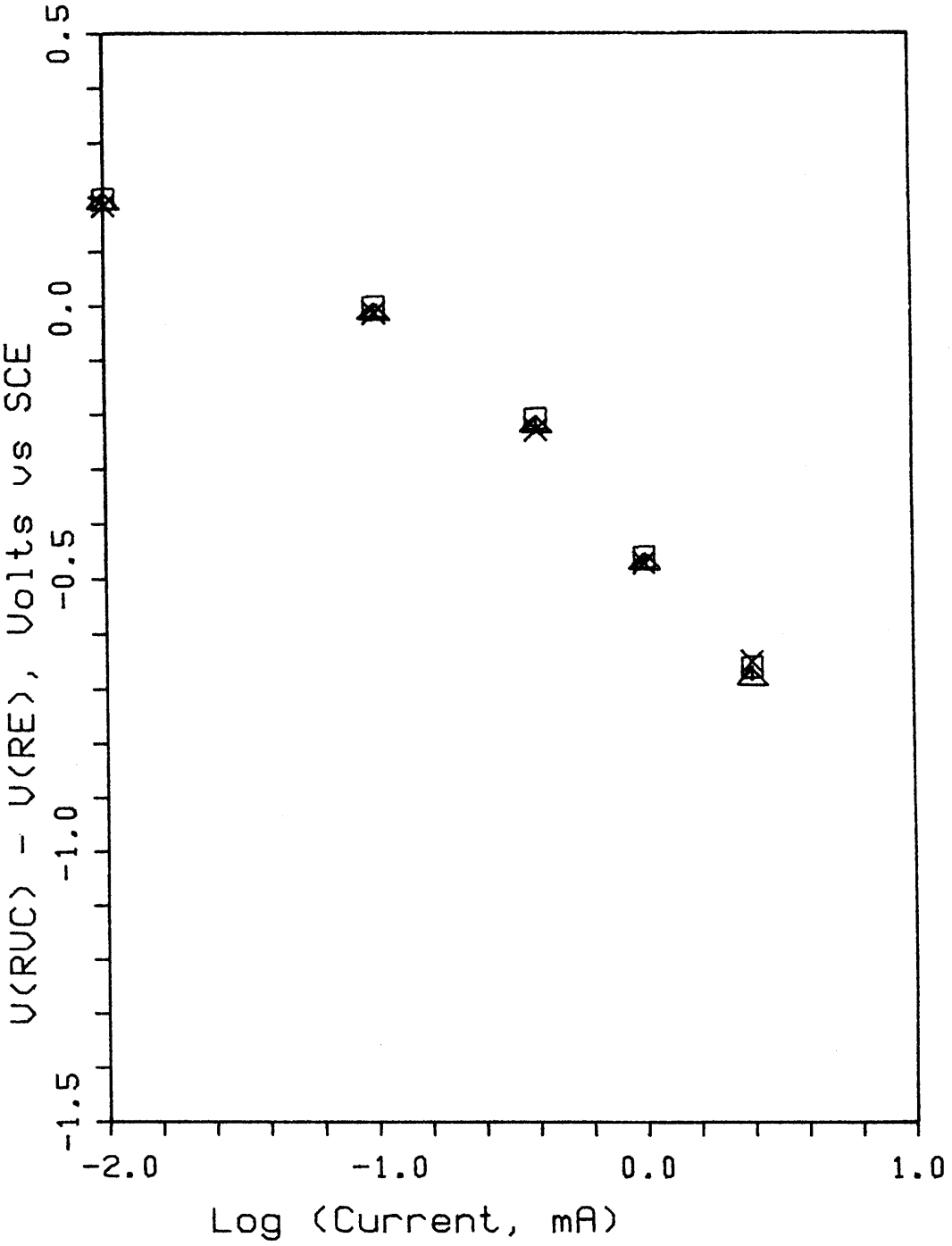

Figure 6. Tafel plot for the uncoated RVC electrode for a 10 mg/l solution of Cu(II) at pH=2.

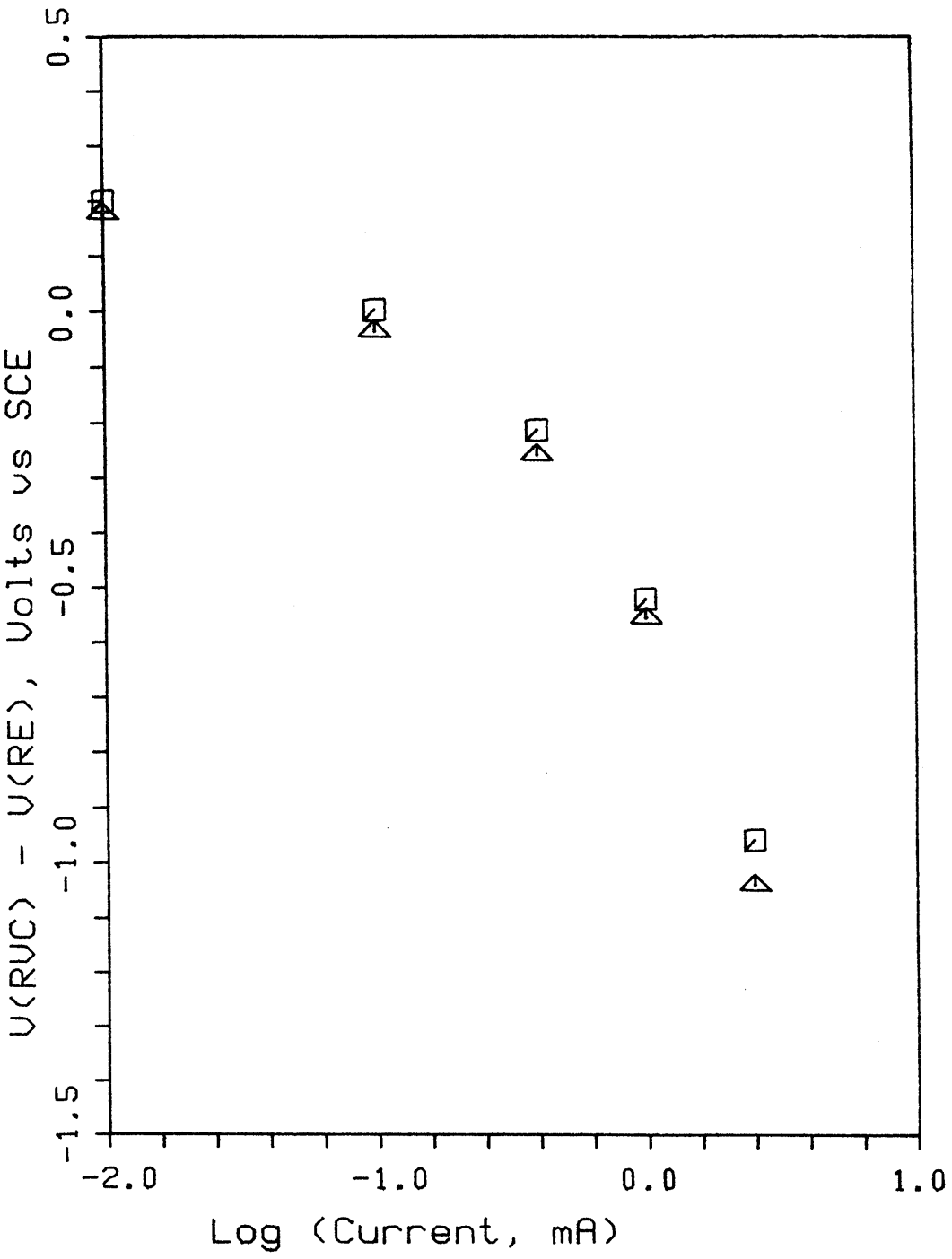

Figure 7. Tafel plot for the uncoated RVC electrode for a 10 mg/l solution of Pb(II) at pH=2.

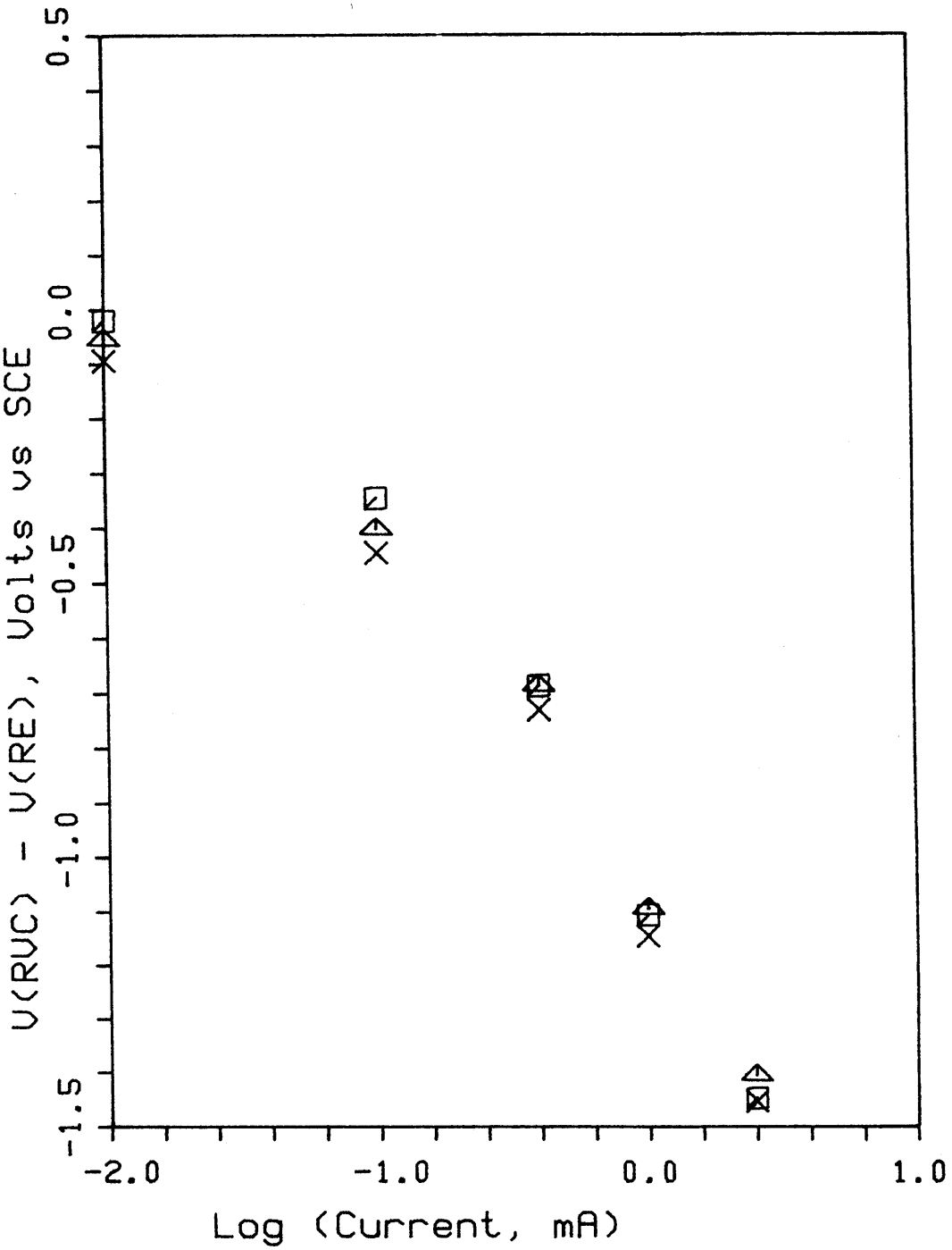

Figure 8. Tafel plot for the uncoated RVC electrode for a 10 mg/l solution of Zn(II) at pH=2.

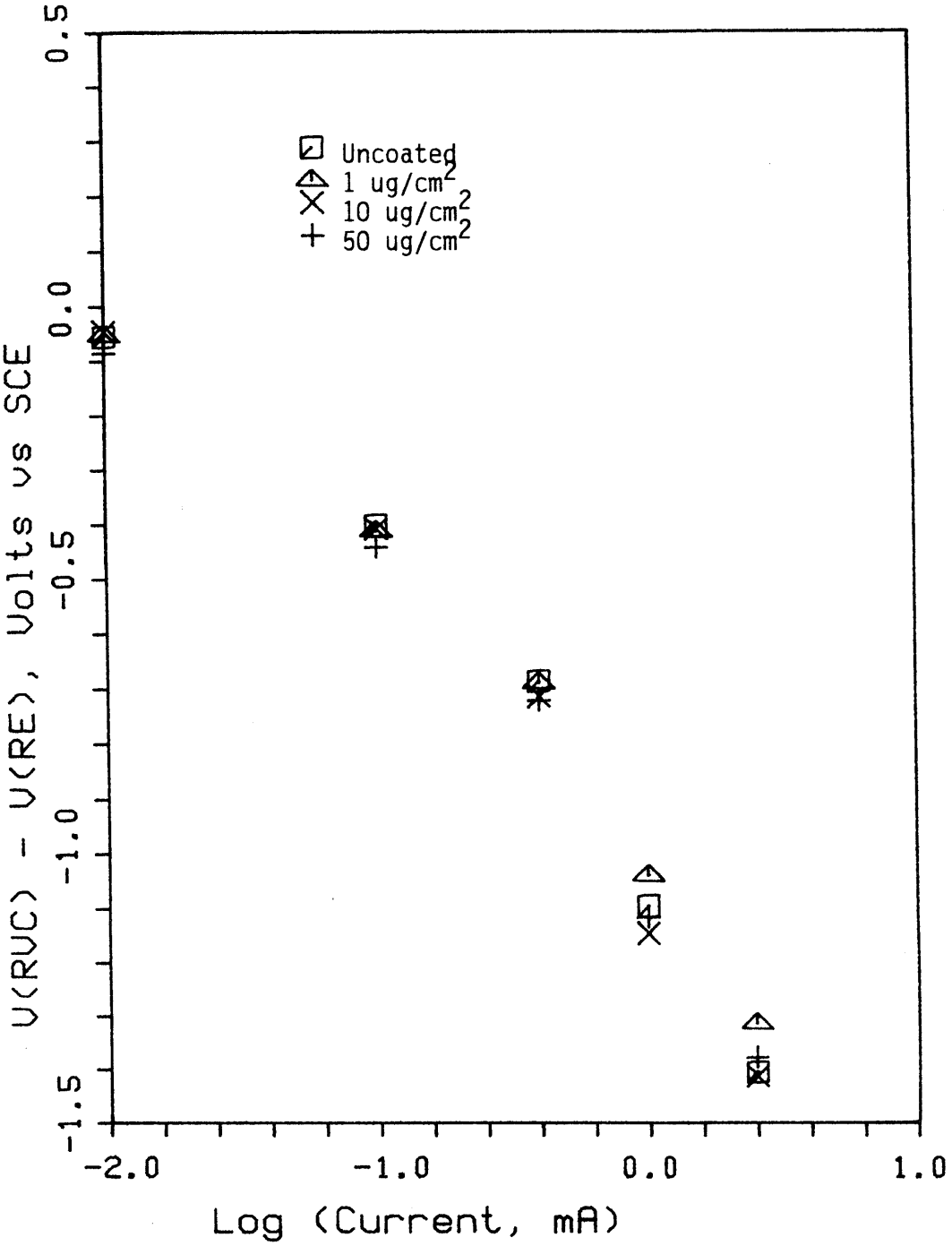

Figure 9. Tafel plot for Zn(II) deposition at a Pb coated RVC electrode from a 10 mg/l solution at pH=2 at various coating levels.

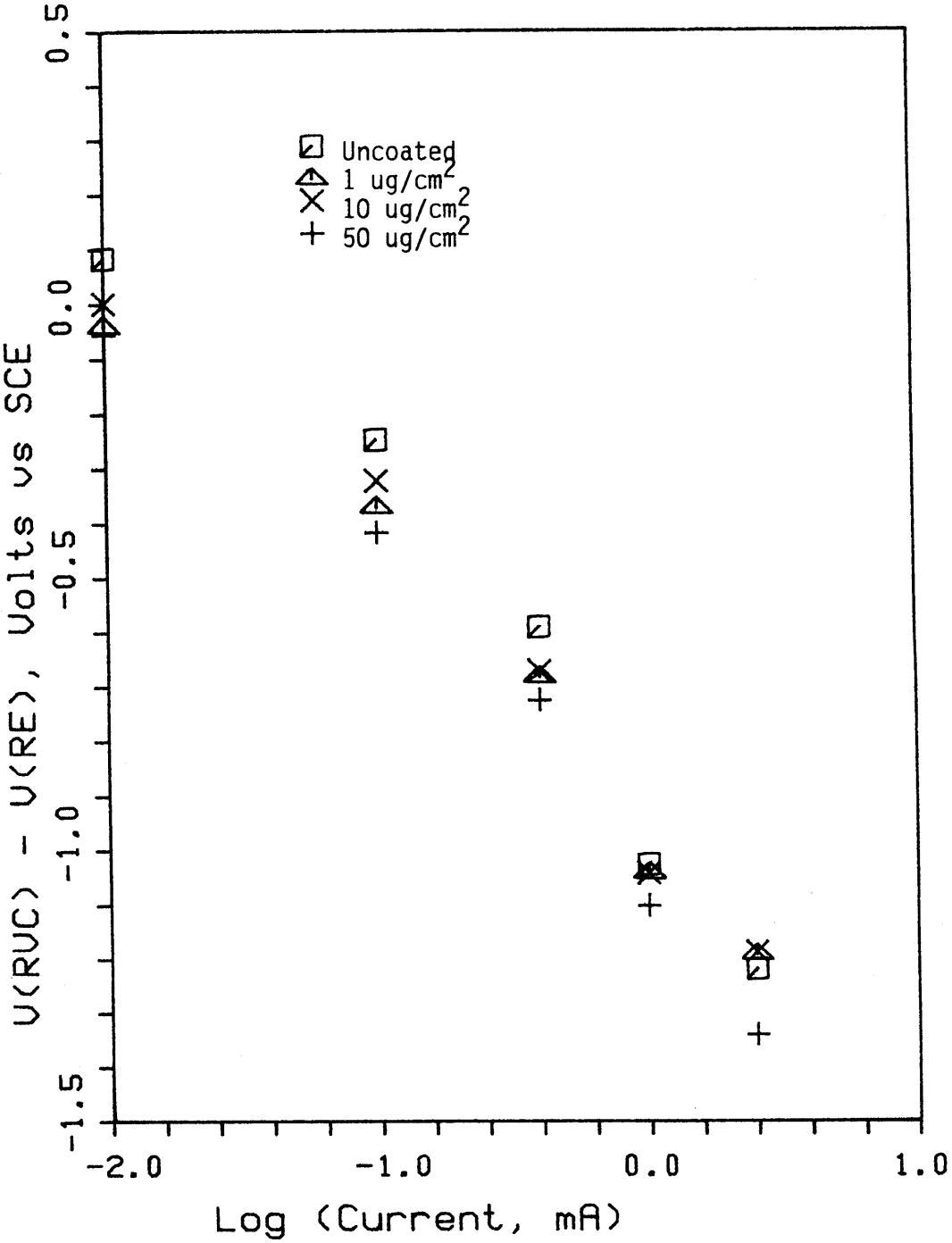

Figure 10. Tafel plot for the Pb coated RVC electrode in the absence of metal ions in the electrolyte at pH=2.

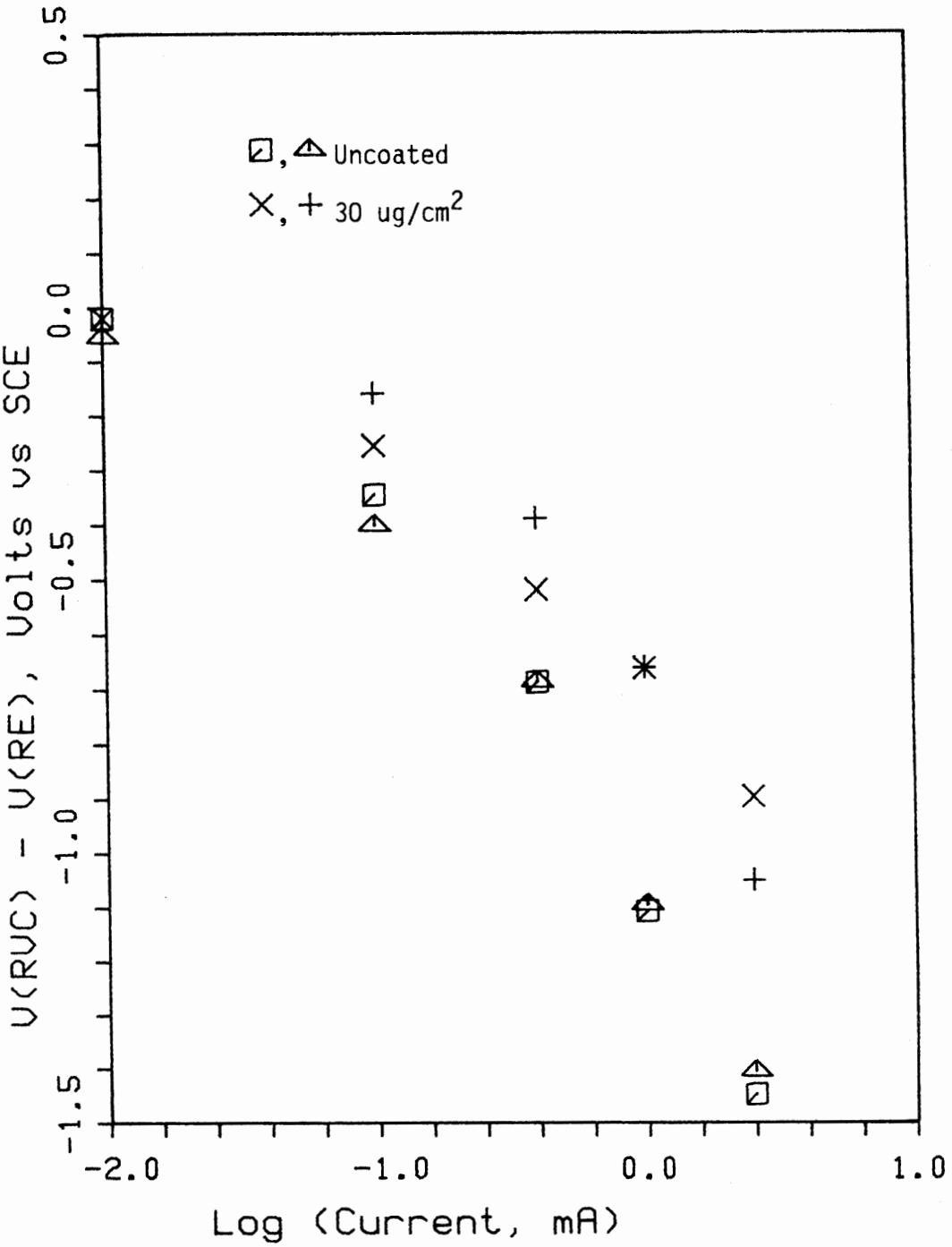

Figure 11. Tafel plot for Zn(II) deposition at a Cu coated RVC electrode (30 ug/cm^2) from a 10 mg/l solution at pH=2.

Figure 12 shows the current-voltage relationship for Zn(II) deposition from a 10 mg/l solution on a RVC plug coated with copper at four loadings: 0, 5, 20, 50 ug/cm^2. This data was obtained by ramping the current from 0 to 2 mA at a rate of 2 uA/sec and simultaneously recording the RVC voltage relative to the upstream calomel reference electrode. Figure 13 shows the current-voltage relationship for Ni(II) deposition from a 10 mg/l solution on a RVC plug coated with copper at four loadings: 0, 5, 20 and 50 ug/cm^2. Figures 14 and 15 show the current-voltage relationship for the oxidation of cyanide ion, CN^-, in the presence of Cu(II) ion at three concentrations: 0, 10, 100 mg/l.

Figures 16 and 17 show the concentration and voltage response obtained with the flow-by reactor processing 400 ml of a simulated copper waste solution operating at a flowrate of 60 ml/min and a current of 15.7 mA.

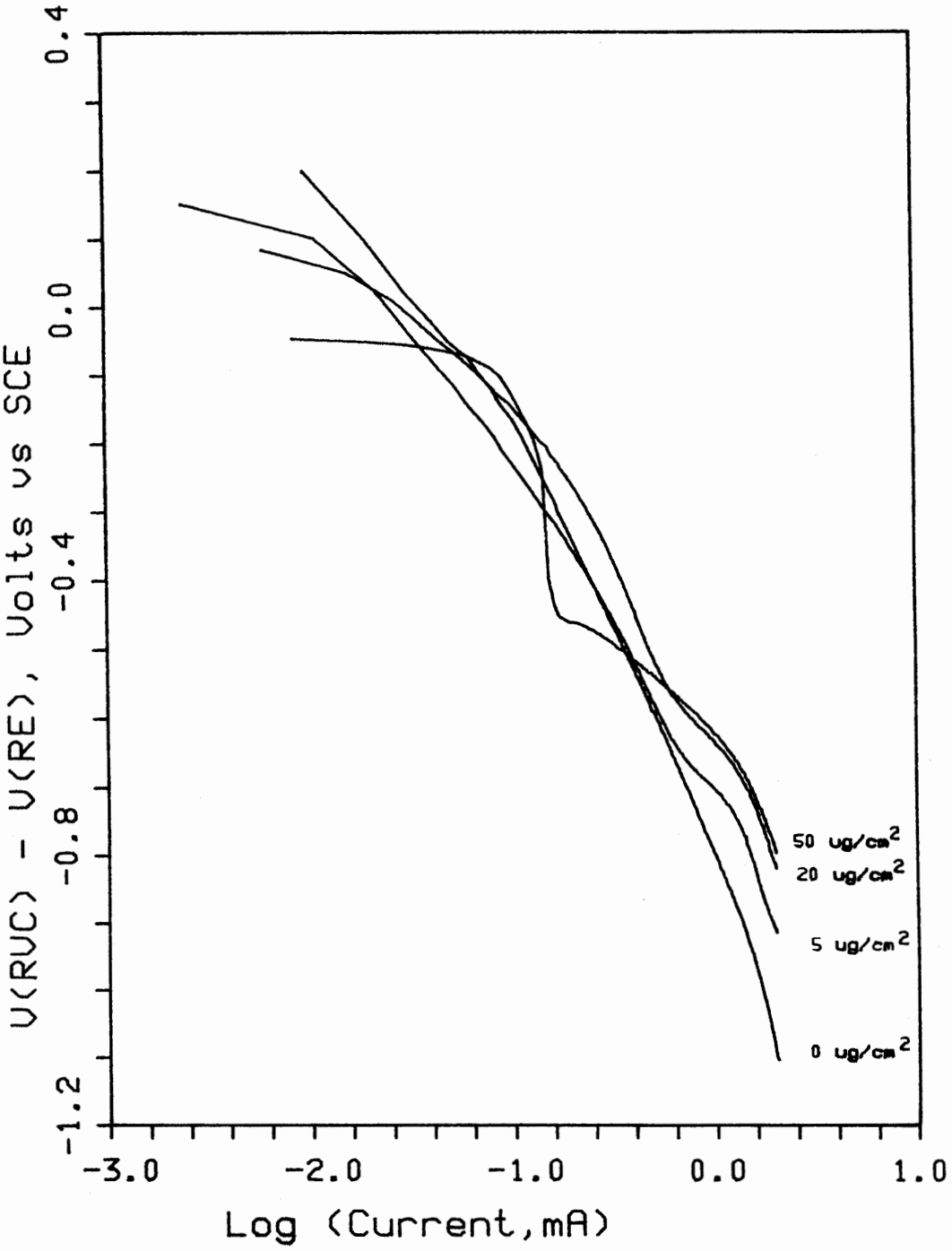

Figure 12. Tafel plot for Zn(II) deposition at a Cu coated RVC electrode from a 10 mg/l solution at pH=2 at coating levels of: 0, 5, 20, and 50 ug/cm^2.

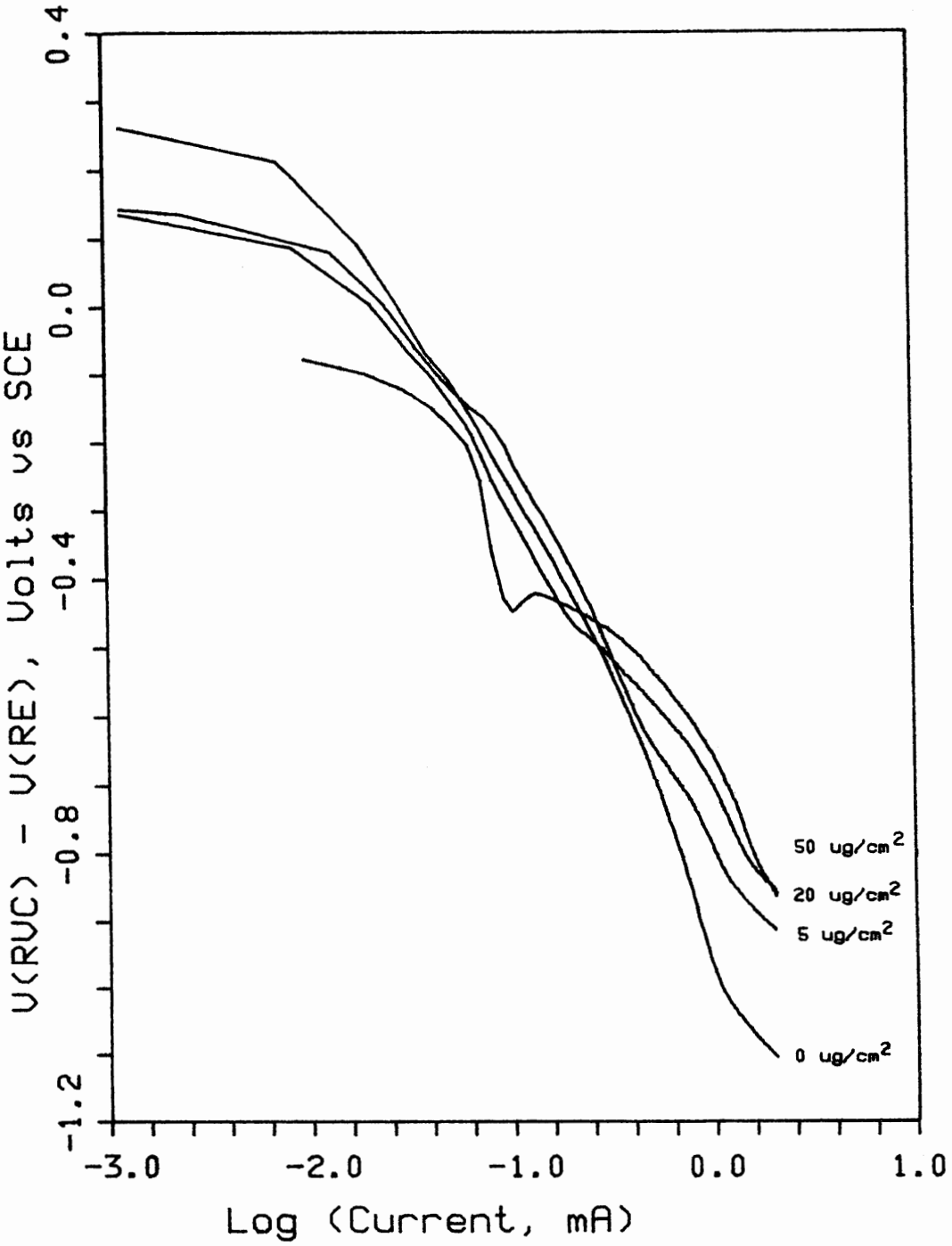

Figure 13. Tafel plot for Ni(II) deposition at a Cu coated RVC electrode from a 10 mg/l solution at pH=2 at coating levels of: 0, 5, 20, and 50 ug/cm^2.

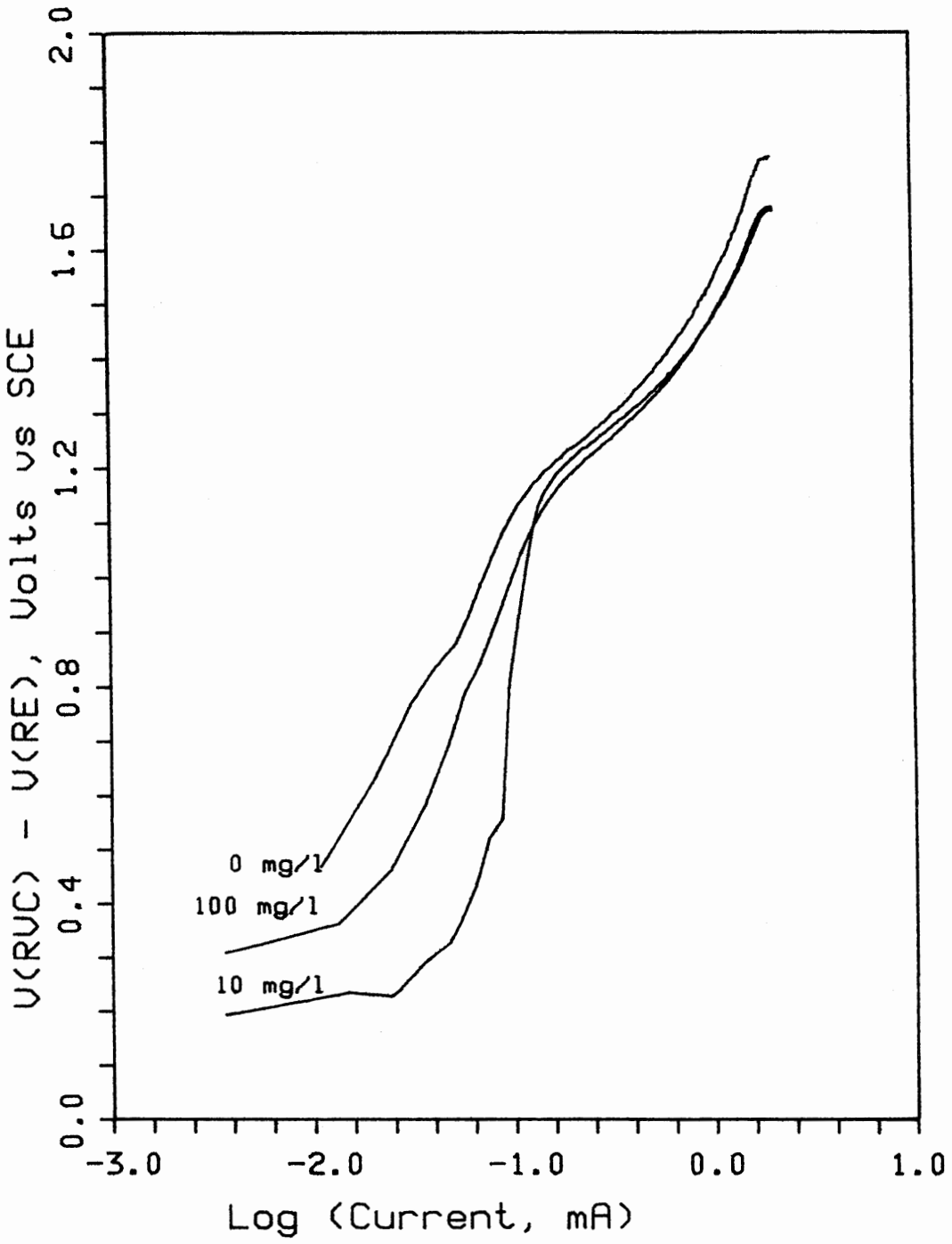

Figure 14. Tafel plot for CN^- electrooxidation at a RVC electrode from a 10 mg/l solution at pH=2 for Cu(II) concentrations of: 0, 10, and 100 mg/l.

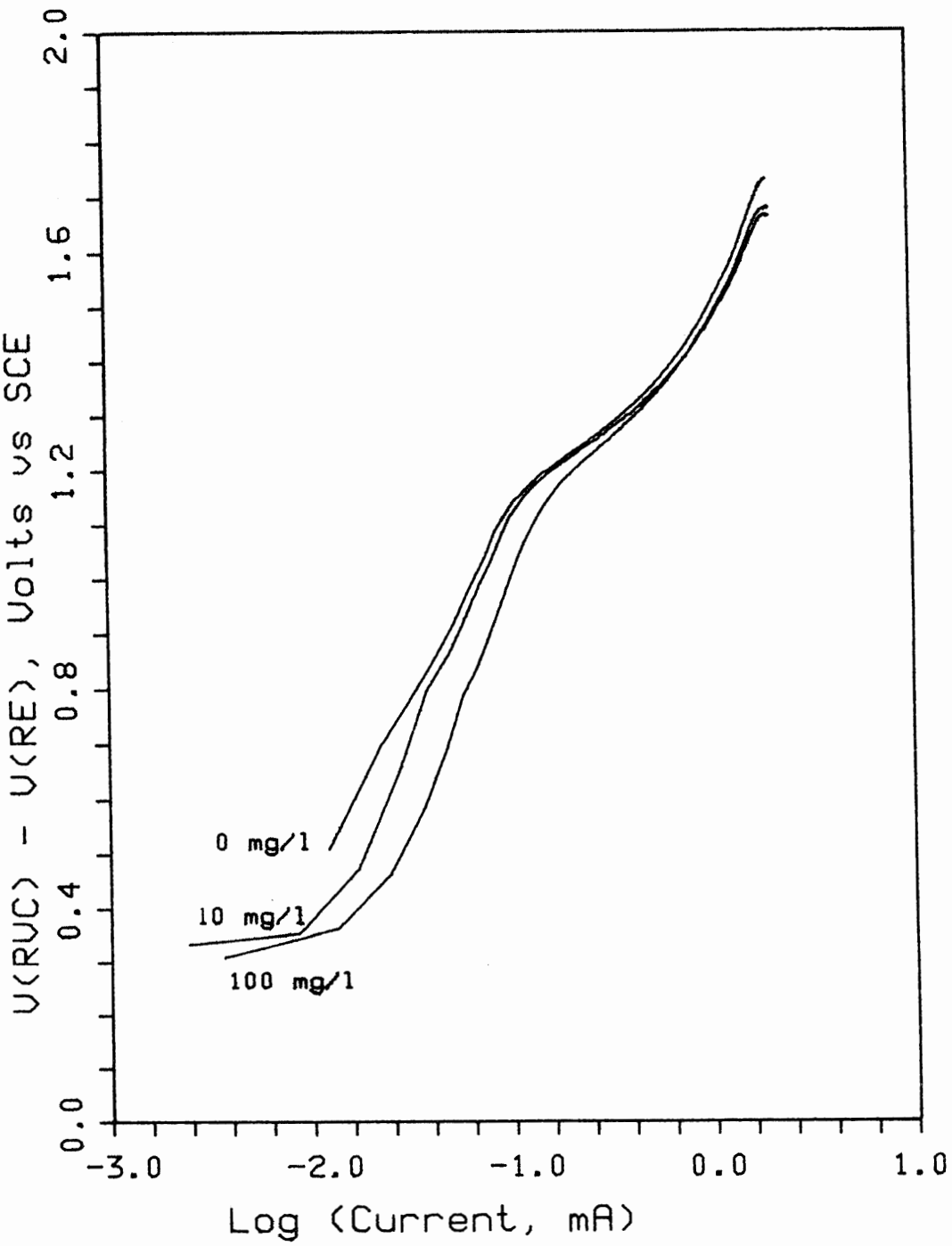

Figure 15. Tafel plot for CN^- electrooxidation at a RVC electrode from a 10 mg/l solution at pH=2 for Cu(II) concentrations of: 0, 10, and 100 mg/l.

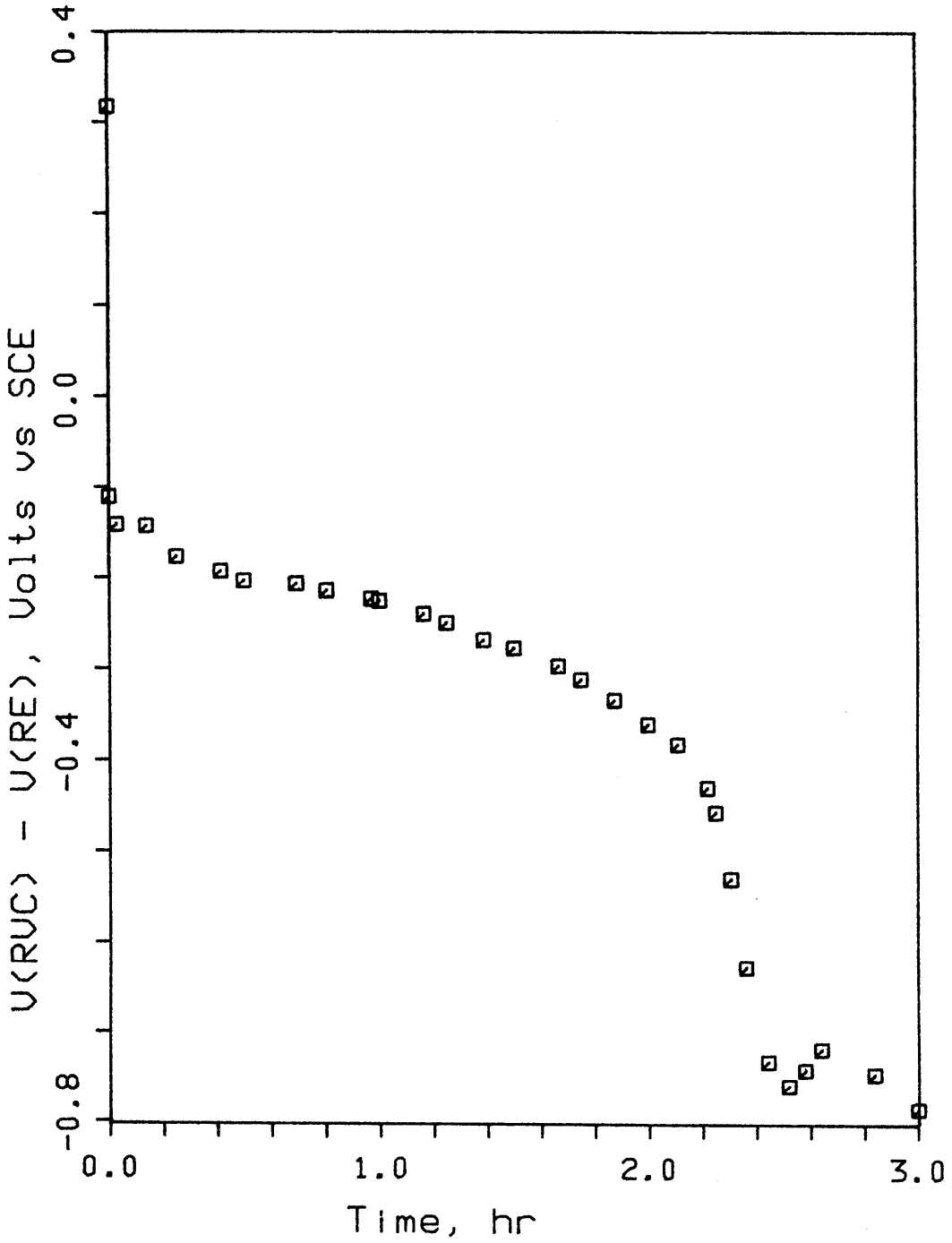

Figure 16. Response of the potential difference between the RVC flow-by electrode and the calomel reference electrode during the reduction of a solution of 94 mg/l Cu(II) at a pH=2 to 0.05 mg/l at a current of 15.7 mA.

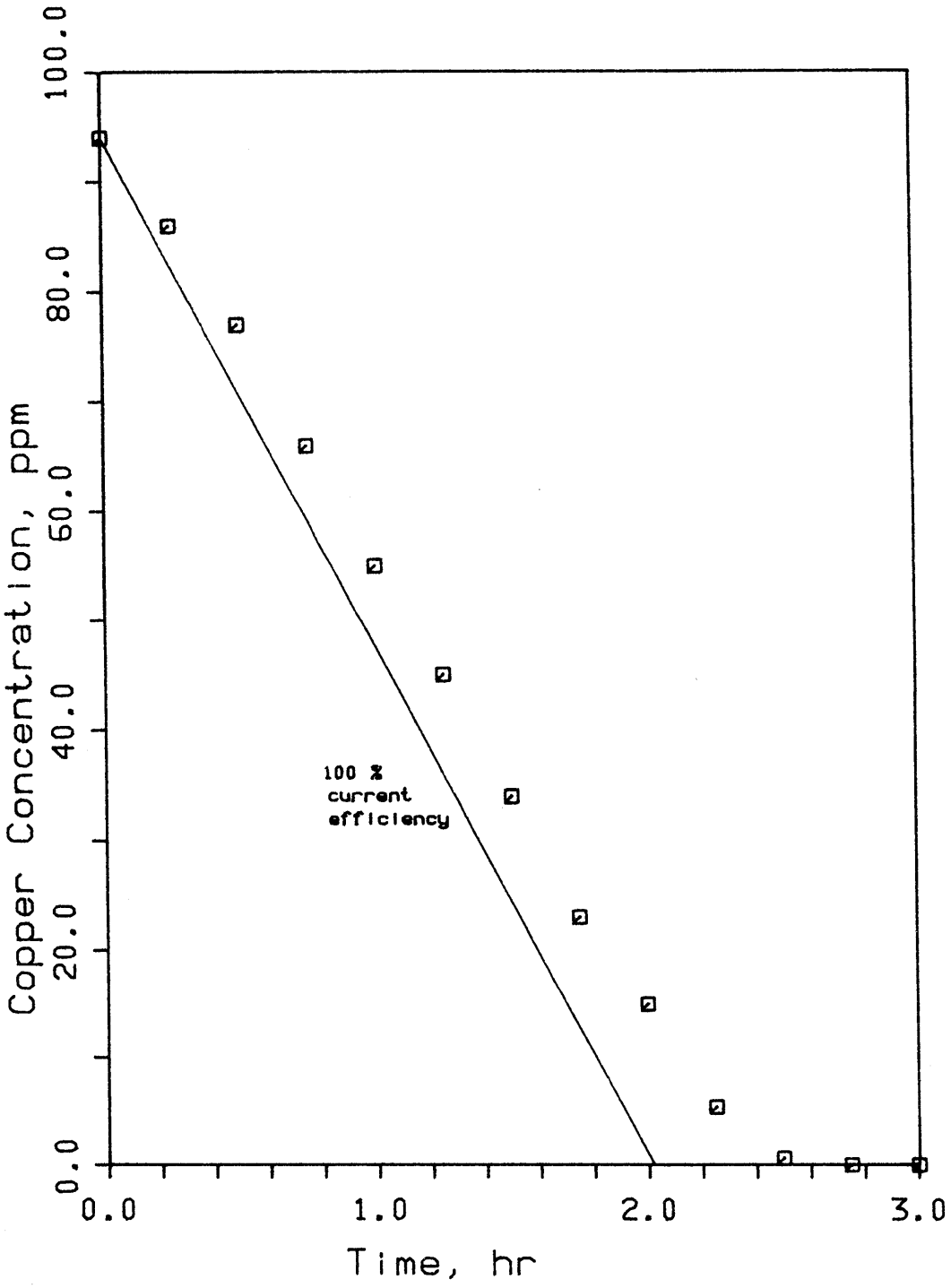

Figure 17. Concentration response of Cu(II) during its reduction in a flow-by RVC electrode from 94 mg/l at a pH=2 to 0.05 mg/l at a current of 15.7 mA.

DISCUSSION

Reactor considerations

It should be emphasized that data collected in the flow-through cell are used to guide the scaleup to the larger, more practical flow-by reactor (Figure 2) in a rational manner. Kinetic data collected in the smaller reactor are more easily measured and interpreted than that collected from a larger cell. On the other hand, the current efficiency and multiple ion removal characteristics of the larger cell are more easily determined.

Thermodynamic considerations

The Nernst equation may be used to calculate the potential either reference electrode must measure before it is thermodynamically possible to carry out a given electrochemical reaction. Table 5 illustrates the results of these calculations with the potentials reported relative to the saturated calomel electrode (SCE) used in our experiments.

Table 5. Equilibrium potential of the RVC relative to a SCE with 10 mg/l solutions of the indicated metal ions at pH=2.

Reaction	E (volt)
$Cu^{+2} + 2e^- = Cu$	-.02
$Pb^{+2} + 2e^- = Pb$	-.50
$Zn^{+2} + 2e^- = Zn$	-1.12
$2H^+ + 2e^- = H_2$	-.30

Metal deposition on RVC

At or below 10 uA, any metal ions which are removed are deposited at potentials anodic relative to the equilibrium potential shown in Table 1. This was an unexpected but highly beneficial result in that a lower electrical driving force is required to remove the metal than would otherwise be required if underpotential deposition did not occur. The underpotential deposition of the metals occurs at the lower current level but this mechanism cannot sustain the reaction at the higher current; however, underpotential deposition may affect the subsequent growth kinetics of bulk deposition.

The deposition kinetics of the metal ions was reproducible as seen by examining the multiple data sets shown Figures 6, 7, and 8. The electrolyte only runs were not; however, this was expected since the electrode reaction in this case is highly sensitive to the residual oxygen and other impurities in the cell which is difficult to reproduce.

In Figure 4, the voltage for the Cu(II) deposition at 1 mA shows an initial cathodic shift followed by a slow anodic recovery. This may be attributed to the lower overvoltage for Cu(II) deposition on the freshly deposited copper surface in comparison to that on a virgin RVC surface.

Evaluation of catalytic effect of lead on metal deposition

The systematic study of the effect of lead coating on the deposition of Zn(II) has been examined at three coating levels: 1, 10, and 50 ug/cm^2. The data shown in Figure 9 illustrate no significant enhancement of the Zn(II) deposition at the lead loadings investigated. The lead, as expected, inhibits the H_2 reaction as shown in Figure 10: at any given current, the voltage is now, in the absense of metal ions, shifted in the cathodic direction. However, note only the highest lead coating is effective in retarding the hydrogen reaction. Possibly higher levels should be examined for the inhibition of hydrogen; the work of Giner and Cahill (5) and Reid (6) et al show that a loading of 100 to 200 ug/cm^2 of lead in combination with gold showed a strong inhibition to hydrogen evolution as evidenced by the very large hydrogen overvoltage measured.

Catalysis, UPD and the electronic work function

Unfortunately, no catalytic effect of the lead coating, at the levels studied to date, has been demonstrated for metal deposition. Catalysis of metal deposition may be accomplished by an energetic attraction between the adsorbate (the reduced form of the metal ion) and the substrate or by supplying additional sites for nucleation. Underpotential deposition provides one possible means for catalysis. Underpotential deposition (UPD) is the deposition of a metal ion at a voltage anodic to the equilibrium potential predicted by the Nernst equation (9). This phenomenon occurs when a metal adsorbate has a greater attraction to a different metal subtrate than its own. To understand UPD behavior, the energetic and entropic effects between the adsorbate and substrate (surface) must be considered. Differences in electronegativity between atoms cause a strong attraction. This attraction may be explained by a transfer of charge which occurs from the less electronegative atom to the more electronegative atom which is similiar to ionic bonding. The more electronegative atom has a greater attraction for the shared electrons in a bond. A more convenient measure of an atom's attraction for electrons is its electronic work function. The electronic work function is defined as the work required to remove a single electron from a solid surface to a vacuum (9). Trasatti has shown a direct correlation between an atom's electronic work function and its electronegativity (38). He showed that a different correlation exists

for the transition metals and the sp metals (38). Values of the electronic work function and effective electronegativities as recommended by Trasatti (38) for several metal atoms of interest are given in Table 6. The effective electronegativities reported by Trasatti (38) are a refinement of Pauling's original values which are made based on relationships observed between the electronic work function, the potential of zero charge, and the electronegativity of diffent groups of atoms. The effect of orientation of water dipoles on the metal surfaces has also been taken into account (38).

Table 6. Selected Work Functions and Effective Electronegativites

Metal	Work Function (eV)	Effective Electronegativity
Au	4.78	2.10
Cd	4.12	1.77
Cr	4.40	1.65
Cu	4.70	2.06
Ni	4.73	1.82
Pb	4.18	1.80
Pt	5.03	2.22
Zn	4.30	1.60

Difference in electronegativies between atoms or, in other words, difference in their Fermi energies (9) can cause a transfer of a partial charge to occur. This results in a bond formed between the two atoms.

A large attraction by the metal adsorbate for a foreign substrate occurs when the work function of the metallic surface is greater than that of the metal adsorbate (7,8,9,27,35,36, and 37). UPD phenomena has not been observed experimentally for systems where the electronic work function of the metal adsorbate was greater than that of the metal substrate (9).

Examination of the difference in the electronic work functions for lead minus zinc is -0.12 eV. Despic (37) reports that Berens found no evidence of UPD for deposition of Zn(II) on lead and noted that the crystals of ordinary electrodeposited zinc were oriented perpendicular to the lead surface (37). The absence of UPD does not exclude the possibility of catalysis; however, the perpendicular orientation of the deposit indicates that lead will probably not act as a site for catalysis since it is more likely to induce 3-D nucleation which is much slower than 2-D nucleation observed following UPD (37).

Catalysis of Zn(II) deposition by copper

It is common practice in the electroplating industry to precoat a work piece with a copper "strike" before plating the desired metal (2). Many metal deposition reactions occur at an enhanced rate on a copper surface. We have exploited this phenomena in our work. In contrast to lead, copper should provide a catalytic effect for Zn(II) deposition since energetic and entropic considerations favor the presence of UPD for

Zn(II) on a copper surface (the work function of copper surface minus Zn adsorbate is +0.40 eV). Despic (37) reports that Berens found that Zn(II) deposition on copper proceeds with the occurrence of underpotential deposition (UPD) before bulk deposition. The hexagonal basal plane of crystals of the deposit were found to lie flat on the substrate indicating a layer growth by 2-D nucleation which is believed to accompany metal deposition for metals which exhibit UPD on foreign substrates (37).

A dramatic decrease in the Zn(II) reaction overvoltage was found when the RVC was coated with copper at 30 ug/cm^2 in comparison to the bare RVC as seen in Figure 11. The overvoltage reduction was found to be dependent upon level of the applied current. At a current of 1 mA, for example, a decrease in overvoltage of 434 mV is observed on the 30 ug/cm^2 copper coated RVC compared to bare RVC. This is a significant decrease in overpotential and will manifest itself in the larger, flow-by reactor by (1) lower power consumption and (2) greater Faradaic current efficiency. Experiments were performed to evaluate the catalytic effect of various copper coating levels on Zn(II) deposition. Implementation of a computer data acquisition system made it possible to modify the experimental procedure in order to obtain a continuous current-voltage relationship. Such experiments were performed by ramping the current from 0 to 2 mA at a rate of 2 uA/sec and recording the resulting voltage at the upstream electrode. As shown in Figure 12, at high current levels

(1 mA and above), 20 to 50 ug/cm^2 of copper showed a significant catalytic effect on Zn(II) deposition as evidenced by the decrease in reduction voltage as compared to the uncatalyzed deposition. At 1 mA, for example, a reduction voltage of -0.604 Volts vs SCE was observed for Zn(II) deposition on a RVC plug loaded with copper at 50 ug/cm^2 as compared to a reduction voltage of -0.798 Volts vs SCE on an uncatalyzed RVC plug. At lower current levels, which correspond to less cathodic voltages, there was no evidence of a catalytic effect. In fact, an inhibition in the reduction reaction at the highest loading of copper is observed. This reduction reaction was not necessarily Zn(II) deposition but might have been the adsorption of hydrogen ions from solution or some other surface reaction. Kolb (9) has shown that the amount of hydrogen adsorbed on a Pt substrate decreases with surface coverage of copper. The reduction voltage for Zn(II) deposition on copper catalyzed RVC was fairly consistent and reproducible when compared to earlier data; however, the reduction voltage for Zn(II) deposition on uncatalyzed RVC was highly variable and not reproducible.

Catalysis of Ni(II) deposition by copper

Ni(II) deposition showed results very similiar to Zn(II) deposition with a significant catalytic effect at the higher current levels for a copper loadings of 20 to 50 ug/cm^2. At 1 mA, a decrease of about 300 mV in overvoltage was observed on the copper coated RVC (50 ug/cm^2) in comparison to bare RVC. At lower current levels, an inhibition in

current was observed as also seen with the Zn(II) deposition. A weak adsorbate-substrate binding energy for nickel onto copper is expected from the difference in electronic work function (work function of copper minus Ni adsorbate = -0.03 eV); however, a favorable energetic interaction is indicated by the difference in electronegativities of +0.24. The effective electronegativity as defined by Trasatti should provide a better means of evaluating the level of energetic interactions when comparing a sp metal and a transition metal.

Copper-lead as a catalyst

Kolb (9) showed that the presence of copper adsorbed on a platinum surface inhibits hydrogen adsorption which is desirable for inhibiting H_2 evolution. A codeposited copper-lead catalytic surface will probably offer an optimal surface on which catalysis of metal deposition is obtained along with inhibition of hydrogen side reaction. It should be noted that other catalysts such as Au and Pt would provide a favorable energetic interaction between adsorbate and surface (9); however, such catalysts are prohibitive due to cost.

Catalysis of cyanide oxidation by Cu(II) in solution

Since at a small anodic overvoltage the dissolution of copper from the electrode is a highly favorable reaction in slightly acidic solutions, it was not used as a surface for the oxidation of cyanide;

however, it has been found that the presence of copper ion in solution catalyzes the oxidation of cyanide (26). Current-voltage relationships for the oxidation of 10 mg/l of cyanide ion are shown in Figure 14 with Cu(II) concentrations: 0, 10, and 100 mg/l. At 0.1 mA, a decrease in voltage of about 130 mV is observed for a Cu(II) concentration of 100 ppm compared to no Cu(II) present. At low currents, a significant catalytic effect is observed when Cu(II) is present at 10 and 100 ppm but diminishes as current is increased indicating a possible shift from the oxidation of cyanide to the evolution of oxygen at the electrode.

Copper removal using flow-by reactor

The flow-by reactor was used to treat 400 ml of a 94 ppm Cu(II) solution which was continuously recirculated from a reservoir. The reactor was operated at a current of 15.7 mA and a flowrate of 60 ml/min which, in the absence of mass transfer effects, is equivalent to a current of 1 mA in the smaller flow-through reactor on a cross-sectional area basis. The concentration and voltage responses are shown in Figures 15 and 16. The concentration is seen to decrease fairly linearly throughout the electrolysis until 95 % of the original amount of Cu(II) is remaining at which point hydrogen evolution becomes the dominating reaction. The voltage-time relationship is that of a typical chronopotentiogram (constant current electrolysis) with a large cathodic increase in voltage occuring as the concentration becomes very small. Analysis of the concentration data indicated that the flow-by reactor

reduced the concentration of Cu(II) to less than .05 ppm (the detection limit of the AA) while operating at a Faradaic efficiency of 87 per cent.

Electrochemical vs precipitation operating costs

The precipitation of an acid Cu(II) waste with caustic (NaOH) is accomplished in four steps(38): (1) Neutralization, (2) Precipitation, (3) Flocculation, and (4) Clarification. A basis of 60 gal/h of 50 ppm Cu(II) acid waste is assumed for the analysis; the flow of copper is then 1.51 lb./h. The waste stream is neutralized with caustic to adjust the pH between 7.5 and 9.5 since Cu(II) is soluble at low pH (38). An amount of 1.0 lb. NaOH per 1000 gal waste (38) at a cost of 9.5 cents per lb. NaOH (39) is required. A caustic cost of 22.6 cents per lb. of copper removed is incurred for neutralization of the acid waste. Additional caustic is added causing the copper hydroxide to precipitate out of solution. Precipitation of copper hydroxide requires 1.99 lb. NaOH per lb. copper removed, resulting in a cost of caustic of 18.9 cents per lb. copper removed. Flocculating agents--such as polymers, alum, or ferrous sulfate--are added to enhance the settling characteristics of the suspended solids (38). Approximately 0.1 lb. of a polyelectrolyte per 1,000 gal waste is added which costs approximately 10 cents per 1,000 gal adding an additional cost of 23.8 cents per lb. copper removed. A total operating cost for chemicals used in precipitation is 65.3 cents per lb. copper removed. An additional cost is incurred in disposing of the sludge generated by the solids settling

in the clarifier. The amount of sludge generated is 4.46 gal per lb. copper removed for precipitation based on a sludge consisting of 4 per cent solids. A value of 10 cents per gal for sludge disposal is used which gives a sludge disposal cost of 44.6 cents per lb. copper. The total operating cost for caustic precipitation is $ 1.10 per lb. copper removed.

The electrochemical scheme consists of recirculating the acid Cu(II) waste from a rinse tank to the flow-by reactor and back to the rinse tank. The same fluid may be used for anolyte and catholyte or separate streams may be used depending upon operating demands. For Cu(II), a current efficiency of 87 percent was obtained operating a flow-by reactor at a circulation rate of 60 ml/min. For a cell voltage of 5 volts and an electric cost of 5.8 cents per kW-h, the operating cost for electricity is 11 cents per lb. of copper removed. The copper deposited on the RVC may be anodically recovered into a concentrated plating solution or left in the RVC to be disposed of as a sludge. The sludge generated would only be .0278 gal per lb. copper removed assuming that the copper deposit occupies 50 per cent of the void volume in the RVC. This would be a cost of .3 cents per lb. copper removed for sludge disposal; however, the cost of electrode replacement prohibits the disposal of the metal-covered electrode. A 6.415 cubic inch RVC electrode is required per lb. of copper based on a copper deposit occupying 50 per cent of the void volume in the reactor. At an electrode cost of 30 cents per cubic

inch, the cost of replacing an electrode is $ 1.92 per lb. copper removed. Instead of disposal, the copper may be returned directly into the concentrated plating solution by anodic dissolution. A conservative estimate of 10 cents per lb. of copper removed has been made for the electricity cost for anodic copper dissolution. The total electrical operating cost of electrochemical removal is 21 cents per pound of copper removed compared to a chemicals and sludge disposal cost of $ 1.10 per lb. copper removed for precipitation. Moreover, a savings in plating chemicals cost of $ 1.90 for $CuCl_2$ per lb. copper recovered is realized when the copper is recovered from the reactor.

WORK REMAINING

1. The kinetics of Cd(II) deposition from a 10 mg/l solution will be studied in the flow-through cell.

2. Copper coating levels from 0 to 50 micrograms/cm^2 will be applied to evaluate their catalytic effect on Pb(II) and Cd(II) reactions and inhibition of hydrogen reaction.

3. The flow-by cell will be used to study the deposition of single ion solutions of Cu(II), Pb(II), Zn(II), Ni(II), and Cd(II) on uncatalyzed and catalyzed RVC.

4. The flow-by cell will be used to measure the effectiveness of the catalyzed electrode in removing metals from multiple ion solutions which would be found in any real wastewater stream. In addition, the reactor will be run with the cyanide salts of the metals to examine the efficiency of the simultaneous removal of metal and cyanide ions from the water.

5. With the data collected from the flow-by cell, an economic comparison between the electrochemical route and the

precipitation technology will be made.

6. Additional studies with co-deposited Cu-Pb catalytic coatings will be studied in order to exploit the catalytic effect of a copper surface on metal ion reactions and the inhibition effect of a lead surface on the adsorption of hydrogen ion and consequent evolution of hydrogen gas.

REFERENCES

1. M. S. Shumann, L. A. Smock and C. L. Haynie, "Metals in the Water, Sediments and Biota of the Haw and New Hope Rivers, North Carolina, " Report No. 124, Water Resources Research Institute of the University of North Carolina (1977).

2. Mr. William Russell, Vice President American Electroplaters Society, North Carolina section, private communication (1982).

3. "Development Document for Effluent Limitations Guidelines and Standards for the Metal Finishing Point Source Category, "EPA 440-1-80-091-A (1977).

4. J. A. Trainham and J. Newman, "A thermodynamic estimation of the minimum concentration attainable in a flow-through porous electrode reactor," J. Appl. Electrochem., 7, 287 (1977).

5. J. Giner and K. Cahill, "Advanced Screening of Electrode Couples, " DOE/NASA/0794-80/1.

6. M. A. Reid, R. F. Gahn, J. S. Ling and M. A. Charleston, "Preparation and Characterization of Electrodes for the NASA REDOX Storage System," submitted to J. Electrochem. Soc., 1981.

7. R. R. Adzic, "Electrocatalysis on Surfaces Modified by Foreign Metal Adatoms," Israel J. Chem., 18, 166 (1979).

8. J. D. McIntyre and W. F. Peck, Jr., "Electrochemical Catalysis by Foreign Metal Adatoms," Proceedings Third Symposium Electrode Process, Electrochemical Society, 322 (1979).

9. D. M. Kolb, "Physical and Electrochemical Properties of Metal Monolayers on Metallic Substrates, " Adv. Electrochem. Engr. Vol. 11, Wiley Interscience, New York, 125 (1978).

10. J. Newman and W. Tiedemann, "Flow-through Porous Electrodes," Adv. Electrochem. Electrochem. Engr. Vol. 11, Wiley Interscience, New York, (1978).

11. P. S. Fedkiw, "Ohmic Potential Drop in Flow-through and Flow-by Porous Electrodes," J. Electrochem. Soc., 128, 831 (1981).

12. J. E. Entwistle, "The Electrolyte Processing of Cyanide Wastes, " Effluent and Water Treatment Journal, 16, 236 (1976).

13. D. N. Bennion and J. Newman, "Electrochemical removal of copper ions from very dilute solutions," J. Appl. Electrochem., 2, 113 (1972).

14. J. Van Zee and J. Newman, "Electrochemical Removal of Silver Ions from Photographic Fixing Solutions Using a Porous Flow-Through Electrode," J. Electrochem. Soc., 124, 706 (1977).

15. G. B. Adams, R. P. Hollandsworth and D. Bennion, "Electrochemical oxidation of ferrous ions in very dilute solutions," J. Appl. Electrochem., 6, 385 (1976).

16. S. Ehdaie, M. Fleischmann and R. E. W. Jansson, "Application of the trickle tower to problems of pollution control. I. The scavenging of metal ions," J. Appl. Electrochem., 12, 59 (1982).

17. E. A. El-Ghaoui and R. E. W. Jansson and C. Moreland, "Application of the trickle tower to problems of pollution control. II. The direct and indirect oxidation of cyanide," J. Appl. Electrochem., 12, 69 (1982).

18. E. A. El-Ghaoui and R. E. W. Jansson, "Application of the trickle tower to problems of pollution control. III. Heavy metal cyanide solutions," J. Appl. Electrochem., 12, 75 (1982).

19. D. Yaniv and M. Ariel, "Electrodeposition and Stripping at Graphite Cloth Electrodes in a Flow-Through Cell," J. Electroanal. Chem., 129, 301 (1981).

20. C. P. C. Poon and K. P. Soscia, "Process for Simultaneous Removal of Cadmium and Cyanide," Indust. Water Engr., 17, 28 (1980).

21. E. Roof, "Electrochemical Reactor and Associated In-Plant Changes at Varland Metal Service, Inc.," Third Conference on Advanced Pollution Control for the Metal Finishing Industry, EPA-60/2-81-028, 16 (1981).

22. "Reticulated Vitreous Carbon," bulletin 176, Fluorocarbon Co., Anaheim, CA (1976).

23. A. J. Bard and H. Lund (ed), Encyclopedia of Electrochemistry of the Elements, Vol. VII, Marcel Dekker, Inc., New York (1976).

24. J. Wang, "Reticulated Vitreous Carbon-A New Versatile Electrode

Material," Electrochim. Acta, 12, 1721 (1981).

25. A. J. Bard and L. R. Faulkner, Electrochemical Methods: Fundamentals and Applications, John Wiley and Sons, New York, (1980).

26. A. Katagiri, S. Yoshimura, Y. Deguchi and S. Yoshizawa, "Catalytic Effect of Copper Ion on the Anodic Oxidation of Cyanide Ion," Proceedings of the Symposium on Electrocatalysis, Electrochemical Society, Vol. 82-2, 336 (1982).

27. D. M. Kolb, "The Structure of Metal Adsorbates formed at Underpotentials," Proceedings of the Symposium on Electocatalysis, Electrochemical Society, Vol. 82-2, 291 (1982).

28. S. Yoshimura, A. Katagiri and S. Yoshizawa," Reaction Products of Anodic Oxidation of Cyanide Ion in the Presence of Copper Ion," Nippon Kagaku Kaishi, 1327 (1980).

29. S. Yoshimura, A. Katagiri and S. Yoshizawa," Application of Packed Bipolar Cell to Electrolytic Treatment of Waste Waters," Nippon Kagaku Kaishi, 1144 (1978).

30. T. Arikado, C. Iwakura, H. Yoneyama and H. Tamura," Anodic Oxidation of Potassium Cyanide on the Graphite Electrode," Electrochim. Acta, 21, 1021 (1976).

31. D. T. Sawyer and R. J. Day, "Electrochemical Oxidation of Cyanide Ion at Platinum Electrodes," J. Electroanal. Chem., 5, 195 (1963).

32. A. Longo and T. Buch, "Complex Cyanides of Copper(II)," Inorg. Chem., 6, 556 (1967).

33. G. Nord and H Matthes, " A Stopped-flow Kinetic Study of the Copper(II) Cyanide Reaction in Water and in Aqueous Methanol," Acta Chem. Scand., A28, 13 (1974).

34. M. C. Dart, J. D. Gentles and D. G. Renton, "Electrolytic Oxidation of Strong Cyanide Wastes," J. Appl. Chem., 13, 55 (1963).

35. A. R. Despic, "Factors Determining Type of Deposit in Electrocrystallization of Metals," Proceedings of the Third Symposium on Electrode Processes, Electrochemical Society, Vol. 80-3, 235 (1979).

36. W. J. Lorenz, " Underpotential Metal Deposition, Phase

Transitions and Electrocrystallization," Proceedings of the Symposium on Electrocrystallization, Electrochemical Society, Vol. 81-6, 81 (1981).

37. A. R. Despic, " Effect of Foreign Metal Adatoms on Metal Deposition and Dissolution," Proceedings of the Symposium on Electrocrystallization, Electrochemical Society, Vol. 81-6, 101 (1981).

38. S. Trasatti, "Work Function, Electronegativity, and Electrochemical Behaviour of Metals," J. Electroanal. Chem., 33(1971).

39. U.S. Environmental Protection Agency, Environmental Pollution Control Alternatives: Economics of Wastewater Treatment Alternatives for the Electroplating Industry, EPA 625/5-79-016, June 1979.

40. Chemical Marketing Reporter, Aug. 22,1983.

41. American Metal Market, Aug. 22,1983.