ABSTRACT

Title of Thesis: Transport Phenomena of Copper Ions Through
an Electromembrane

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Thesis Directed by

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A separation process based on a new class of membrane (the electromembrane) was studied. Experiments were performed using three types of electromembrane to remove copper ions from aqueous solution. A Separation Cell Unit was designed and set up to investigate the transport of copper ions through the electromembranes under the influence of both an electric field and a concentration gradient. Fluxes achieved were much greater than those reported for other membrane processes, and the energy consumption was one half that of electrolytic deposition.

TRANSPORT PHENOMENA
OF
COPPER IONS THROUGH AN ELECTROMEMBRANE

by
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INTRODUCTION

Heavy metals, including mercury, cobalt, lead, cadmium, chromium, silver, radium, copper etc., are among the most harzarous materials contaminated in our environment, affecting the nation's water resources. Water contamination is one of the major environmental problems confronting the nation today. The heavy metals mostly come from the chemical processing industries, metal-finishing, and electroplating industries. These industries have an ever-growing problem in controlling the effects of its wastewaters. The wastewaters, if discharged into the environment without treatment can pollute our natural resources, inhibit or destroy natural biological activities, and adversely affect materials of construction. Specific examples of these detrimental effects include the toxicity of heavy metals to various forms of aquatic life [1], and the deleterious effect of copper and chromium on biological sewage treatment processes because of their toxicity to the microflora [2].

Heavy metals removal and/or recovery from wastewaters is very difficult and costly. For instance, for its Edison plant, the Ford Motor Co. built a $4 million federally mandated wastewater treatment facility. The conventional treatment of such wastewater impurities takes place at the end-of-line and involves treatment of large volumes of wastewater by chemical precipitation. This operation entails large capital costs and produces vast volumes of metal-containing sludges. Consequently, several other technologies are being investigated to reduce or eliminate the end-of-line treatment by removing metallic impurities at the source. Examples of such treatment are ion exchange, reverse osmosis[3], electrodialysis, and electrolytic cleanup of wastewater[4]. Recently, the combination of membrane with electrophoresis has attracted greater attention. A solid/liquid separation process based on electrofiltration was investigated by Henry[5] to prevent deposition of particles in oil-in-water emulsions. A separation technique on electrofiltration of dewatering a dispersed slurry was developed by James[6]. A study on performance of electrofiltration using a rotary drum vacuum filter to enhance the throughput has been suggessted by Yukawa[7]. However, there were no other breakthrough techniques on cost-effective membrane preparation since the anisotropic membrane proposed by Leob and Sourivaian at the University of Califoria in 1960[8], and hallow fiber membranes of Nylon polymer developed by E. I. Dupont de Nemours & Co. Inc[9,10].

Extraction of heavy metals, such as uranium from wet process phosphoric acid, has been performed by liquid membrane process[11], but the major challege to the development of the liquid membrane is its demulsification process, which is the complete breakup of an emulsion into its component parts. Troublesome emulsification and demulsification operations limit the practical applications of liquid membrane process to the separation technology. Another liquid membrane processes consisting of a liquid layer containing ion-exchange carriers which are imposed between two aqueous phases have been studied by many researchers[12-14]. These membranes have not yet found application as a separation medium because of their lack of stability, thus their use has been limited to situations in which the adjacent aqueous phases are maintained within narrow limits of composition, temperature, and pressure. The source of the difficulty was found to be the formation of a separate aqueous phase within the liquid membrane layer. It is not easy to overcome this difficulty in practical industrial separation processes.

A new electromembrane liquid separation process, which has been developed by professor Lin recently[15], will be studied in this experiment. The electromembrane can be charged either positivoly or negatively to provide the effective process in separation technique of heavy metals. Electromembrane process for the removal of heavy metals from liquid has the advantages that no cake will be formed on the membranes with high throughput and low operating and epuiqment cost. The electromembrane process is also different from electrolytic deposition method developed by

Kim and Weininger at General Electric Company[16]. The principal differences of these two methods are summarized in Table 1. Essentially, the electromembrane process provides a higher removal rate with minimum flow resistance, allowing no cake formation during the operation, resulting in savings of capital and operateng cost.

Experiments are performed with emphasis on removal of copper by using the electromembrane process. Some transport phenomena of ions through the electromembrane are being investigated and discussed. The objectives of this experiment are to explore the use of electromembrane to the removal of copper ions and to make a primary economic analysis of this new class of separation technique.

Electromembrane process is a separation system for rapidly removing metal ions from wastewater by means of electrically chargeable membranes under an applied low direct electric current. It is easy to scale up because the basic apparatus is inherently modular. It is simple because the removal rate is controlled electrically. It is flexible because the basic modules in the apparatus can be adapted with little modifications from one application to another. The advantages of the electromembrane process include: (1) High permeation flux of charged species: Low flow resistance provides an increase in removal rate, causing a cheap and fast treatment of metal-containing wastewater, soil and sludges. (2) Simpler construction of apparatus: Electric Separation cell of D.C.-Unit has a simple structure, which results in easy operation and the potential for further wastewater treatment. (3) Operation at room temperature and atmosphere pressure. This is very important for practical operation with low capital investment.

THEORETICAL

A. Flux Through Electromembrane Due to Concentration Gradient

As shown in Fig. 1, the flux of copper ions across the membrane on the left side of compartment 2, $\overleftarrow{J}_+$, is given by the product of three terms, a proportionality constant, concentration C_+, and driving force[17,18]. The flux due to diffusion $\overleftarrow{J}_+(d)$ caused by the force represented by the gradient of chemical potenial, $-dU_+/dx$, is given by

$$\overleftarrow{J}_+(d) = \frac{\overleftarrow{D}_+(d)}{R\ T} C_+\left(-\frac{dU_+}{dX}\right) = -\overleftarrow{D}_+(d)\ C_+\frac{d\ln a_+}{dX} \qquad (1)$$

where $\overleftarrow{D}_+(d)$ is the diffusion coefficient toward left cathode side. For same chemical potenial difference, $\overleftarrow{D}_+(d) = \overrightarrow{D}_+(d)$, where $\overrightarrow{D}_+(d)$ is diffusion coefficient toward right anode side.

Substituing for $a_+ = C_+\ r_+$.

$$\overleftarrow{J}_+(d) = -\overleftarrow{D}_+(d)\ \left(\frac{dC_+}{dX} + C_+\frac{d\ln r_+}{dX}\right) \qquad (2)$$

when r_+ is a constant, thus the flux Eq.(2) reduces to Fick's first law

$$\overleftarrow{J}_+(d) = -\overleftarrow{D}_+(d)\ \frac{dC_+}{dX} \qquad (3)$$

where $\overleftarrow{J}_+(d)$ is the flux of copper ions across electromembrane due to diffusion caused by concentration difference.

Because it is difficult to measure the concentration gradient in the membrane, a procedure was used by Stewart[19] who measured the changes in concentration across the membrane in a known period of time and used the unintegrated form of Fick's equation

$$\overleftarrow{J}_+(d) = \frac{\Delta C \quad V}{t \quad A} = D_{app}\frac{C_t}{d} \qquad (4)$$

where A is area of the memgrane; Δ c is change in concentration of copper ions on either side of the membrane in time t; V is the equal volume of solution on either side of the membrane; C_t is the concentration on high concentration side of the copper ions at the end of time t ; d is thickness of membrane; D_{app} is the apparent diffusion coefficient. From the observed flux, the value of the apparent diffusion coefficient was calculated.

B. Flux Through Electromembrane Due to Electric Field

The flux of copper ions across an electromembrane due to an electric field $-dE/dx$ is given by

$$\overleftarrow{J}_+ (e) = - m_+ Z_+ C_+ \frac{dE}{dX} \tag{5}$$

$\overleftarrow{D}_+ (e)$, diffusion coefficient toward left cathode side, is related to mobility m_+ by the Nernst-Einstein relation :

$$\overleftarrow{D}_+ (e) = \left(\frac{R\ T}{F} \right) m_+ \tag{6}$$

The total flux of copper ions through a membrane is given by

$$\overleftarrow{J}_+ = \overleftarrow{J}_+ (d) + \overleftarrow{J}_+ (e) \tag{7}$$

Substituting for $\overleftarrow{J}_+ (d)$ and $\overleftarrow{J}_+ (e)$

$$\overleftarrow{J}_+ = - \overleftarrow{D}_+ (d) \left(\frac{dC_+}{dX} + C_+ \frac{d\ln r_+}{dX} \right) - \overleftarrow{D}_+ (e) \left(Z_+ \frac{F}{RT} C_+ \frac{dE}{dX} \right) \tag{8}$$

Eq.(8) is similar to the Nernst-Plank flux eqution.

Assuming the flux due to concentration gradient is very small compared with the flux due to electric field (this will be proved by the experiment here), so neglecting $\overleftarrow{J}_+ (d)$

$$\overleftarrow{J}_{+} \div \overleftarrow{J}_{+}(e) = - m_{+} Z_{+} C_{+} \frac{dE}{dX} \qquad (9)$$

The velocity of copper ions proportional to the ionic charge z_{+},

$$U_{+} = - m_{+} Z_{+} \frac{dE}{dX} \qquad (10)$$

The flux, $\overleftarrow{J}_{+}$, is the product of the velocity, U_{+}, and the concentration.

$$\overleftarrow{J}_{+} = U_{+} C_{+} \qquad (11)$$

Ionic flux is related to the electric current density, I, by Faraday's constant and the valence.

$$I = F Z_{+} \overleftarrow{J}_{+} \qquad (12)$$

The amount of copper ions removed from a depleting solution in a membrane separation process is given by[20] .

$$R = \eta I / F Z_{+} \qquad (13)$$

where R is the removal rate.

The energy consumption is given by

$$P = V I \qquad (14)$$

where, P is the electric power in Kw; V is voltage; I is electric current.

The major limitation of the removal rate achievable in electromembrane process is concentration polarization. As the electric current density is increased, interfacial concentration become lower on the entering side (right side of positive electromembrane) and higher on the other side (left side of positive electromembrane). As the current density is increased still more, the concentration of copper ions at the entering interface infinitesimal. At this current density, limiting current density I_{lim} , hydrogen and hydroxyl ions formed by ionization of water begin to be conducted through the electromembrane and take a significant part in carring the current. These phenomena have been occured in ion-exchanger membranes and studied by a number of investigators[21,22]. Like the ion-exchanger membranes, those phenomena may be also occurred in electromembranes. At current densities in excess of the limiting current density, little additional transfer of the desired ions, copper ions, is obtained because they are not available at the entering side. The increment of current above the limiting values results mostly in conduction of hydrogen and hydroxyl ions from the so-called splitting of water, and in only a small amount of additional transport of copper ions. The transport of hydrogen and hydroxyl ions results in locally high and low PH level at the membrane surface, which can damage the membrane[23] . Thus, concentration polarization imposes a real limitation on the removal rate of copper ions in an electromembrane process.

APPARATUS AND EXPERIMENTAL PROCEDURE

A. Apparatus

A Separation Cell Unit has been set up by arranging the two electrodes connected with a D.C.-power supply. The Cell Unit consists of three compartments separated by two electromembranes as shown schematically in Fig. 1. The entire unit is about 2 ft. long, 8 in. wide, 8 in. high. Operating condition is at room temperature 25 °c.

Experiments are performed with removal of copper at first step. The electromembranes are separated from each other by spaces which form compartments. Compartment 2 having positive electromembrane on the left side facing the negatively charged electrode (cathode) is ion depleting compartment, decreasing in concentration of copper ions during the experimental period. The copper ions transfer through positive electromembrane from compartment 2 to compartment 1. The compartment 1 is an ion enriching compartment, increasing in concentration of copper ions during the experimental period. Concentration changes of copper ions observed occurred in compartment 1 and compartment 2 are due to transport of copper ions across the positive electromembrane.

The Cell Unit is designed so that the following variables can be independently varied: electrical field strength, concentration of solution in each compartment, and resistances connected with electromembranes (R1 and R2). Some detail specification and dimesion of Cell Unit are presented as following: (1). Regulated D.C. power supply has constant voltage control from 0-50 volts; (2). Anode is a 10*10 cm platinum plate; (3). Negative electromembrane (N-EM), a metallic gauze, is the product of TETKO Inc., material: s/s 3042, specification: 325*2300, area: 6.1*5.2 cm, thickness: 0.01 cm; (4). Positive electromembrane (P-EM), a metallic gauze, is also the product of TETKO Inc., material: s/s 3042, specification: 325*2300, area: 6.1*5.2 cm, thickness: 0.01 cm; (5). Cathode is a 10*10 cm Cu-Ni alloy plate; (6),(7). are Variable Resistance operating range from 500 to 2000Ω; (8). Polyacrylate plate form three compartments; each has 3 litters in volume.

B. Procedure

Three known concentrations of copper nitrate solutions, prepared with reagent grade copper nitrate in distilled water, were put into compartments, then a D.C. voltage was applied across the solution compartments and electromembranes. The cations, copper ions, tended to migrate toward the cathode and anions, nitrate ions, tended to migate toward the anode due to electrophoresis. The positive electromembrane had a trend to permit only the positively charged ion, i.e. copper ions, to pass and to retain the negatively charged ions, i.e. nitrate ions behind under an electric field. The negative electromembrane had a trend to permit only the negatively charged ions to pass and to retain the positively charged ions behind under an electric field. As a result, copper ions transfered through positive electromembrane from compartment 2 to compartment 1, decreasing in concentration of copper ions at compartment 2, and increasing in concentration of copper ions at compartment 1.

The concentration of copper ions in three compartments varied within a range from 0 to 2000 p.p.m. and the only anions present were nitrate ions. The concentration in compartment 2 was several times higher than in the other two compartments to permit the easy study of remove rate of copper ions from this compartment. During the experiment period, the concentration of copper ions in the three compartments were all a function of time, one can obtain the flux of copper ions across the membranes. The concentration of solution in each compartment would be determined by a Spectrophotometer. The operational manual and measuring methods are described at next section.

C. Spectrophotometer

The Spectronic 710 Spectrophotometer has been used to measure the concentration of solution in this experiment. The flux of copper ions across the electromembrane can be calculated after the concentrations of solution on the both sides of membrane have been measured. To obtain optimum instrument performence, one can read the manual published by BAUSCH & LOMB CO.[24]. The manual provides concise information on the operation and maintenance of the spectrophotometer.

The Spectronic 710 Spectrophotometer actually provides photometric readout in absorbance on a 4-place digital display. Since the absorbance is directly proportional to concentration, a graph of standard curre can be plotted of absorbance versus the concentrotion of standard solutions containing copper ions as Fig. 2. The concentration of unknow samples may be read from the standard curve if the analytical conditions are identical to those used to construct the standard curve. Some information of operating conditions to construct standard curve in absorbance readout are presented as following: (1).Set Mode Selector Switch at Absorbance; (2). Select Tungsten for Source Lamp; (3). Set Wavelength at 630 nm; (4). Set Gain Switch to X1.

RESULT AND DISCUSSION

A. Flux Through Electromembrane Due to Concentration Gradient

To obtain the flux due to concentration gradient, two experiments was undertaken. In Run 1, three equal volumes of known concentration of copper nitrate solutions, which were prepared with reagent grade coppper nitrate in distilled water, were separately put into the three compartments of the Separation Cell Unit. The initial concentration of copper ion in compartments were o p.p.m. in compartment 1, 1500 p.p.m. in compartment 2, and o p.p.m. in compartment 3, respectively. In Run 2, the initial concentration in compartment 1 and 3 was changed from 0 to 500 p.p.m. and the concehtration in compartment 2 was kept the same as for Run 1, The volume of solutions was all equal at three litters. In order to determine the diffusion flux of copper ions across the Electromembranes, the concentration in three comparments were taken measurement from time to time. The copper concentration of the samples was measured by the Spectronic 710 Spectrophotometer. The concentration changes of copper ions in each compartment varied with time and are presented in Table 2 for the Run 1, and Table 3 for the Run 2. The plots of the concentration of copper ions versus time are shown in Fig. 3 for the Run 1 and Fig. 4 for the Run 2. Compartment 2 is the depleting compartment for both runs, decreasing in concentration of the copper ions. The copper ions transfer through membrane I from compartment 2 to compartment 1 and transfer through membrane II to compartment 3 due to concentration gradient. Compartment 1 and compartment 3 are increasing in concentration during the experiment period. From the concentration changes in three compartments, one can obtain the flux, then use the Eq. (4) to calculate the apparent diffusion coefficient D_{app}.

The value of the observed flux and calculated D_{app} are shown in Table 4 for the Run 1, and in Table 5 for Run 2. The average value of D_{app} is about 1.2×10^{-7} cm^2/hr in the Run 1 in which the initial concentration difference between compartment 2 and compartment 1 or 3 is 1500 p.p.m. and D_{app} is about 0.5×10^{-7} cm^2/hr in the Run 2 in which the initial concentration difference beteween compartment 2 and compartment 1 or 3 is 1000 p.p.m. The average flux due to concentration gradient of each run, 5×10^{-5} for Run 1 or 2.5×10^{-5} g/cm^2/hr for Run 2, is so small in comparison with the flux due to electric field, shown to be 6×10^{-3} g/cm^2/hr in electromembrane process, that one can neglect this difusion flux, $\overleftarrow{J}_{+}(d)$, when it is combined with electric flux, $\overleftarrow{J}_{+}(e)$, i.e. $\overleftarrow{J}_{+} = \overleftarrow{J}_{+}(e)$ shown in Eq.(9) before.

B. Flux Through Electromembrane Due to Electric Field

Three kinds of electromembranes were tested to obtain the flux of copper ions transfering through them. They were neutral, positive, and negative electromembrane. The electromembrane which had been charged positively was positive electromembrane, P-EM; the electromembrane charged negatively was negative electromembrane, N-EM; the electromembrane which had no charge at all was neutral electromembrane , n-EM. Three equal volume of three litters copper nitrate solutions were separately put into the three compartments of the Cell Unit. The initial concentration of copper ions in solution of each compartment was kept the same while different kinds of electromembranes were tested, they were 1500 p.p.m. in compartment 2, and 0 p.p.m. in both compartment 1 and 3.

(1). The Flux Through Neutral Electromembrane (n-EM)

A D.C. voltage was applied in two electrodes of the Cell Unit only and there were no connections between membranes and power supply source, so the membranes were neutral electromembrane. After the passage of electrical current, the copper ions in compartment 2 began to transfer through neutral electromembrane to compartment 1 due to electrophoresis. Three runs of experiment were made here. The electrical field strengthes were varied for each run, which were 10,15, and 20 volts for Run 1,2, and 3, respectively.

The procedure to measure the concentration of copper ions is the same as before. The experimental conditions and the concentration changes as a function of time in each compartment of each run are presented in Table 6,7, and 8. The plots of the concentration changes of copper ions versus time of each run are also shown in Fig. 5,6,7 for compartment 1, and in Fig. 8,9,10 for compartment 2. Because copper ions transfer from compartment 2 to 1, compartment 2 is always decreasing in concentration, while compartment 1 is increasing. The fluxes of copper ions through the n-EM, which can be found from the slopes of curves, are summarized in Table 15.

(2). The Flux Through Positive Electromembrane (P-EM)

The membrane on the left side of compartment 2 was charged positively in addition to a D.C. voltage applied in two electrodes of the Cell Unit. This kind of membrane was called positive electromembrane. The flux through positive electromembrane was determined by the resistance R which connected the membrane with positive pole of power supply source and by the operating voltage applied on the system. After the passage of electrical current,the copper ions in compartment 2 began to transfer across the positive electromembrane to compartment 1 due to electrophresis. A few runs of experiment were made. The experimental conditions and the concentration changes in each compartment for different positive electromembranes are all presented in Table 9,10, and 11. The plots of the concentration changes of copper ions versus time for each kind of P-EM are shown in Fig. 5,6,7 for compartment 1, and in Fig. 8,9,10 for compartment 2. Obviously, the flux through a positive electromembrane is larger than that through a neutral electromembrane. A further discussion about the copper ions transfering through P-EM will be made later.

(3). The Flux Through Negative Electromembrane (N-EM)

The membrane on the left side of the compartment 2 was charged negatively, so it was called negative electromembrane. The flux through this kind of electromembrane was determined by the resistance R which connected the membrane with negative pole of power supply source and by the operating voltage applied on the system. A few runs of experiment were made to obtain the flux across different kinds of N-EM. The experimental conditions and the concentration changes in each compartment for each run are presented in Table 12,13, and 14. The plots of the concentration changes of copper ions versus time for each kind of N-EM are shown in Fig. 5,6,7 for compartment 1, and in Fig. 8,9,10 for compartment 2. The fluxes found from the slopes of curves are summarized in Table 15.

From Table 15 which lists all the fluxes of three kinds of electromembranes, three things are evident : (1). At same operating electric field strength, P-EM has larger flux than n-EM. (2). At same operating electric field strength, N-EM has smaller flux than n-EM. (3). The P-EM R1000 has the largest flux, while N-EM R1000 has the smallest for each same operating voltage. Those experimental results show that the major function of positive electromembrane is its good ionic selectivity that permits the positively charged ions, copper ions, to pass easily. Especially, the P-EMR1000 provides the flux larger by two times than n-EM at the same operating voltage. For instance, at 15 volts the flux of a n-EM is 3.08×10^{-3} $g/cm^2/hr$, while the flux of the P-EMR1000 is 6.35×10^{-3} $g/cm^2/hr$. In contrast to P-EM, the N-EM retains the positively charged copper ions to pass. Hence, the flux through a negative electromembrane decreases to almost half of that through a neutral electromembrane. Because some copper ions were deposited on the surface of N-EMR1000 interrupting the ions to pass, the N-EMR1000 has the smallest flux.

(4). Flux Through Both Positive and Negative Electromembrane Simultaneously (Combined P-EM and N-EM)

In order to see the difference between the neutral electromembrane process and combined positive and negative electromembrane process, a few experiments of two cases were made. Three equal volume of 3 litters copper nitrate solutions were separately put into the three compartments of the Cell Unit. The initial concentration of copper ions in solution of each compartment was kept the same during each run, which were 0 p.p.m. in compartment 1, 1500 p.p.m. in compartment 2, and 500 p.p.m. in compartment 3.

At first, a neutral electromembrane process was tested. A D.C. voltage was applied in two electrodes only, and there were no connections between two electromembranes and power supply source. The electrical field strength were varied for each run, which were 5,10,15,20, and 30 volts for Run 1,2,3,4, and 5, respectively. The experimental conditions and the concentration changes as a function of time in each compartment of each run are presented in Table 16,17,18,19,and 20. In order to obtain the removal rate more easily, the plots of the concentration changes of copper ions in compartment 2 versus time of each run are shown in Fig. 11. The removal rate, the concentration decreasement in compartment 2, is the net value of the flux transfering out through the membrane on the left side of compartment 2 minus the flux transfering in through the membrane on the right side of compartment 2. The removal rate of copper ions and coulomb efficiency calculated by Eq. (13) of each run are summarized in Table 21. That removal rate is proportional to the current density is in reasonable good agreement with the theoretical Eq. (12). It is comprehensiblle that the coulomb efficiencys for five runs are lower than 30% because some copper ions transfer from compartment 3 to 2. This flux has the negative effect on remove rate of copper ions from compartment 2. The flux through two neutral electromembrane on both sides of compartment 2 are listed later in Table 29.

In a combined positive and negative electromembrane process, a lot of runs of experiment were tried to obtain the optimum operation conditions at which one can get the highest removal rate of copper ions. A D.C. voltage was applied not only in two electrodes but also in the electromembranes which had been connected to the power supply. The membrane which had been charged positively was positive electreomembrane. Oppositely, the membrane which had been charged negatively was negative electromembrane. More detail about this Separation Cell Unit has been shown in Fig. 1.

When the electrical current passed through the system, the cations, copper ions, tended to migrate toward the cathode and the anions, nitrate ions, tended to migrate toward the anode due to electrophoresis. The positive electromembrane had a trend to permit the positively charged ions, copper ions to pass and to retain the negative nitrate ions behind. On the other hand, the negative electromembrane had a trend to permit the nitrate ions to pass and to retain the copper ions behind. The flux of copper ions through a electromembrane depended on how much of electrical current either positively or negatively charged on them. By adjusting the two variable resistances R and R different positive and negative electromembranes had been tested. The fluxes through different positive and negative electromembranes are listed in Table 22 and Table 23, respectively. The highest removal rate of copper ions can be reached if one selected a combination of a positive electromembrane with the highest flux of copper ions transfering through it and a negative electromembrane with the lowest flux of copper ions across it. At any operating voltage the P-EMR 1000 provided the largest flux. Because N-EMR 1000 had a little copper ions deposited on the surface of it after a long experiment time, the N-EMR 1500 was selected. These two charged electromembranes had been used through the following experimental runs to investigate some transfer phenomena of ions across electromembranes and to obtain the optimum operation conditions where the highest efficiency reached. Five runs of experiment were made here. The operating voltage of each run was kept the same as that of the equivalent run in the neutral electromembrane. The concentration changes of copper ions varied with time in each compartment of each run and are presented in Table 24,25,26,27, and 28. The removal rates, the concentration decrease in compartment 2, were read from the slopes of curves in Fig. 12. The fluxes through positive electromembrane on the left side of compartment 2 and the fluxes through negative electromembrane on the right side of compartment 2 are listed in Table 29. From Table 29, in combined positive and negative electromembranes process, the fluxes through P-EM is almost twenty times over those through N-EM; while the fluxes through n-EM on the left side is only two times over the other one on the right side in neutral electromembrane process. This is the major factor that affects the removal rates of compartment 2.

The removal rate and coulomb efficiency of each operating voltage are summarized in Table 30. Comparing attainable remove rate at the same operating voltage of two processes, neutral electromembrane and charged positive and negative electromembrane used simultaneously, for example, while the voltage is 15 volts, the remove rate is $6.05*10^{-3}$ $g/cm^2/hr$ in charged positively and negatively electromembrane; that in neutral electromembrane is $1.74*10^{-3}$ $g/cm^2/hr$, less than one third of former. One concludes that charged electromembrane process has the advantage of higher removal rate than neutral electromembrane process. The achievement of higher removal rate and efficiency in charged positively and negatively electromembrane process are shown in Fig. 13 and 14. From Fig. 14, three things are evident : (1). When the current density is 6.1 mA/cm^2, while operating voltage is 15 volts, one has the higest efficiency; (2). If the current density lower than 6.1 mA/cm^2, the higher the current density, the larger the removal rate, the larger efficiency; (3). The current density higher than 6.1 mA/cm^2 results in higher the current density, only a little increase in removal rate, but lower the efficiency. It is very interesting to observe the current density at 6.1 mA/cm^2 is a critical point. This current density can be considered as the limiting current density I_{lim}. As expected, at current density in excess of the I_{lim} little additional transfer of copper ions is obtained. The increment of current above the limiting values results mostly in conduction of hydrogen ions from the splitting of water, and in only a small amount of desired copper ions. Experimental results show a good agreemwnt with the above explanations. Considering the current density at 13.2 mA/cm^2 which is two times I_{lim}, the flux increases no more than 15% with respect to 6.05×10^{-3} g/cm^2/hr at I_{lim} 6.1 mA/cm^2. There is only a 0.53×10^{-3} g/cm^2/hr increment as the current density raises from 6.1 to 8.7 mA/cm^2. Thus, the separating Cell Unit had better operation under limiting current density to obtain the highest efficiency, also to avoid concentration polarization occuring.

C. Efficiency Comparison and Economic Analysis of the Electromembrane

In Moore's liquid ion exchange membranes, the fluxes of potassium and sodium have been estimated to be respectively 6.63×10^{-5} and 4.30×10^{-5} g/cm^2/hr. These fluxes are 100 times smaller than those obtained using a positive electromembrane (corresponding to a flux of 6.3×10^{-3} g/cm^2/hr at 0.195A and 15 volts). A typical commercial electrodialysis in Reed's[25] report provides a flux of 2.24×10^{-4} g/cm^2/hr, only one-thirtieth of the positive electromembrane's

The energy consumption calculated by Eq. (14) for a typical positive electromembrane operating at 15 volts and two other separation processes are also presented in Table 31. This shows that the charged electromembrane is the most economic process, consuming less than one half the energy of Kim's[16] electrolytic deposition method to remove one gram of copper.

CONCLUSIONS

The Electromembrane process is a new separation method for rapidly removing metal ions from wastewater by means of electrically chargeable membranes and low voltage direct current.

The diffusional flux through the electromembrane due to a concentration gradient has been measured to be 5×10^{-5} $g/cm^2/hr$ for a concentration difference of 1500 ppm or 2.5×10^{-5} $g/cm^2/hr$ for a concentration difference of 1000 ppm. This flux is so small in comparison with the flux due to the electric field (6×10^{-3} $g/cm^2/hr$) that one can neglect the diffusional flux.

The flux of copper ions through an electromembrane depends on the sign of the applied DC voltage. The positive electromembrane (P-EM) will exhibit a larger flux than the neutral electromembrane (n-EM) (to which no change is applied). In turn, the n-EM has a larger flux than the negative electromembrane (N-EM). The P-EMR1000 membrane has the largest flux among charged electromembranes at the same operating conditions. The flux through P-EMR1000 membrane is 6.35×10^{-3} $g/cm^2/hr$ at 15 volts, which is thirty times the flux of an ion-exchanger membrane (Which is 2.24×10^{-4} $g/cm^2/hr$ in commercial electrodialysis), and one hundred times the flux of Moor's liquid membrane. In addition, the removal rate of the charged electromembrane process is almost two times Kim's result of 3.24×10^{-3} $g/cm^2/hr$ using electrolytic deposition.

For a combined P-EM and N-EM separation process, the removal rate of copper ions has reached 6.05×10^{-3} $g/cm^2/hr$, with an optimum operating current of 0.193 A and electric field strength of 15 volts. In addition, the charged electromembrane is also an economic separation process. For removing one gram of copper, the charged electromembrane process consumes less than one half the energy of Kim's[16] method.

A batch type separation Cell Unit has been designed and operated in the present work. However, in practical industrial separation processes, a continuous process must be used in order to save capital and operating costs. Further study will be to develop the fundamental equations for the design of continuous equipment.

TABLE 1

Characteristics of Electrolytic Deposition and Electromembranes Process

	Electrolytic Deposition	Electromembrane
Metal Removal	Deposited on cathode before going through separator	Metal ion transfer through positive electromembrane
Characteristics	Pure water going through seperator	Metal ion going through membrane
Cake Formation	Yes	No
Electrodes	Carbon fibers	Metal
Electrode Replacement	Difficult	Easy
Recommendation	Metal without sludge	Metals with sludge

Taken from C-C, Lin's proposal at N.J.I.T.

Table 2

Concentration Change of Copper Ions Due to Concentration Gradient

	Concentration of copper ions in solution					
Time	Compartment 1		Compartment 2		Compartment 3	
(hr.)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
0	0	0	1.050	1500	0	0
0.5	0	0	1.050	1500	0	0
1	0	0	1.050	1500	0	0
1.5	0	0	1.050	1500	0	0
2	0	0	1.048	1497	0.001	2
2.5	0.001	2	1.046	1495	0.002	3
3	0.001	2	1.046	1495	0.002	3
4	0.002	3	1.046	1495	0.002	3
5	0.002	3	1.046	1495	0.002	3
7	0.002	3	1.046	1495	0.002	3
10	0.004	5	1.043	1490	0.004	5
12	0.004	5	1.043	1490	0.004	5
15	0.007	10	1.039	1485	0.007	10
20	0.010	15	1.029	1470	0.010	15
25	0.021	30	1.015	1450	0.017	25

* Run 1, The initial concentration difference is 1500 P.P.M.

Table 3

Concentration Change of Copper Ions Due to Concentration Gradient

	Concentration of copper ions in solution					
Time	Compartment 1		Compartment 2		Compartment 3	
(hr.)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
0	0.350	500	1.050	1500	0.350	500
0.5	0.350	500	1.050	1500	0.350	500
1	0.350	500	1.050	1500	0.350	500
1.5	0.350	500	1.050	1500	0.350	500
2	0.350	500	1.050	1500	0.350	500
2.5	0.351	501	1.048	1497	0.351	501
3	0.351	501	1.048	1497	0.351	501
4	0.351	501	1.048	1497	0.351	501
5	0.351	502	1.046	1495	0.351	502
7	0.351	502	1.046	1495	0.351	502
10	0.352	503	1.045	1495	0.352	503
12	0.352	503	1.045	1495	0.352	503
15	0.352	503	1.043	1490	0.354	505
20	0.355	507	1.040	1485	0.356	508
25	0.358	510	1.035	1480	0.358	510

* Run 2, The initial concentration difference is 1000 P.P.M.

Table 4

Flux Through Electromembrane Due to Concentration Gradient

Time (hr.)	Δ C (P.P.M.)	Flux $\times 10^5$ (g/cm^2/hr)	C_t (P.P.M.)	$D_{app} \times 10^7$ (cm^2/hr)
0	0	0	1500	0
0.5	0	0	1500	0
1	0	0	1500	0
1.5	0	0	1500	0
2	2	9.46	1497	2.11
2.5	3	11.36	1495	2.53
3	3	9.46	1495	2.11
4	3	7.10	1495	1.58
5	3	5.68	1495	1.27
7	3	4.06	1495	0.91
10	5	4.73	1490	1.05
12	5	3.94	1490	0.90
15	10	6.31	1485	1.42
20	15	7.10	1470	1.61
25	25	9.46	1450	2.11

* The area of the membrane A = 6.1 * 5.2 cm = 31.7 cm^2

* The thickness of the membrane d = 0.01 cm

* Run 1, The initial concentration difference is 1500 P.P.M.

Table 5

Flux Through Electromembrane Due to Concentration Gradient

Time (hr.)	ΔC (P.P.M.)	Flux$\times 10^{5}$ (g/cm^2/hr)	C_t (P.P.M.)	$D_{app}\times 10^{7}$ (cm^2/hr)
0	0	0	1500	0
0.5	0	0	1500	0
1	0	0	1500	0
1.5	0	0	1500	0
2	0	0	1500	0
2.5	1	3.78	1497	8.43
3	1	3.15	1497	7.02
4	1	2.36	1497	5.28
5	2	3.78	1495	8.44
7	2	2.70	1495	6.03
10	3	2.84	1493	6.34
12	3	2.70	1493	6.03
15	5	3.15	1490	7.05
20	8	3.78	1485	8.48
25	10	3.78	1480	8.51

* The area of the memgrane A = 6.1 * 5.2. cm = 31.7 cm^2

* The thickness of the membrane d = 0.01 cm

* The initial concentration difference is 1000 P.P.M.

Table 6

Concentration Change of Copper Ions Through Neutral Electromembrane Due to Electric Field

	Concentration of copper ions in solution					
Time	Compartment 1		Compartment 2		Compartment 3	
(min)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
0	0	0	1.050	1500	0	0
15	0.003	5	1.046	1495	0	0
30	0.007	10	1.043	1490	0	0
45	0.011	17	1.036	1480	0	0
60	0.016	22	1.036	1480	0	0
90	0.021	32	1.029	1470	0	0
120	0.032	45	1.022	1460	0	0
150	0.041	60	1.009	1440	0	0

* Electric Field strength = 10 Volts

Table 7

Concentration Change of Copper Ions Through Neutral Electromembrane Due to Electric Field

Time	Concentration of copper ions in solution					
	Compartment 1		Compartment 2		Compartment 3	
(min)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
0	0	0	1.050	1500	0	0
15	0.004	6	1.043	1490	0	0
30	0.012	17	1.041	1485	0	0
45	0.018	23	1.036	1480	0	0
60	0.021	32	1.029	1470	0	0
90	0.031	45	1.021	1460	0	0
120	0.045	65	1.008	1440	0	0
150	0 056	80	0.994	1420	0	0

* Electric field strenth = 15 Volts

Table 8

Concentration Change of Copper Ions Through Neutral Electromembrane Due to Electric Field

Time	Concentration of copper ions in solution					
	Compartment 1		Compartment 2		Compartment 3	
’min)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
0	0	0	1.050	1500	0	0
15	0.007	10	1.043	1490	0	0
30	0.014	20	1.041	1485	0	0
45	0.021	30	1.029	1470	0	0
60	0.031	45	1.022	1460	0	0
90	0.047	68	1.001	1430	0	0
120	0.063	90	0.987	1410	0	0
150	0.080	115	0.966	1380	0	0

* Electric field strenth = 20 Volts

Table 9

Concentration Change of Copper Ions Through Positive Electromembrane Due to Electric Field

		Concentration of copper ions in solution					
Electro-membrane	Time	Compartment 1		Compartment 2		Compartment 3	
	(min)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
P-EMR500	0	0	0	1.050	1500	0	0
	15	0.007	10	1.043	1490	0	0
	30	0.014	20	1.036	1480	0	0
	45	0.020	30	1.025	1465	0	0
	60	0.028	40	1.022	1460	0	0
	90	0.038	55	1.008	1440	0	0
	120	0.048	70	1.005	1435	0	0
	150	0.062	90	0.994	1420	0	0
P-EMR1000	0	0	0	1.050	1500	0	0
	15	0.010	15	1.036	1480	0	0
	30	0.015	21	1.036	1480	0	0
	45	0.024	35	1.030	1470	0	0
	60	0.031	45	1.022	1460	0	0
	90	0.045	65	1.001	1430	0	0
	120	0.062	90	0.987	1410	0	0
	150	0.076	110	0.970	1385	0	0
P-EMR2000	0	0	0	1.050	1500	0	0
	15	0.005	7	1.043	1490	0	0
	30	0.010	13	1.040	1485	0	0
	45	0.015	20	1.036	1480	0	0
	60	0.020	30	1 030	1470	0	0
	90	0.031	45	1.022	1469	0	0
	120	0.041	60	1.008	1440	0	0
	150	0.050	70	1.001	1430	0	0

* Electric field strength = 10 Volts

P-EMR500 : Positive Electromembrane Operating at R = 500 Ω

P-EMR1000: Positive Electromembrane Operating at R =1000 Ω

P-EMR2000: Positive Electromembrane Operating at R =2000 Ω

Table 10

Concentration Change of Copper Ions Through Positive Electromembrane Due to Electric Field

		Concentration of copper ions in solution					
Electro-membrane	Time	Compartment 1		Compartment 2		Compartment 3	
	(min)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
P-EMR500	0	0	0	1.050	1500	0	0
	15	0.010	15	1.043	1490	0	0
	30	0.017	25	1.030	1470	0	0
	45	0.028	40	1.001	1460	0	0
	60	0.038	55	1.015	1450	0	0
	90	0.055	80	0.994	1420	0	0
	120	0.076	110	0.973	1390	0	0
	150	0.090	130	0.960	1370	0	0
P-EMR1000	0	0	0	1.050	1500	0	0
	15	0.012	18	1.036	1480	0	0
	30	0.025	35	1.030	1470	0	0
	45	0.035	50	1.015	1450	0	0
	60	0.048	70	1.001	1430	0	0
	90	0.070	100	0.980	1400	0	0
	120	0.090	130	0.960	1370	0	0
	150	0.115	165	0.937	1340	0	0
P-EMR2000	0	0	0	1.050	1500	0	0
	15	0.007	10	1.043	1490	0	0
	30	0.015	20	1.036	1480	0	0
	45	0.020	30	1.030	1470	0	0
	60	0.028	40	1 022	1460	0	0
	90	0.041	60	1.008	1440	0	0
	120	0.054	80	0.994	1420	0	0
	150	0.070	100	0.980	1400	0	0

* Electric field strength = 15 volts

Table 11

Concentration Change of Copper Ions Through Positive Electromembrane Due to Electric Field

Concentration of copper ions in solution

Electro-membrane	Time	Compartment 1		Compartment 2		Compartment 3	
	(min)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
P-EMR500	0	0	0	1.050	1500	0	0
	15	0.015	20	1.036	1480	0	0
	30	0.025	35	1.022	1460	0	0
	45	0.038	55	1.008	1440	0	0
	60	0.050	70	1.001	1430	0	0
	90	0.072	105	0.973	1390	0	0
	120	0.098	140	0.962	1360	0	0
	150	0.125	175	0.931	1330	0	0
P-EMR1000	0	0	0	1.050	1500	0	0
	15	0.015	20	1.036	1480	0	0
	30	0.028	40	1.022	1460	0	0
	45	0.041	60	1.008	1440	0	0
	60	0.052	75	0.997	1425	0	0
	90	0.076	110	0.973	1390	0	0
	120	0.105	150	0.945	1350	0	0
	150	0.130	185	0.925	1320	0	0
P-EMR2000	0	0	0	1.050	1500	0	0
	15	0.010	15	1.040	1485	0	0
	30	0.020	30	1.030	1470	0	0
	45	0.035	50	1.015	1450	0	0
	60	0.045	65	1 001	1430	0	0
	90	0.070	100	0.980	1400	0	0
	120	0.090	130	0.960	1370	0	0
	150	0.115	165	0.931	1330	0	0

* Electric field strength = 20 volts

Table 12

Concentration Change of Copper Ions Through Negative Electromembrane Due to Electric Field

Electro-membrane	Time	Concentration of copper ions in solution					
		Compartment 1		Compartment 2		Compartment 3	
	(min)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
N-EMR1000	0	0	0	1.050	1500	0	0
	15	0.001	2	1.048	1498	0	0
	30	0.003	4	1.046	1495	0	0
	45	0.004	5	1.046	1495	0	0
	60	0.004	6	1.044	1493	0	0
	90	0.007	10	1.043	1490	0	0
	120	0.008	12	1.041	1488	0	0
	150	0.010	15	1.040	1485	0	0
N-EMR1500	0	0	0	1.050	1500	0	0
	15	0.003	4	1.046	1495	0	0
	30	0.006	6	1.044	1493	0	0
	45	0.006	9	1.043	1491	0	0
	60	0.008	12	1.041	1488	0	0
	90	0.012	18	1.038	1482	0	0
	120	0.016	23	1.032	1475	0	0
	150	0.021	30	1.029	1470	0	0
N-EMR2000	0	0	0	1.050	1500	0	0
	15	0.004	5	1.046	1495	0	0
	30	0.006	9	1.043	1490	0	0
	45	0.008	12	1.043	1490	0	0
	60	0.010	15	1 040	1485	0	0
	90	0.017	25	1.032	1475	0	0
	120	0.022	32	1.029	1470	0	0
	150	0.028	40	1.022	1460	0	0

* Electric field strength = 10 volts

N-EMR1000: Negative Electromembrane Operating at R =1000 Ω

N-EMR1500: Negative Electromembrane Operating at R =1500 Ω

N-EMR2000: Negative Electromembrane Operating at R =2000 Ω

Table 13

Concentration Change of Copper Ions Through Negative Electromembrane Due to Electric Field

		Concentration of copper ions in solution					
Electro-membrane	Time	Compartment 1		Compartment 2		Compartment 3	
	(min)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
N-EMR1000	0	0	0	1.050	1500	0	0
	15	0.001	2	1.048	1498	0	0
	30	0.003	4	1.046	1495	0	0
	45	0.004	5	1.046	1495	0	0
	60	0.005	7	1.044	1493	0	0
	90	0.008	11	1.041	1488	0	0
	120	0.010	15	1.040	1485	0	0
	150	0.014	20	1.026	1480	0	0
N-EMR1500	0	0	0	1.050	1500	0	0
	15	0.002	3	1.047	1497	0	0
	30	0.005	7	1.044	1493	0	0
	45	0.007	10	1.043	1490	0	0
	60	0.009	13	1.040	1485	0	0
	90	0.014	20	1.036	1480	0	0
	120	0.018	26	1.032	1475	0	0
	150	0.024	35	1.025	1465	0	0
N-EMR2000	0	0	0	1.050	1500	0	0
	15	0.004	5	1.046	1495	0	0
	30	0.007	10	1.043	1490	0	0
	45	0.009	13	1.040	1485	0	0
	60	0.014	20	1 036	1480	0	0
	90	0.021	30	1.029	1470	0	0
	120	0.024	35	1.025	1465	0	0
	150	0.031	45	1.015	1450	0	0

* Electric field strength = 15 volts

Table 14

Concentration Change of Copper Ions Through Negative Electromembrane Due to Electric Field

		Concentration of copper ions in solution					
Electro- membrane	Time	Compartment 1		Compartment 2		Compartment 3	
	(min)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
N-EMR1000	0	0	0	1.050	1500	0	0
	15	0.002	3	1.046	1495	0	0
	30	0.004	5	1.046	1495	0	0
	45	0.005	7	1.043	1490	0	0
	60	0.007	10	1.043	1490	0	0
	90	0.010	15	1.040	1485	0	0
	120	0.014	20	1.036	1480	0	0
	150	0.017	25	1.032	1475	0	0
N-EMR1500	0	0	0	1.050	1500	0	0
	15	0.004	5	1.046	1495	0	0
	30	0.007	10	1.043	1490	0	0
	45	0.010	15	1.040	1485	0	0
	60	0.014	20	1.036	1480	0	0
	90	0.021	30	1.029	1470	0	0
	120	0.028	40	1.022	1460	0	0
	150	0.035	50	1.015	1450	0	0
N-EMR2000	0	0	0	1.050	1500	0	0
	15	0.004	6	1.046	1495	0	0
	30	0.008	12	1.040	1485	0	0
	45	0.012	18	1.040	1485	0	0
	60	0.017	24	1 032	1475	0	0
	90	0.025	36	1.022	1460	0	0
	120	0.035	50	1.015	1450	0	0
	150	0.042	60	1.007	1440	0	0

* Electric field strength = 20 volts

Table 15

Flux Through Electromembranes Due to Electric Field

Electro-membrane	Operating Voltage (volts)	Current Density (mA/cm^2)	Flux × 10^3 ($g/cm^2/hr$)
n-EM	10	3.78	2.24
P-EM R500	10	3.95	3.47
P-EM R1000	10	4.23	4.24
P-EM R2000	10	3.90	2.78
N-EM R1000	10	3.50	2.54
N-EM R1500	10	3.60	1.12
N-EM R2000	10	3.75	1.54
n-EM	15	5.70	3.08
P-EM R500	15	6.05	5.19
P-EM R1000	15	6.16	6.35
P-EM R2000	15	5.92	3.93
N-EM R1000	15	5.50	0.73
N-EM R1500	15	5.60	1.31
N-EM R2000	15	5.65	1.77
n-EM	20	7.88	4.28
P-EM R500	20	8.48	6.51
P-EM R1000	20	8.75	6.88
P-EM R2000	20	8.56	6.14
N-EM R1000	20	7.60	0.93
N-EM R1500	20	7.75	1.78
N-EM R2000	20	7.80	2.23

Table 16

Concentration Change of Copper Ions Across Neutral Electromembrane Due to Electric Field

Time	Concentration of copper ions in solution					
	Compartment 1		Compartment 2		Compartment 3	
(min)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
0	0	0	1.050	1500	0.350	500
15	0.002	3	1.048	1498	0.348	498
30	0.004	6	1.047	1496	0.347	497
45	0.007	10	1.046	1495	0.347	496
60	0.009	13	1.044	1492	0.346	495
90	0.014	20	1.041	1488	0.346	492
120	0.018	26	1.040	1486	0.341	488
150	0.022	32	1.038	1483	0.340	485

* Electric Field Strength = 5 Volts

Table 17

Concentration Change of Copper Ions Across Neutral Electromembrane Due to Electric Field

Time	Concentration of copper ions in solution					
	Compartment 1		Compartment 2		Compartment 3	
(min)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
0	0	0	1.050	1500	0.350	500
15	0.004	6	1.046	1495	0.348	498
30	0.007	10	1.044	1492	0.346	495
45	0.012	18	1.043	1490	0.345	492
60	0.017	24	1.041	1485	0.343	490
90	0.024	34	1.036	1480	0.340	485
120	0.033	48	1.030	1472	0.336	480
150	0.040	58	1.029	1470	0.332	475

* Electric Field Strength = 10 Volts

Table 18

Concentration Change of Copper Ions Across Neutral Electromembrane Due to Electric Field

Time	Concentration of copper ions in solution					
	Compartment 1		Compartment 2		Compartment 3	
(min)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
0	0	0	1.050	1500	0.350	500
15	0.005	8	1.046	1495	0.346	496
30	0.011	16	1.043	1490	0.345	492
45	0.017	24	1.041	1485	0.343	490
60	0.022	33	1.036	1480	0.340	486
90	0.035	50	1.030	1472	0.335	478
120	0.045	65	1.025	1464	0.329	470
150	0.056	80	1.019	1455	0.325	465

* Electric Field Strength = 15 Volts

Table 19

Concentration Change of Copper Ions Across Neutral Electromembrane Due to Electric Field

Time	Concentration of copper ions in solution					
	Compartment 1		Compartment 2		Compartment 3	
(min)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
0	0	0	1.050	1500	0.350	500
15	0.008	12	1.043	1492	0.346	495
30	0.016	23	1.040	1486	0.343	490
45	0.024	35	1.036	1480	0.340	486
60	0.031	45	1.030	1472	0.337	482
90	0.047	68	1.020	1458	0.330	472
120	0.063	90	1.010	1444	0.325	464
150	0.080	115	1.000	1428	0.319	455

* Electric Field Strength = 20 Volts

Table 20

Concentration Change of Copper Ions Across Neutral Electromembrane Due to Electric Field

Time	Concentration of copper ions in solution					
	Compartment 1		Compartment 2		Compartment 3	
(min)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
0	0	0	1.050	1500	0.350	500
15	0.011	16	1.043	1490	0.346	494
30	0.022	32	1.036	1480	0.342	488
45	0.033	48	1.029	1470	0.337	482
60	0.045	64	1.022	1460	0.332	475
90	0.067	96	1.007	1440	0.323	462
120	0.090	128	0.994	1420	0.315	450
150	0.112	160	0.980	1400	0.306	437

* Electric Field Strength = 30 Volts

Table 21

Remove Rate of Copper Ionns in Neutral Electromembrane Process

Run	Operatin Voltage (Volts)	Current Density (mA/cm^2)	Remove Rate $*10^3$ (g/cm^2/hr)	Coulomb Efficiency (7%)
1	5	2.05	0.70	29
2	10	3.78	1.29	29
3	15	5.70	1.74	28
4	20	7.88	2.61	28
5	30	11.98	3.68	26

Table 22

The Flux Through Positive Electromembrane In Combined P-EM and N-EM Process

Positive Electro-membrane	External Conc. (P.P.M.)	Operating Voltage (Volts)	Current Density (mA/cm^2)	Flux $*10^3$ ($g/cm^2/hr$)
P-EMR500	1500	5	2.18	2.01
P-EMR1000	1500	5	2.35	2.40
P-EMR2000	1500	5	2.15	1.65
P-EMR500	1500	10	3.90	3.47
P-EMR1000	1500	10	4.20	4.24
P-EMR2000	1500	10	3.86	2.78
P-EMR500	1500	15	6.00	5.19
P-EMR1000	1500	15	6.10	6.35
P-EMR2000	1500	15	5.93	3.93
P-EMR500	1500	20	8.50	6.51
P-EMR1000	1500	20	8.70	6.88
P-EMR2000	1500	20	8.60	6.14
P-EMR500	1500	30	14.00	6.84
P-EMR1000	1500	30	13.20	7.17
P-EMR2000	1500	30	14.20	6.46

Table 23

The Flux Through Negative Electromembrane In Combined P-EM and N-EM Process

Positive Electro-membrane	External Conc. (P.P.M.)	Operating Voltage (Volts)	Current Density (mA/cm^2)	Flux $*10^3$ ($g/cm^2/hr$)
N-EMR1000	500	5	2.18	0.20
N-EMR1500	500	5	2.35	0.22
N-EMR2000	500	5	2.15	0.37
N-EMR1000	500	10	3.90	0.27
N-EMR1500	500	10	4.20	0.28
N-EMR2000	500	10	3.86	0.76
N-EMR1000	500	15	6.00	0.28
N-EMR1500	500	15	6.10	0.31
N-EMR2000	500	15	5.93	1.05
N-EMR1000	500	20	8.50	0.28
N-EMR1500	500	20	8.70	0.31
N-EMR2000	500	20	8.60	1.41
N-EMR1000	500	30	14.00	0.30
N-EMR1500	500	30	13.20	0.31
N-EMR2000	500	30	14.20	1.60

Table 24

Concentration Change of Copper Ions Across in Combined P-EM and N-EM Electromembrane Due to Electric Field

Time	Concentration of copper ions in solution					
	Compartment 1		Compartment 2		Compartment 3	
(min)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
0	0	0	1.050	1500	0.350	500
15	0.004	6	1.047	1496	0.349	499
30	0.009	13	1.043	1490	0.349	499
45	0.012	18	1.040	1485	0.349	498
60	0.018	25	1.037	1482	0.348	497
90	0.026	38	1.030	1471	0.347	496
120	0.034	49	1.024	1462	0.346	495
150	0.042	62	1.014	1452	0.345	494

* Electric Field Strength = 5 Volts

Positive Electromembrane used is P-EMR1000

Negative Electromembrane used is N-EMR1500

Table 25

Concentration Change of Copper Ions Across in Combined P-EM and N-EM Electromembrane Due to Electric Field

Time	Concentration of copper ions in solution					
	Compartment 1		Compartment 2		Compartment 3	
(min)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
0	0	0	1.050	1500	0.350	500
15	0.007	10	1.044	1491	0.349	499
30	0.013	20	1.036	1480	0.349	498
45	0.024	35	1.028	1468	0.348	497
60	0.031	45	1.021	1459	0.348	497
90	0.045	65	1.009	1439	0.346	495
120	0.063	90	0.995	1420	0.346	495
150	0.076	110	0.980	1400	0.343	490

* Electric Field Strength = 10 Volts

Positive Electromembrane used is P-EMR1000

Negative Electromembrane used is N-EMR1500

Table 26

Concentration Change of Copper Ions Across in Combined P-EM and N-EM Electromembrane Due to Electric Field

Time	Concentration of copper ions in solution					
	Compartment 1		Compartment 2		Compartment 3	
(min)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
0	0	0	1.050	1500	0.350	500
15	0.012	18	1.040	1486	0.349	499
30	0.024	35	1.030	1472	0.349	498
45	0.035	50	1.022	1460	0.348	497
60	0.049	70	1.008	1440	0.347	496
90	0.070	100	0.987	1410	0.346	495
120	0.087	125	0.970	1385	0.344	493
150	0.115	164	0.948	1355	0.343	490

* Electric Field Strength = 15 Volts

Positive Electromembrane used is P-EMR1000

Negative Electromembrane used is N-EMR1500

Table 27

Concentration Change of Copper Ions Across in Combined P-EM and N-EM Electromembrane Due to Electric Field

Time	Concentration of copper ions in solution					
	Compartment 1		Compartment 2		Compartment 3	
(min)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
0	0	0	1.050	1500	0.350	500
15	0.014	20	1.037	1483	0.349	499
30	0.028	40	1.025	1465	0.349	498
45	0.041	60	1.015	1450	0.348	497
60	0.055	80	1.001	1430	0.348	497
90	0.076	110	0.980	1400	0.346	495
120	0.105	150	0.952	1360	0.345	493
150	0.130	185	0.931	1330	0.343	490

* Electric Field Strength = 20 Volts

Positive Electromembrane used is P-EMR1000

Negative Electromembrane used is N-EMR1500

Table 28

Concentration Change of Copper Ions Across in Combined P-EM and N-EM Electromembrane Due to Electric Field

Time	Concentration of copper ions in solution					
	Compartment 1		Compartment 2		Compartment 3	
(min)	Absor.	P.P.M.	Absor.	P.P.M.	Absor.	P.P.M.
0	0	0	1.050	1500	0.350	500
15	0.014	20	1.035	1480	0.349	499
30	0.028	40	1.025	1464	0.348	498
45	0.041	60	1.012	1445	0.348	497
60	0.055	80	0.997	1425	0.348	497
90	0.084	120	0.973	1390	0.346	495
120	0.105	150	0.948	1355	0.345	493
150	0.133	190	0.924	1320	0.343	490

* Electric Field Strength = 30 Volts
Positive Electromembrane used is P-EMR1000
Negative Electromembrane used is N-EMR1500

Table 29

Flux Through Electromembrane in Separation Unit Cell

	Neutral Electromembrane			Charged Electromembrane		
Operating voltage (Volts)	Flux 1 $*10^{3}$	$\frac{\text{Flux 1}}{\text{Flux 2}}$	Flux 2 $*10^{3}$	Flux 3 $*10^{3}$	$\frac{\text{Flux3}}{\text{Flux4}}$	Flux 4 $*10^{3}$
5	1.26	2.26	0.56	2.4	10.76	0.223
10	2.24	2.36	0.95	4.24	14.93	0.284
15	3.08	2.30	1.34	6.35	20.89	0.304
20	4.28	2.56	1.67	6.88	22.63	0.304
30	6.08	2.53	2.40	7.17	23.59	0.304

Flux 1 = Flux across n-EM on the left side of compartment 2

Flux 2 = Flux across n-EM on the right side of compartment 2

Flux 3 = Flux across P-EM on the left side of compartment 2

Flux 4 = Flux across N-EM on the right side of compartment 2

* P-EM used is P-EMR1000 and N-EM used is N-ENR1500

Table 30

Remove Rate of Copper Ionns in Combined Electromembranes Process

Run	Operatin Voltage (Volts)	Current Density (mA/cm^2)	Remove Rate *10^3 (g/cm^2 /hr)	Coulomb Efficiency (7%)
1	5	2.35	2.18	62
2	10	4.2	3.98	77
3	15	6.1	6.05	80
4	20	8.7	6.58	61
5	30	13.2	6.87	40

* P-EM used is P-EMR1000 and N-EM used is N-EMR1500.

Table 31

Energy Consumption of Electromembrane

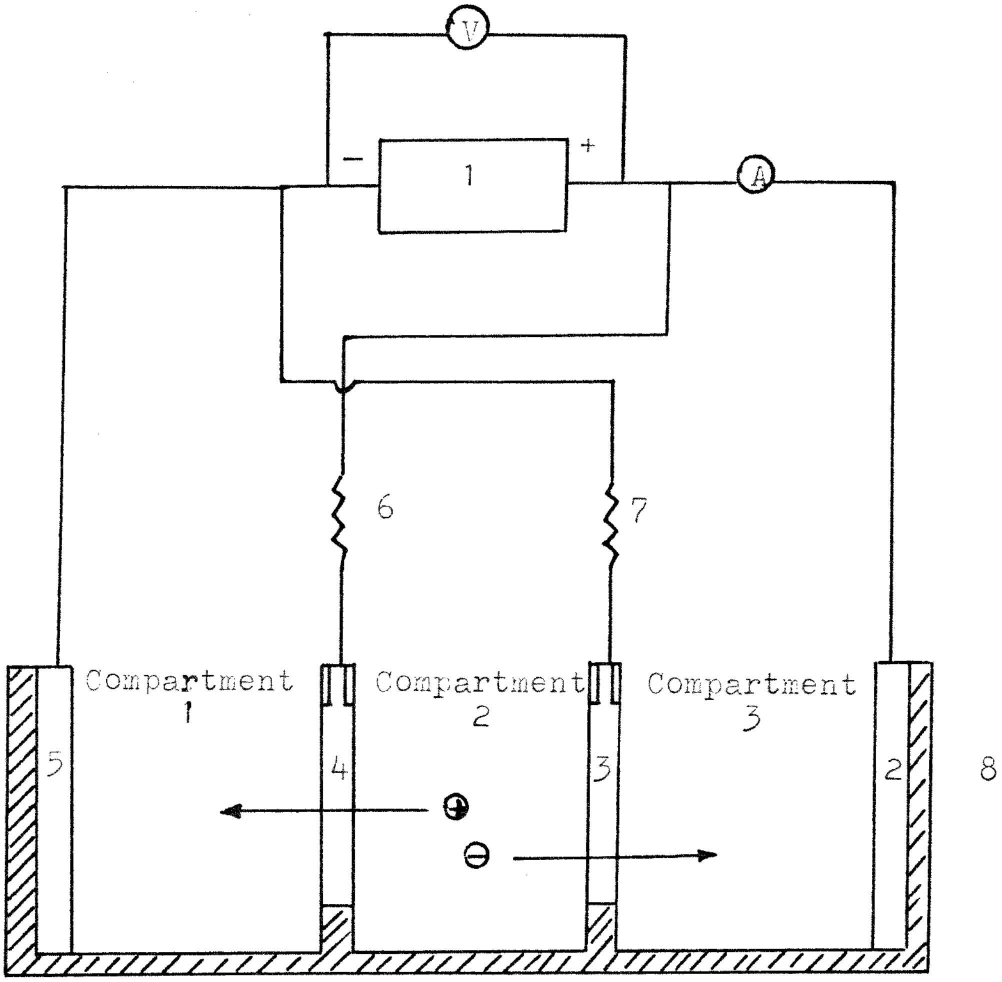
	Electrolytic Deposition (a)	Electodialysis (b)	Electromembrane P-EMR1000 (c)
Operating Voltage (volts)	12	2-8	15
Current Density (mA/cm^2)	6.7	10	6.1
Flux or Remove rate ($g/cm^2/hr$)	$3.24*10^{-3}$	$2.24*10^{-4}$	$6.05*10^{-3}$
Work power (d) (KW/cm^2)	$8.04*10^{-5}$	$2 *10^{-5}$	$9.15*10^{-5}$
Energy Consumption (kw-hr/g)	0.025	0.08	0.015

(a) Taken from Kim's report[16]

(b) taken from Reed's report[25]

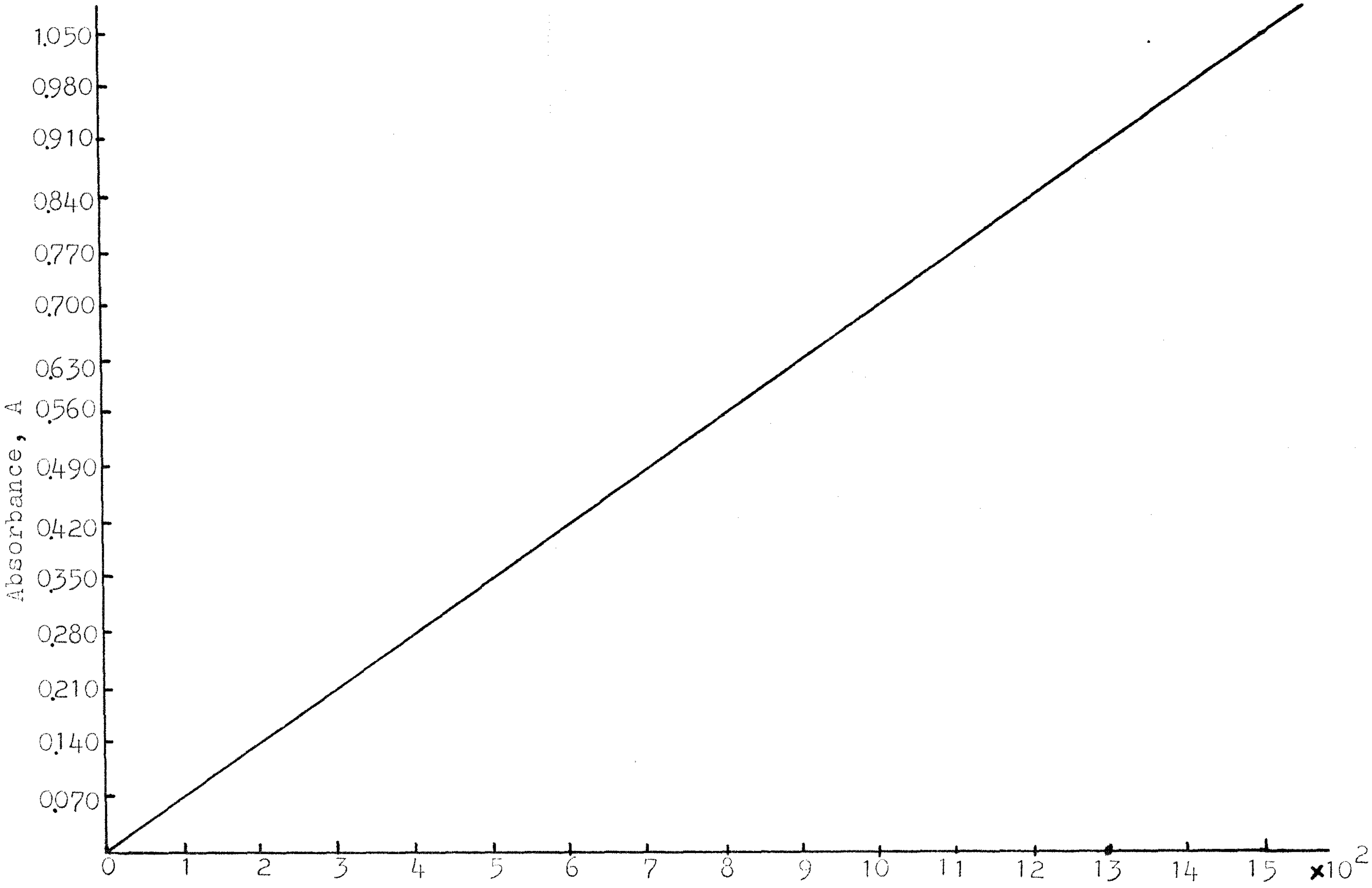
(c) Taken from this experiment

(d) Calculated by Eq.(14)



1	D.C. Power Suppiy	5	Cathode
2	Anode	6	Resistance R
3	Negative Electromembrane	7	Resistance R
4	Positive Electromembrane	8	Polyacylate Plate

Fig. 1 Electromembrane Separation Cell Unit



Concentration of Copper Ion, P.P.M.

Fig.2,Standard Absorbance Curve

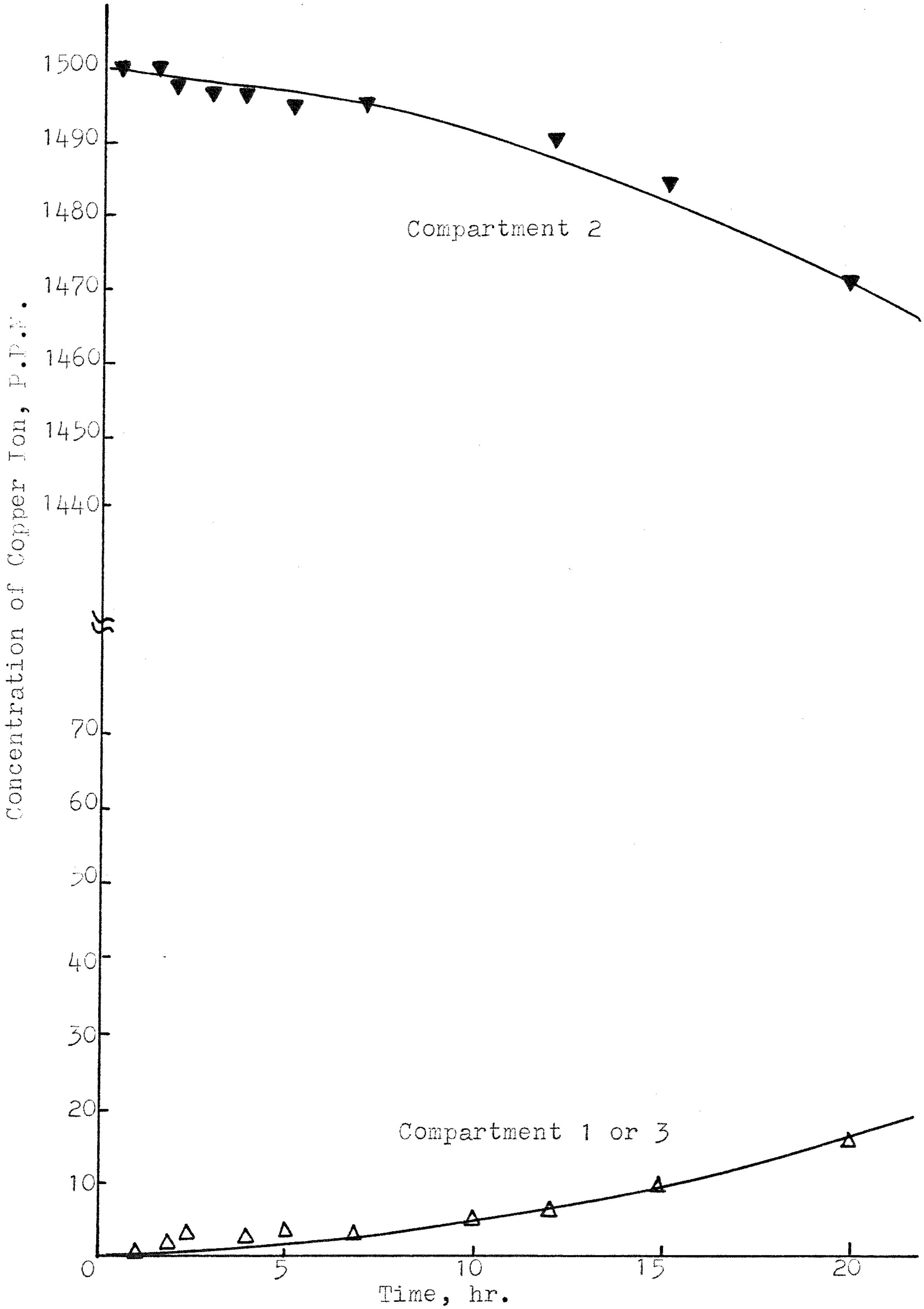


Fig. 3 Concentration of Copper Ion V.S. Time

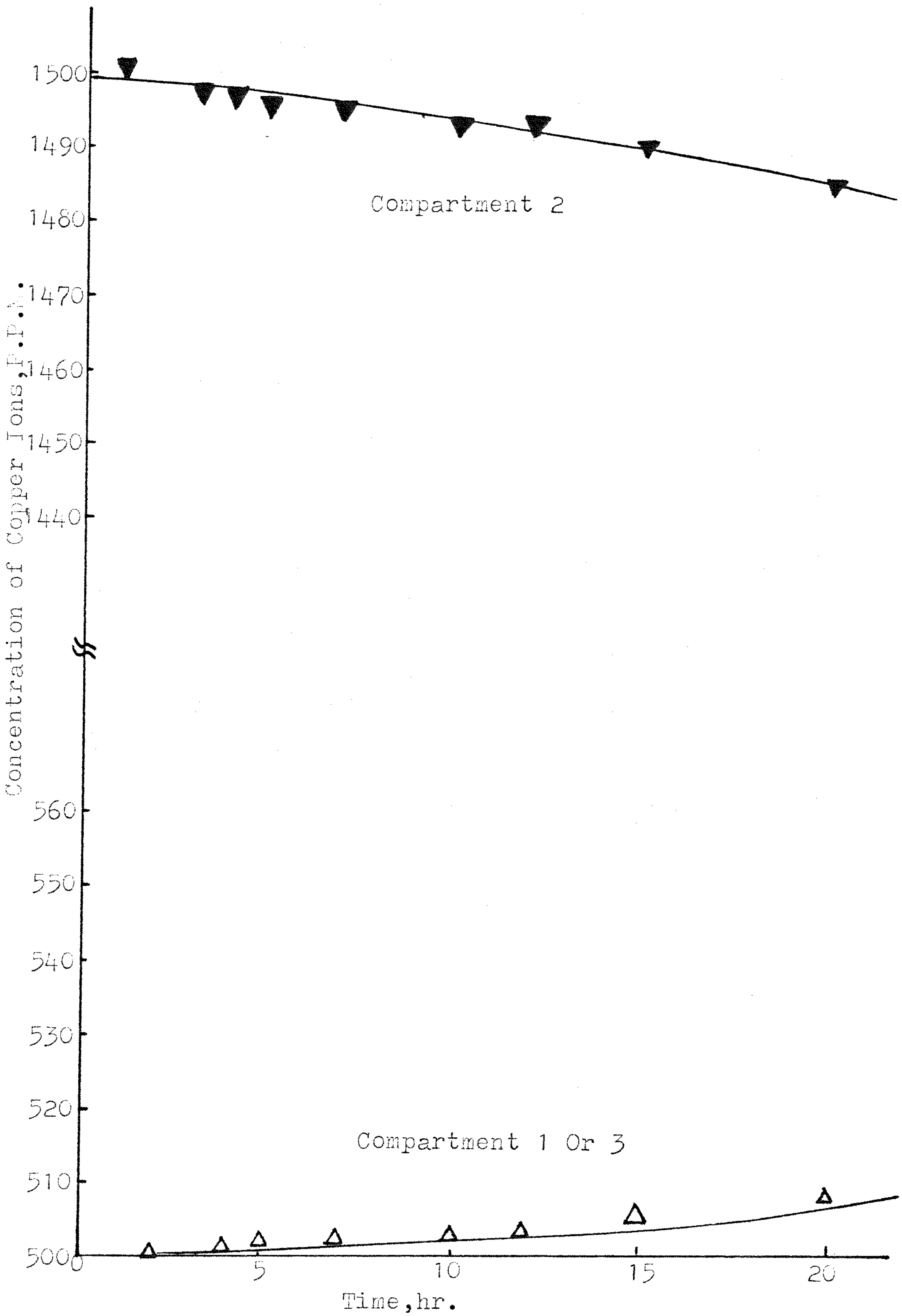


Fig. 4 Concentration of Copper Ions V.S. Time

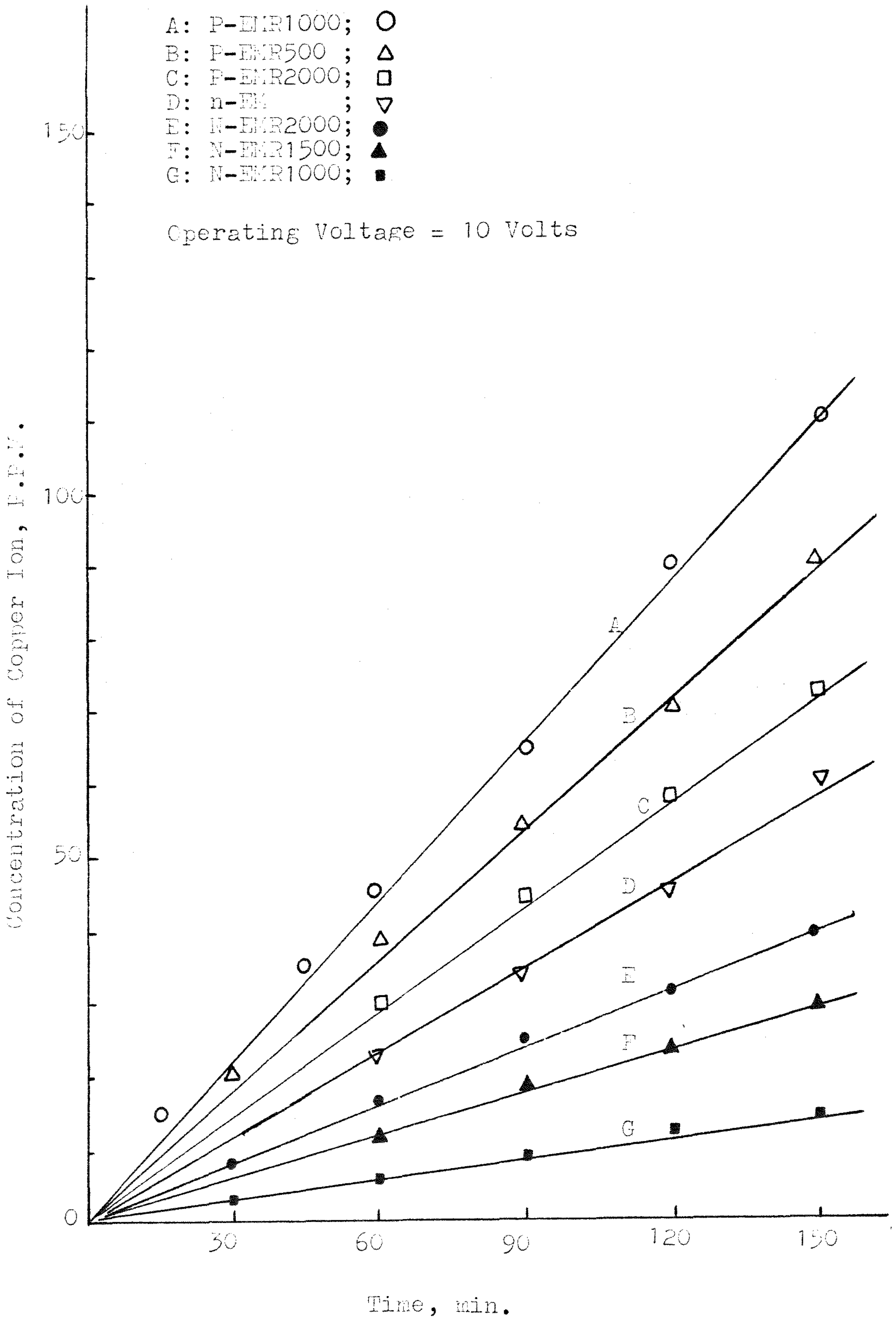


Fig. 5 Concentration Change of Copper Ion

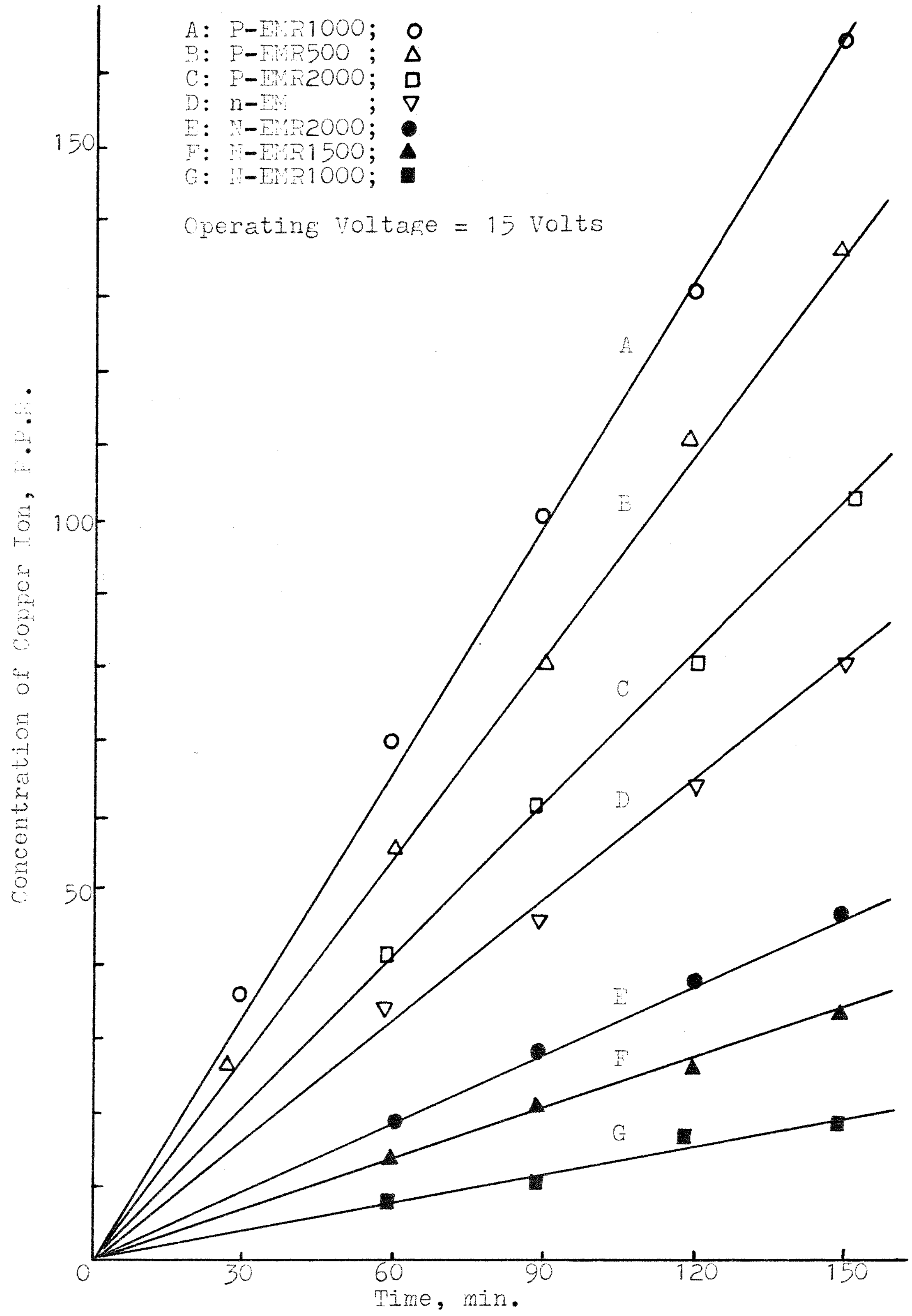


Fig. 6 Concentration Change of Copper Ion in Compartment 1

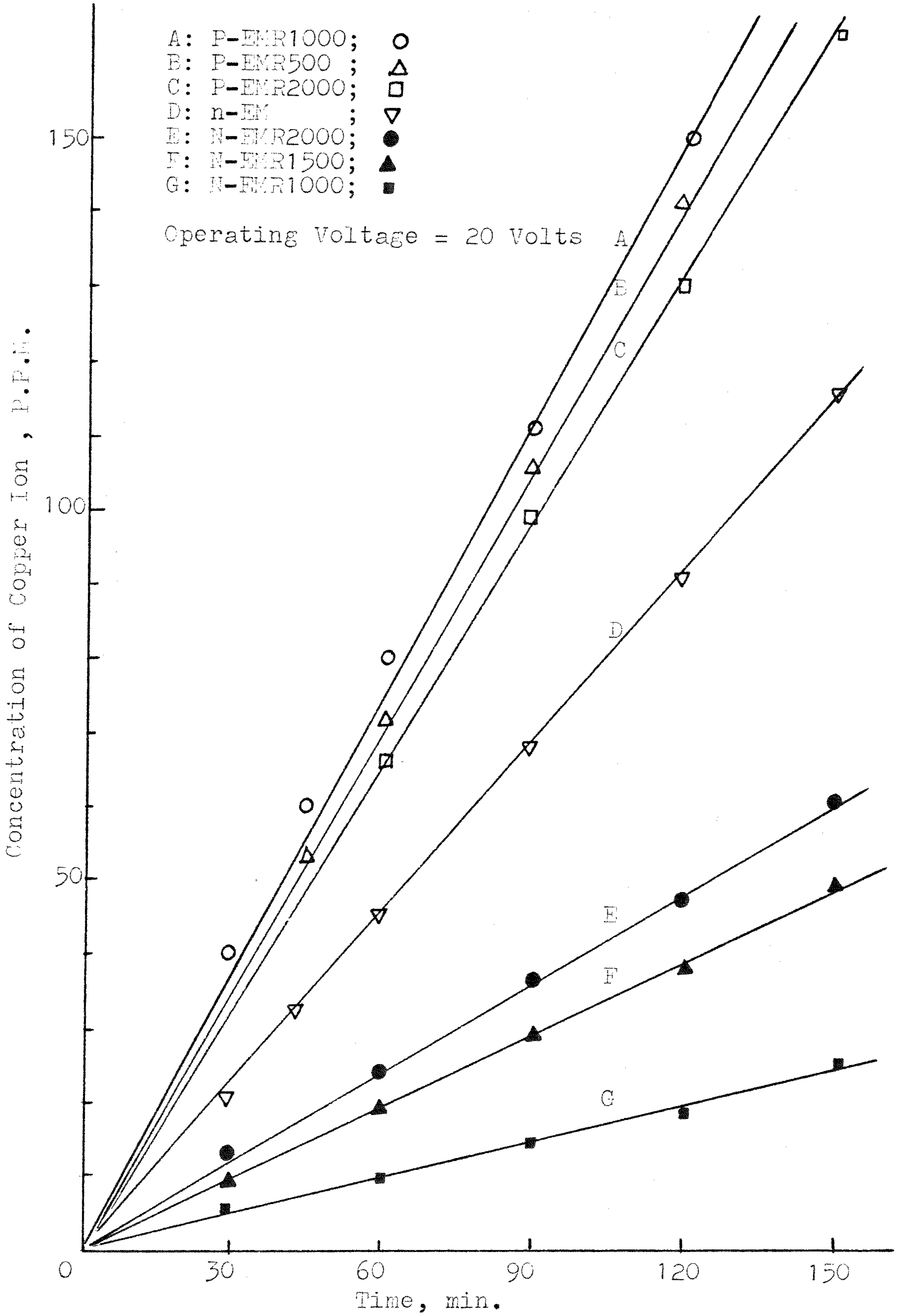


Fig. 7 Concentration Change of Copper Ion in Compartment 1

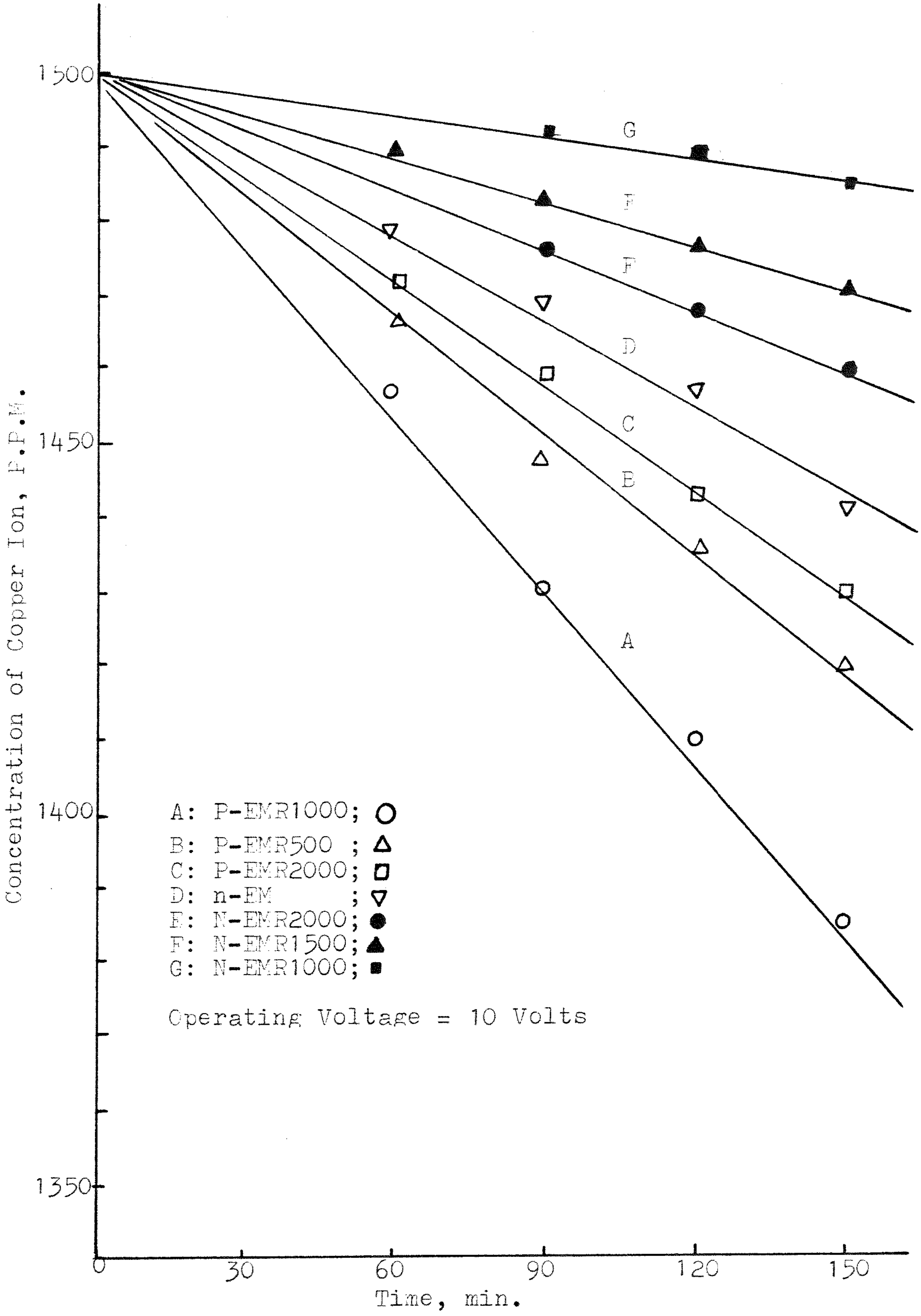


Fig. 8 Concentration Change of Copper Ion in Compartment 2

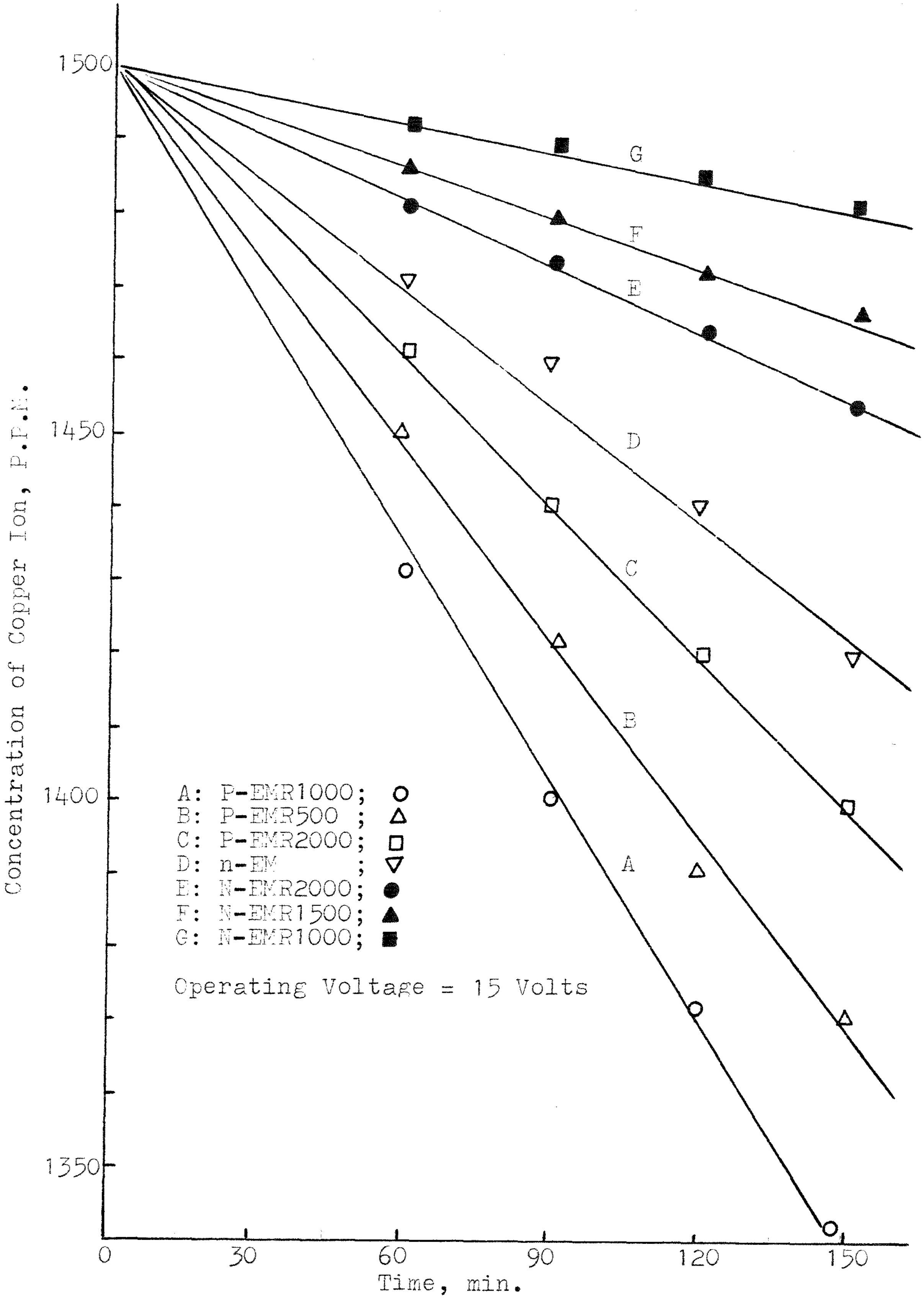


Fig. 9 Concentration Change of Copper Ion in Compartment 2

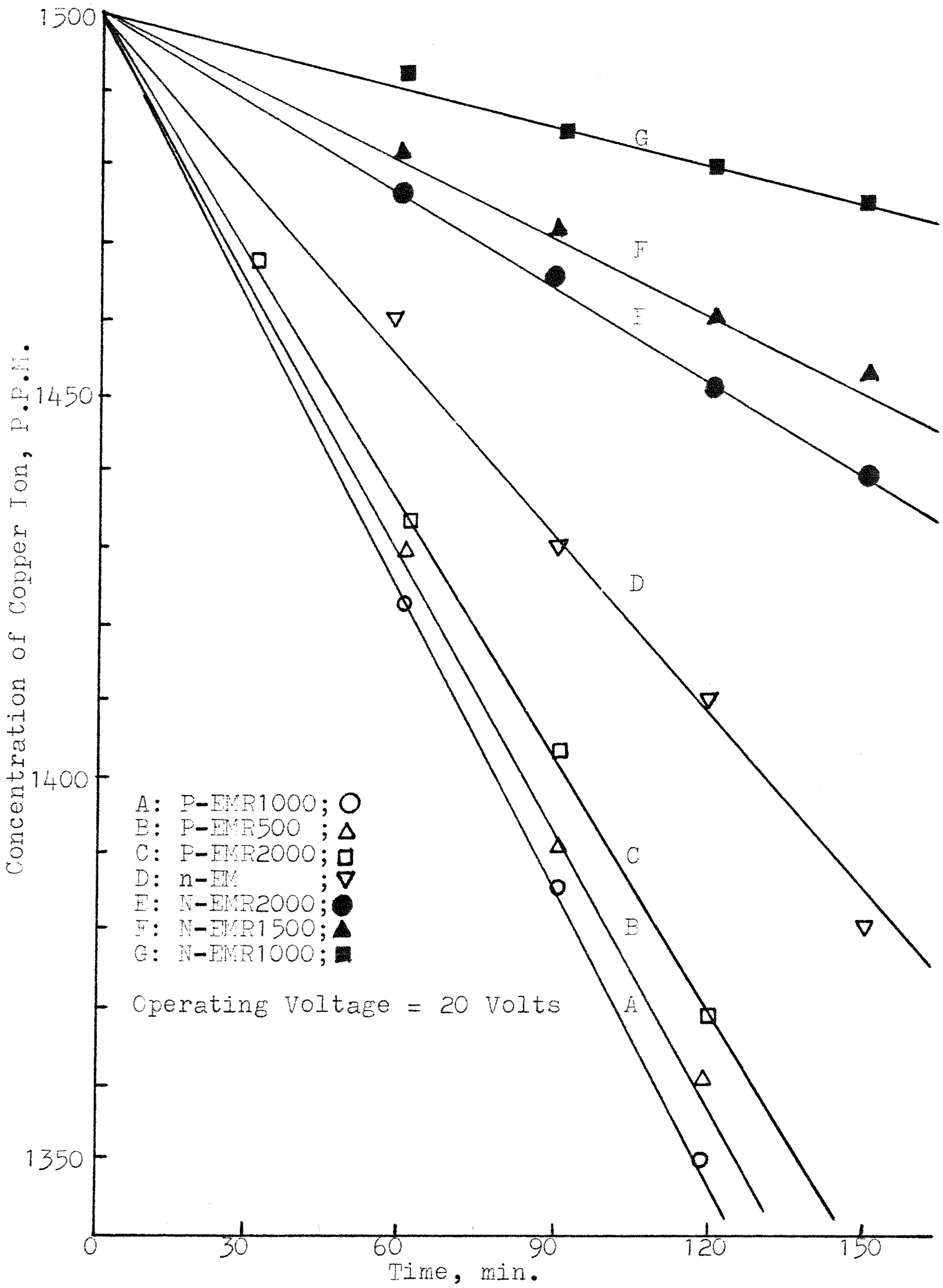


Fig. 10 Concentration Change of Copper Ion in Compartment 2

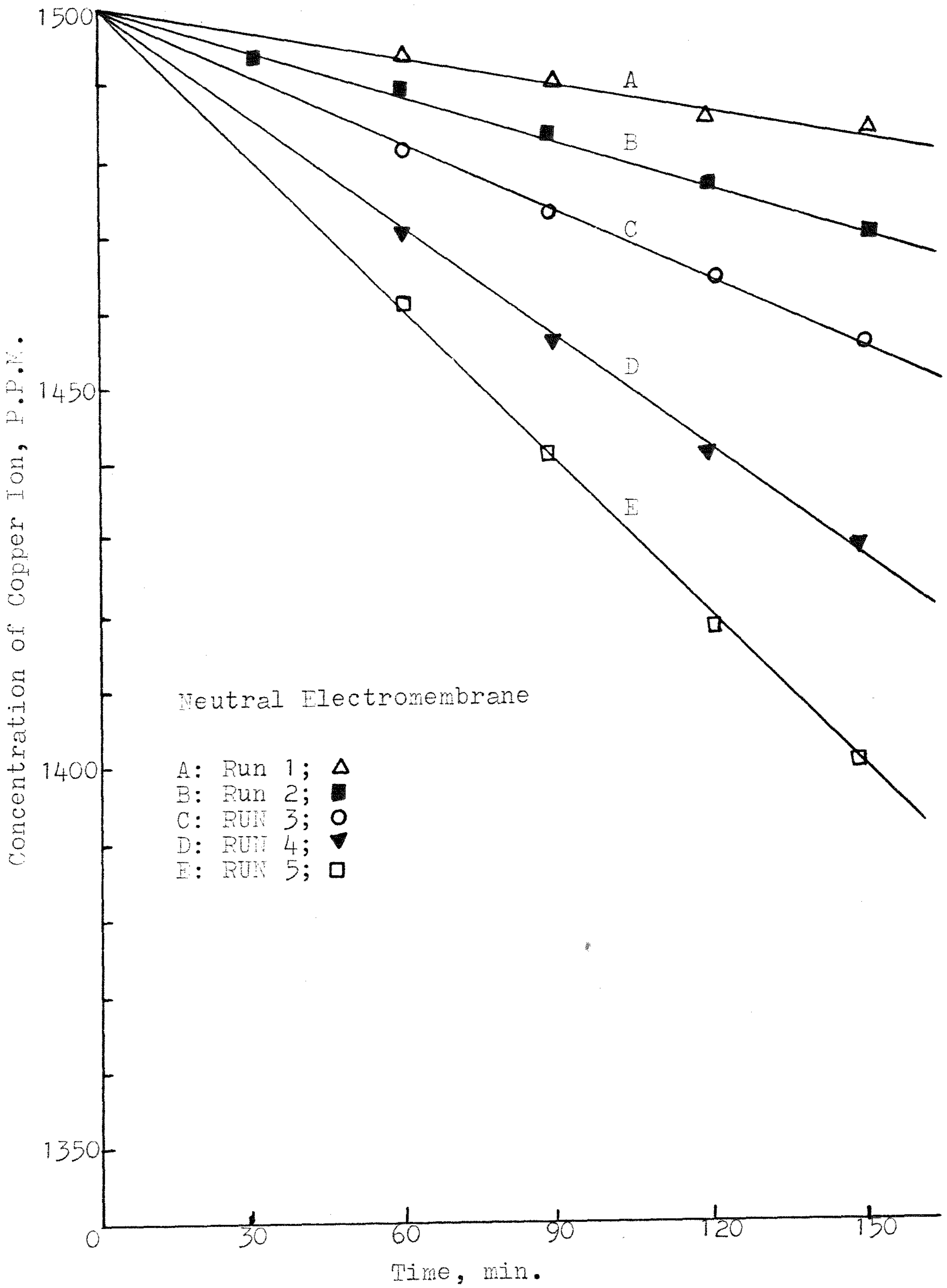


Fig. 11 Concentration Change of Copper Ion in Compartment 2

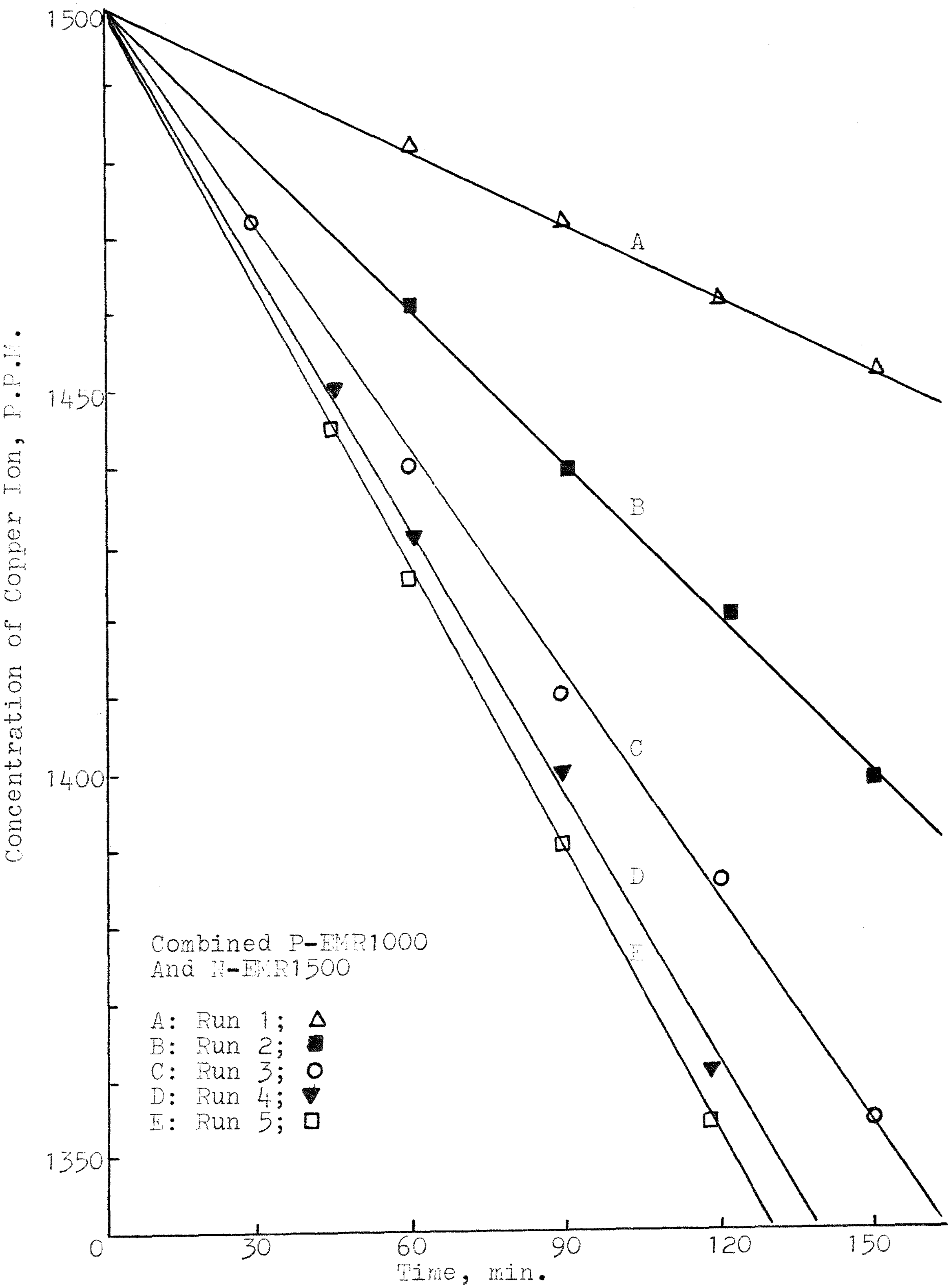


Fig. 12 Concentration Change of Copper Ion in Compartment 2

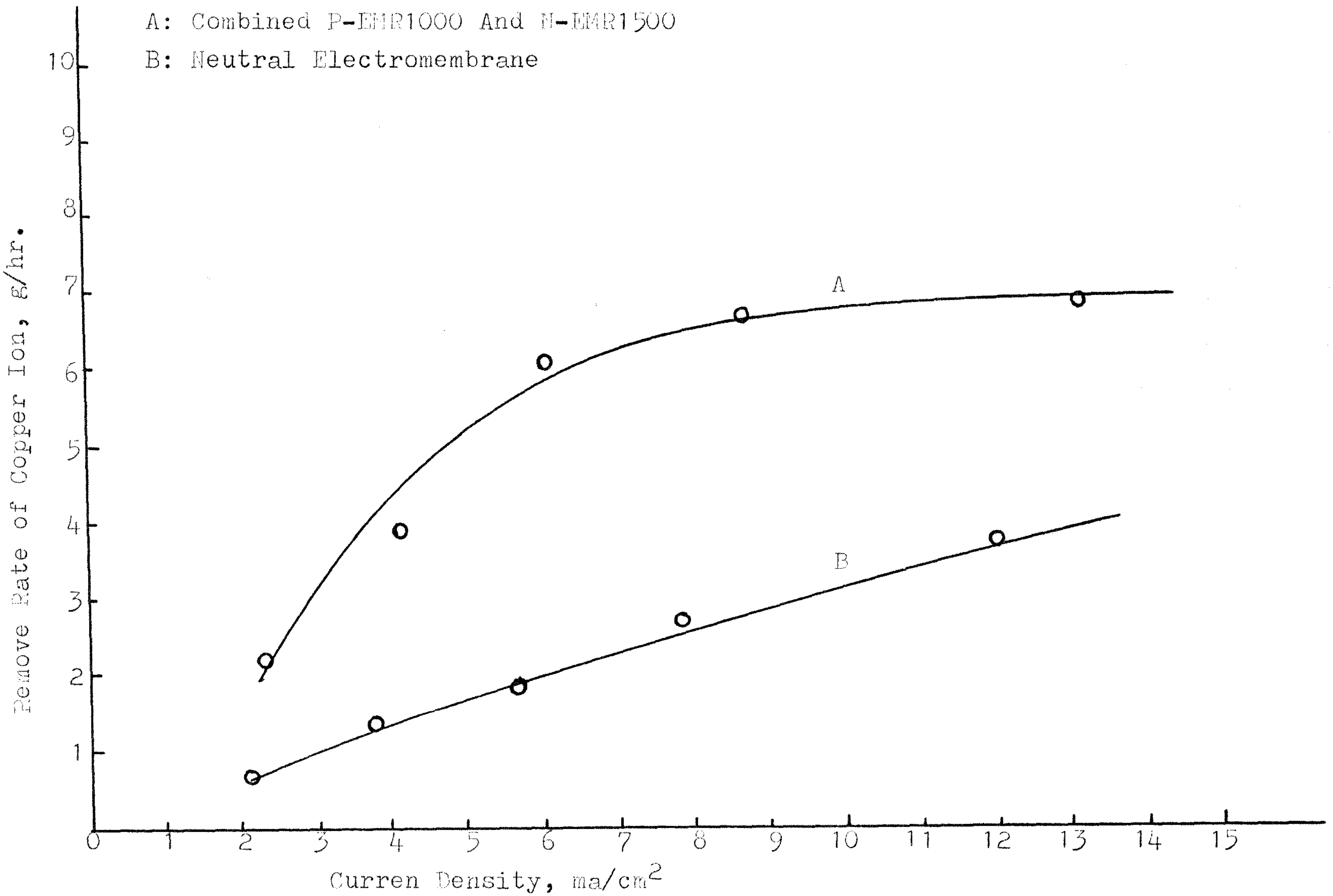


Fig. 13 Remove Rate as a Function of Current Density

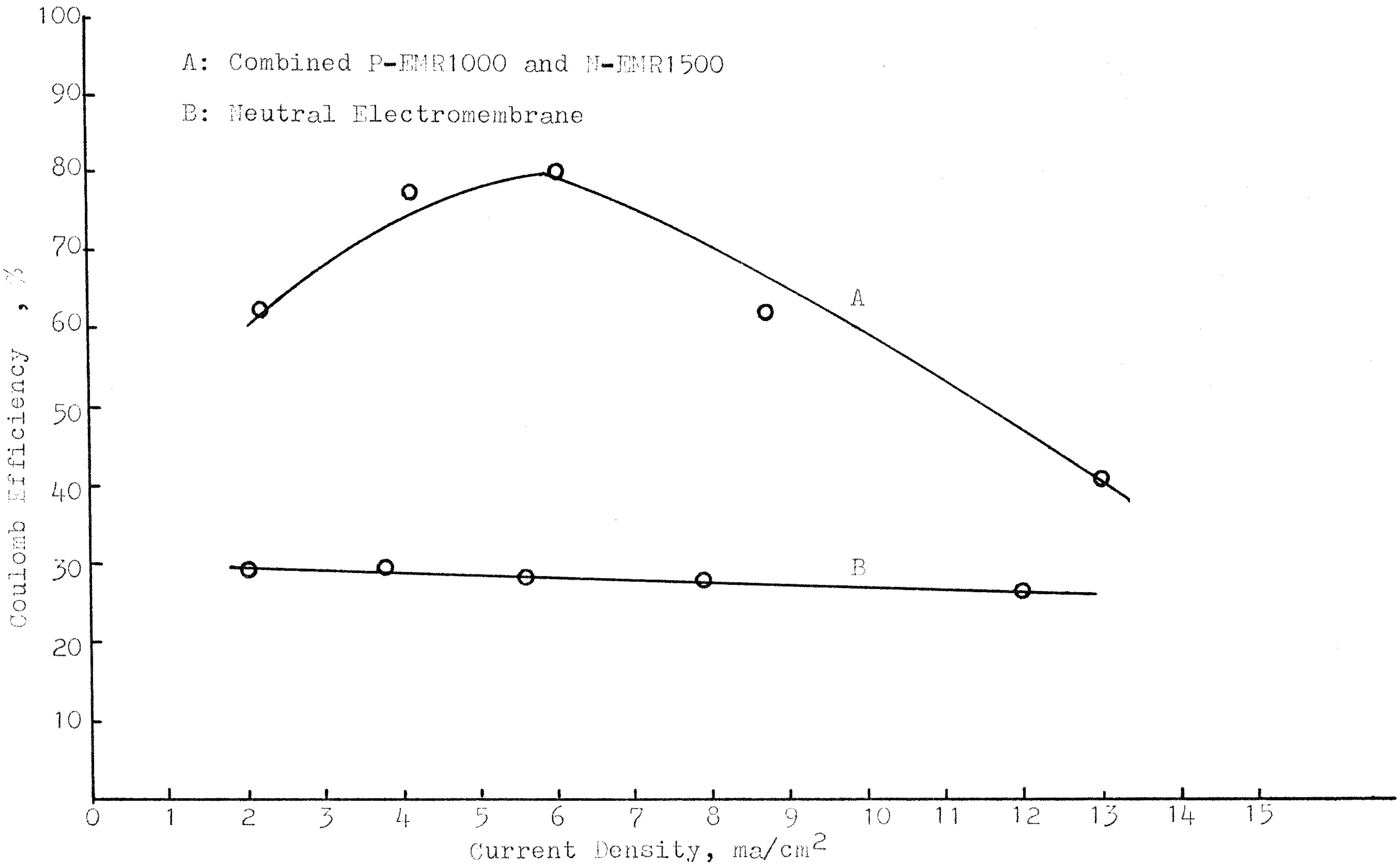


Fig. 14 Coulomb Efficiency as a Function of Current Density

ABBREVIATIONS

A	area of The membrane
a_+	activity of copper ion
C_+	concentration of copper ion
$\overleftarrow{D}_+(d)$	diffusion coefficient of copper ion
D_{app}	apparent diffusion coefficient
d	thickness of the membrane
E	energy consumption
F	Faraday's constant
I	current density
I_{lim}	limiting current density
$\overleftarrow{J}_+$	flux of copper ions across the membrane
$\overleftarrow{J}_+(d)$	flux caused by concentration diffusion
$\overleftarrow{J}_+(e)$	flux caused by electric field
M_+	mobility of copper ions in electric field
P	electric work power
R	remove rate of copper ions
U_+	velocity of copper ions in electric field
V	electric field strength
Z_+	charge of copper ions
η	coulomb efficiency

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