THE REMOVAL AND RECOVERY OF FLUOBORATE FROM PLATING RINSE WATERS

BY

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ABSTRACT

Fluoborate poses a problem to electroplaters when discharged in their wastestreams. Therefore, a method for removing fluoborate from rinse waters is necessary. An ion floatation technique using a surfactant was developed at N.J.I.T. to perform this job. However, this technique requires long time periods therefore other methods were investigated.

Ultrafiltration was investigated as a replacement for the ion floatation technique. It would cut down the time required for the fluoborate removal. Also, electrolysis and the addition of excess acetic acid were tried in an attempt to separate the fluoborate and the surfactant in the ultrafiltration retentate. This system was evaluated using dilute rinse solutions. For concentrated rinses, electrodialysis was employed.

Results showed that when using a 1,000 molecular weight cut-off membrane, ultrafiltration succeeded in removing the surfactant-fluoborate complex from solution. Therefore, ultrafiltration can replace the ion floatation technique. Also, the results achieved using electrolysis to separate the surfactant-fluoborate complex were encouraging. However, further experimentation should be done in this area.

In utilizing electrodialysis as a means of removing fluoborate from concentrated rinse waters, positive results were achieved. Also, electrodialysis can be employed to recover plating solutions from the rinse waters.

APPROVAL OF THESIS

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BY

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FOR

DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING

NEW JERSEY INSTITUTE OF TECHNOLOGY

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PREFACE

This research work was a follow-up of Mr. R.H. Haralson's work in ion floatation, which was done in pursuit of his Doctorate Degree in Environmental Engineering. As a result of Mr. Haralson's research, an EPA Grant #101-601 was obtained from the Industrial Environmental Research Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio. The research covered in this thesis was funded by this EPA Grant.

ACKNOWLEDGEMENTS

I wish to extend my sincere gratitude to my advisor, Dr. J. Liskowitz; to faculty members, Prof. V. Cagnati, Dr. A. Perna and Dr. R. Trattner; and to Mr. R. Haralson for their supervision and assistance throughout my research and study programs. I would also like to express my thanks to the Foundation at N.J.I.T. for its financial support during my graduate studies.

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I. INTRODUCTION

A recognition of the detremental effects of industrial pollution on our environment has surfaced in recent years. Along with this awareness came Federal Regulations calling for reduction of industrial discharges into the environment. One such piece of legislation, the Federal Water Pollution Control Act (PL 92-500) was enacted in 1972. This law advocates the attainment of "Zero Discharge" of pollutants into the nations waterways by 1983. Present commonly used industrial waste water treatment practices are not capable of achieving "Zero Discharge". The metal finishing industry is an example of an industry which will need to apply new technology in order to meet this discharge requirement.

The metal finishing industry in the United States includes approximately twenty thousand facilities, the majority of which are associated with the automotive, electronic, and jewelry industries. These facilities encompass both job- and captive-shops. The major operations performed at metal finishing facilities include cleaning and pickling, annealing, case hardening, polishing, buffing, immersion plating, electroplating, phosphating, conversion coating, oxidizing, painting, electropainting, and anodizing.

Metal finishing operations can be divided into three general areas:

1. Cleaning and Conditioning
2. Deposition of Metal
3. Passivation

Cleaning is one of the final steps in preparing a metal surface for finishing. Preceding fabrication steps contribute to the surface finish and to the soil and oxides that must be removed to obtain a satisfactory electroplate. This is so because the appearance and acceptance of the finished articles depend on a sound foundation for the finish, which is achieved with a clean and active substrate. Inadequate cleaning may result in the following defects:

- Poor Adhesion
- Irregular Plate
- Pitting
- Bare Spots
- Poor Corrosion Resistance
- Roughness
- Hydrogen Embrittlement
- Etching
- Staining
- Excessive Graininess
- And Powdery Coatings

The deposition of metals onto a substrate is achieved by adding electrons to the dissolved metal ions. This deposition can be achieved by either the electroless or electroplating processes. In electroplating electrons are supplied from an external source. In electroless plating, the electrons are furnished by chemical reducing agents included in the bath formulation.

The purpose of passivation is to render the substrate inactive to corrosion from the atmosphere in which the part will be used. An example is the passivation of steel with zinc dichromate. Zinc is used as a sacrificial coating on the steel. Zinc dichromate is then added and reacts with the zinc to form a protective insoluable coating of variable composition.

After each stage of treatment of the work piece, water rinses are employed to reduce the carry-over of process solutions into the next tank. The work piece is transferred from tank to tank, either manually or automatically. Large pieces are carried on racks while while smaller parts are placed in baskets or rotating barrels. Each type of transport has its own inherent rinsing problems associated with it.

The waste water produced in metal finishing operations is mainly generated in two ways. Concentrated wastes come from the dumping of solutions which have become used or fouled. This is especially true of cleaning, stripping, passivating and anodizing solutions. The dilute wastes, which are the larger volume wastes, come from the rinse waters. These rinses wash off the process solution that has adhered to the surface or was entrapped in crevices due to the shape of the processed piece. The drag out of solution into the rinse tank may vary considerably, depending upon the shape of the work piece, the position of the part on the rack, the time allowed for drainage, and the number of pieces being processed. Other generators of waste include accidental spillage, leakage, equipment cleanup and washdown, entrainment of mist in ventilation ducts, regeneration of ion exchange units, and sludge deposits in process tanks.

Depending upon the types of baths which are employed at a specific facility, the waste water generated may be either acidic or alkaline. It can also contain toxic contaminants such as cyanide, fluoride or chromate along with metal cations such as copper, zinc, nickel or cadmium and many other pollutants such as surfactants, deoxidants oil and grease, organic solvents and wetting agents. Acid wastes will predominate at chrome plating, nickel plating, aluminum anodizing, copper stripping, aluminum, copper, zinc cleaning and bright dipping, and steel and magnesium pickling operations. Some operations where alkaline wastes are prevalent are copper, brass, zinc, bronze, cadmium, silver and gold plating, and alkaline cleaning.

Presently, the most common used procedure for treating metal finishing waste waters includes the following operations:

- Separation of Oil and Grease
- Oxidative Destruction of Cyanides
- Reduction of Chromates
- Neutralization of Acids and Alkalies
- Precipitation of Metal Hydroxides
- Disposal of Sludge

These operations are usually performed at the facility's central waste treatment plant prior to the waste streams discharge to a receiving water or sanitary sewer system. Problems arise with the above procedures in regard to the federal legislative goal of "Zero Discharge" of pollutants. Also, the precipitated heavy metal sludges present a potential pollution problem when they are disposed of on land. Alternatives are the recovery and recycle of wastes from their point of generation, or the substitution of toxic process chemicals with less objectionable ones.

Among the more attractive recovery techniques are reverse osmosis, ion exchange, evaporation, ultrafiltration and electrodialysis. In specific areas, these processes have been applied to the recovery of metals from plating rinse waters, or the concentration of the rinse waters for the reuse in the plating bath.[1] The application of these technologies must be evaluated on an individual basis due to the diversity of waste stream composition encountered in the metal finishing industry.

Substitution of process chemicals is practical only when the substitution does not compromise the quality of the finished product. One such substitution is the use of fluoborate to replace cyanides as a conducting salt in plating baths. Fluoborate has been found to be an excellent carrier ion which gives a uniform, bright, well-thrown covering. Also, fluoborate is much less toxic than cyanide, and therefore, provides for a safer plating room. For these reasons, many platers of cadmium, zinc, tin, lead, solder, copper, nickel and iron are replacing their cyanide baths with fluoborate baths.

Commercial fluoborate solutions are presently available

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[1] Waste Treatment - Upgrading Metal Finishing Facilities to Reduce Pollution, EPA Technology Transfer Seminar Publication, January, 1974.

for the plating of copper, indium, iron, lead, nickel, tin and their alloys. Also, fluoboric acid (HBF_4) is used in various pretreatment operations, such as stripping and cleaning. The concentration of these rinse waters is variable, depending upon the rinsing technique which is employed. Dilute rinses would be typical of single tank rinsing, while the concentrated rinse water would be attributed to multiple tank countercurrent or series rinsing.

The fluoborate ion is an ion in which boron is covalently saturated by fluorine. This ion forms salts in which there is a true cation with no covalent bonding to the anion. Fluoborate is a very small, tightly bound tetrahedron with a uniform charge. It apparently does not polarize.

Fluoborate by itself is relatively non-hazardous. However, it will hydrolize in water yielding boric acid and fluorine in accordance with the following equilibrium reaction:[2]

$$BF_4^- + 3H_2O \longrightarrow B(OH)_3 + 4F^- + 3H^+$$

The presence of this resulting fluoride in our receiving waters is undesirable. Previous testing has

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[2] Sharp, D.W.A., Fluoboric Acids and Their Derivatives. London, England: Bullersworth, 1960, pp. 69-80.

shown that the hydrolysis is relatively slow at ambient temperature and pH, or a decrease in concentration.[3]

There are presently no specific discharge limitations on fluoborate. However, when a waste stream is analyzed for fluoride by the approved method (Bellack Distillation), any fluoborate present will be hydrolyzed yielding inflated fluoride concentrations. For each fluoborate ion present in a sample the test will show four fluoride ions. This gives a false indication of fluoride concentration and can show a National Pollution Discharge Elimination System permit (NPDES) violation where none exists. If the goal of PL 92-500 is to be realized, fluoborate must be removed from or kept out of our waste waters.

Few processes are known for the removal of fluoborate from plating rinse waters. It is a small tight molecule and is not easily rejected by membrane processes such as reverse osmosis. Presently, there is no known ion exchange resin which will remove fluoborate from solution. Battele Memorial Institute in their January 1974 draft of the <u>Development Document for Limitations for Electroplating Point Sources</u>, suggested the hydrolysis of the fluoborate

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[3] Cagnati, Haralson, Hunter, Liskowitz, Perna, Trattner, "Removal of Fluoborate From Plating Wastewater: Technique and Mechanism," <u>Water-1977</u>, American Institute of Chemical Engineers, pp. 309-315.

to fluoride, followed by lime precipitation as a possible treatment. Tests have proven this method to be unrealistic because the hydrolysis reaction is too slow at any reasonable temperature.

Vacuum evaporation is currently being used as a means of recycling stannous fluoborate rinse waters back into the plating tank as make-up solution. However, despite its closed loop performance, evaporation is an energy intensive operation.

Adsorptive bubble separation techniques have been used for separating or concentrating solid particles from a liquid medium. This separation is achieved by diffusing bubbles through a column of solution to disperse or suspend the solid particles. The process depends upon differences in the surface activity of the species to be separated. The particles are selectively adsorbed or attached to the solution to effectively control the surface activity of the constituent to be removed.

The surfactant is usually a long chained organic with a hydrophyllic and a hydrophobic end. The hydrophyllic end attaches to the particle in solution and the hydrophobic end attaches to a bubble of diffused air and is floated out of solution.

The most widespread use of floatation processes is in the separation of ores. In ore floatation, the surfactant is designed to preferentially adhere to one type of solid allowing it to be floated from solution while the other solids settle.

Recently floatation techniques have been applied to the removal of specific ions from solution. Ion floatation has been applied to the separation of hexavalent chromium and cyanide complexed by iron. Recently, an ion floatation process for the removal of dilute concentrations of fluoborate from aqueous solutions was developed at N.J.I.T., employing the addition of a cationic surfactant, thorough mixing, application of air from a diffuser and foam skimming.[4] Experimentation was conducted to optimize the above process using the laboratory apparatus depicted in Figure 1. A tallow amine acetate (Armac-T) was found to be the most usable surfactant tested when employed at a 3.5:1 molar ratio of surfactant to fluoborate.

An inherent problem of the ion floatation process is the amount of time necessary to carry it to completion. Foaming times in excess of 20 hours were necessary to achieve maximum removal of surfactant from solution.

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[4] Cagnati, Haralson, Hunter, Liskowitz, Perna, Trattner, "Removal of Fluoborate From Plating Wastewater: Technique and Mechanism," Water-1977, American Institute of Chemical Engineers, pp. 309-315.

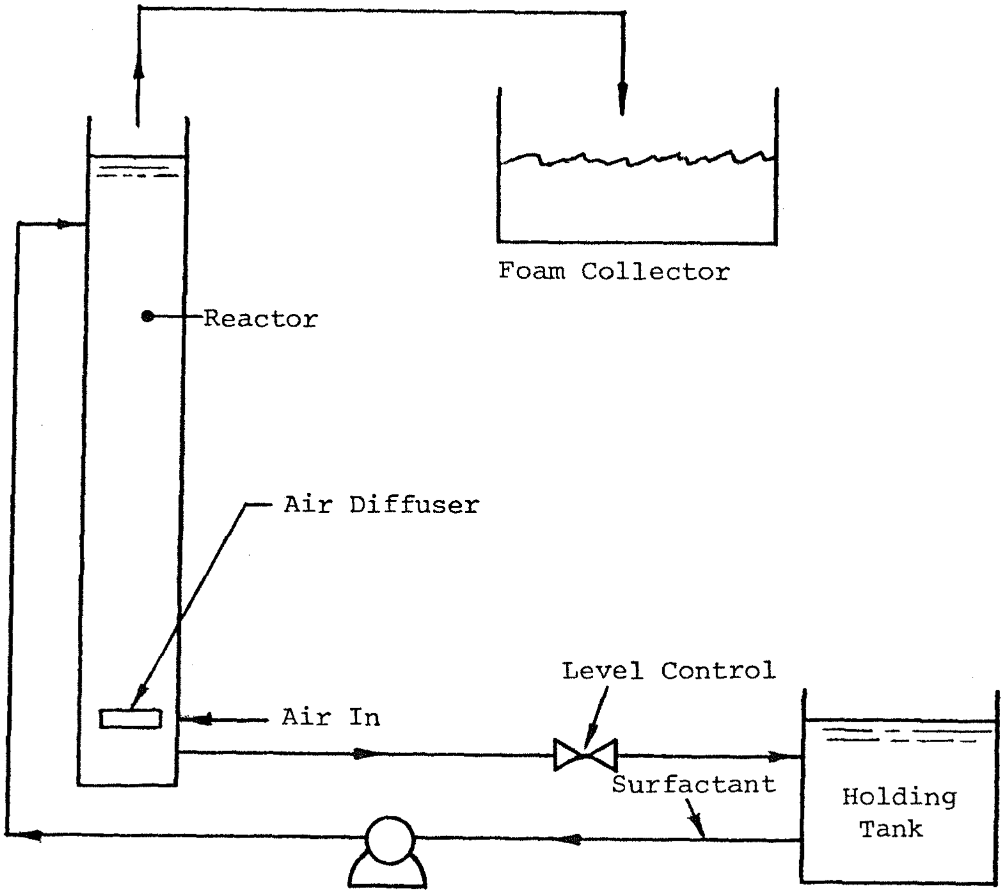

FIGURE 1, FOAMING APPARATUS

Although this time requirement could be coped with, other possibilities for removing the surfactant-fluoborate adduct from solution should be considered. An alternative removal technique is the use of ultrafiltration.

Ultrafiltration involves using semipermeable polymetric membranes to separate molecular or colloidal materials dissolved or suspended in a liquid phase while a pressure is being exerted on the liquid. The membrane acts as a molecular screen which separates molecular particles based on differences in size, shape, and chemical structure. The membrane retains dissolved or dispersed molecules which have a greater molecular weight than a predetermined molecular weight cut-off, while it allows the passage of the solvent and lower molecular weight solutes. At present, ultrafilter membranes are commercially available with nominal molecular weight cut-offs ranging from 1,000 to 100,000.

It was only during the past decade that ultrafiltration has advanced from laboratory to industrial applications. Current applications of ultrafiltration in the finishing industry includes the following:[5]

Ultrafiltration of Electrocoated Paint,

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[5] Del Pico, Joseph and White, Paul W., "Reverse Osmosis and Ultrafiltration," <u>Metal Finishing</u>, August, 1974, pp. 29-31.

Ultrafiltration of Aqueous Enamel Overspray Rinsewater,

Ultrafiltration of oil emulsified wastes.

Ultrafiltration offers a means of removing the surfactant-fluoborate adduct from solution. Although the apparent molecular weight of Armac-T is 330, it was found from conductivity and spectrophotometric measurements that Armac-T forms a micellar system when the concentration is above 12ppm. Therefore, at the concentrations of Armac-T required to complex the fluoborate, the surfactant will exhibit an apparent molecular weight much higher than 330.[6]

To determine the feasibility of employing ultrafiltration to concentrate the surfactant-fluoborate adduct, equipment from the Millipore Corporation was used. Initially, different membranes were tested in conjunction with a low through-put pressure cell. Then, based on favorable results with the above system the Millipore High Volume Pellicon Cassette System was evaluated.

For either ion floatation or ultrafiltration to be a practical solution for the removal of fluoborate, a

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[6] Cagnati, Haralson, Hunter, Liskowitz, Perna, Trattner, "Removal of Fluoborate From Plating Wastewater: Technique and Mechanism," Water-1977, American Institute of Chemical Engineers, pp. 309-315.

method for breaking the surfactant-fluoborate complex must be developed. Once the adduct is separated, the fluoborate solution could be recyled as makeup plating bath. Two methods of breaking the complex were investigated; the addition of acetic acid and the use of electrolysis.

Previous experimentation showed that the mechanism for removal of the fluoborate, using a surfactant, involved the replacement of the acetate in the surfactant by the fluoborate.[7] Therefore, the excess acetic acid was added in an attempt to liberate the fluoborate from the complex by reversing the binding mechanism.

Electrolysis was also used in an attempt to break the surfactant-fluoborate complex. Electrolysis is the decomposition of a chemical complex by the addition of an electric field to a solution. The negatively charged ions will migrate to the anode while the positive ions are drawn toward the cathode. Therefore, in the case of the surfactant-fluoborate complex, the liberated fluoborate should move toward the anode while the gelatinous tallow amine should plate out on the cathode.

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[7] Cagnati, Haralson, Hunter, Liskowitz, Perna, Trattner, "Removal of Fluoborate From Plating Wastewater: Technique and Mechanism," Water-1977, American Institute of Chemical Engineers, pp. 309-315.

Ion floatation and ultrafiltration are feasible only for dilute rinse solutions such as those obtained from single tank rinsing. The addition of the required quantities of surfactant to more concentrated rinse solutions yields a dense non-workable solution unsuitable for ion floatation and ultrafiltration. However, concentrated rinses do exist where countercurrent or series rinsing is employed. Electrodialysis was used to investigate the recycling of concentrated rinse waters.

Electrodialysis is a membrane process which can be used for the separation, removal or concentration of ionized species in aqueous solutions.[8] The above is accomplished by using an electromotive force to selectively transport ions through an ion-exchange membrane. These ion-exchange membranes are permeable to either cations or anions, but not both. The membranes are thin sheets of ion-exchange material reinforced by a synthetic fabric backing. The resin matrix is usually copolymerized styrene divinylbenzene, the exchange capacity being imparted by sulfonic acid groups for cation exchange membranes and quaternary ammonium groups for anion exchange membranes.[9]

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[8] Eisenmann, John L., "Recovery of Nickel From Plating Bath Rinse Waters by Electrodialysis," _Plating and Surface Finishing_, November, 1977, pp. 34-38.

[9] Ibid., pp. 34-38.

A simple electrodialysis system consists of an anode and a cathode, separated by an anion permeable membrane near the anode and a cation permeable membrane near the cathode. Thus a cathode chamber, an anode chamber, and a center chamber are formed. When the electric charge is applied, anions pass from the center chamber to the anode chamber while cations pass from the center chamber to the cathode chamber. Therefore, the concentration of salt in the center chamber is decreased. The application of a simple electrodialysis cell in the separation of a potassium sulfate solution is shown in Figure 2.

In practical electrodialysis installations, there are ten to hundreds of compartments between one pair of electrodes. These units are referred to as electrodialysis stacks. These stacks include specially designed spacers to separate the membranes and form flow directing cells between adjacent membranes. The feed solution is distributed and collected from these cells by two internal hydraulic circuits; one for diluting cells and one for concentrating cells. An electrodialysis stack can be characterized by its number of cell pairs. A cell pair includes the following components:

- Cation Selective Membrane
- Diluting Spacer

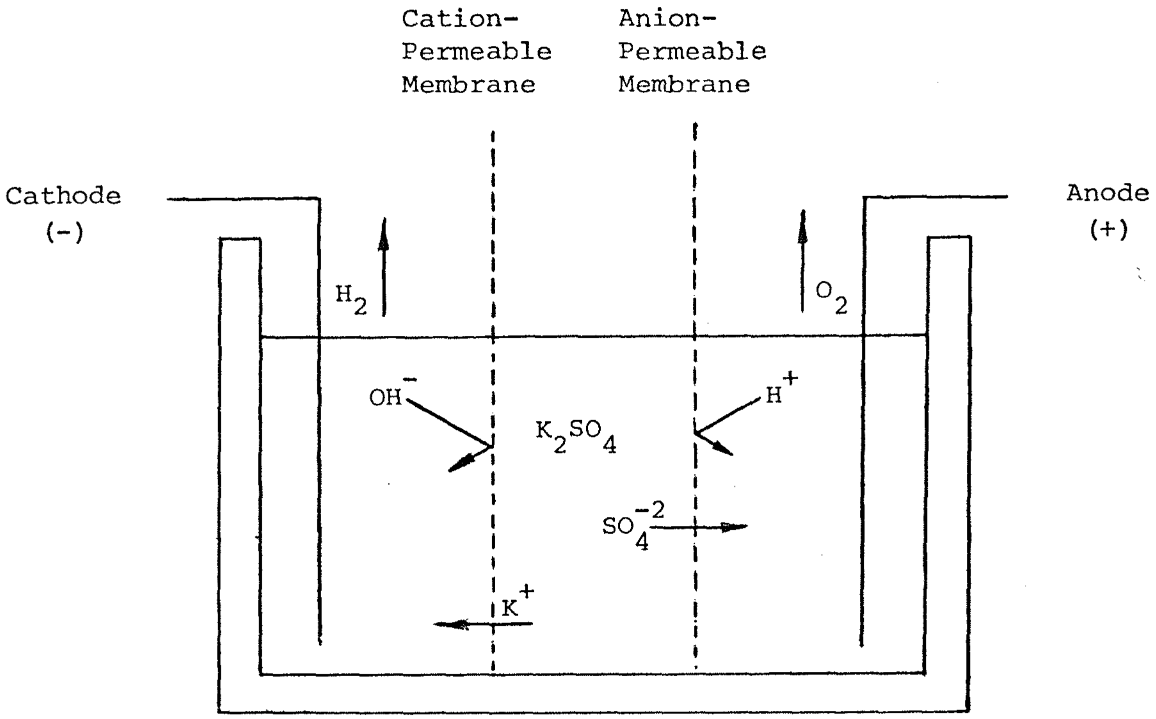

FIGURE 2, A SCHEMATIC OF A SIMPLE ELECTRODIALYSIS CELL

- Anion Selective Membrane
- Concentrating Spacer

Passing a direct current through the stack causes ions to leave the diluting cells and collect in the concentrating cells.

The most frequently used application of electrodialysis is in the desalination of brakish water.[10] Another major application is the deashing of whey. Some recent investigations relating to the metal finishing industry include the recovery of nickel from plating rinse waters and closed loop control of cyanide rinse waters.[11] Electrodialysis was investigated here as a means of concentrating fluoborate plating rinsewaters for recycle back to the plating bath.

A major portion of this experimental work relied on the measurement of the fluoborate in the solution. For this an ion-selective electrode was used. Ion-selective electrodes are widely recognized as an important tool for chemical analysis.[12]

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[10] Birkett, Dr. James D., "Electrodialysis - An Overview," Industrial Water Engineering, September, 1977, pp. 6-10.

[11] Eisenmann, John L., "Recovery of Nickel From Plating Bath Rinse Waters by Electrodialysis," Plating and Surface Finishing, November, 1977, pp. 34-38.

[12] Ion Selective Electrodes, HNU Systems Incorporated, Newton Upper Falls, Massachusetts, 1978.

Selective ion electrodes are used to measure a wide variety of ions and dissolved gases in solution and are relatively inexpensive and simple to use. Virtually all of the ions which are of interest to platers can be measured with such electrodes.[13]

Recently, a specific ion electrode was developed for the measurement of the fluoborate ion in aqueous solutions. Prior to the electrode's development, there was no method for readily determining fluoborate concentrations. Wet chemical methods were tedious and could not be performed rapidly. Also, a method of detection utilizing the fluoride specific ion electrode was employed which was also time consuming. The initial flouride concentration would be measured using the electrode, then an acid digestion process would be performed to hydrolyze the fluoborate, and the final concentration determined. The difference between the final and initial fluoride concentrations was attributed to the hydrolysis of the fluoborate. Therefore, for every four parts of fluoride there would be one part of fluoborate present.

With the development of the fluoborate electrode,

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[13] Frant, M.S., Application of Specific Ion Electrodes to Electroplating Analyses, 56th Annual Convention, American Electroplaters' Society, June 16, 1969.

detection of the ion has been simplified. There are presently two types of fluoborate probes offered by Orion Research Incorporated, the original (Orion 92-05) and it's replacement (Orion 93-05). The 93 series electrode had been used in previous research work at N.J.I.T. and was found to produce usable results in the concentration ranges of interest. This electrode was used in conjunction with an Orion 90-02 double junction reference electrode.

The 93 series electrode could not perform in the presence of an organic surfactant. The surfactant had an adverse effect on the probe's membrane, therefore, the older 92 series electrode was considered. The 92 series electrode has replaceable membranes and it was determined that this probe would yield five to ten reliable readings before the membrane necessitated replacement. An Orion 90-01 single junction reference electrode is specified for use with the 92 series probe.

Due to the presence of the surfactant in solution, during the electrolysis experiments the 92 series electrode was utilized. Since there was no surfactant present during the electrodialysis experiments, the 93 series electrode was employed. Both electrode systems were used along with a pH/mv meter and operated as outlined in Orion's instruction manual.

Two methods were used to determine the presence of the tallowamine acetate surfactant (TA) in solution. One technique was a dye test, while the other mode was the total organic carbon (TOC) test.

The dye test was used only during the simple cell ultrafiltration experiments. This test provided evidence of the presence or absence of TA in the filtrate solution by visual inspection. Bromophenol blue, which was the dye that was used, gave a rough quantitative indication of the TA in solution. When TA was present a blue color was formed in the solution. When no TA was present the solution remained clear and colorless. The deepness of the blue increased as the concentration of TA increased. Therefore, the dye test was a good preliminary indication of the passage of the surfactant-fluoborate complex through the ultrafiltration membrane. However, a more exacting test was required to determine the overall efficiency of ultrafiltration. For this TOC tests were used.

TA is a long chained carbon organic compound. Therefore, as it's concentration in solution increased the TOC of the solution will increase. This correlation between the concentration of TA and the TOC gives all indications of being proportional. Therefore, TOC was used to represent the concentration of TA in solution during all phases of the ultrafiltration experimentation. This testing was performed on an automatic TOC analyser.

In light of the above discussion, the following experimental work was performed: ultrafiltration was evaluated as a means of removing the surfactant-fluoborate complex from solution, the addition of excess acetic acid and electrolysis were assessed as a means of breaking the surfactant-fluoborate complex, and electrodialysis was investigated as a method of recycling fluoborate rinsewaters.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

Ultrafiltration

Simple Cell. The equipment used was the Millipore Corporation's 47mm stirred cell, catalogue number XX42 047 10. The membranes were Millipore's Pellicon membranes, PSAC type.

The two membranes which were evaluated were 1,000 and 10,000 nominal molecular weight limit (nmwl) membranes. The nmwl is a rough guide to the size above which most molecules are efficiently retained by that membrane. The nmwl is not a sharp cut-off.

The simple stirred cell, which is depicted in Figure 3, is a cylindrical plastic unit designed to hold membrane discs for the ultrafiltration of small fluid volumes. The cell barrel is polycarbonate with silicone O-rings for seals at the base and cap. The capacity of the cell is 80ml, the cell takes a 47mm membrane disc which has a filtration area of 10.5cm^2.

In the evaluation of the two different membranes, the set-up that is shown in Figure 3 was used. Seventy-five milliliters of solution was placed in the cell. Pressure was applied by filtered air from the house pressure line by means of a Luer connection on the cap.

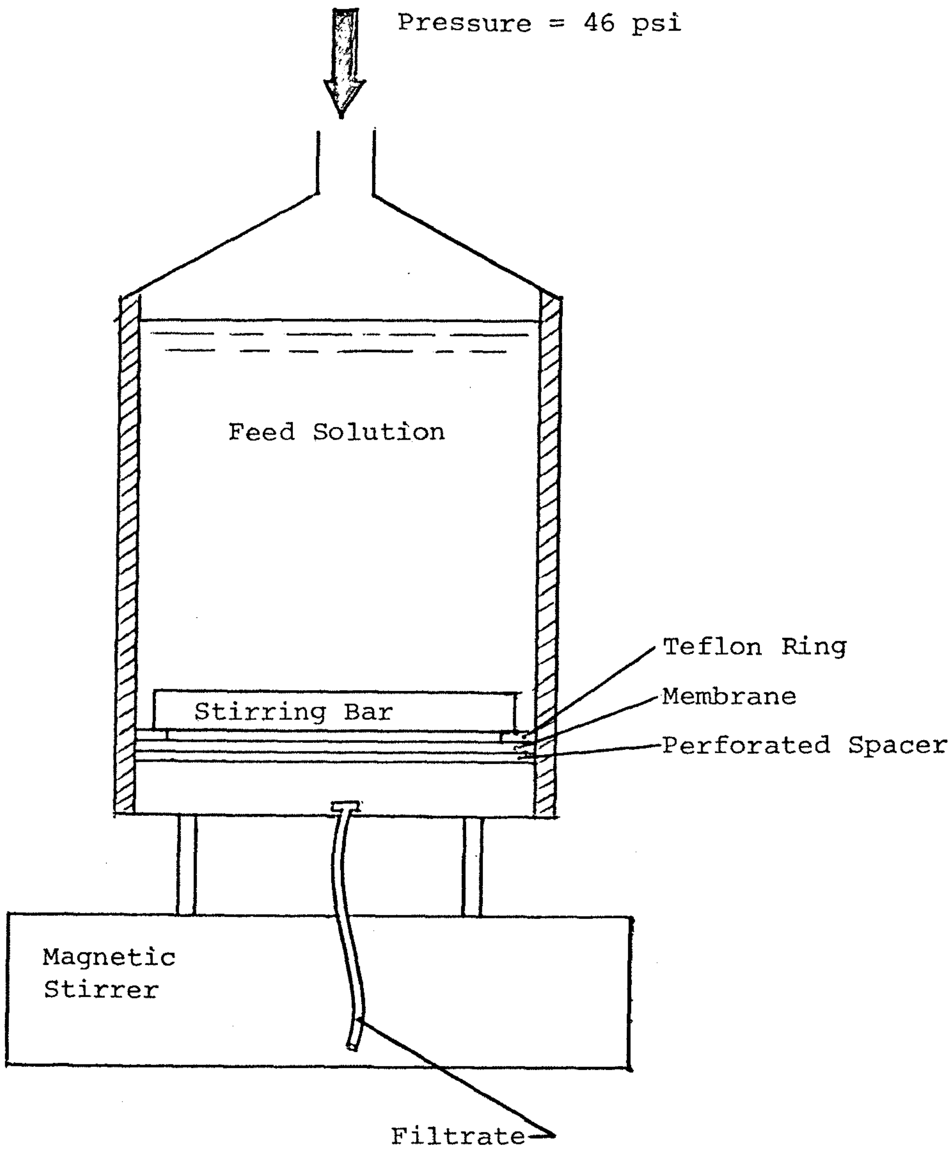

FIGURE 3, SCHEMATIC OF A SIMPLE ULTRAFILTRATION CELL

The pressure was maintained at 46 psi. The cell was mounted on a magnetic stirrer and stirred by means of a magnetic stirring bar inside the cell. This reduced the possibility of membrane polorization. The filtrate was collected in test tubes from the plastic tube which was inserted in the base of the cell.

Experiments were run using 1500 ppm of TA and 100 ppm of BF_4^- as the initial solution. During the evaluation of the 10,000 nmwl membrane the dye test was used to determine the presence of TA in the filtrate. While assessing the 1,000 nmwl membrane, the dye test was initially used on the filtrate. Then an additional experiment was run utilizing TOC analysis on the filtrates.

High Volume Cassette. In light of encouraging results achieved using the 1,000 nmwl membrane in the simple cell, a larger unit was purchased and evaluated. This unit was the Millipore High Volume Cassette System as shown in Figure 4. The cassette system is 10" wide x 9" deep x 12" high. Membranes for this system have a filtration area of $465 cm^2 (0.5 ft^2)$.

The system was run utilizing a variable speed tubing pump to transport pressurized solution to the cassette's feed port. Pressure at the feed port was regulated by the pump speed. A needle valve was placed at the

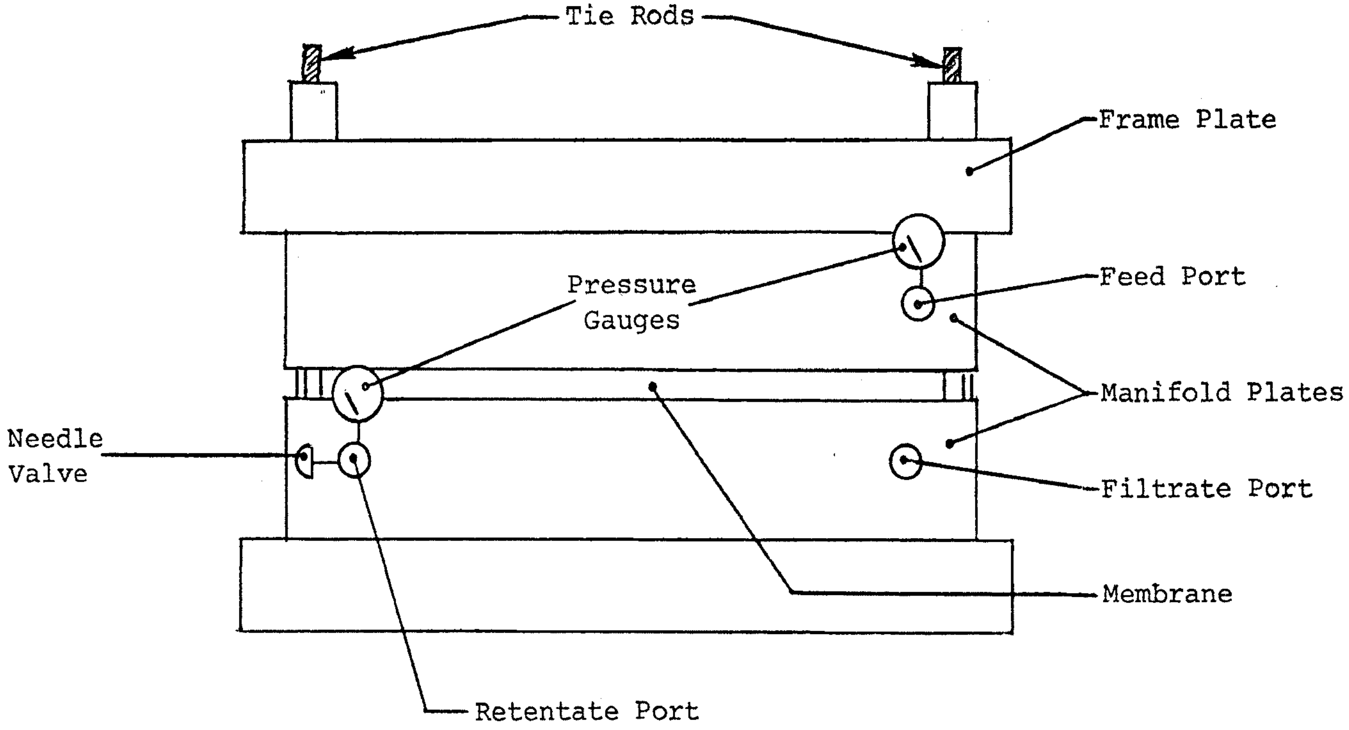

FIGURE 4, SCHEMATIC OF AN ULTRAFILTRATION CASSETTE retentate port in order to maintain pressure over the entire membrane area. Using this system, two types of experiments were run. They were single pass flow and recirculating flow as depicted in Figures 5 and 6, respectively. During both experiments the same feed solution (1500 ppm of TA and 100 ppm of BF_4^-) was used.

Operating pressures were maintained at 30 psi at the feed port and 21 psi at the retentate port, during the single pass flow experiment. Due to the viscosity of the feed solution, only 5.7 ml of filtrate was collected per litre of feed. Millipore's operating manual recommends using recirculating flow when the application requires removing more fluid from the sample than the cassette unit can accomplish in one pass. Therefore, the recirculating flow system was investigated.

During the recirculating flow experiment the retentate was run back into the sample vessel. The sample vessel was mounted on a magnetic stirrer and the solution was stirred to maintain a homogeneous feed. The pressures were maintained at 30 psi at the feed port and 22 psi at the retentate port.

The filtrates from both the single pass flow and the recirculating flow experiments were analyzed for TOC to determine the surfactant-fluoborate complex removal.

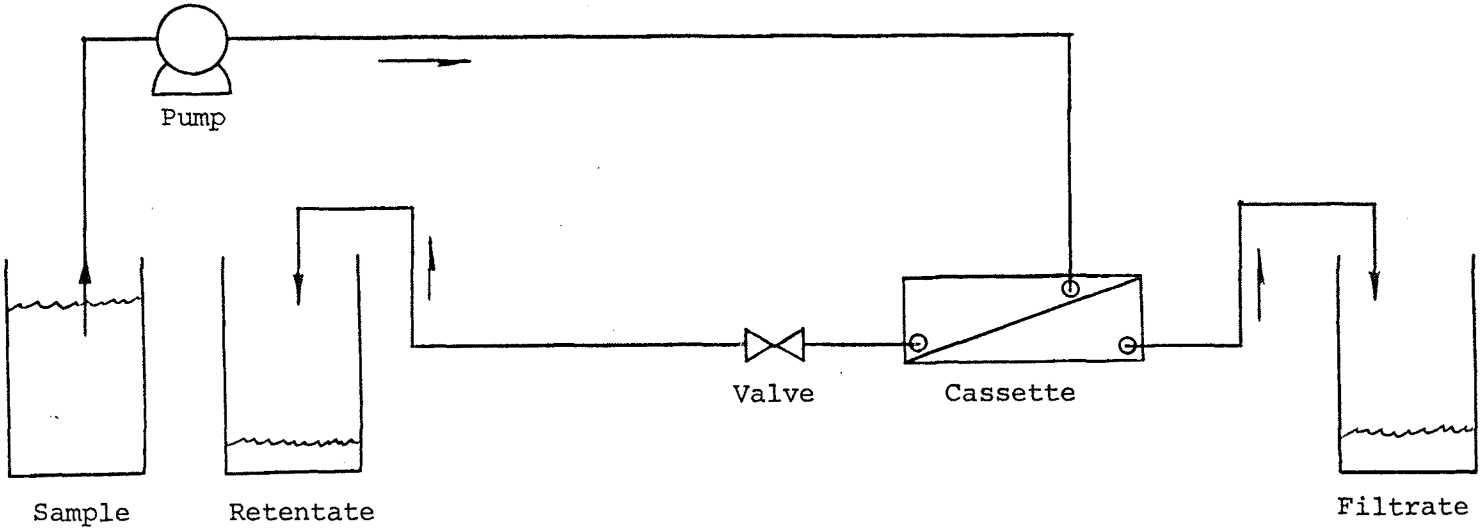

FIGURE 5, SINGLE PASS FLOW SYSTEM

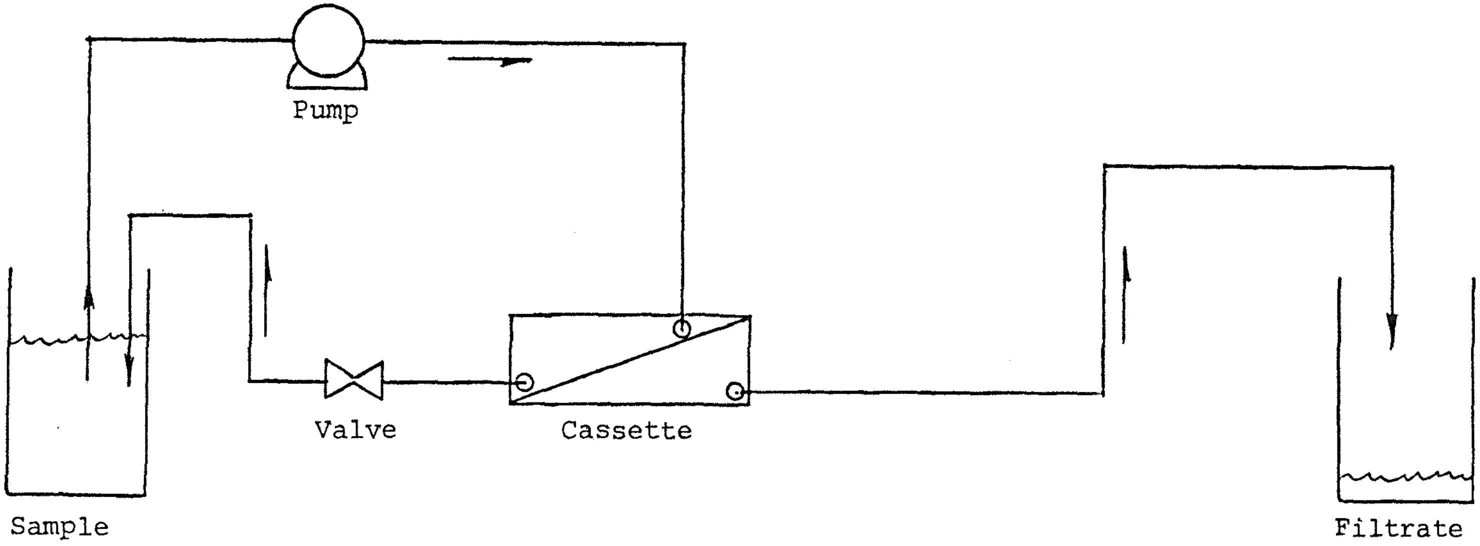

FIGURE 6, RECIRCULATING FLOW SYSTEM

Breaking the Complex

Addition of Excess Acetic Acid. In an attempt to reverse the equilibrium of the surfactant-fluoborate complex and break the complex, the addition of excess acetic acid was tried. A one litre solution of 2,000 ppm of BF_4^- and 30,000 ppm of TA was prepared. Concentrated acetic acid was pipeted into this solution at an initial volume of 0.5 ml. The solution was stirred utilizing a magnetic stirrer to produce a homogeneous sample. The concentrated acetic acid was added in increments of 0.5 ml. After each addition of acid, the concentration of BF_4^- was monitored using the Orion 92 series electrode system.

Electrolysis. Electrolysis was also investigated as a means for separating the surfactant-fluoborate complex. A simple electrolysis cell was set up as shown in Figure 7. The components were a pyrex beaker, a spiraled platinum anode, a copper cathode, a direct current (D.C.) power supply and various clamps and wiring.

The D.C. power supply was kept constant at 45 volts ($<$ 1% ripple). This achieved a current density at the cathode of approximately 3.7 Amps/Ft^2.

A surfactant-fluoborate solution (1500 ppm of TA and 100 ppm of BF_4^-) was added to the system. The power supply

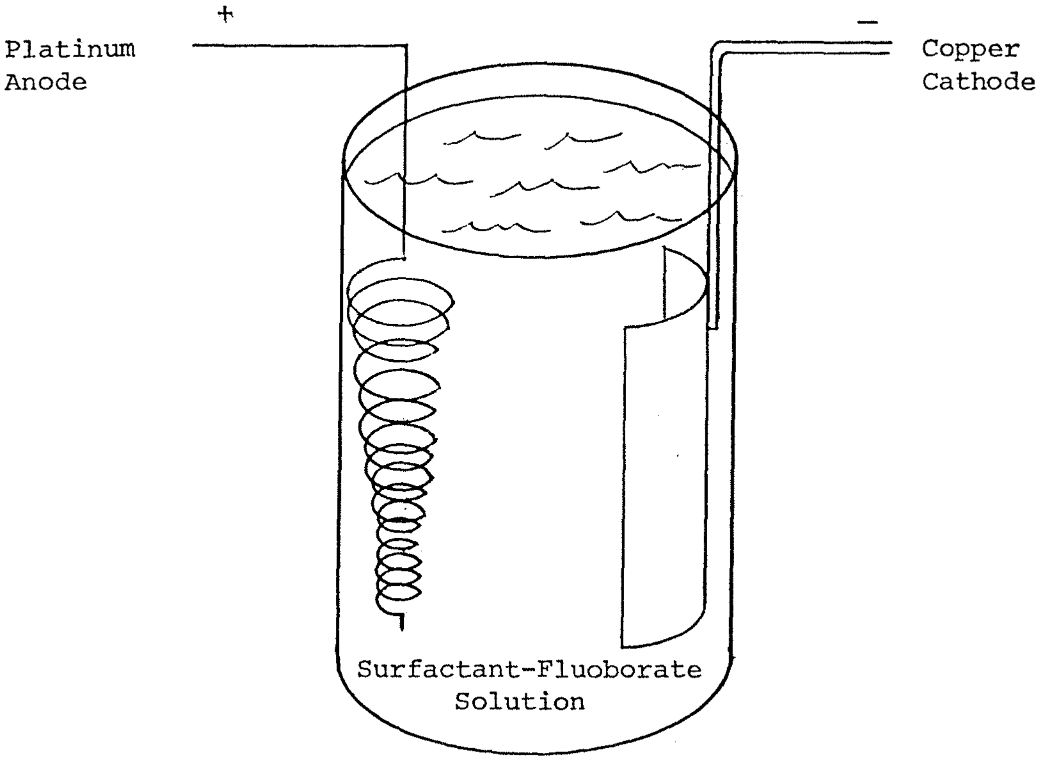

FIGURE 7, SCHEMATIC OF ELECTROLYSIS SET-UP was turned on at TIME = 0. Using the 92 series fluoborate electrode system, the fluoborate concentration was determined periodically. These concentrations were then plotted versus time to determine the rate of disassociation of the complex.

Using the above system, disassociation of the following four solutions were examined:

1. Solution A: TA (1500 ppm) + N_aBF_4 (100 ppm); Stirred for 90 minutes.
2. Solution B: Same constituents as Solution A; Stirred for 8 hours.
3. Solution C: TA (1500 ppm) + Lead and Tin Fluoborate, BF_4^- = 100 ppm; Stirred overnight.
4. Solution D: TA (1500 ppm) + Lead and Tin Fluoborate, BF_4^- = 100 ppm + Brighteners; Stirred overnight.

The concentrations of these solutions coincide with the previously decided optimum molar ratio of surfactant to fluoborate of 3.5:1.

Electrodialysis

Electrodialysis was investigated here as a means of concentrating fluoborate plating rinse waters for recycle back to the plating bath. To carry out the related experimentation, an electrodialysis stack which was purchased from the Micro-Pore Research Company was used. The stack consisted of ten cell pairs and was arranged as illustrated in Figure 8.

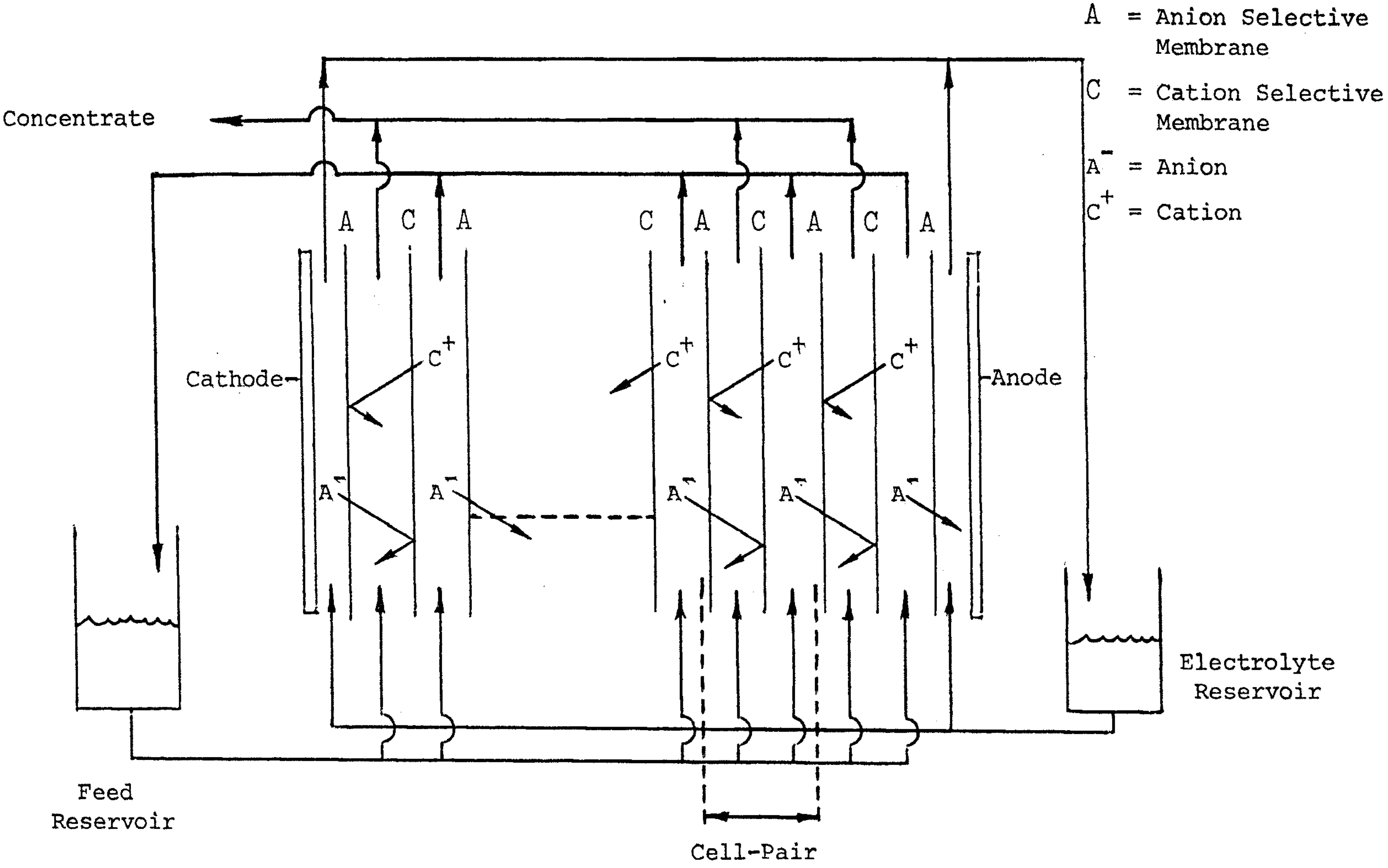

FIGURE 8, SCHEMATIC OF AN ELECTRODIALYSIS STACK

The size of the membranes and electrodes was 55.9 cm x 30.5 cm (22"x12"). Approximately 65% of the area of the membranes was used for ion transfer. The spacers and membranes delineated an S-shaped flow pattern which incorporates the advantages of the more common sheet flow and tortuous path designs. Alternate cells were connected to internal feed or product manifolds. The ends of the stack were terminated with the two electrodes. The cathode was stainless steel 316 while the anode was platinized titanium. A hydraulically isolated electrode rinse solution consisting of a mixture of HBF_4 and $NaBF_4$ in solution was recirculated from a small reservoir.

Other related supplies included pumps for both the feed solution and the electrode rinse solution (electrolyte), reservoirs for the feed and the electrolyte, collecting vessels for the concentrated products, an exhaust over the electrolyte reservoir to remove electrolyte gases, a rectifier and necessary piping and valving.

The system was operated as follows:

1. Recirculate the electrolyte through the cathode and anode cells.
2. Recirculate the feed solution through the feed cells.
3. Turn on the D.C. power supply.
4. Collect product samples and feed samples.

The flows of electrolyte and feed solutions were brought up to operating rates slowly. The flows were regulated by gate valves to maintain a pressure of 10 psi at both the electrolyte and feed inlets. Also, the temperature of the solution at the feed outlet was monitored in order to prevent possible membrane damage due to the overheating of the stack. At the end of each experiment, the hydraulics were run for 2-3 minutes after the current was shut off. Also, between experiments the stack was flushed with distilled water until no fluoborate could be detected.

Various experiments were run using the following fluoborate rinse solutions as feed:

Solution E:	Technical Grade Sodium Fluoborate
Solution F, G and H:	Copper Fluoborate
Solution I:	Solder Fluoborate (60:40 ratio of Tin:Lead)
Solution J:	Stannous Fluoborate

After each run the concentration of fluoborate in the product and feed samples was determined using the 93 series electrode system. These concentrations were ultimately plotted against time.

III. RESULTS AND DISCUSSION

Ultrafiltration

Evaluation of the ultrafiltration membranes utilized a low through-put pressure cell. In the cell, experiments were run with 10,000 and 1,000 molecular weight cut-off membranes. Experiments with the 10,000 molecular weight cut-off membrane were unsuccessful. The solution passed right through the membrane.

The 1,000 molecular weight cut-off membrane was effective in filtering a solution of plating rinse water containing fluoborate ions complexed with the tallowamine acetate surfactant (TA).[15] As shown in Table 1 the removal that was achieved averaged 80%. (The concentration of TA in the solutions was represented by the total organic carbon (TOC) of the solution.)

Table 1, Results of low through-put pressure cell experiment

SOLUTION	VOLUME (ml)	TOC (mg/l)	% REMOVAL
Initial	75	1,063.7	-
1st filtrate	1.2	191.5	82
2nd filtrate	2.6	212.7	80

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[15] Cagnati, Haralson, Hunter, Liskowitz, Perna, Trattner, "Removal of Fluoborate From Plating Wastewater: Technique and Mechanism," Water-1977, American Institute of Chemical Engineers, pp. 309-315.

Table 1 (Cont.)

SOLUTION	VOLUME (ml)	TOC (mg/l)	% REMOVAL
3rd filtrate	10.6	202.1	81
4th filtrate	43.0	234.0	78
5th filtrate	2.4	223.4	79
		Average =	80%

Although the molecular weight of TA is approximately 330, it was determined from conductivity and spectrophotometric measurements that TA forms a micellar system at concentrations greater than 12 ppm. Therefore, at the concentration of TA that is required to complex the fluoborate, it will exhibit an apparent molecular weight much greater than 330.[16]

Experiments utilizing the 1,000 molecular weight cutoff membrane in the Millipore Cassette ultrafiltration apparatus showed favorable results. As illustrated in Table 2, the removal of the complex during the single pass experiment averaged 94%.

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[16] Cagnati, Haralson, Hunter, Liskowitz, Perna, Trattner, "Removal of Fluoborate From Plating Wastewater: Technique and Mechanism," Water-1977, American Institute of Chemical Engineers, pp. 309-315.

Table 2, Results of single pass experiment, Millipore Cassette

SOLUTION	VOLUME (ml)	TOC (mg/l)	% REMOVAL
Initial	1,000	1,044.5	-
1st filtrate	2	50.7	95
2nd filtrate	3.7	73.0	93
			Average = 94%

Recycling the retentate back into the ultrafiltration cassette resulted in an average removal of surfactant of 86%, as shown in Table 3.

Table 3, Results of recycled retentate experiment, Millipore Cassette

SOLUTION	VOLUME (ml)	TOC (mg/l)	% REMOVAL
Initial	1,000	1,072.9	-
1st filtrate	20	86.3	92
2nd filtrate	50	173.0	84
3rd filtrate	10	165.1	85
4th filtrate	50	185.3	83
			Average = 86%

These ultrafiltration experiments produced the same components as the ion flotation technique, i.e., a solution with trace amounts of the surfactant-fluoborate complex and a concentrate of the complex. On experimental ion-flotation equipment, foaming times in excess of 20 hrs.

were not unusual to reach maximum removal of the surfactant-fluoborate complex from solution.[17] The experimental recycled ultrafiltration equipment achieved this separation in approximately 5 hours. The ion flotation time cannot be reduced by industrial scale-up; however, the time required for ultrafiltration can be minimized by increasing the number of membranes. The Millipore model can handle a maximum of 50 membranes.[18] Therefore, the industrial scale-up of such an ultrafiltration apparatus would facilitate the handling of large volumes (e.g., 1,000 gal.) of TA complexed rinse waters.

Separation of Surfactant-Fluoborate Complex

Two methods were evaluated for breaking the surfactant-fluoborate complex. They were the addition of excess concentrated acetic acid and electrolysis. It was proven that the addition of concentrated acetic acid failed to reverse the equilibrium of the solution and separate

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[17] Cagnati, Haralson, Hunter, Liskowitz, Perna, Trattner, "Removal of Fluoborate From Plating Wastewater: Technique and Mechanism," Water-1977, American Institute of Chemical Engineers, pp. 309-315.

[18] Pellicon Cassette System, Assembly, Operation and Maintenance, Millipore Corporation, Bedford, Massachusetts, 1975.

the surfactant-fluoborate complex.[19] Even with the addition of copious quantities of acetic acid, only a small amount of fluoborate was liberated from the complex.

Electrolysis of the surfactant-fluoborate complex was assessed. Using a copper cathode and a spiraled platinum anode at 45 volts direct current and a current density of the cathode of approximately 3.7 amps/ft.^{2}, four separate solutions were examined. They were the following:

1. Solution A: TA (1500 ppm) + $NaBF_4$ (100 ppm); Stirred for 90 minutes.
2. Solution B: Same constituents as Solution A; Stirred for 8 hours.
3. Solution C: TA (1500 ppm) + lead and tin fluoborate, $BF_4^- = 100$ ppm; Stirred overnight.
4. Solution D: TA (1500 ppm) + lead and tin fluoborate, $BF_4^- = 100$ ppm + brighteners; Stirred overnight.

In all cases the solutions were prepared with the optimum molar ratio of surfactant to fluoborate of 3.5:1.[20]

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[19] Cagnati, Haralson, Hunter, Liskowitz, Perna, Trattner, "Removal of Fluoborate From Plating Wastewater: Technique and Mechanism," Water-1977, American Institute of Chemical Engineers, pp. 309-315.

[20] Ibid., pp. 309-315.

The results of these experiments are plotted as ppm of BF_4^- formed as a function of time. Figure 9 illustrates the effect of electrolyzing solutions A and B. These plots show a release of approximately 87% of BF_4^-. The variation between the two curves is believed to be caused by the stirring time, which reinforces the fact that formation of the complex is a function of contact time.

Figures 10 and 11 correspond to the electrolysis of solutions C and D respectively. In both cases the formation of approximately 90% of BF_4^- is seen. The concave up slope of Figure 11 is probably due to the presence of the brighteners. These brighteners presumably complex the metal ions thereby causing a slow release phenomenon.[21]

In this electrolysis process the surfactant is plated out on the cathode as the complex is broken. This causes the initial turbid solution to be clear and colorless after electrolysis. Also the surfactant can be removed from the electrode and ultimately reused.

In light of these results, electrolysis is a feasible method for breaking the surfactant-fluoborate complex. Further work must be performed, however, on the complex

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[21] Cagnati, Haralson, Hunter, Liskowitz, Perna, Trattner, "Removal of Fluoborate From Plating Wastewater: Technique and Mechanism," Water-1977, American Institute of Chemical Engineers, pp. 309-315.

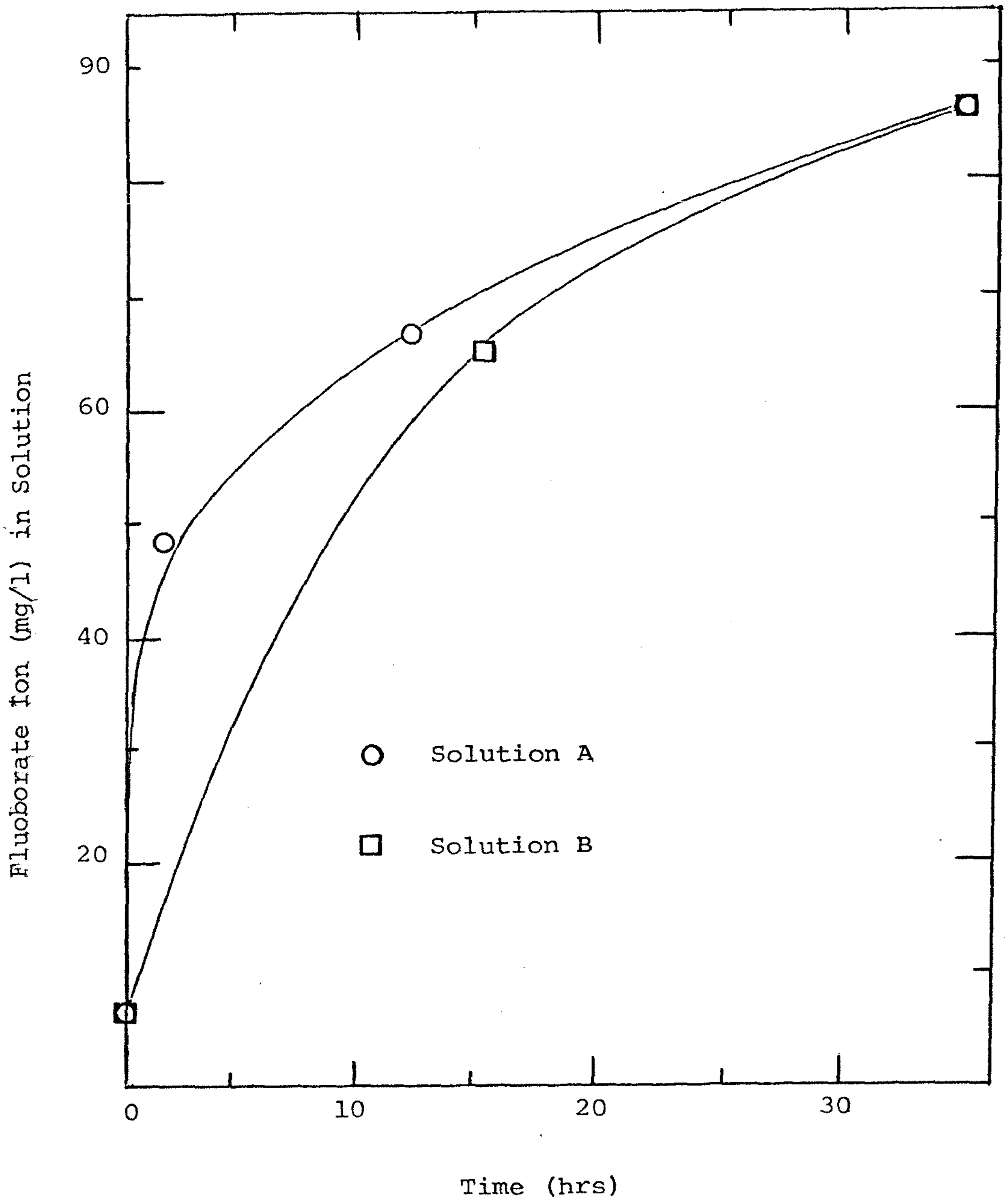

FIGURE 9, ELECTROLYSIS OF SOLUTIONS A AND B

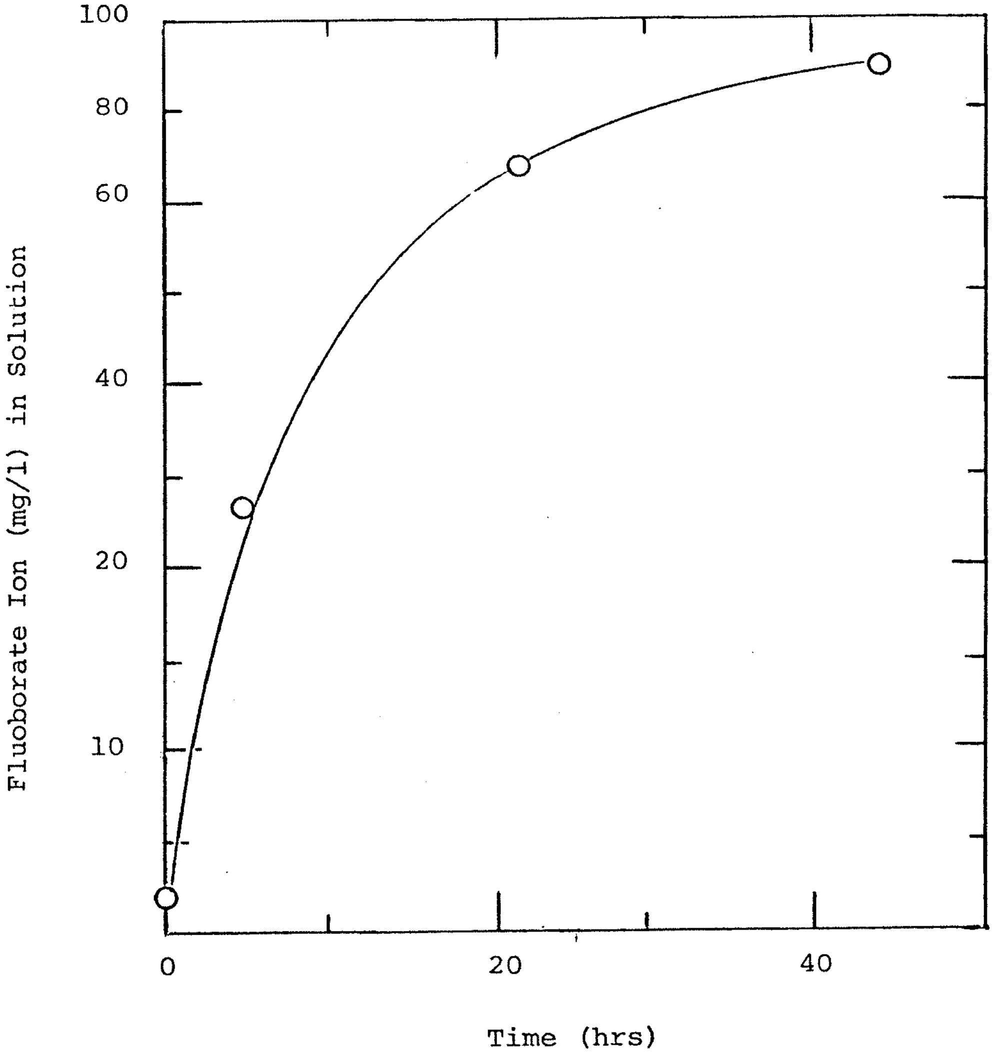

FIGURE 10, ELECTROLYSIS OF SOLUTION C

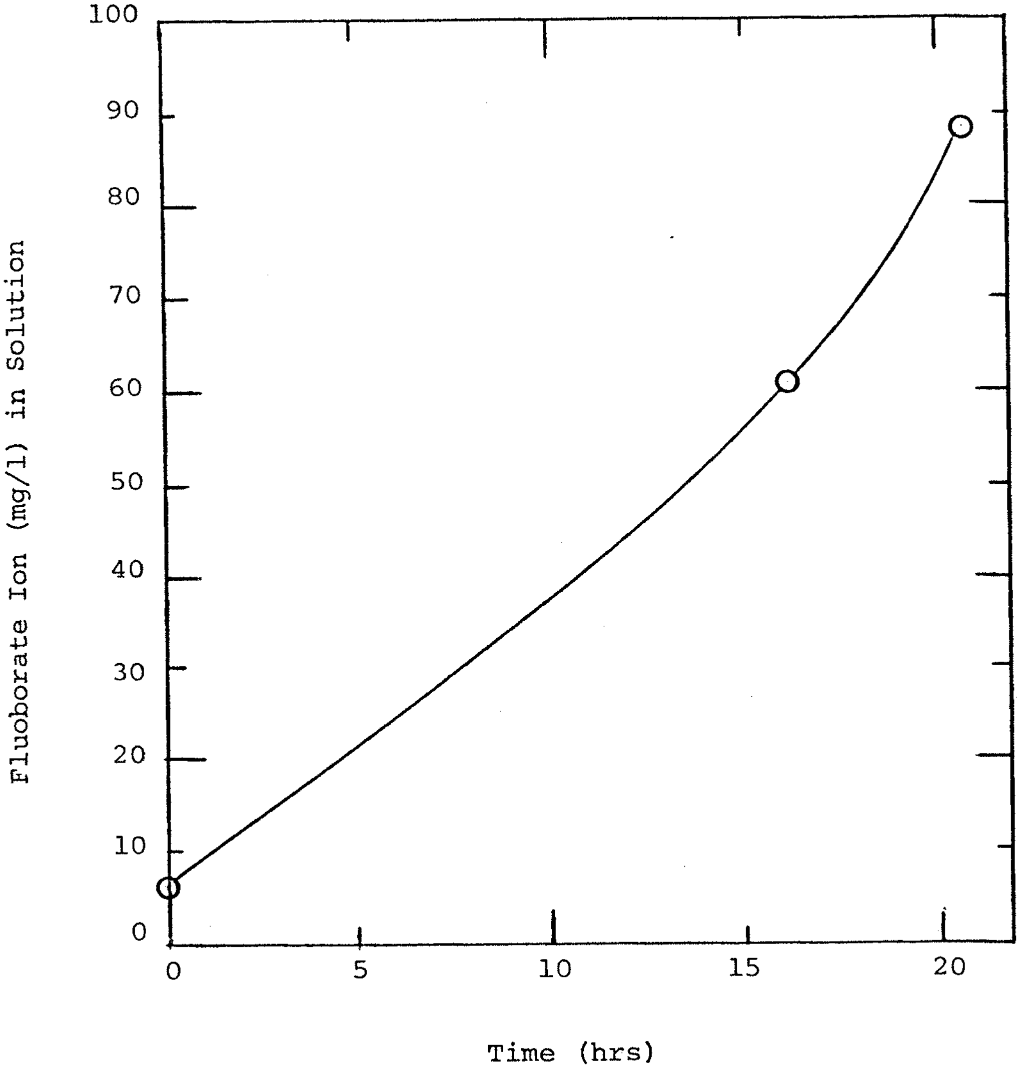

FIGURE 11, ELECTROLYSIS OF SOLUTION D

concentrate (i.e foam from the ion exchange process or retentate from the ultrafiltration process) to determine if electrolysis can be employed as part of a closed loop recycling process.

Electrodialysis

Electrodialysis was investigated as a means for recycling concentrated fluoborate rinse waters. These concentrated rinses are characteristic of countercurrent or series rinsing. The following solutions were run through the electrodialysis stack which was purchased from the Micro-Pore Research Company;

Solution E: Sodium Fluoborate (4,500 mg/l)
Solution F: Copper Fluoborate (15,947 mg/l)
Solution G: Copper Fluoborate (10,202 mg/l)
Solution H: Copper Fluoborate (7,638 mg/l)
Solution I: Solder Fluoborate (5,955 mg/l), (60:40 ratio of tin:lead)
Solution J: Stannous Fluoborate (2,489 mg/l)

For all of these experiments, a solution of fluoboric acid, $[BF_4^-]$ = 19,500 mg/l was used as the electrolyte.

Solution E was used as the feed in the first run of the electrodialysis equipment. This was done with a simple solution in order to determine the workability of the system. Samples of the product were taken at various times during the five hour experiment. The concentrations of these products are plotted in Figure 12. This showed that the electrodialysis stack did indeed concentrate the solution. However, what was of more interest was the dilution of the feed solution. From the initial and final feed solution concentrations, 4,500 mg/l and 1,376 mg/l respectively, it was calculated that the removal of BF_4^- from the feed solution was approximately 70%.

The following three experiments were performed with $CU(BF_4)_2$ in the feed solution at varying concentrations. Figure 13 depicts the BF_4^- concentration in the feed, using solution F, as a function of time. The removal after 5 hours and 15 minutes of electrodialysis time was 65%. The concentrations of the product are shown in Figure 14.

Solution G was fed into the electrodialysis stack. The concentration of solution G was made less that that of solution F to evaluate the effects of concentration on the removal. Results show that even at this lower concentration, comparable results were seen. The removal, as illustrated in Figure 15, was 67% in just under 2 hours. This leads one to believe that if the experiment utilizing solution F was allowed to run for additional time, increased removals would have been achieved.

The next experiment using $Cu(BF_4)_2$ as the feed solution

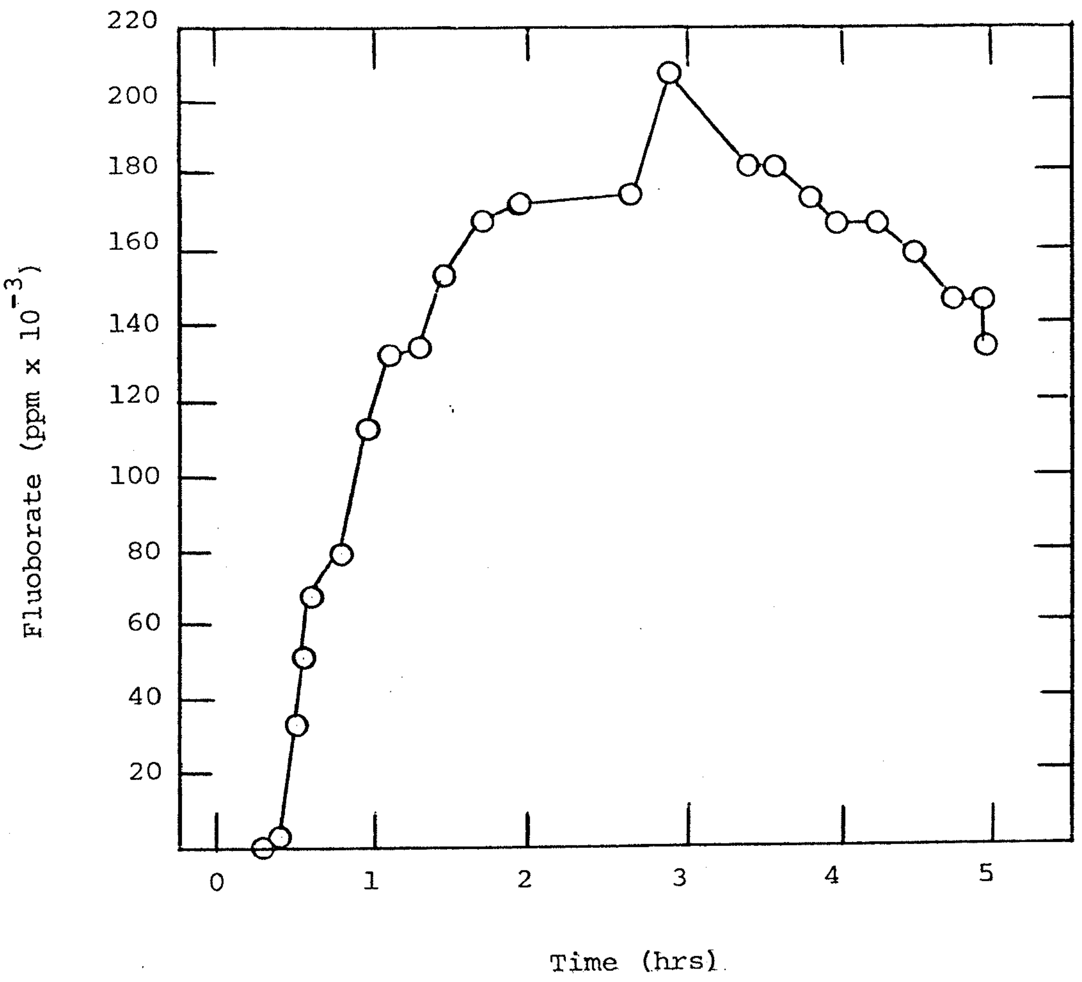

FIGURE 12, $[BF_4^-]$ IN FEED-ELECTRODIALYSIS OF SOLUTION E

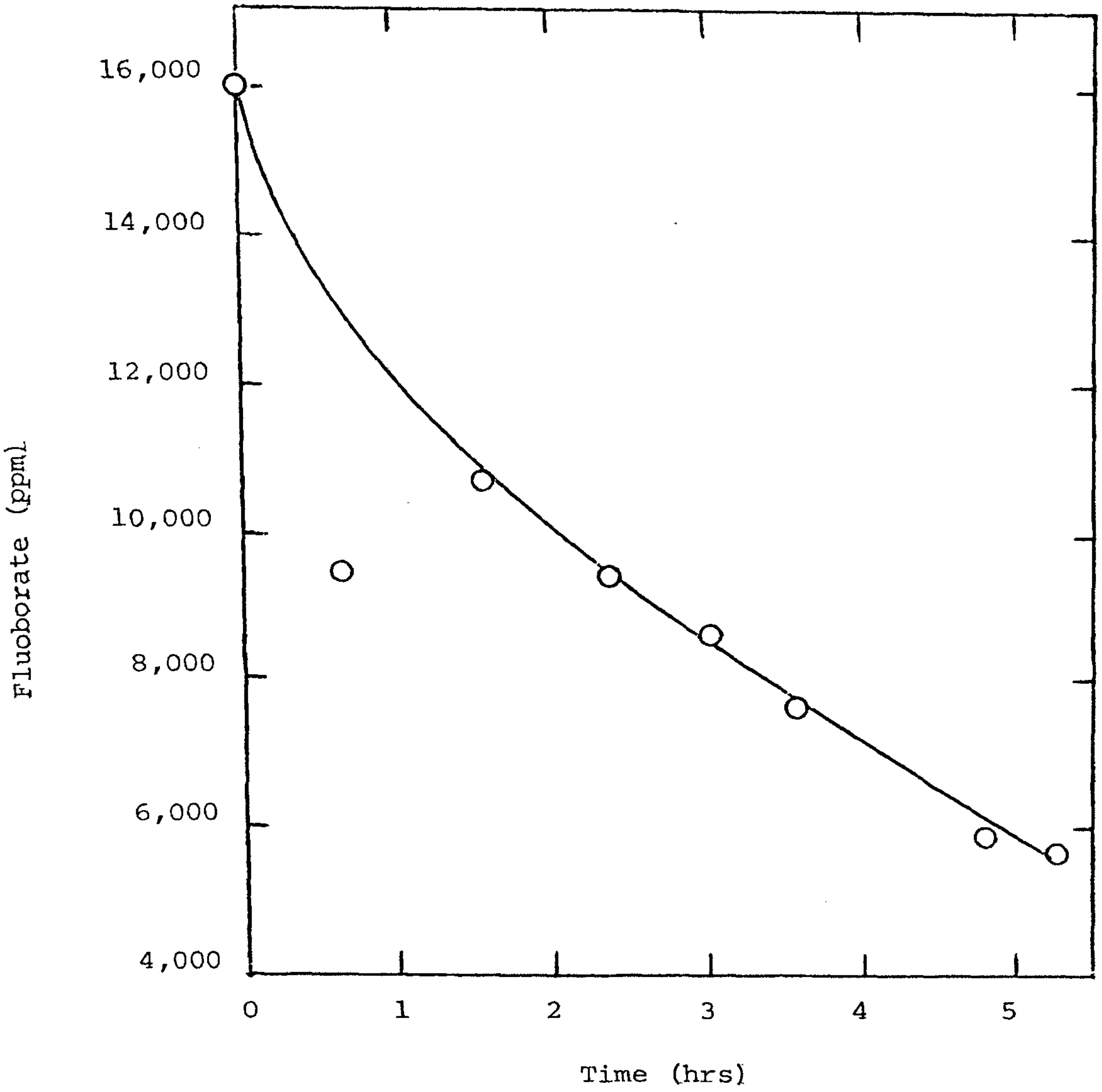

FIGURE 13, $[BF_4^-]$ IN FEED-ELECTRODIALYSIS OF SOLUTION F

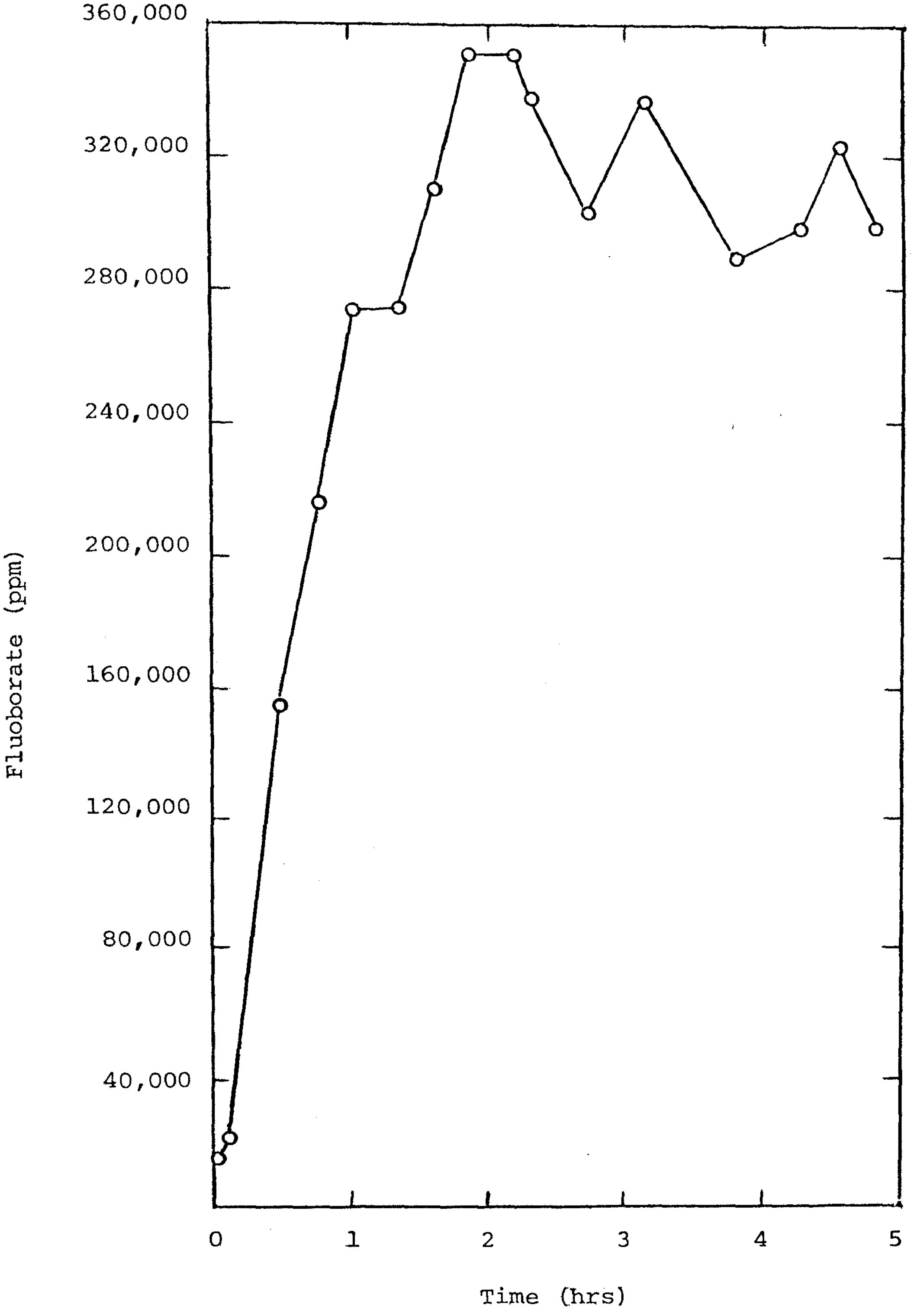

FIGURE 14, $\left[BF_4^-\right]$ IN PRODUCT-ELECTRODIALYSIS OF SOLUTION F

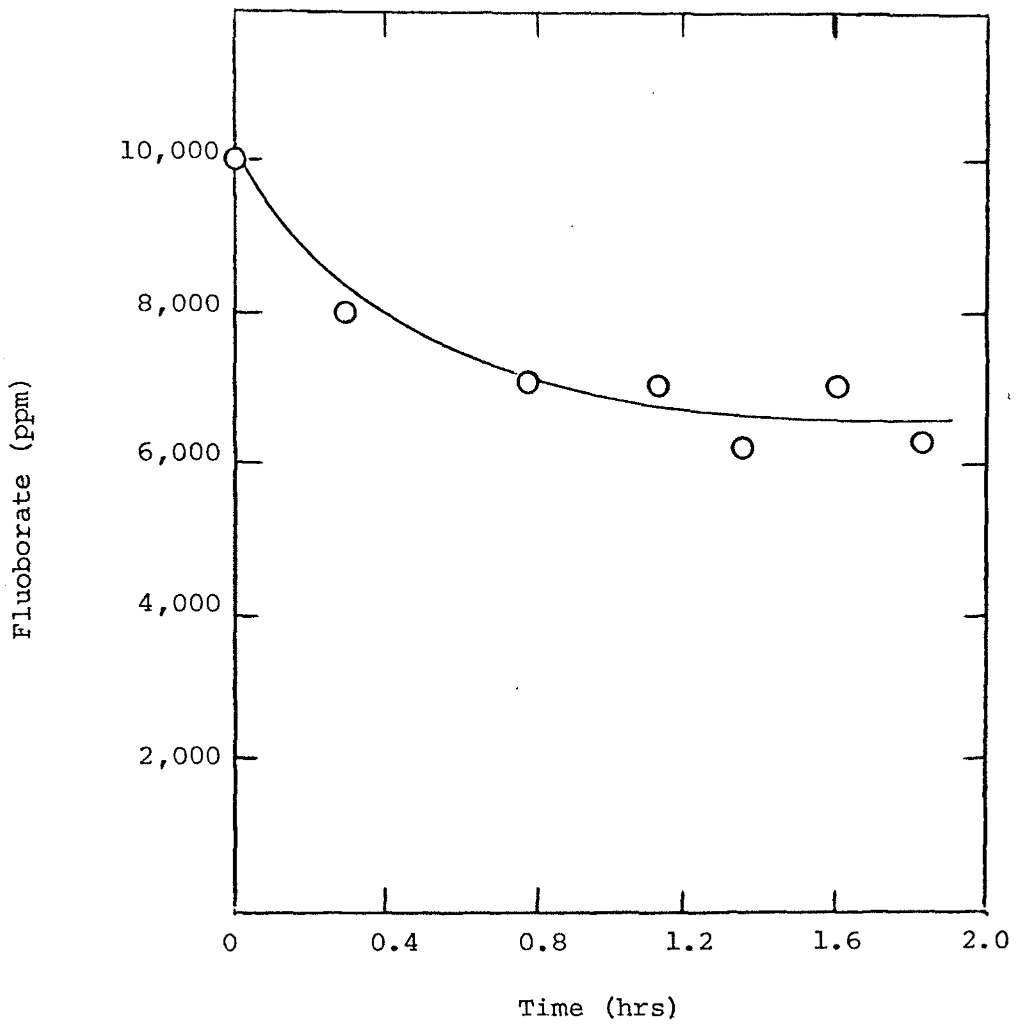

FIGURE 15, $[BF_4^-]$ IN FEED-ELECTRODIALYSIS OF SOLUTION G was performed with solution H. Solution H had a lower concentration (7,638 mg/l) and the experiment was run for 6 hours. A reduction of 90% in fluoborate concentration in the feed was achieved as illustrated in Figure 16. The concentrations of the product are plotted in Figure 17.

There is no definite rationale for the increased removal efficiency. However, it may be attributed to the lower concentration of the initial feed solution. To confirm this, solution F should have been run for 13 hours to see if the results correlated with the composite of the three runs using $Cu(BF_4)_2$.

Next, solution I was used as the feed solution. This was a solder fluoborate solution consisting of 60% stannous fluoborate and 40% lead fluoborate. Two cell pair were removed as they were worn and damaged due to the dismantling of the stack each time a different type of feed was going to be run.

Solution I was recycled through the electrodialysis stack for 6½ hours. The fluoborate concentrations of the feed and product are shown in Figures 18 and 19 respectively. A removal of 44% of BF_4^- in the feed solution was achieved.

Solution J, a stannous fluoborate solution was run

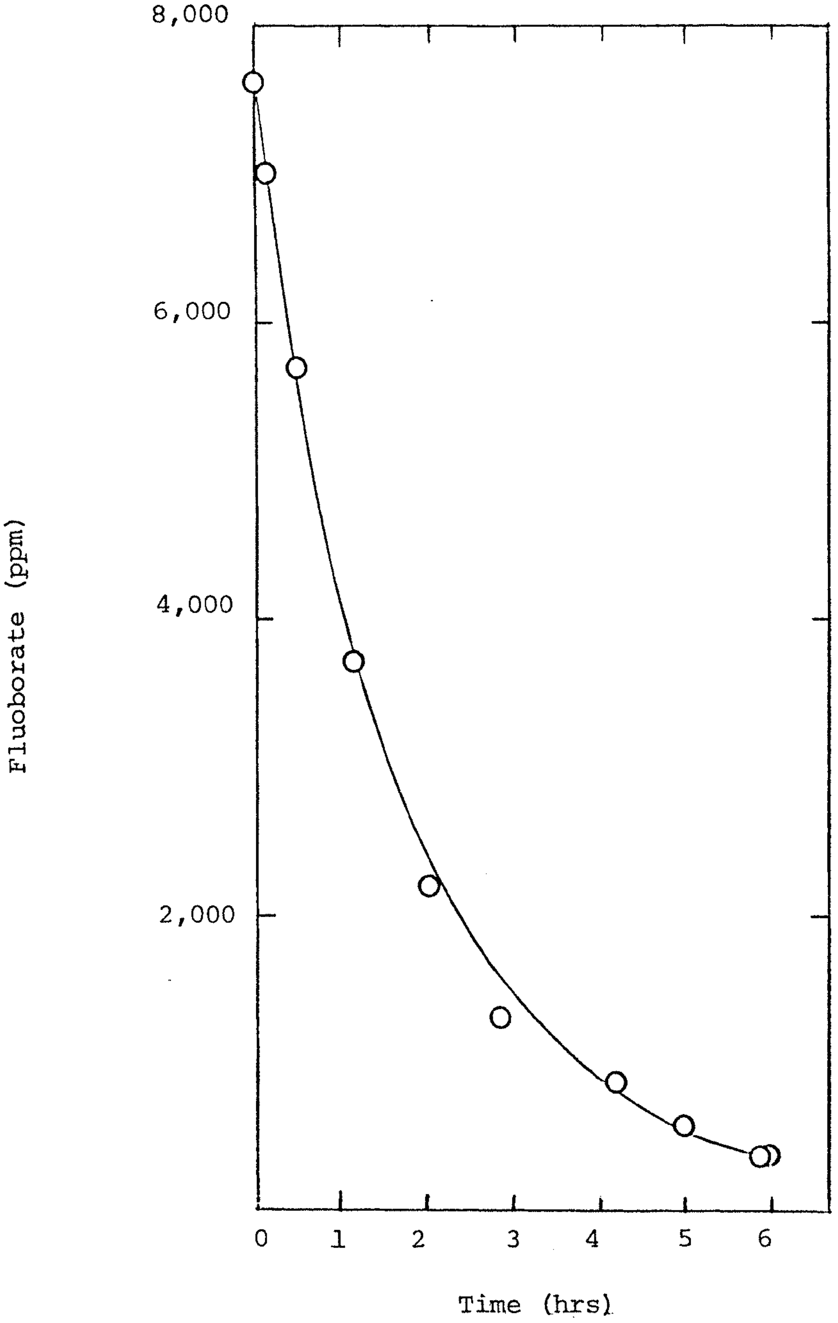

FIGURE 16, $[BF_4^-]$ IN FEED-ELECTRODIALYSIS OF SOLUTION H

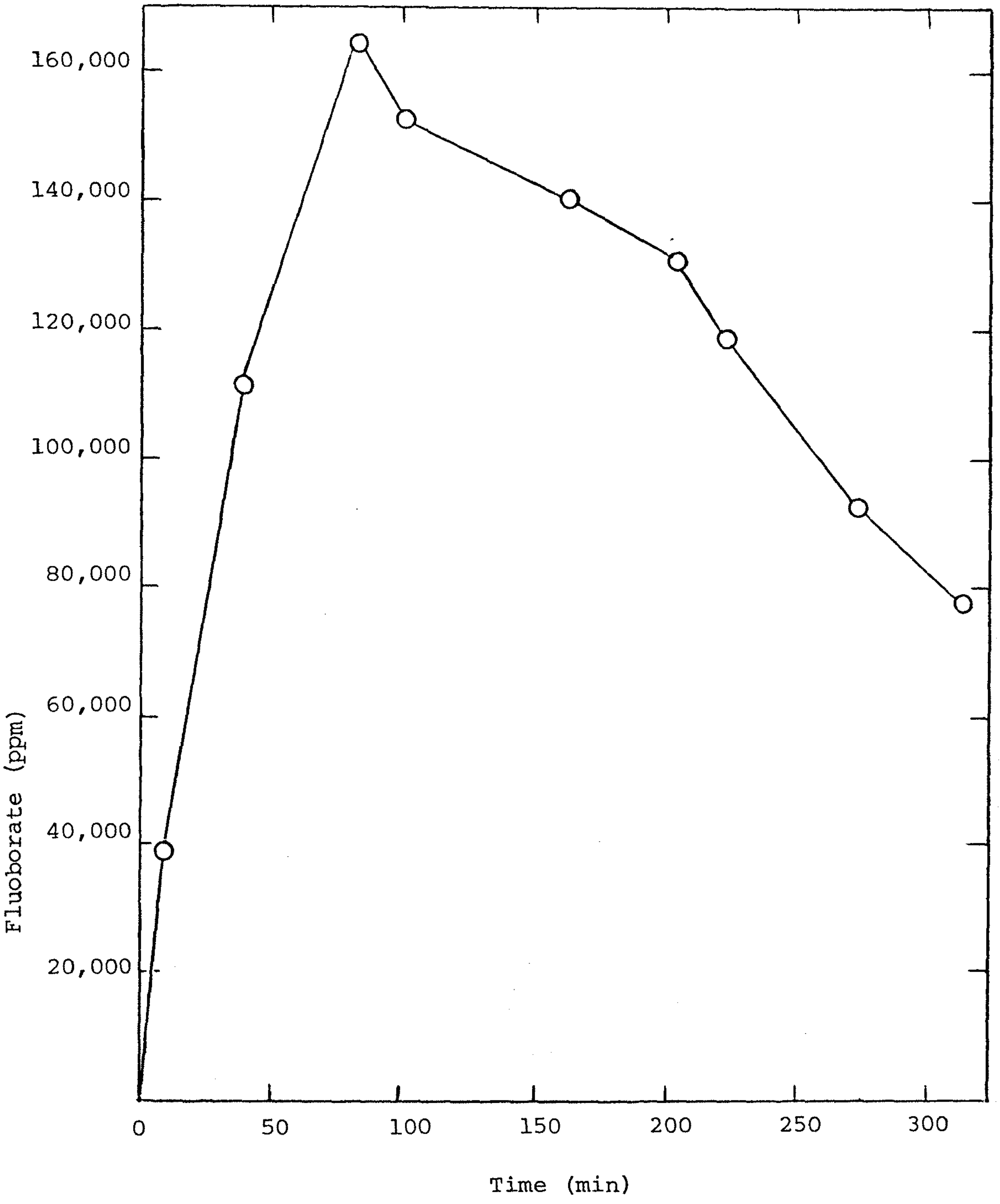

FIGURE 17, $[BF_4^-]$ IN PRODUCT-ELECTRODIALYSIS OF SOLUTION H

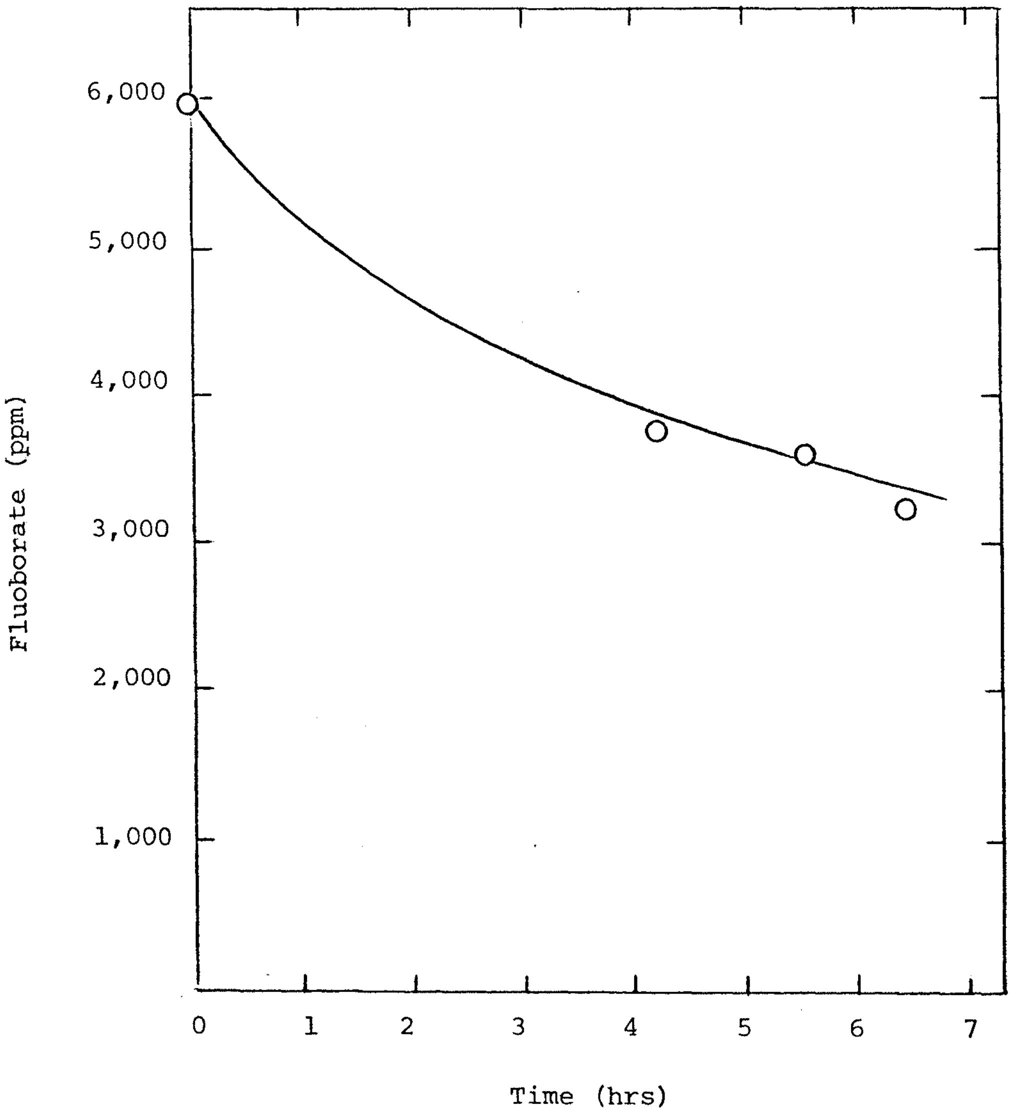

FIGURE 18, $[BF_4^-]$ IN FEED-ELECTRODIALYSIS OF SOLUTION I

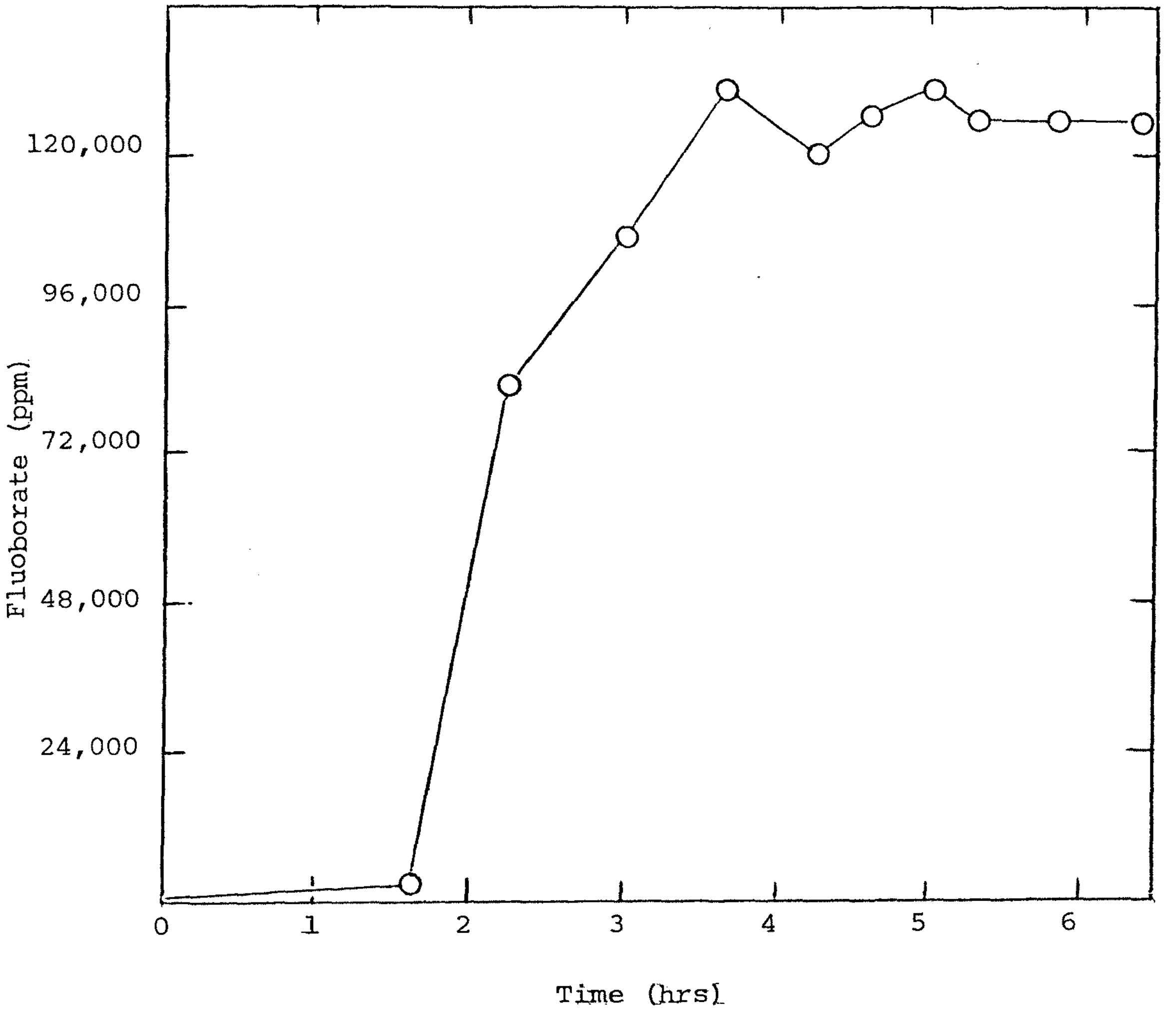

FIGURE 19, $[BF_4^-]$ IN PRODUCT-ELECTRODIALYSIS OF SOLUTION I through the stack. This solution also had minute quantities of a leveler and a brightener. The experiment was run for 10 hours, shut down and started up the following morning and run for an additional 5 hours. The feed concentrations are illustrated in graph form in Figure 20. The total removal for the 15 hour period was 44% which was definitely less than was expected. However at that low of a concentration, the conductivity was also low which may have led to this result. The concentration of the product samples for the first 4½ hours are shown in Figure 21. This graph shows, as do the majority of the plots of products, that the product reaches a peak concentration and then tappers off downwardly.

These results show that electrodialysis is indeed a viable way of removing and recovering plating solutions from rinse waters. However, much work is still needed to be done, such as the variation of electrolyte solutions and anode materials. Also, a single feed solution should be chosen and used for all experimentation to minimize the variables.

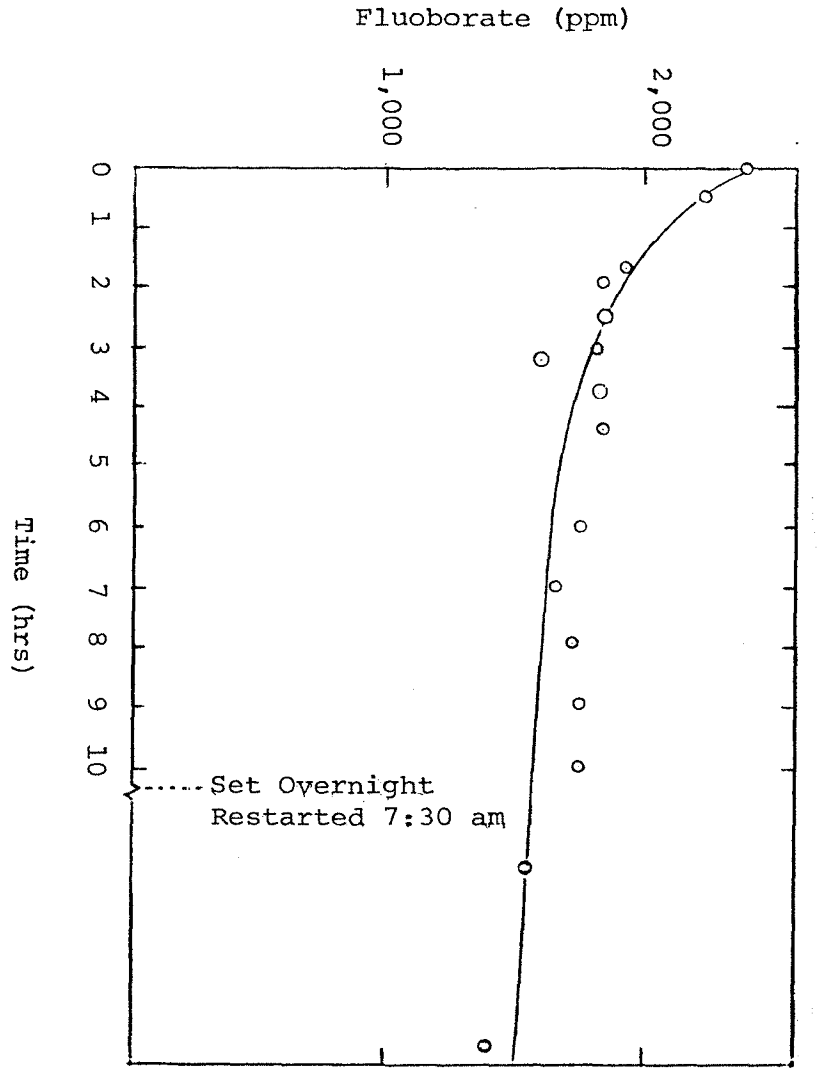

FIGURE 20, $[BF_4^-]$ IN FEED-ELECTRODIALYSIS OF SOLUTION J

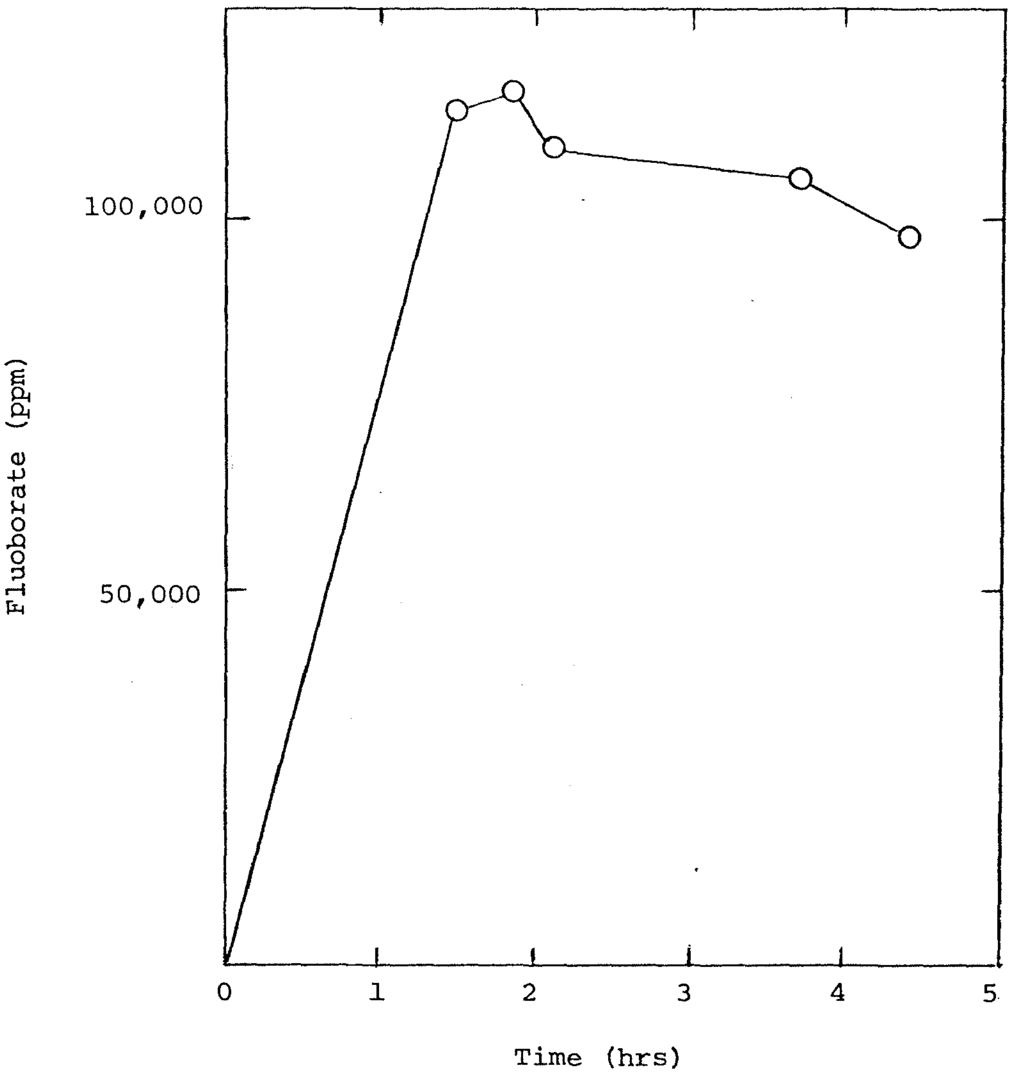

FIGURE 21, $\left[BF_4^-\right]$ IN PRODUCT-ELECTRODIALYSIS OF SOLUTION J

IV. CONCLUSIONS

Experimentation exhibits that ultrafiltration succeeds in removing the surfactant-fluoborate complex from solution. A 1,000 molecular weight cut-off membrane is adequate for this separation using the Millipore Cassette ultrafiltration apparatus. Therefore, due to the reasons cited in the results and discussion, ultrafiltration is a more efficient operation than ion floatation for this particular application.

Also, the results that were achieved using electrolysis in separating the surfactant-fluoborate adduct are encouraging. However, the solution which was electrolized (i.e. 1500 mg/l TA and 100 mg/l BF_4^-) was dilute. Further experimentation should be carried out utilizing a concentrated surfactant-fluoborate complexed solution (i.e. the retentate from the ultrafiltration process) to determine electrolysis' feasibility as an operation involved in recycling fluoborate rinse waters.

Experimental results obtained by utilizing electrodialysis on concentrated fluoborate plating rinse waters proved positive. Electrodialysis can be employed to recover plating solutions from rinse waters.

Although much experimental work must still be done with electrodialysis, it seems to be the most viable solution for recycling electroplating rinse waters containing fluoborate. It has advantages over the ultrafiltration and electrolysis processes. First of all, no additives (such as a surfactant) are necessary for electrodialysis to work. Also, electrodialysis can handle high concentrations of plating solution in the rinse waters.

This leads to the utilization of more efficient rinsing techniques and ultimately a marked savings in water usage. The most important aspect supporting electrodialysis is the fact that the products of the operation can be recycled. The concentrated product water can be recycled back into the plating bath and the diluted feed can be run through a clarifier to precipitate the metals and ultimately discharged, or directly discharged if acceptable dilution is achieved.

V. RECOMMENDATIONS

Evaluation of the utilization of ultrafiltration to remove the surfactant-fluoborate complex from solution was carried out adequately. Conclusive results proved that the ultrafiltration process removed the complex from solution. However, more experimentation will be necessary to determine the kinetics of the operations, which would be necessary for industrial scale-up.

Experimentation involving electrolysis showed that it is a feasible method for breaking the surfactant-fluoborate complex. During this experimentation a dilute solution of the complex was ued. In order to make sure that electrolysis can be coupled with ultrafiltration to recycle fluoborate rinse waters, additional experimentation must be carried out. In this experimentation, the solution which will be electrolyzed should be the actual retentate obtained from an ultrafiltration run.

In light of the positive results of the electrodialysis experiments, further work should be carried out in this area. Electrodialysis has advantages over an operation using ultrafiltration coupled with electrolysis to recycle fluoborate rinse waters. First off, electrodialysis uses no additives, such as the surfactant needed to complex the fluoborate in the other process. Also, a more concentrate rinse may be handled by electrodialysis. Therefore, more efficient rinsing techniques can be employed which will provide a substantial savings in water usage. More important, the products of electrodialysis can be directly recycled to the plating bath while the dilute feed can be reused as rinse water or ultimately run through a clarifier to precipitate the metals and discharged.

If electrodialysis is the direction that is taken for recycling fluoborate rinse waters, further experimentation should be carried out. In this experimentation, a single feed solution should be chosen so that the effects of varying other constituents can be readily seen. Among these other factors which should be evaluated are the electrolyte solution and the anode material.

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