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Coupled Transport Systems for Control of Heavy Metal Pollutants

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COUPLED TRANSPORT SYSTEMS FOR CONTROL OF HEAVY METAL POLLUTANTS

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

The study described in this report was undertaken to demonstrate the applicability of a new separation method to the recovery of metal values from plating rinse waters. The process is referred to as coupled transport. In this brief, four-month study, it was demonstrated that coupled transport membranes can be used to separate copper, nickel, and chromium from these rinse waters and to "chemically pump" these metal ions against very large concentration gradients. High recoveries of metal values can thereby be effected, producing recycle streams sufficiently concentrated for direct return to the plating bath. The economics of the process appear favorable relative to existing technology.

For further information on this subject, contact the Industrial Pollution Control Division, Metals and Inorganic Chemicals Branch.

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ABSTRACT

This report describes a process for separating and concentrating heavy metals from electroplating rinse waters. Metal ions can be "chemically pumped" across a coupled transport membrane against large concentration gradients by allowing the counterflow of a coupled ion such as hydrogen ion. The process is carried out within a microporous membrane containing within its pores an organic, water immiscible complexing agent. The complexing agent acts as a shuttle, picking up metal ions on one side of the membrane, carrying them across the membrane as a complex, and preserving electrical neutrality by carrying hydrogen ions in the opposite direction.

The importance of coupled transport is its high selectivity and flux. High selectivity derives from the use of specific complexing agents. High flux is possible because these are actually liquid membranes with diffusivities many times greater than those in solid membranes.

CONTENTS

Foreword iii
Abstract iv
Acknowledgement vi

1. Introduction and Summary 1
2. Principles of Coupled Transport Membranes 2
   - Co-transport 2
   - Counter Transport 4
   - Applicability of Coupled Transport Membranes to Plating Wastes 5
3. Experimental 7
   - Distribution Coefficients 7
   - Membranes and Permeability Apparatus 7
   - Analytical Methods 9
   - Reagents 9
4. Results 11
   - Distribution Coefficients 11
   - Demonstration of Coupled Transport 11
   - Effect of Diluents on Flux 15
   - Simulation of Actual Plating Rinse Conditions 15
     - General Considerations 15
     - Chromium 20
     - Copper and Nickel 22
5. Economics 29
6. Future Work 31

Appendices
A. Steady State Concentration Factors 32
B. Exponential Decay 34

ACKNOWLEDGMENT

Our work on coupled transport membranes began under a contract with the Bureau of Mines (Contract No. H0252066), in which we are examining the hydrometallurgical recovery of copper and other metals from low grade ores. Some of the data reported in Figures 4, 5, 6b, 7, and 9 of the present report were obtained in the course of that ongoing, parallel work.

SECTION I

INTRODUCTION AND SUMMARY

This is the final report on Phase I of American Electroplaters' Society Project No. 43, entitled "Coupled Transport Systems for Control of Heavy Metal Pollutants in Metal Finishing Solutions". It covers the period from October 22, 1976 - January 21, 1977.

The goal of this program is to demonstrate the applicability of coupled transport membranes to the processing of electroplating rinse waters. These waters are a serious pollution problem. However, they also have an intrinsic value in the metals they contain. Recovering these metal values and recycling the rinse water has been a long standing challenge. Of considerable promise in this regard is a new membrane process that we refer to as coupled transport membrane processing.

In the next section, the principles of coupled transport membranes are described. The bulk of this report is concerned with an experimental study of these membranes and their application to plating wastes. Initially, some range-finding studies were performed to find membranes and conditions that would be suitable for processing dilute solutions of chromium, copper, and nickel. The dependence of the transmembrane flux of these metal ions on such conditions as pH and concentration was measured in laboratory permeation cells. We then carried out a series of experiments in which the conditions that would exist in a counter-current coupled transport concentrator were simulated. These results were used to carry out an economic analysis of the process for chrome-plating rinse waters. The results showed that the capital costs of such a coupled transport unit would be substantially lower than the annual savings realized in chromium recovery. Favorable economics are also predicted for copper plating rinse waters. Less favorable were the projected economics with nickel wastes because of the lower nickel fluxes observed to date.

SECTION II

PRINCIPLES OF COUPLED TRANSPORT MEMBRANES

In a coupled transport membrane, the flow of the permeant of interest is coupled to the flow of some second species. Under the right conditions, the flow of this second species can force the permeant of interest to flow against its own concentration gradient thereby, for example, separating this species from other species and concentrating it as well. These membranes can thus be considered a kind of selective chemical pump.

More specifically, the coupled transport membranes being developed at Bend Research consist of a suitable liquid complexing agent constrained by capillary forces to the pores of a microporous membrane. Thus, these are essentially liquid membranes. The complexing agent is specific for the permeant of interest under certain conditions. The desired permeant is complexed at one interface between the membrane and an external solution. The complex diffuses across the liquid membrane to the downstream interface where the reaction is reversed because of some appropriate change in conditions. The free complexing agent then diffuses back across the membrane where it picks up more of the desired permeant. The complexing agent thus acts as a shuttle, carrying both the desired permeant and some second, coupled species across the membrane.

In the work described here, the coupled species is the hydrogen ion. This ion can either cross the membrane in the same direction as the metal ion of interest (a case we refer to as "co-transport") or opposite to the metal ion (referred to as "counter-transport"). Because of the requirement to maintain electroneutrality across the membrane, the hydrogen ion must move in the same direction as the metal ion if the metal is present in anionic form, e.g. chromium as the chromate ion. On the other hand, with free metal ions such as copper and nickel in solution, the flow of hydrogen ions must be counter to the flow of metal ion. These two cases are discussed below.

CO-TRANSPORT

Consider the case in which a coupled transport membrane separates a dilute aqueous solution of chromic acid at low pH from a less acidic solution of sodium chromate. The membrane contains a complexing agent for the chromate, R, which could be a water immiscible tertiary amine, for example. These conditions are depicted schematically in Figure 1a. At the left-hand membrane-solution interface, the chromate will partition into the amine phase in the membrane where one molecule of chromate complexes with two molecules of chromate, forming the neutral complex $(RH)_2CrO_4$. This complex is soluble only in the amine phase. The complex will diffuse down its concentration gradient to the opposite or downstream interface. There, because of the higher pH, the complex dissociates, freeing the chromate to

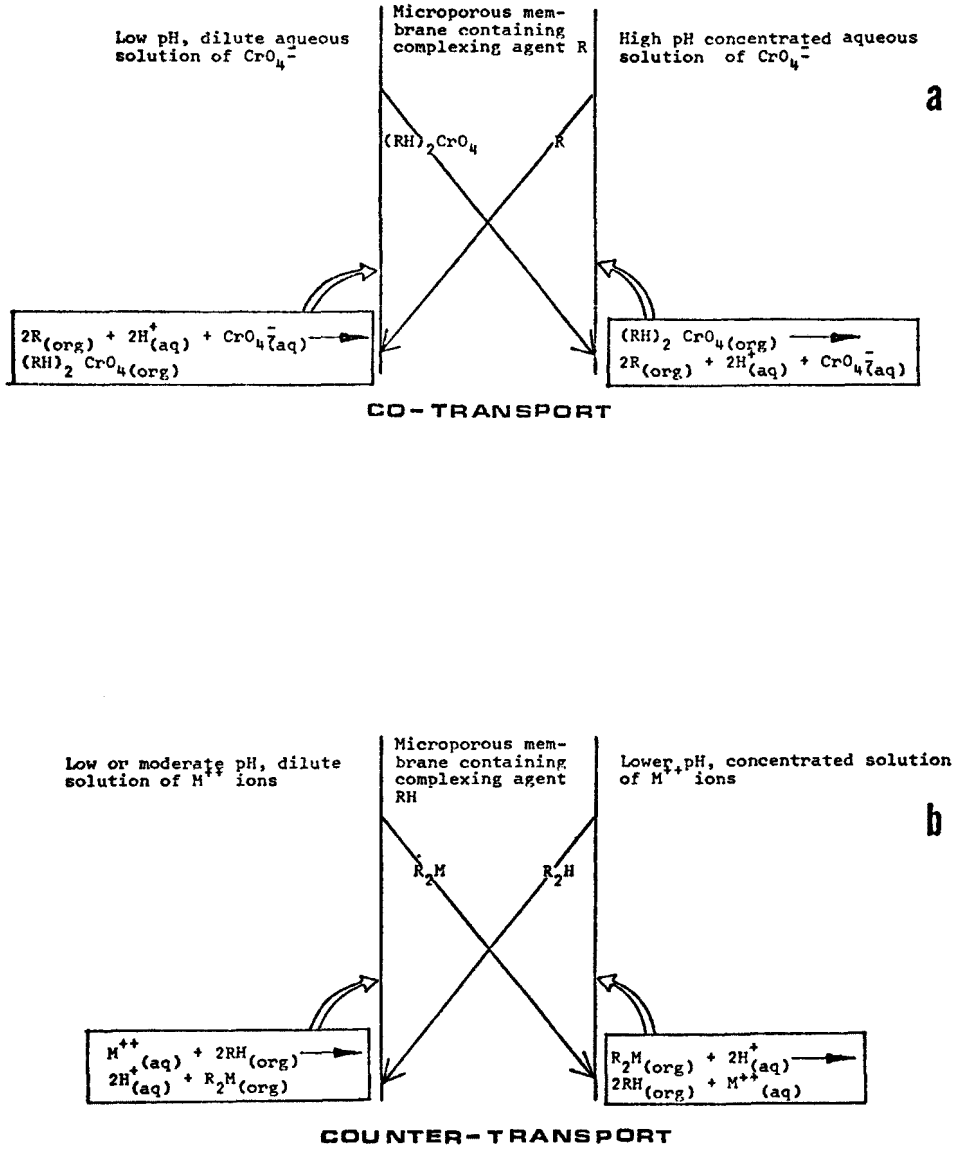


Figure 1. Schematic representation of co-transport (a), and counter-transport (b).

the aqueous phase and regenerating the neutral amine, R. The amine then diffuses down its own concentration gradient toward the left-hand interface (or "feed" side of the membrane) where it combines with more chromate and the cycle is repeated. The equilibrium existing across the aqueous-organic phase boundaries is this:

$$2R(org) + 2H^{+}(aq) + CrO_4^{=}(org) \rightleftharpoons (RH)_2CrO_4(org) \ . \qquad (1)$$

At the feed interface, the hydrogen ion concentration is high and the reaction is forced to the right. At the downstream interface, the reaction is shifted to the left because of the higher pH. Thus, the amine is a carrier. Hydrogen and chromate ions permeate the membrane in the same direction, from left to right in Figure 1a. Note that an increase in H^+ concentration on the left-hand side of the membrane or, equivalently, a decrease in H^+ concentration on the right-hand side will favor the left-to-right flux of chromate. (The situation is not quite this simple because of the equilibrium that exists in solution between $CrO_4^{=}$ and $Cr_2O_7^{=}$, but the essential result is the same).

With a suitable pH gradient, chromate can be "chemically pumped" against its own substantial concentration gradient. It can be shown in fact (see Appendix A) that in the co-transport case the steady state concentration ratio of the divalent chromium anion across the membrane depends on the hydrogen ion concentration ratio in the following way:

$$\frac{\left[CrO_4^{=}\right]_o}{\left[CrO_4^{=}\right]_\ell} = \left(\frac{\left[H^+\right]_\ell}{\left[H^+\right]_o}\right)^2 , \qquad (2)$$

where the subscripts o and ℓ refer to the feed and downstream solutions, respectively (i.e. the left-hand and right-hand solutions in Figure 1a). Thus, a pH difference across the membrane of two units should produce a chromate ion concentration ratio of 10,000, with the less acidic solution being more concentrated in chromium. The chromate ion will diffuse from the dilute solution into the concentrated solution until the condition indicated in equation (2) is satisfied.

COUNTER TRANSPORT

Consider next the situation depicted in Figure 1b. Here, the metal ions exist as cations and because we are interested in copper and nickel, we have shown them as divalent. The complexing agent in the membrane in this case could be an oxime, for example, denoted in the Figure as RH. Again, two moles of oxime will react with one mole of the metal ion, and the equilibrium existing at the membrane-solution interfaces is:

$$M^{++}(aq) + 2RH(org) \rightleftharpoons 2H^{+}(aq) + R_2M(org) \ . \qquad (3)$$

The metal-oxime complex is again soluble only in the organic phase. At the left-hand interface, the equilibrium is shifted to the right, because of the

low concentration of H^+ ions, and the metal-oxime complex partitions into the liquid membrane. The reverse reaction occurs at the downstream or right-hand interface. Thus, metal ions are again chemically pumped from left to right in the figure while hydrogen ions flow the other way.

It can be shown (see Appendix A) that the steady state ratio of divalent metal ion concentrations across the membrane is given by:

$$\frac{\left[M^{++}\right]_o}{\left[M^{++}\right]_\ell} = \left(\frac{\left[H^+\right]_o}{\left[H^+\right]_\ell}\right)^2 \tag{4}$$

The metal ions can again be pumped against a substantial concentration gradient but in this case the concentrated metal ion solution will be at the lower pH.

While we have not attempted to derive it here, it can also be shown that the same pH conditions that favor high concentration factors across the membrane also favor high metal ion flux across the membrane. Thus, in the co-transport case, metal ion flux will be enhanced by increasing the hydrogen ion concentration gradient in the same direction. In the counter-transport case, metal ion flux is enhanced when the hydrogen ion concentration gradient is increased in the opposite direction.

APPLICABILITY OF COUPLED TRANSPORT MEMBRANES TO PLATING WASTES

Coupled transport membranes could be assembled into a concentrator. The way in which such a concentrator would be applied to the treatment of plating wastes is illustrated in Figure 2. The rinse water containing metal ions would be fed to one side of the membrane concentrator. The metal ions would be transported across the membrane by the coupled transport process. Under favorable conditions, the metal could be concentrated in the unit to produce a solution of sufficient concentration to feed back to the plating bath, while the rinse water, almost totally stripped of its metal values, would be returned to the rinse bath. Alternately, a partially depleted rinse water could be discharged.

Under favorable conditions, then, the plating and rinse operation could be run closed-loop. No metal is wasted and no make-up water is required for the rinse bath.

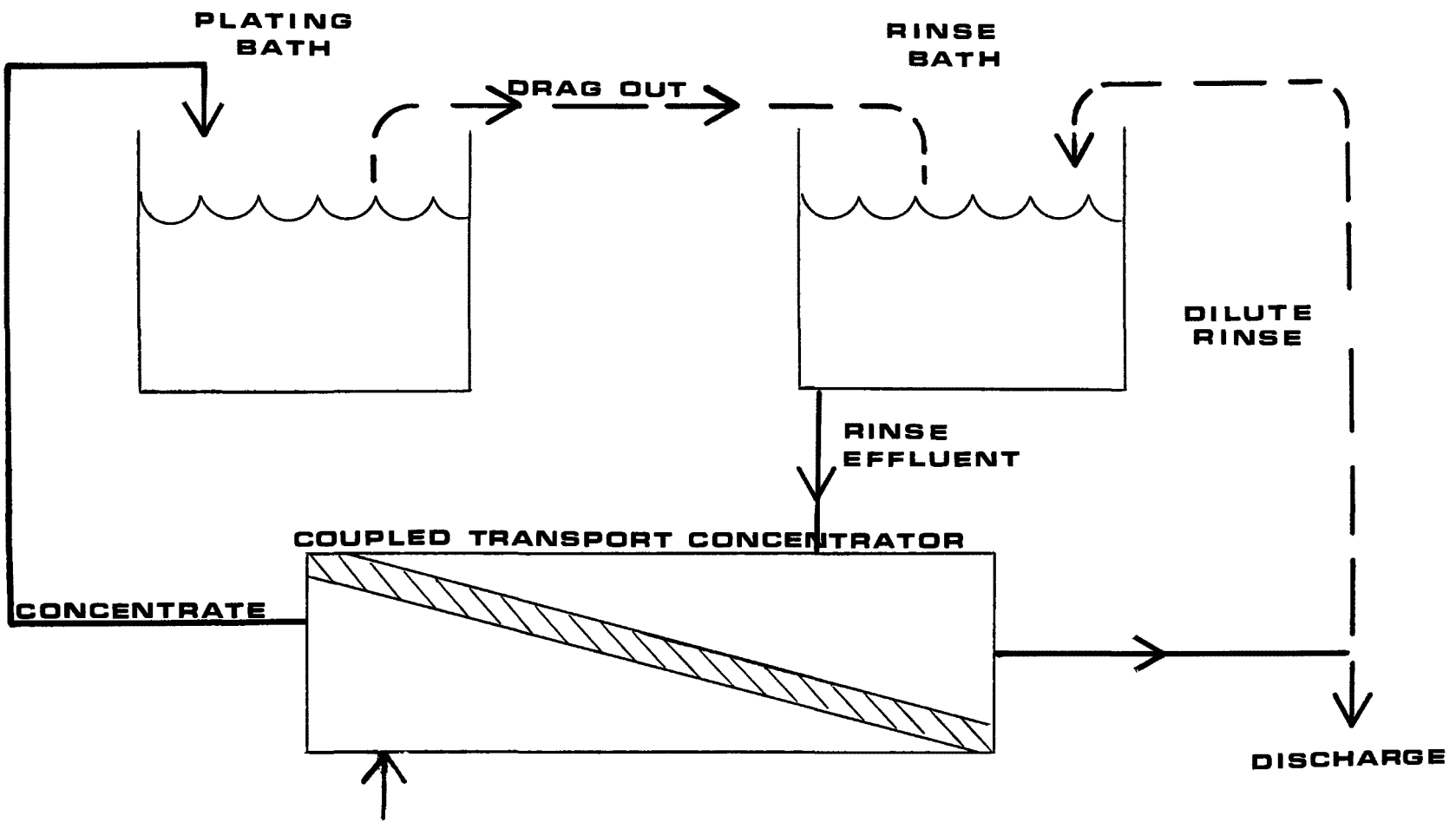


Figure 2. Simple schematic of coupled-transport concentrator as applied to plating rinse water effluent.

SECTION III

EXPERIMENTAL

Two sorts of experiments were performed in this reporting period. In the first of these, we examined suitable complexing agents for chromium, copper, and nickel. This search was performed by measuring distribution coefficients of the metal ions between organic liquids (known to complex these ions) and aqueous solutions at known pH. An ideal complexing agent is one that is highly water immiscible and which forms a very stable complex at a given pH. The complex should also be highly soluble in the complexing agent but insoluble in water. Finally, the complex should be unstable at some higher or lower pH. Having identified suitable complexing agents, we then prepared liquid membranes from them and carried out a number of permeation experiments to measure the metal ion flux across the membrane and its dependence on pH and other conditions.

The second type of experiment was designed to simulate the conditions that would exist in an actual coupled transport membrane concentrator. The purpose of these experiments was to obtain data representative of what might be achieved in practice so that an economic assessment of the process could be made.

DISTRIBUTION COEFFICIENTS

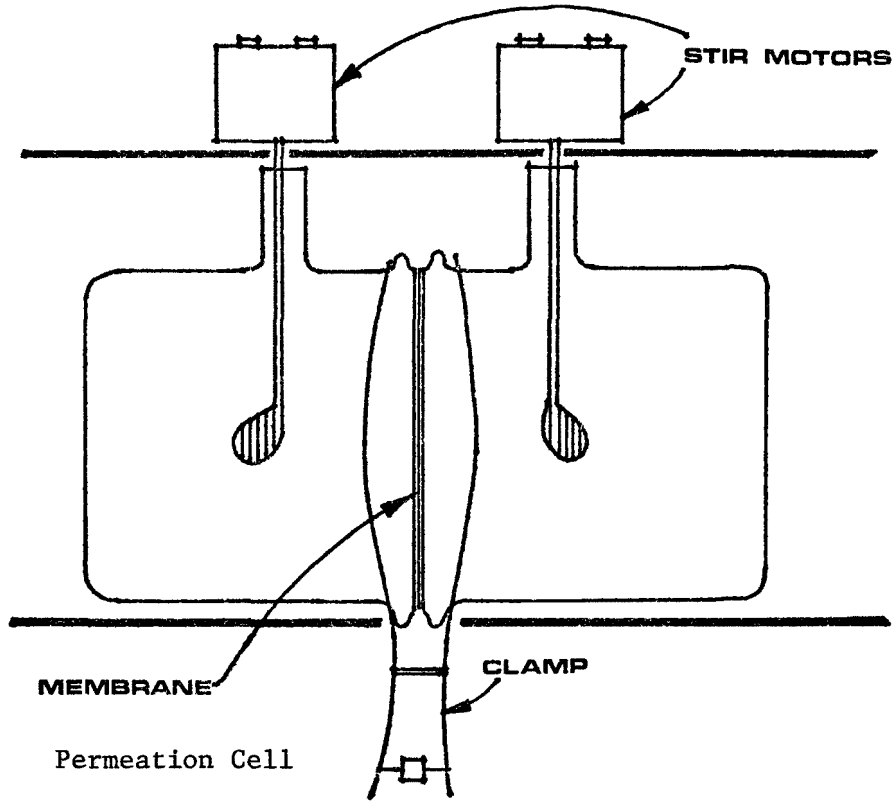
These were obtained simply by shaking the complexing agent for two minutes with an aqueous solution of the metal ion at a known pH in a separatory funnel at room temperature. After allowing the phases to separate, a sample of the aqueous solution was removed and analysed for metal ion. The concentration in the organic phase was then obtained from the known volumes and mass balance considerations. Acid or base was then added to the aqueous phase and the process was repeated at a new pH.

MEMBRANES AND PERMEABILITY APPARATUS

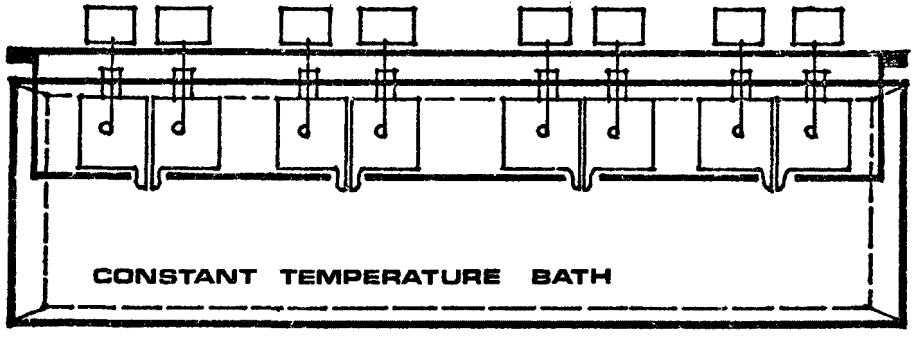
Coupled transport membranes were prepared by simply immersing a microporous membrane in the liquid complexing agent of interest. The liquid was rapidly sorbed into the pores by capillary action. For our initial studies, we chose Celanese Celgard® 2400 as the microporous membrane. It is made of polypropylene and is highly resistant to acids.

Permeation experiments were carried out in standard two-compartment glass cells shown in Figure 3. The membrane was mounted without a gasket between the half cells, held together by a standard ball-joint clamp. The volume of each half cell was 100 cm^3, and the membrane area was 20 cm^2. The

cells were supplied with stirrers to avoid concentration polarization effects. The cells were mounted in a constant temperature bath. All permeation measurements were performed at 30 ± 1°C.



Permeation Cell



Permeation Cells in Water Bath

Figure 3. Permeability apparatus for testing coupled transport membranes.

The pH and metal ion concentration were periodically determined in the course of a run by removing small samples from the cell, through sampling ports not shown in the figure, and replacing with fresh solution at the same pH. Metal ion fluxes were obtained from the concentration-vs.-time data after correcting for sampling.

ANALYTICAL METHODS

Chromate concentrations have been measured spectrophotometrically at 350 nm. The pH of the samples was first raised to 12 to insure that the dichromate ion would not interfere.

Copper and nickel analyses have been made with a Perkin-Elmer model 290 atomic absorption spectrophotometer. With this instrument, both copper and nickel can be measured in aqueous and organic solutions at concentrations as low as 15 ppm with a precision of ± 2%.

REAGENTS

The complexing agents studied were Alamine 336, a tertiary amine from General Mills; LIX 63, LIX 64N, and LIX 70, all oximes from General Mills; and Kelex 100, a substituted quinoline from Ashland Chemical. All of these are common industrial liquid ion exchangers. Their chemical structures are presented in Table I.

In many permeation experiments, these complexing agents were diluted with a compatible, inert carrier, principally to reduce their viscosity. The diluents used were Solvesso from Exxon and kerosene. In some cases, a small amount (2 vol%) of isohexadecyl alcohol from American Hoechst was also added to the diluted complexing agents in order to prevent the formation of a separate phase.(1) Apparently, this agent promotes the solubility of the metal ion complex in the organic complexing agent.

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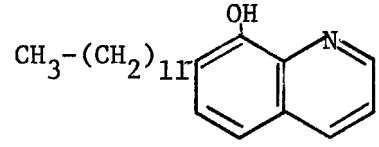
(1) C.J. Lewis, "Liquid Ion Exchange in Hydrometallurgy", in Recent Developments in Separation Science Vol. II, N. N. Li (Ed.), CRC Press, Cleveland, Ohio 1972.

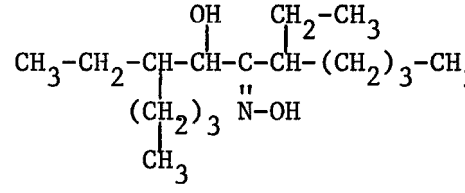
Table I

COMPLEXING AGENTS FOR COPPER, NICKEL, AND CHROMIUM

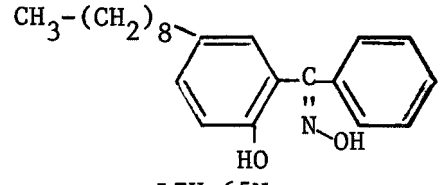
Kelex 100
(Ashland Chemical)



LIX 63
(General Mills)

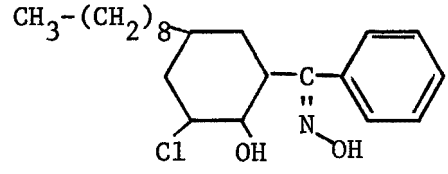


LIX 64N, a mixture of 10% LIX 63 and 90% LIX 65N
(General Mills)



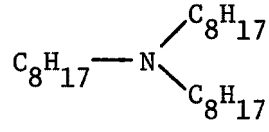
LIX 65N

LIX 70
(General Mills)



+ LIX 63

Alamine 336
(General Mills)



SECTION IV

RESULTS

DISTRIBUTION COEFFICIENTS

The distribution coefficient is defined here as:

$$K = \frac{\text{Concentration of metal in the organic phase}}{\text{Concentration of metal in the aqueous phase}} .$$

Distribution coefficients for copper with several complexing agents are presented in Figure 4 as a function of the pH of the aqueous phase. The complexing agents were diluted to a 10 vol% solution in kerosene in all cases.

Similar data for nickel are presented in Figure 5. Note the hysteresis effect. The data connected by the upward-pointing arrows were taken while nickel was being loaded into the organic phase, i.e. on increasing pH, while the downward-pointing arrows connect data taken while nickel was being stripped from the organic phase. The hysteresis effect was reflected in the permeation experiments as well, as is discussed below.

DEMONSTRATION OF COUPLED TRANSPORT

The results of a coupled transport experiment with CrO_3 are presented in Figure 6a. The complexing agent was Alamine 336 diluted to 40 vol% with Solvesso. The feed side of the permeation cell initially contained 50 ppm CrO_3 while the downstream side was buffered at either pH 7 or 11, and it initially contained no CrO_3. Clearly, chromium was transported in the direction of decreasing hydrogen ion concentration. Because the two cell compartments are of equal volume, we can see that beyond the point where the downstream concentration reached 25 ppm, the chromium was diffusing uphill. The flux was higher at the higher downstream pH as is predicted from the analysis presented in Part II. Almost complete removal of chromium from the feed solution was observed in the course of the experiment when the downstream pH was 11, and it is predictable that the same effect would have occurred at a downstream pH of 7 at some longer time.

Coupled transport of copper was demonstrated using a 10% solution of Kelex 100 in kerosene as the liquid membrane. The results are presented in Figure 6b. The initial feed solution contained either 0 or 100 ppm copper at pH 2.5, while the downstream solution was initially at pH 1.0 with either 3.0 or 9.3 wt% copper, the latter being an essentially saturated solution of copper sulfate. In Figure 6b, the feed concentration is plotted against time. In all cases, the copper was transported counter to

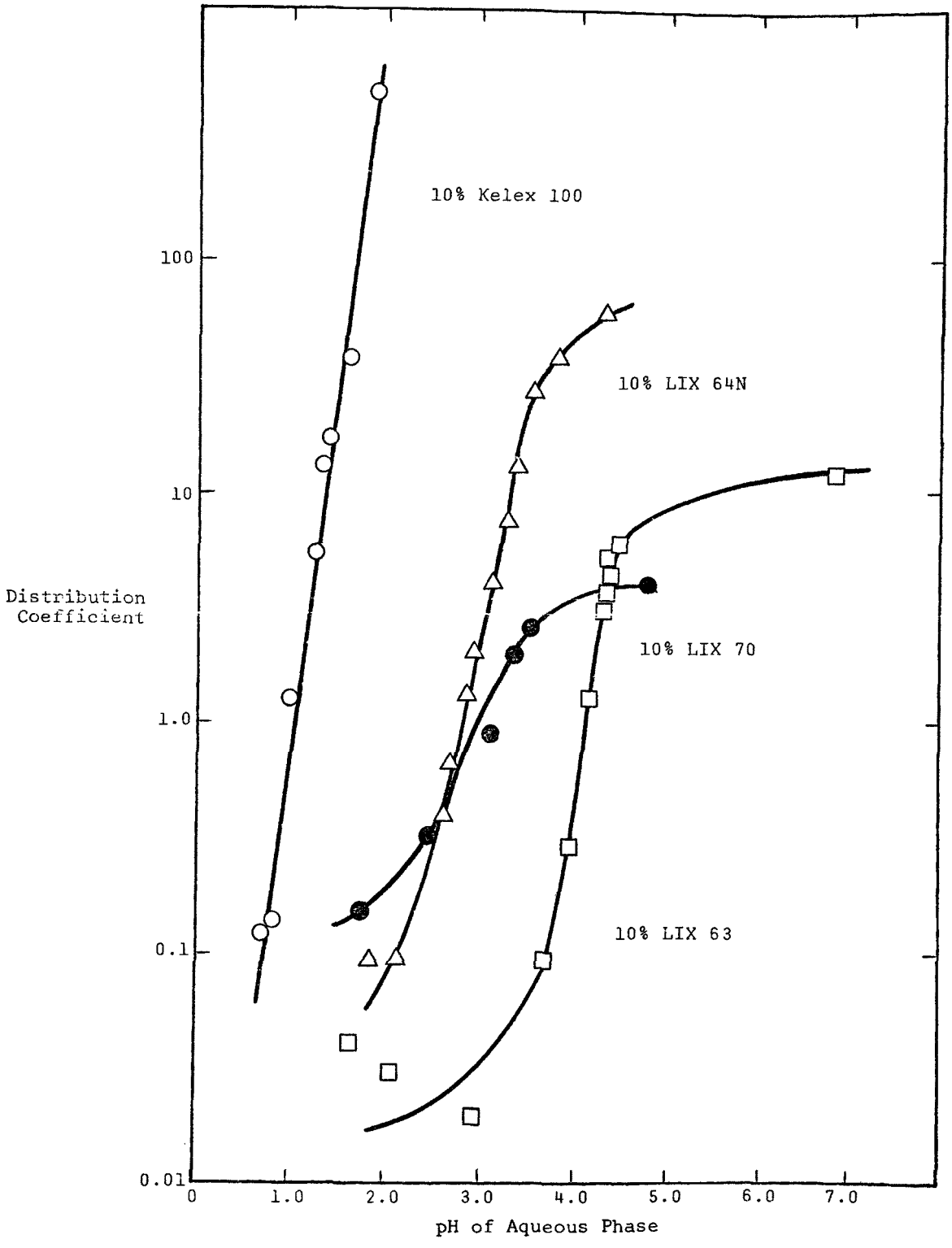


Figure 4. Distribution coefficients of Cu^{++} vs. pH for several liquid ion exchangers dissolved in kerosene.

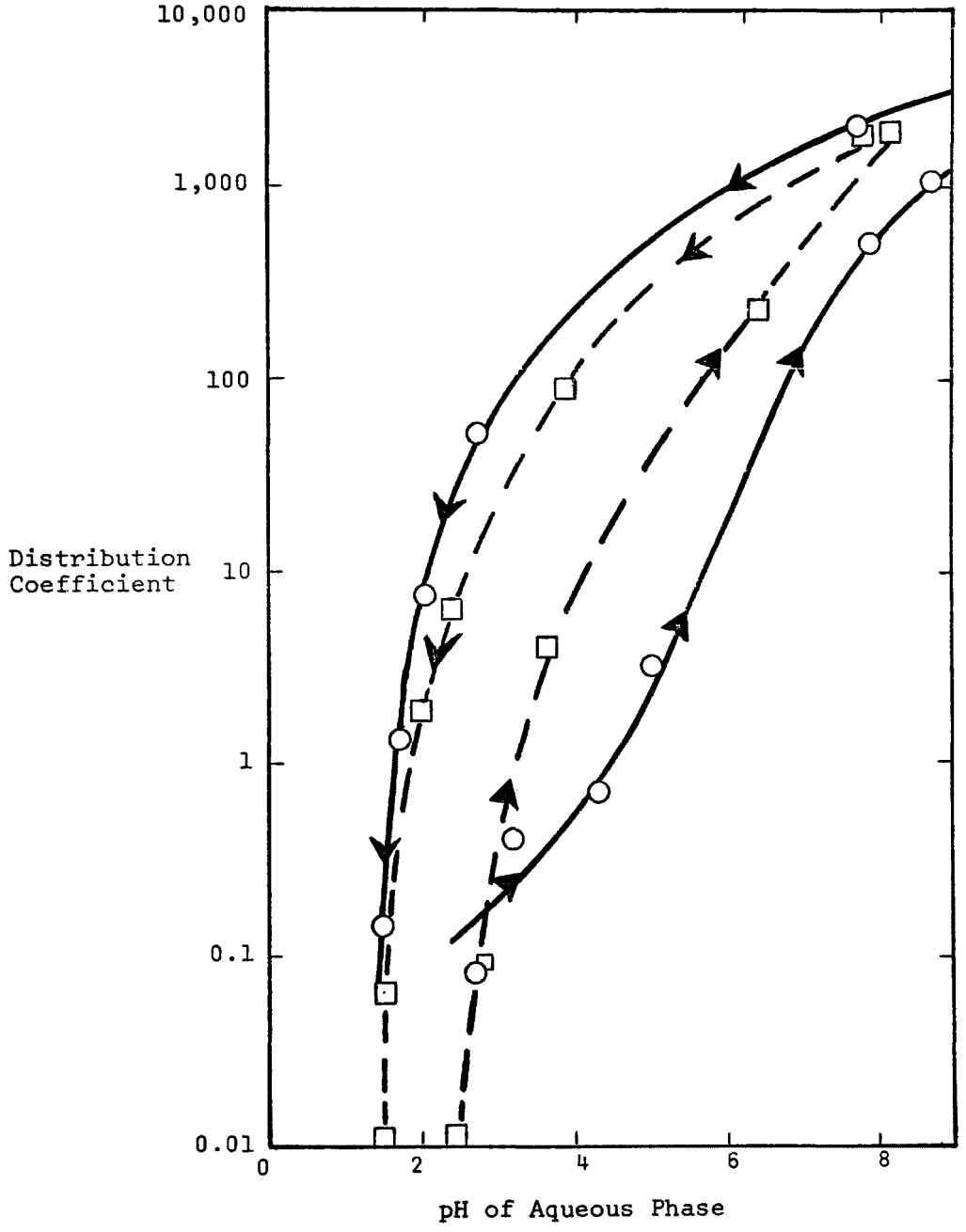


Figure 5. Distribution coefficients for nickel vs. pH in 10% LIX 64N in kerosene (—) and 10% Kelex 100 in kerosene (---).

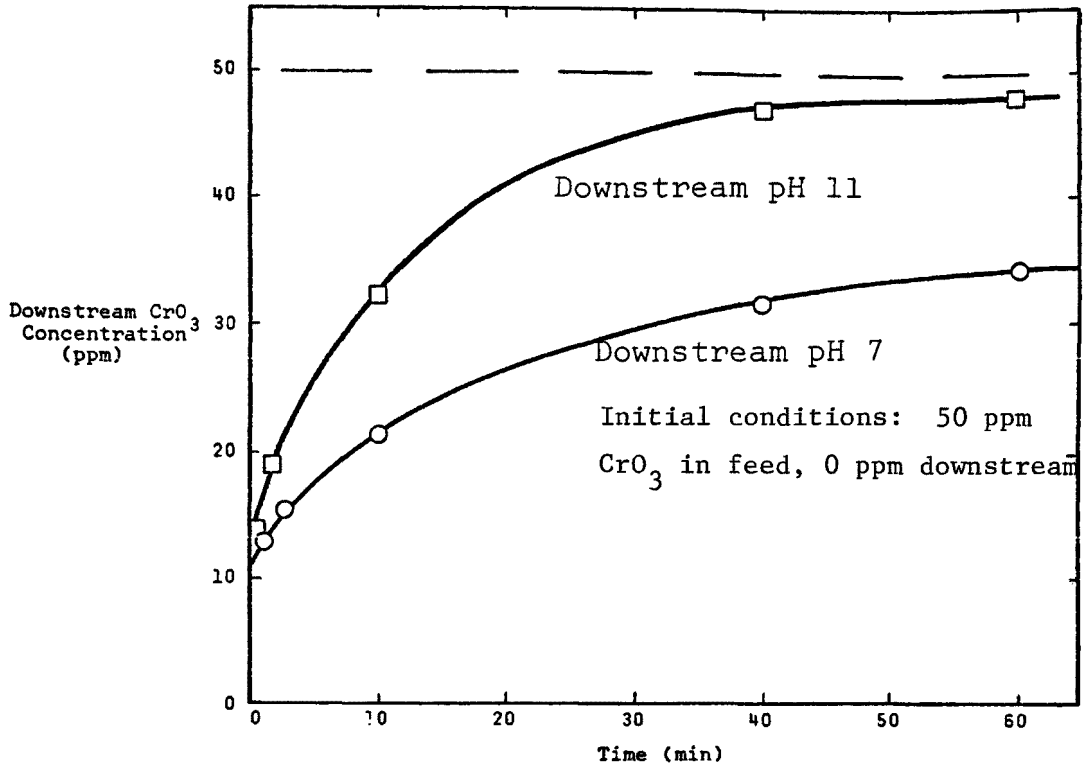


Figure 6a. Downstream chromate concentration vs. time.

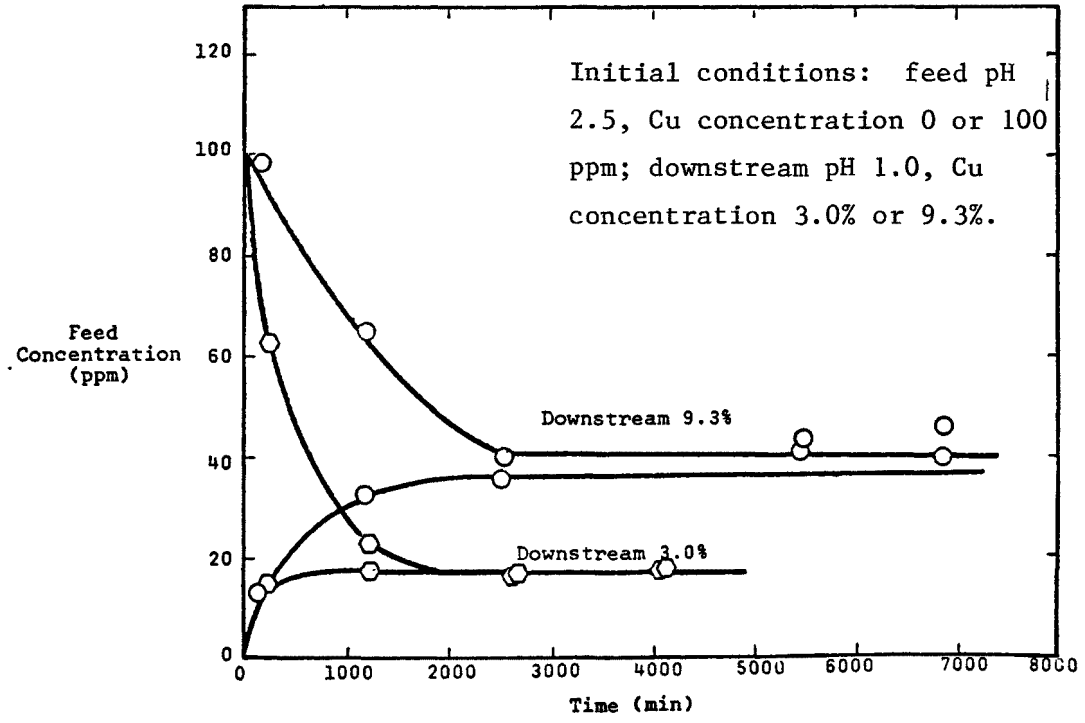


Figure 6b. Concentration of copper in the feed vs. time.

the hydrogen ion concentration gradient. In these experiments, the steady state concentration factor was attained from both directions, i.e. both the 0 ppm and the 100 ppm copper feed solutions reached a final concentration of about 20 ppm when the downstream compartment was 3.0 wt% Cu. The steady state copper concentration factors were in the range 1500-2000 in these two cases.

A series of steady state concentration factors for copper were measured as a function of the pH difference across the membrane. The results are presented in Figure 7. Note that at a pH difference of less than 2 units, copper was concentrated against its own concentration gradient by about 4000-fold. In fact, the slope of the line in this essentially log-log plot is 2, which is just the value predicted by equation (4).

EFFECT OF DILUENTS ON FLUX

The diluent added to the complexing agent can be expected to have two effects on the flux of metal ions across coupled transport membranes. First, because the diluent displaces some of the complexing agent, less of the metal ion complex will be formed, and we could expect a lower metal flux as a result. Opposing this effect, however, is the fact that the diluents are lower molecular weight compounds and hence are much more fluid at room temperature than the complexing agents. The reduced viscosity of the liquid membrane in the presence of diluent should enhance the diffusivity of the metal ion complex (according to the Stokes-Einstein equation) and hence increase the flux. These two effects thus run counter to one another.

The effect of the concentration of complexing agent in the diluent on the flux of metal was measured. Typical results for chromium are presented in Figure 8. The complexing agent was Alamine 336 and the diluent was Solvesso. The feed solution contained 5000 ppm chromic acid, while the downstream solution was maintained essentially free of chromium and at pH 7 throughout the experiment. A maximum occurred in the flux at about 40% Alamine, apparently the result of the opposing effects described above. Because of this maximum, we carried out our further chromium experiments at this concentration of complexing agent.

Similar data are plotted in Figures 9 and 10 for copper and nickel, respectively. The liquid membrane used in the copper experiments was Kelex 100 diluted with kerosene; for the nickel experiments, the Kelex was diluted with Solvesso. Flux maxima occurred in both cases, and we again carried out our further experiments at the complexing agent concentrations at which the maxima occurred.

It is noteworthy that the maximum flux in the chromium experiments was 3-4 times the maximum observed with either copper or nickel.

SIMULATION OF ACTUAL PLATING RINSE CONDITIONS

General Considerations. In Figure 2 we indicated in a general way how a coupled transport membrane concentrator might be applied to the treatment of plating rinse waters. An ideal system would be one that could be run closed-loop, i.e. with no discharge of metal ions and with complete

recycle of the purified rinse water. This ideal situation will generally not prevail in a coupled transport membrane concentrator, because there is always a flow of coupled ion across the membrane along with the flow of metal. In co-transport, the co-permeating species (or another ion used to

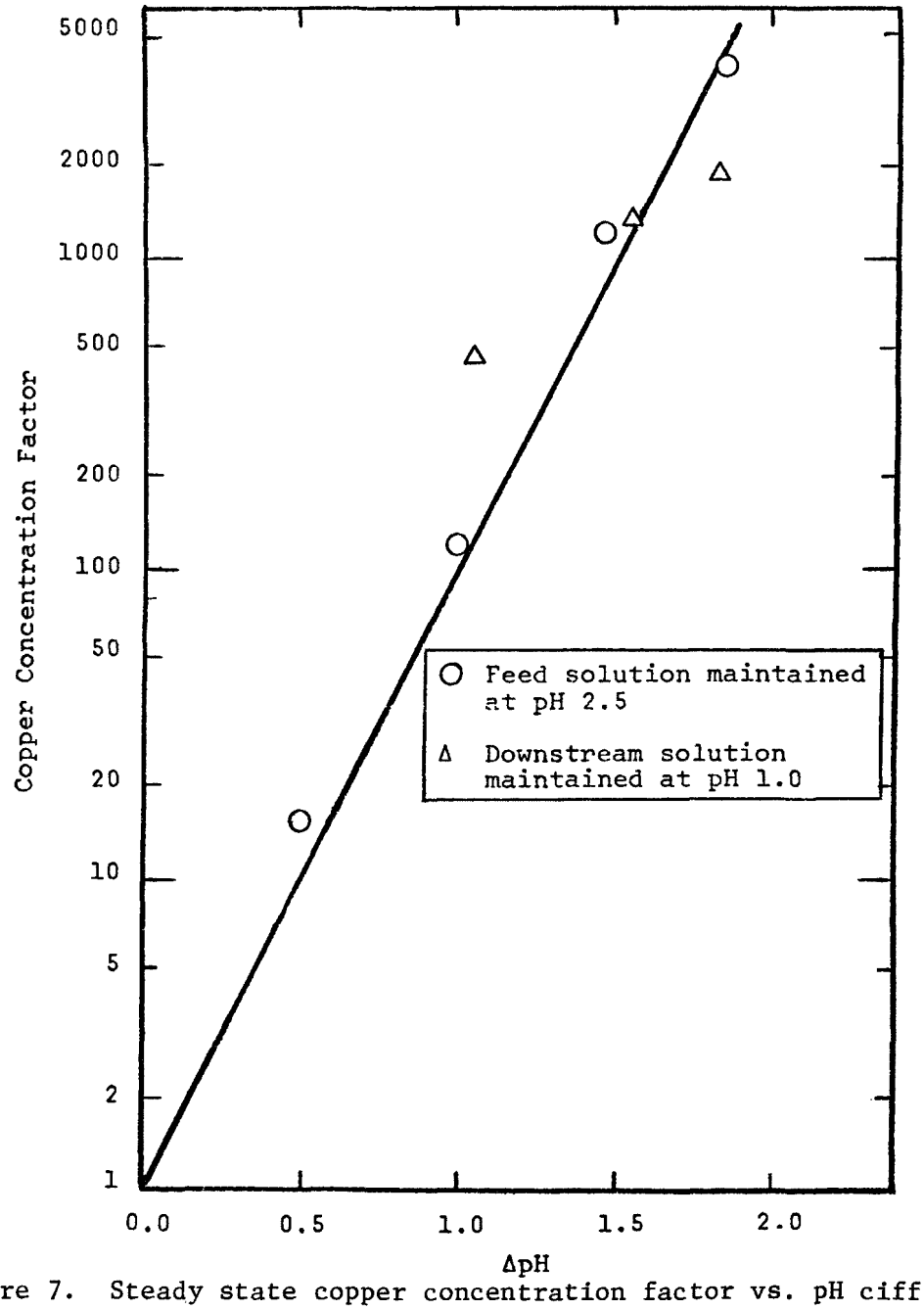


Figure 7. Steady state copper concentration factor vs. pH cifference across the membrane.

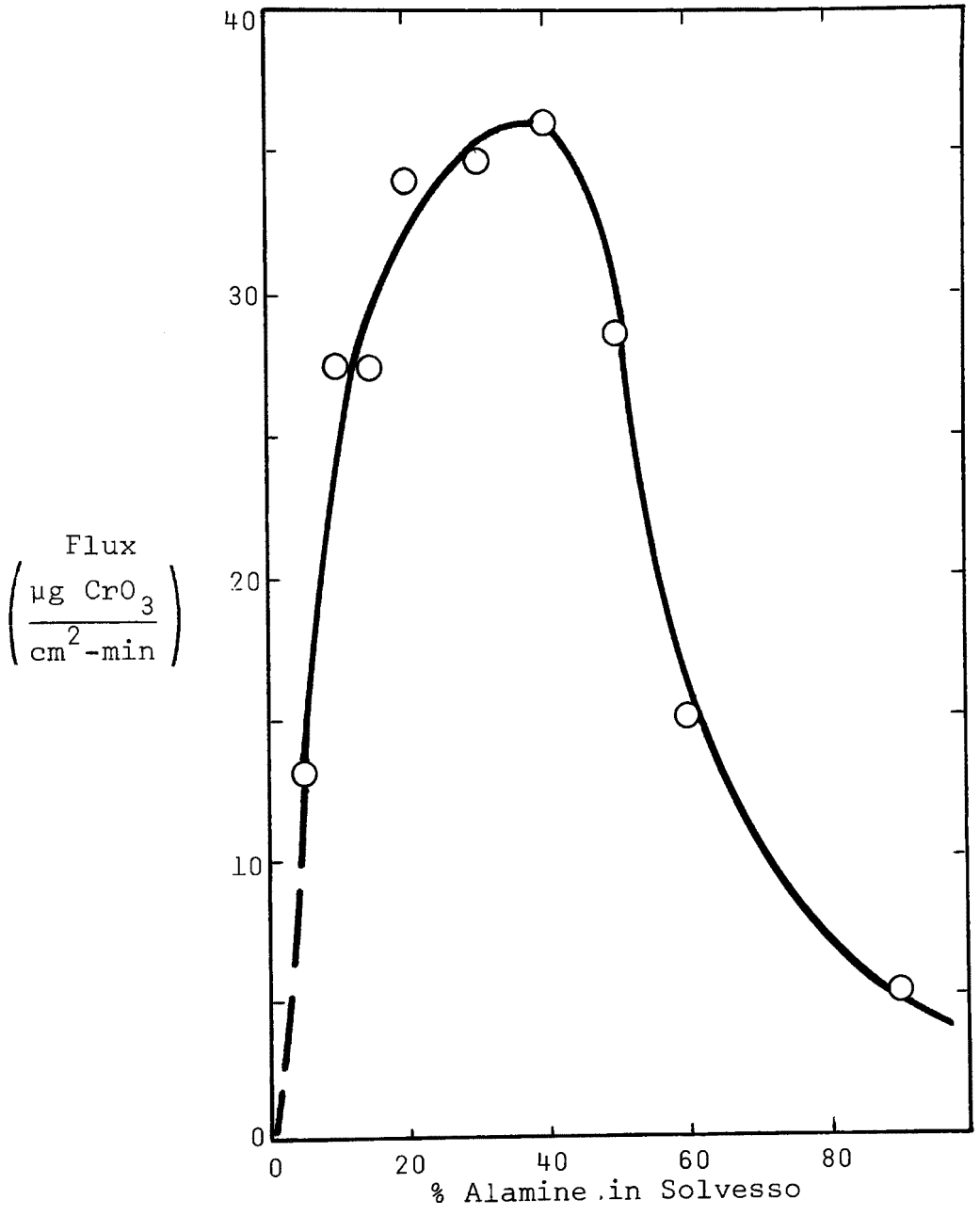


Figure 8. CrO_3 flux vs. concentration of Alamine 336 in Solvesso.

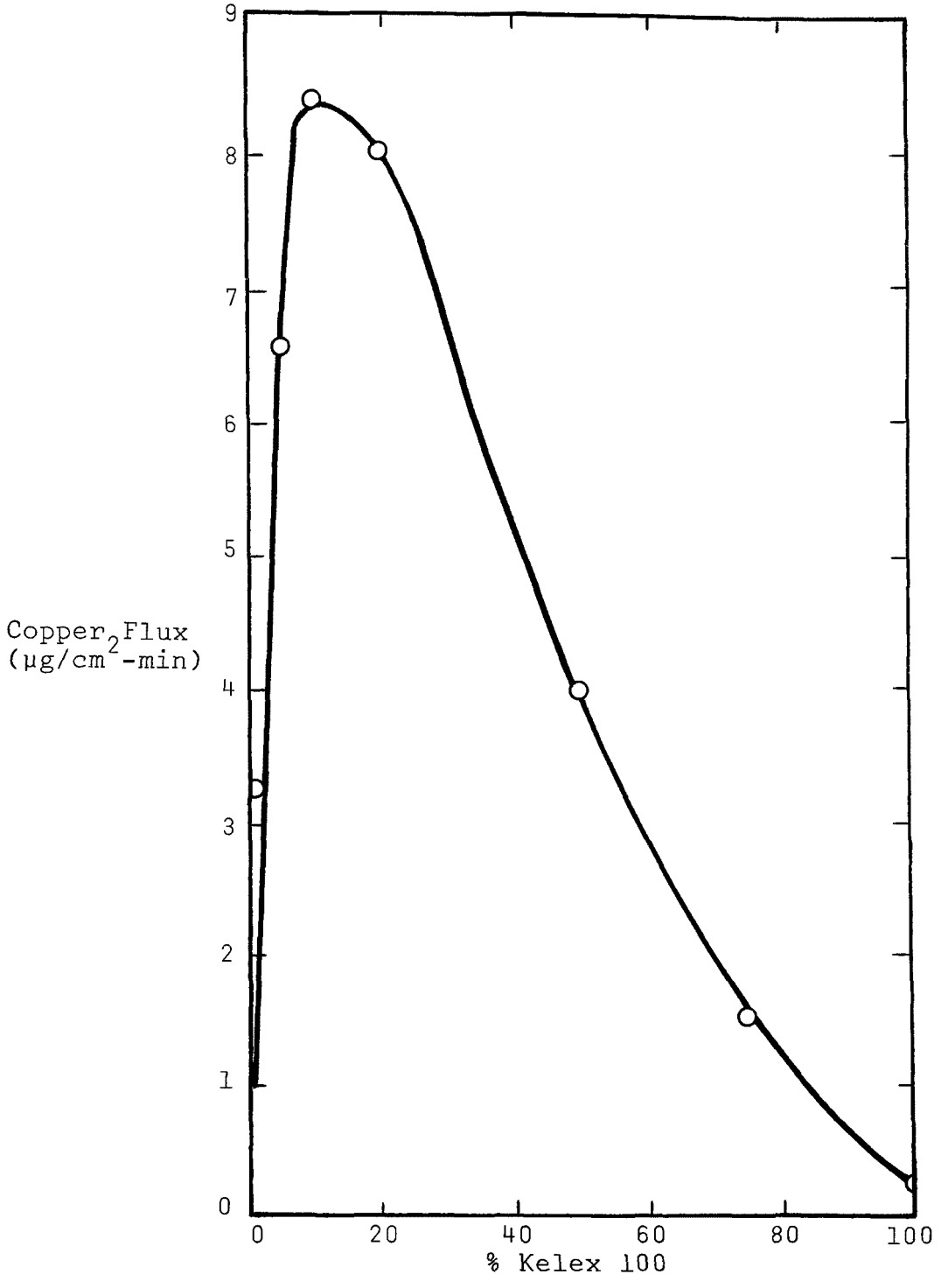


Figure 9. Copper flux vs. concentration of Kelex 100 in kerosene.

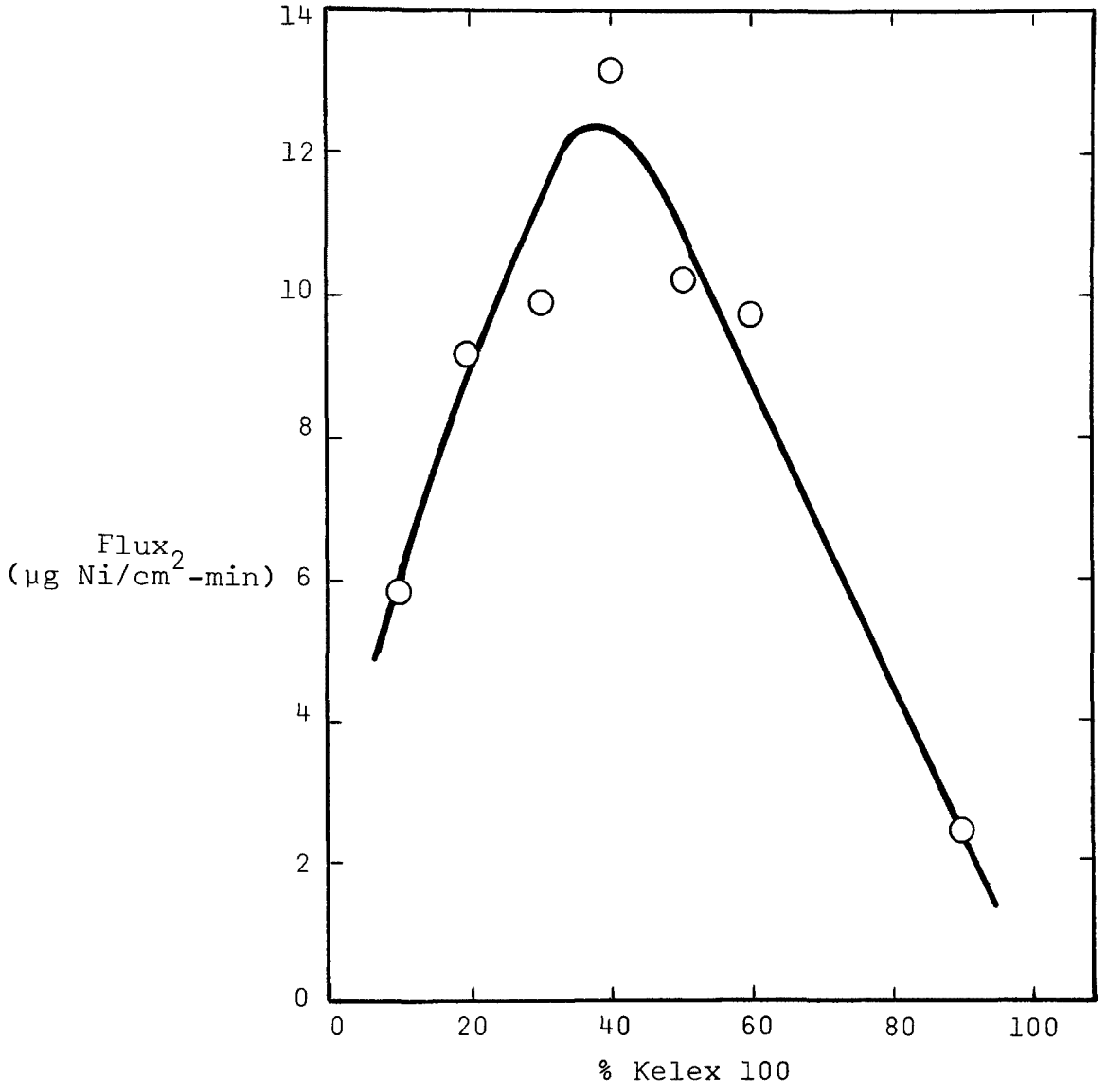


Figure 10. Ni flux vs. concentration of Kelex 100 in Solvesso.

neutralize it) would add to the concentrated stream. Before this stream could be fed back to the plating bath, this contaminant would have to be removed, in general. In counter-transport, the coupled ion contaminates the rinse water feed from which the metal ion was removed. These contaminants may be simple to remove, but it should be recognized that in general only one of the two streams emanating from the concentrator could be reused without some further treatment. In this section, we describe a series of experiments designed to simulate the conditions that might exist in such a concentrator.

Chromium. In Figure 11, we present a diagram showing how the concentrator might operate on a chrome plating rinse bath. The following assumptions have been made: the plating bath contains 25 wt% CrO_3[2] and there is a constant dragout rate equal to 2% of the flow rate of water through the rinse baths, producing a CrO_3 concentration in the first rinse bath of 5000 ppm.[3] This solution would be fed to one end of the membrane concentrator, and depleted of chromium as it passed through the concentrator from left-to-right in the figure. To drive the chromate ion across the membrane against its concentration gradient, we must either acidify this feed stream or make the downstream side of the membrane basic. Because we want to reuse the treated rinse water, we do not want to contaminate it with acid and hence we chose to add sufficient base to the downstream side of the membrane to neutralize the chromic acid that is transported across the membrane. The most favorable conditions will be achieved when the feed and downstream solutions flow counter to one another so that high concentration gradients are established everywhere.

The concentrated downstream solution emerging from the concentrator thus contains Na_2CrO_4. If we assume that a 50-fold concentration factor is achieved in the concentrator, the emerging concentrate stream will contain 41% Na_2CrO_4, which has the same chromium content as the plating bath. However, the chromium would have to be recovered from this stream as CrO_3 before it could be returned to the plating bath. This might be achieved, for example, by the addition of H_2SO_4 followed by fractional crystallization.[4] In this case, $NaHSO_4$ would become a by-product.

To simulate the changing concentrations that would exist in an operating concentrator, we arbitrarily divided the length of the concentrator into four zones of decreasing chromium concentration. Within each zone, we assumed a certain CrO_3 concentration and calculated the concentrations of Na_2CrO_4 and NaOH that would exist within that zone. These concentrations are

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(2) A. Logazzo, Metal Finishing Guidebook and Directory, Metals and Plastics Publications, Inc. Hackensack, N.J. 1976.

(3) E. McGuire, Crown City Plating Co., El Monte, CA, personal communication.

(4) J.R. Partington, General and Inorganic Chemistry, MacMillan, London 1954.

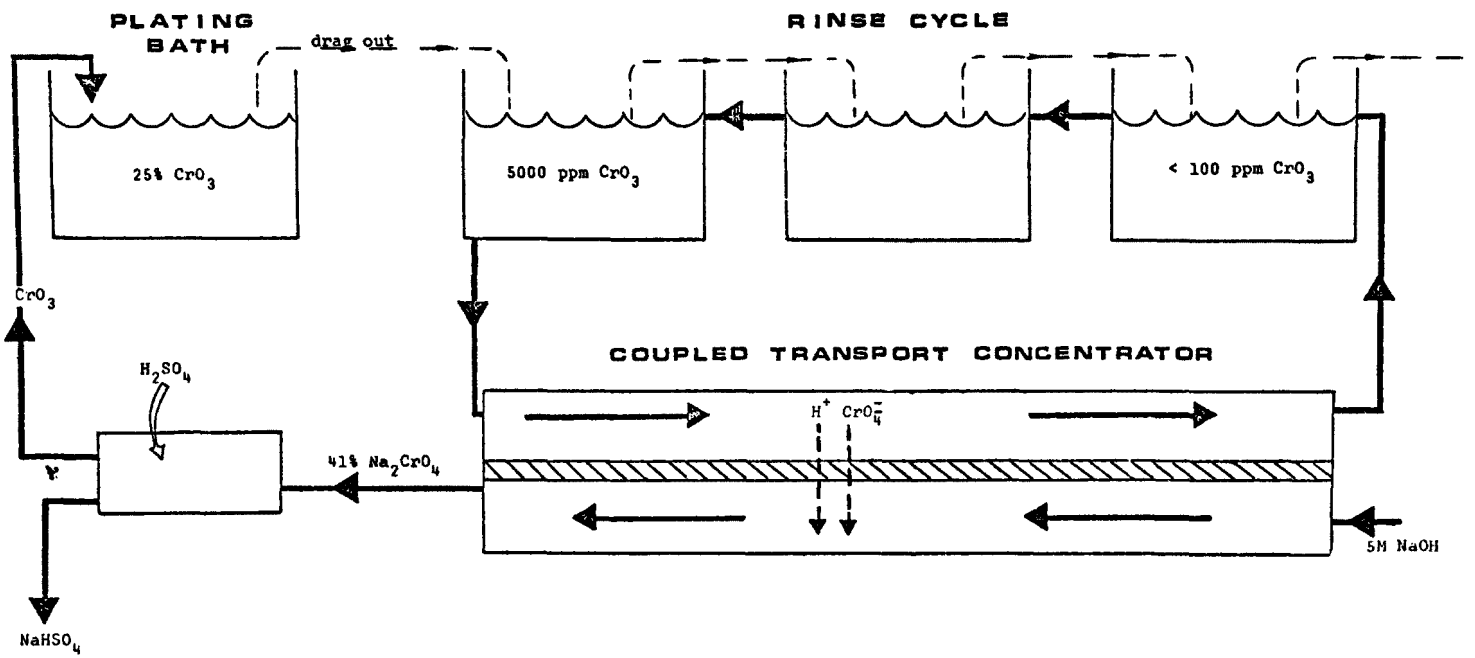

Figure 11. Schematic representation of coupled transport concentrator as applied to chromium plating wastes.

summarized in Table II.

TABLE II

ZONAL CONCENTRATIONS IN A SIMULATED COUPLED TRANSPORT MEMBRANE CONCENTRATOR FOR CHROMIUM

Zone	1	2	3	4
Feed CrO_3 Concentration (ppm)	5000	2500	1000	100
Downstream NaOH Concentration (M)	0.0	2.5	4.0	5.0
Downstream Na_2CrO_4 Concentration (wt%)	41	20	8	0.0

A series of experiments was then performed in permeation cells under each of these four sets of conditions, and the chromium flux was measured. The liquid membrane consisted of 40% Alamine 336 in Solvesso. The results are presented in Figure 12. Particularly noteworthy are the very high chromium fluxes over most of the concentration range and the linear dependence of flux on the concentration of CrO_3 in the feed.

Copper and Nickel. The analogous situation that would occur in the treatment of rinse waters from the acid plating of copper or nickel is shown in Figure 13. Typical compositions were again taken from Reference 3. Here hydrogen ion will flow counter to the metal ions, acidifying the depleted rinse water. This water could thus not be fed directly back to the rinse bath, as in the case of chrome plating rinse waters, but it might be reused after neutralization in an ion exchange column, for example. The concentrated downstream solution emerging from the concentrator could be fed directly back into the plating bath.

The concentrations of metals and acids in the hypothetical zones of the concentrator are presented in Table III. (For copper we arbitrarily selected five zones instead of four). These were calculated using the same considerations applied to the chromium case, above. In the nickel case, we have assumed conditions typical of a Watts bath. The boric acid present in these baths is used as a mild buffering agent and it would not significantly affect the coupled transport process.

The simulation experiments with copper were carried out using Kelex 100 as the complexing agent diluted to 10% in kerosene. This choice was based on the fact that Kelex complexes effectively with copper at the pH at which the concentrator would be operated (i.e. pH approximately 1), whereas the other complexing agents do not.

The results for copper are presented in Figure 14. Again, the copper flux is plotted against feed copper concentration when the composition of the solutions is that shown in Table IIIA. These data produced the dashed line. The copper fluxes in this case were less than 1$\mu g/cm^2$-hr, well below the data in Figure 9 for the same Kelex concentration. However, this flux was markedly enhanced when the pH of the feed solution was increased. The solid line in Figure 14 represents comparable data obtained when 0.03 M/liter

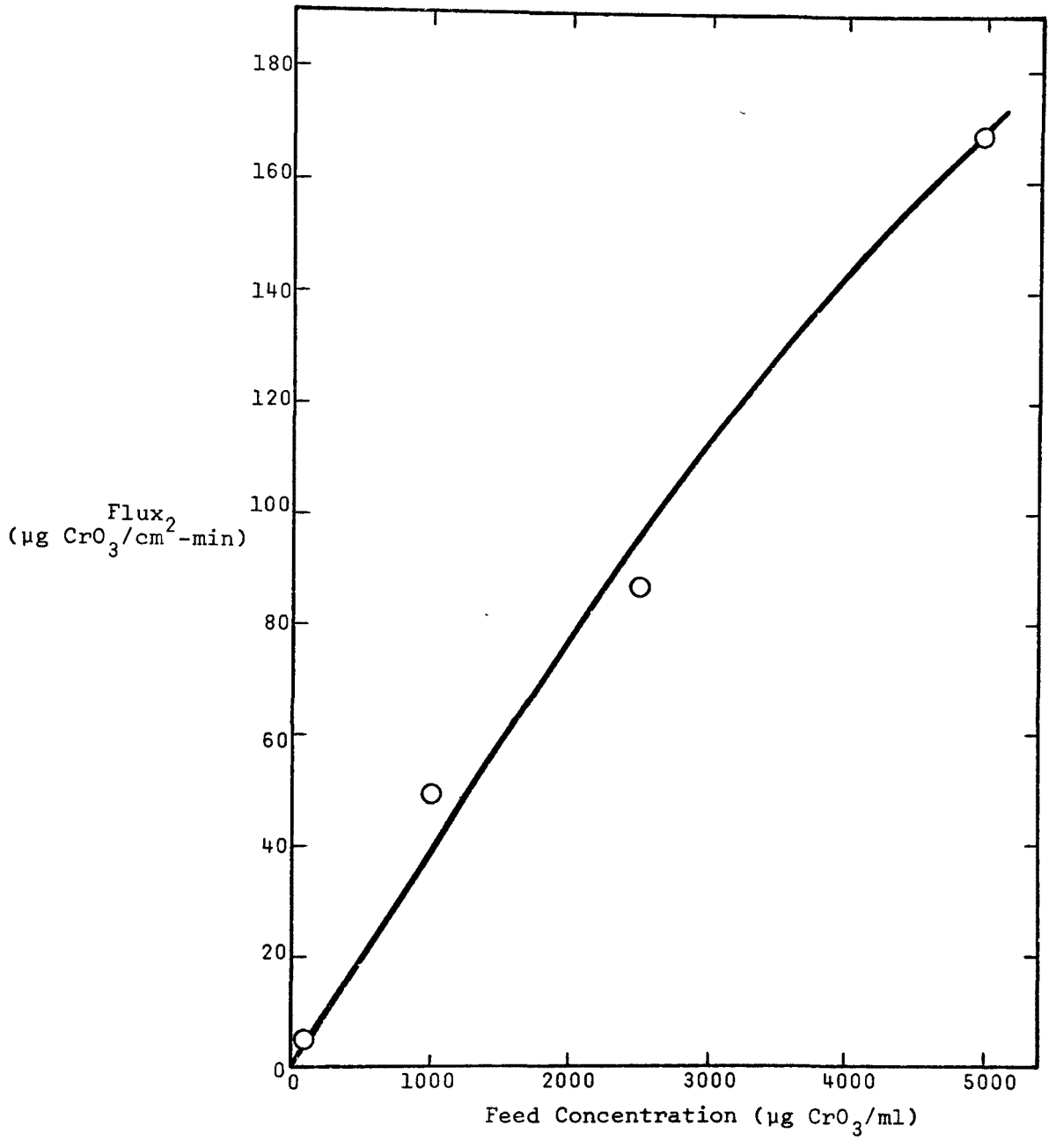

Figure 12. CrO_3 flux vs. feed concentration. All other conditions simulate those in a coupled transport concentrator. (See Table II).

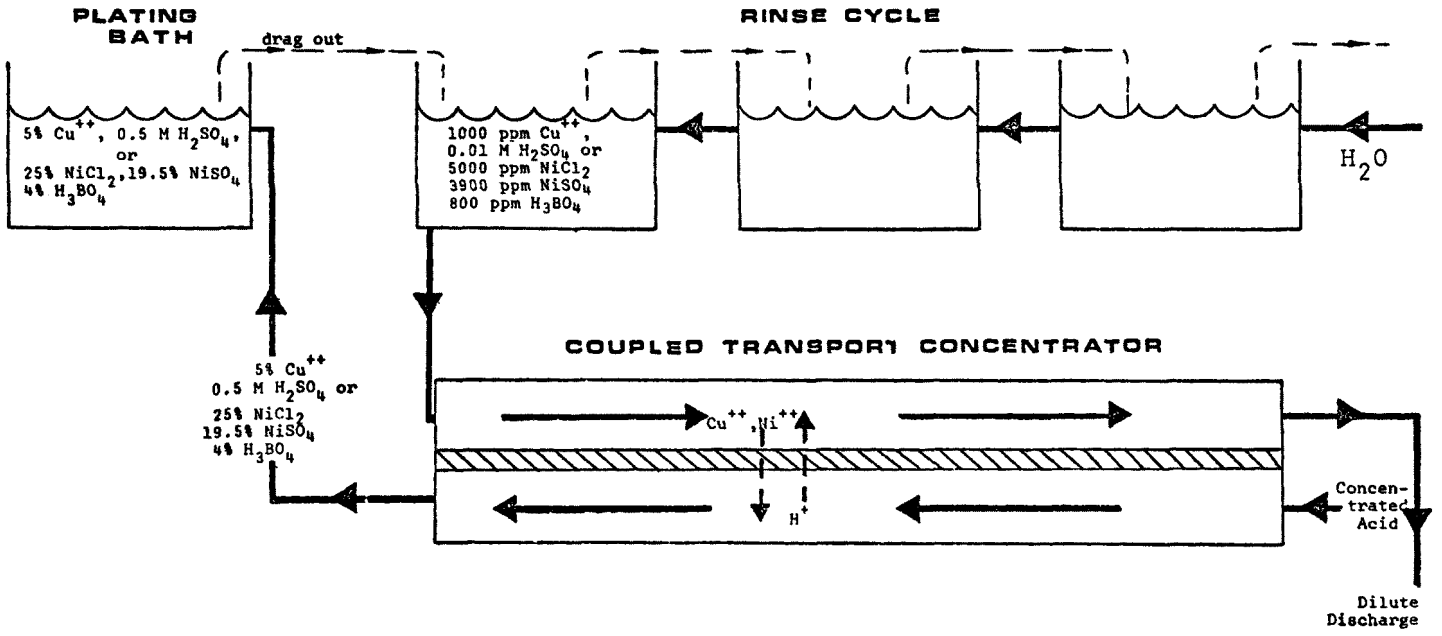

Figure 13. Schematic representation of coupled transport concentrator as applied to nickel or copper plating wastes.

Table III

ZONAL CONCENTRATIONS IN A SIMULATED COUPLED TRANSPORT MEMBRANE CONCENTRATOR FOR COPPER AND NICKEL

A. Copper

Zone	1	2	3	4	5
Feed Cu (ppm)	1000	500	250	100	50
Feed H_2SO_4 (M)	0.01	0.0175	0.0213	0.0235	0.0250
Downstream Cu (wt%)	5	2.5	1.25	0.5	0.0
Downstream H_2SO_4 (M)	0.5	0.875	1.06	1.18	1.25

B. Nickel

Zone	1	2	3	4
Feed $NiCl_2$ (ppm)	5000	2500	1000	100
Feed $NiSO_4$ (ppm)	3900	1950	780	78
Feed HCl (M)	0	0.017	0.026	0.033
Feed H_3BO_3 (ppm)	800	800	800	800
Feed H_2SO_4 (M)	0	0.009	0.014	0.0174
Downstream $NiCl_2$ (wt%)	25	12.5	5	0
Downstream $NiSO_4$ (wt%)	19.5	9.75	1.95	0
Downstream HCl (M)	0	0.96	1.38	1.72
Downstream H_3BO_3 (wt%)	4	4	4	4
Downstream H_2SO_4 (M)	0.0	0.44	0.70	0.81

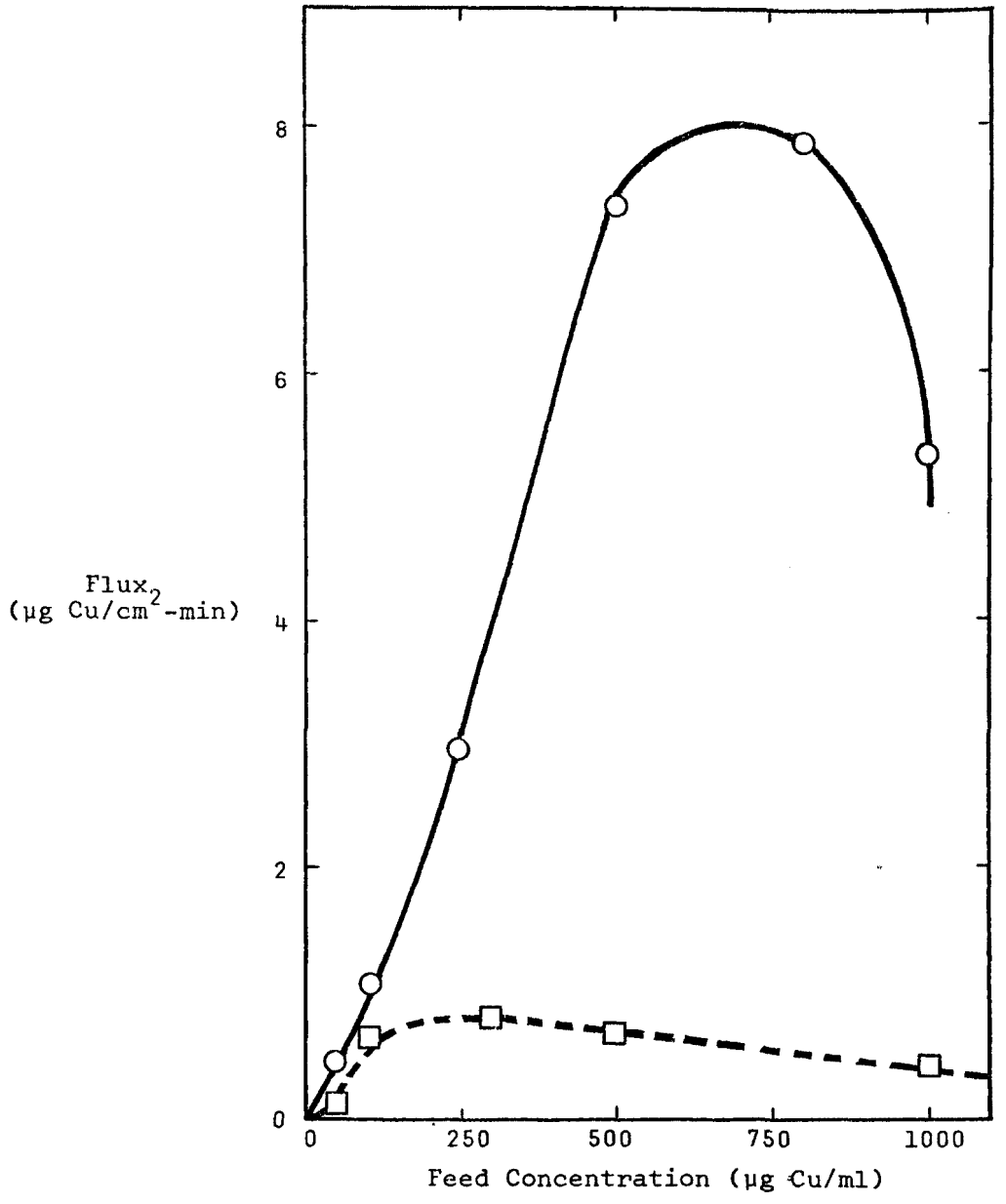

Figure 14. Cu flux vs. feed concentration. Dashed curve: conditions simulate those in a coupled transport concentrator. (See Table IIIA) Solid curve: 0.03 M/liter NaOH added to feed solution.

of NaOH was added to each of the feed solutions. (This is just the amount of base needed to neutralize the acid permeating counter to the copper.)

Nickel removal from rinse waters is similar in principle to copper removal. However, the hysteresis observed in the distribution coefficient measurements with both Kelex 100 and LIX 64N adds some complexity. Large pH gradients would be required to drive the nickel across the membrane, and, as can be seen from Table IIIB, such large pH gradients would not normally occur in the concentrator. Furthermore, addition of base to the feed solution to increase the pH gradient could not be tolerated because nickel precipitates above pH 6, where the concentrator would operate. The much narrower pH differences existing under these simulated conditions produced much lower nickel fluxes than we observed under more favorable conditions. The nickel fluxes are plotted against feed concentration in Figure 15.

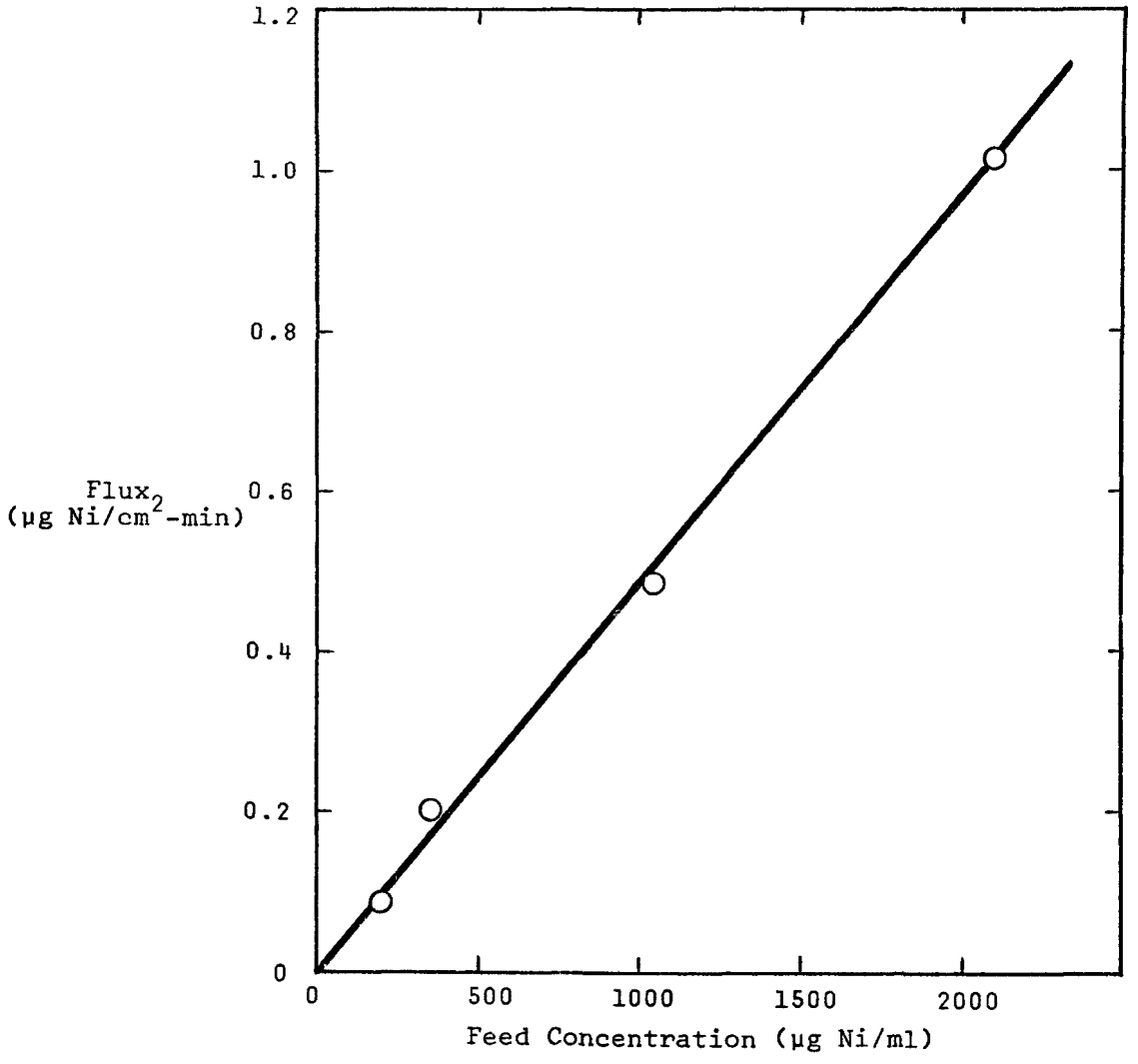

Figure 15. Ni flux vs. feed concentration. All other conditions simulate those in a coupled transport concentrator. (See Table IIIB).

SECTION V

ECONOMICS

Using the flux data generated under these simulated processing conditions, we are in a position to crudely evaluate the economic feasibility of the coupled membrane transport process. We consider here only chromium for the present, which, because of the large observed fluxes, is the most favorable case.

We begin by calculating the membrane area required to process a given volume of rinse water per unit time. An effective membrane permeability can be obtained from Figure 12. The flux-vs.-concentration curve in Figure 12 can be fitted by a straight line of slope k, where

$$k = \frac{170\ \mu g/cm^2\text{-min}}{5000\ \mu g/cm^3} = 0.034\ cm^3/cm^2\text{-min.}$$

Thus, k is a kind of "clearance rate", expressing the volume of solution that is depleted of chromium per unit area per unit time. As shown in Appendix B, the concentration of chromium, C, in a volume, V, of solution in contact with a unit area, A, of membrane will decay according to a first-order rate law:

$$C = C_o \exp(-kAt/V) \ ,$$

where C_o is the initial concentration of chromium in the rinse water. If we assume that C_o = 5000 ppm and if we further assume that we want to reduce the concentration to 100 ppm for return to the rinse bath, we have that C/C_o = 0.02 from which we have that $V/At = 8.7 \times 10^{-3}\ cm^3/cm^2\text{-min}$. This, then, is the volume of rinse water that can be treated per minute by 1 cm^2 of membrane.

The amount of chromic acid recovered from this rinse water is 4900 $\mu g/cm^2$. At a price of 60¢/lb (or 13¢/gram) of chromic acid, the chromic acid recovered has a value of \$26 per ft^2 of membrane per year. This is well below the expected capital cost of a coupled transport membrane concentrating unit. We believe that these units could be constructed for a cost comparable to that of current reverse osmosis units, which are comparable in complexity. These units sell for approximately \$10/ft^2 of membrane. Thus, the expected payback time for the membrane concentrator, ignoring operating costs, could be less than 6 months.

Under favorable circumstances where complete recycle was practiced, there would be an additional saving in the cost of make-up water for the rinse bath. This could amount to a savings of 1000 gallons of water per ft^2 of membrane per year, or approximately $\$1/ft^2$ of membrane per year.

In spite of the lower fluxes observed for copper and the lower cost of this metal, the economic picture for copper is also quite favorable. Only for nickel is the present economic projection unfavorable, because of the low fluxes observed to date.

SECTION VI

FUTURE WORK

The work we proposed to do in Phase I of this project is now essentially completed.

In Phase II, we propose to design and construct a 50 ft^2 mobile membrane concentrator for use in the field. The membranes would be prepared in the form of small, microporous polysulfone hollow fibers. These would be assembled into a multiple tube-in-shell configuration and ultimately field tested on plating rinse waters. The unit will be designed for continuous, unattended operation.

Appendix A

Steady State Concentration Factors

First, consider the reaction

$$CrO_4^- + 2H^+ + 2R \rightleftharpoons (RH)_2CrO_4 \ ,$$

for which there is an equilibrium constant:

$$K_{eq} = \frac{\left[(RH)_2CrO_4\right]}{\left[CrO_4^-\right]\left[H^+\right]^2\left[R\right]^2} \ .$$

Let us denote the two sides of the membrane by the subscripts o and ℓ. There will be no flux of CrO_4^- across the membrane when $\left[(RH)_2CrO_4\right]_o = \left[(RH)_2CrO_4\right]_\ell$.

Under these conditions, it follows that $\left[R\right]_o = \left[R\right]_\ell$. Thus, because the equilibrium constant must hold at both membrane-solution interfaces, a steady state is established when

$$\left(\frac{1}{\left[CrO_4^-\right]\left[H^+\right]^2}\right)_o = \left(\frac{1}{\left[CrO_4^-\right]\left[H^+\right]^2}\right)_\ell$$

or

$$\frac{\left[CrO_4^-\right]_o}{\left[CrO_4^-\right]_\ell} = \left(\frac{\left[H^+\right]_\ell}{\left[H^+\right]_o}\right)^2 \ .$$

(This development, of course, strictly applies only at pH > 7. Below this pH the chromate-dichromate equilibrium becomes important).

Next, consider the reaction

$$M^{++} + 2RH \rightleftharpoons R_2M + 2H^+$$

$$K_{eq} = \frac{\left[H^+\right]^2\left[R_2M\right]}{\left[M^{++}\right]\left[RH\right]^2} .$$

As above, there will be zero flux when $\left[R_2M\right]_o = \left[R_2M\right]_\ell$, and under these conditions $\left[RH\right]_o = \left[RH\right]_\ell$.

Thus,

$$\left(\frac{\left[H^+\right]^2}{\left[M^{++}\right]}\right)_o = \left(\frac{\left[H^+\right]^2}{\left[M^{++}\right]}\right)_\ell$$

or

$$\frac{\left[M^{++}\right]_o}{\left[M^{++}\right]_\ell} = \left(\frac{\left[H^+\right]_o}{\left[H^+\right]_\ell}\right)^2 .$$

Appendix B

Exponential Decay of $\left[CrO_3\right]$ in a Concentrator

The removal of CrO_3 from the feed follows first order kinetics:

$$\frac{d\left[CrO_3\right]}{dt} = -\frac{kA}{V}\left[CrO_3\right],$$

where k is the slope of the flux-vs.-concentration curve, A is the membrane area, and V is the volume of the feed solution. Set $\left[CrO_3\right]$ at t=0 equal to C_o and $\left[CrO_3\right]$ at time t equal to C. We can then integrate:

$$\int_{C_o}^{C} \frac{dC}{C} = \int_{o}^{t} -\frac{kA}{V}dt$$

or

$$\ln(C/C_o) = -kAt/V$$

and

$$C/C_o = \exp(-kAt/V) \ .$$

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(Please read Instructions on the reverse before completing)

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16. ABSTRACT

This report describes a process for separating and concentrating heavy metals from electroplating rinse waters. Metal ions can be "chemically pumped" across a coupled transport membrane against large concentration gradients by allowing the counterflow of a coupled ion such as hydrogen ion. The process is carried out within a microporous membrane containing within its pores an organic, water immiscible complexing agent. The complexing agent acts as a shuttle, picking up metal ions on one side of the membrane, carrying them across the membrane as a complex, and preserving electrical neutrality by carrying hydrogen ions in the opposite direction.

The importance of coupled transport is its high selectivity and flux. High selectivity derives from the rise of specific complexing agents. High flux is possible because these are actually liquid membranes with diffusivities many times greater than those in solid membranes.

17. KEY WORDS AND DOCUMENT ANALYSIS

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