MONTANA STATE UNIVERSITY

Recovery of copper by biopolymer gel and polymer regeneration by electrowinning and ion exchange technologies

by Ramakrishna Raju Kallepalli

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Environmental Engineering

Montana State University

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Abstract:
Biopolymer gel beads of calcium alginate and alginic acid have high affinities for divalent metal ions such as Cu 2+. Hence they may be useful materials for recovering copper from aqueous solutions. The copper sorbed by the calcium alginate gel beads could be completely eluted and the metal recovered in a salable metallic form by using a combination of ion-exchange and electrowinning technologies. In such processes, the calcium alginate gel beads are fully regenerated. The resorption capacity of the gel beads did not decrease significantly during up to three sorption-desorption-electrowinning cycles. Distribution ratios of copper between the gel and liquid phases were measured using a batch method. Distribution ratios of copper for gel beads of calcium alginate ranged from 0.3 to 0.9 liter solution/gram dry sodium alginate [(mg Cu2+ / gram dry sodium alginate)/(mg Cu2+ / liter solution)]. Distribution ratios of copper for gel beads of alginic acid ranged from 0.47 to 0.84 liter solution/gram dry sodium alginate [(mg Cu 2+ / gram dry sodium alginate)/(mg Cu2+ / liter solution)]. The equilibrium data were consistent with the ion-exchange reaction between cupric ions and calcium alginate/alginic acid.

Maximum sorption capacities of the gel beads of calcium alginate and alginic acid were determined by comparing the experimental data with theoretical predictions. Maximum sorption capacities of the gel beads were found to be 5.21 X 10 -3 kmol/ kg dry sodium alginate and 4.11 X 10-3 kmol/ kg dry sodium alginate for calcium alginate and alginic acid respectively. 3.2% sodium alginate in water was used to make the gel beads of calcium alginate and alginic acid. Scale up of the technology was studied in a fluidized bed reactor and electrowinning cell designed for this purpose. Calcium alginate gel beads were reused up to three times for absorption of copper after regeneration using ion exchange and electrowinning technologies. This technology reduced the influent copper concentration by 63%.

RECOVERY OF COPPER BY BIOPOLYMER GEL AND POLYMER REGENERATION BY ELECTROWINNING AND ION EXCHANGE TECHNOLOGIES

by

Ramakrishna Raju Kallepalli

A thesis submitted in partial fulfillment
of the requirements for the degree

of

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in

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

Biopolymer gel beads of calcium alginate and alginic acid have high affinities for divalent metal ions such as Cu^{2+}. Hence they may be useful materials for recovering copper from aqueous solutions. The copper sorbed by the calcium alginate gel beads could be completely eluted and the metal recovered in a salable metallic form by using a combination of ion-exchange and electrowinning technologies. In such processes, the calcium alginate gel beads are fully regenerated. The resorption capacity of the gel beads did not decrease significantly during up to three sorption-desorption-electrowinning cycles. Distribution ratios of copper between the gel and liquid phases were measured using a batch method. Distribution ratios of copper for gel beads of calcium alginate ranged from 0.3 to 0.9 liter solution/gram dry sodium alginate [(mg Cu^{2+} / gram dry sodium alginate)/(mg Cu^{2+} / liter solution)]. Distribution ratios of copper for gel beads of alginic acid ranged from 0.47 to 0.84 liter solution/gram dry sodium alginate [(mg Cu^{2+} / gram dry sodium alginate)/(mg Cu^{2+} / liter solution)]. The equilibrium data were consistent with the ion-exchange reaction between cupric ions and calcium alginate/alginic acid.

Maximum sorption capacities of the gel beads of calcium alginate and alginic acid were determined by comparing the experimental data with theoretical predictions. Maximum sorption capacities of the gel beads were found to be 5.21×10^{-3} kmol/ kg dry sodium alginate and 4.11×10^{-3} kmol/ kg dry sodium alginate for calcium alginate and alginic acid respectively. 3.2% sodium alginate in water was used to make the gel beads of calcium alginate and alginic acid. Scale up of the technology was studied in a fluidized bed reactor and electrowinning cell designed for this purpose. Calcium alginate gel beads were reused up to three times for absorption of copper after regeneration using ion exchange and electrowinning technologies. This technology reduced the influent copper concentration by 63%.

STATEMENT OF GOALS AND OBJECTIVES

The main goal of this work was to develop a technology to recover copper from dilute aqueous solutions using alginate gel beads and to regenerate the copper saturated alginate gel beads for further use. The following seven objectives were set in developing the technology.

1) Measure the distribution ratios for copper between the gel and liquid phases with calcium alginate and alginic acid gel beads.

2) Determine the maximum sorption capacities of alginic acid and calcium alginate gel beads.

3) Based on maximum sorption capacity, select alginic acid or calcium alginate gel beads for copper recovery and alginate regeneration.

4) Evaluate regeneration of copper saturated alginic acid or calcium alginate gel beads by elution (ion exchange) with concentrated HCl or $CaCl_2$, respectively.

5) If step (4) is not sufficient to fully regenerate copper saturated alginic acid or calcium alginate, study the feasibility of regeneration by the simultaneous desorption and electrowinning of copper from the gel and liquid phases respectively.

6) Design a batch reactor for demonstration of the technology for regeneration.

7) Scale up of the alginate gel bead technology to a continuous fluidized bed reactor for absorption of copper and regeneration of the biopolymer.

INTRODUCTION

Many industries such as electroplating and printed circuit board industries (Wong et. al., 1993) discharge effluent containing relatively high levels of heavy metals. The toxicity of copper to microorganisms is well documented. In addition, even the presence of relatively low concentrations of Cu(II) in sewage could significantly reduce the efficiency of biological sewage treatment, such as the activated sludge process. Thus there is a need to remove Cu(II) from industrial effluents before biological treatment. The EPA discharge limit for Cu(II) for discharge to sewers is one mg/l (Farkas 1985).

Existing Technologies

The heavy metal removal technologies currently in use include chemical precipitation, electrowinning, and ion exchange processes. Chemical precipitation processes include alkaline-neutralization, carbonate, sulfide and organic precipitation processes.

Chemical precipitation is increasingly becoming inadequate, because of the high operating costs, high cost of sludge disposal, and the worldwide trend towards reducing heavy metal discharge limits. (Fries and Chew, 1993)

Electrolysis is an environmental friendly technology. Properly designed electrochemical processes need not produce unwanted effluents, use toxic or hazardous materials, or introduce hazards of their own. The wide applicability of Electrochemical cells (ECs) derives from the fact that the electron is a versatile reagent. Unlike standard

chemical reagents, electrons can be readily removed or added, without the byproducts of the reagents. Depending on the electrode potential, various chemical species can be either oxidized or reduced to convert them into profitably salable products (Pletcher and Weinberg, 1992). Electrowinning of copper is an age-old practice. About 15% of the copper produced is obtained by electrowinning (Cooper, 1985). However, all of the commercially available electrowinning processes are limited by low mass transfer rates at low metal concentrations and are prone to undesirable byproduct formation if higher current densities are used to enhance mass transfer rates. They are generally limited in removing metals to below 1000 mg/l (Farkas 1985).

Synthetic polymers such as ion exchange resins and chelating resins have been widely used as commercial sorbents to collect toxic metals, precious metals, base metals, and radio nuclides from aqueous solutions (Konishi et.al., 1993). The use of biopolymer as a new sorbent material for collecting various metal ions is getting increased attention because of their low production costs and their excellent selectivity for multivalent metal ions.

Biopolymer

The use by man of polymers for ion exchange has ancient history. Desalination of sea water by sands or soils was noted by Aristotle, but two thousand or so years elapsed before both Thompson and Way in 1850 reopened the investigation and for Wiegner in 1912 to show that the ability of soils to exchange cations was due in part to organic material in the form of humic acids. Kullgren in 1931 applied the ion-exchange

properties of a modified cellulose to an analytical purpose when he showed that unbleached sulphite wood pulp, i.e., sulphite cellulose, could quantitatively take up copper ions from water and that recovery of the metal ion could be achieved by washing with acid. Since the late 1950's, both cation and anion exchange cellulose, dextran and other seaweed polysaccharides have become commercially available with a variety of exchange groups secondarily substituted onto the polymer. (Hunt, 1986). These, however, found greatest use only in analytical and preparative biochemical work.

Many polymers of biological origin are known to bind metals, these include fungal biomass (Volesky, 1986), natural polymers from seafood processing waste (Yang and Zall, 1984), plant tissue (Scott, 1992), barks (Randall, 1977), sodium alginate (Jang et. al., 1990, 1991 and 1994),calcium alginate (Smisrød and Haug, 1968; Jang, et. al., 1990), alginic acid (Scweiger, 1961; Cozzi et. al., 1969; Konishi et. al., 1992 and 1993; Hassan, 1991 and 1993) immobilized cells (Wong, 1993), nonliving biomass of seaweed (Kuyucak and Volesky, 1989), and extracellular polymers from activated sludge (Rudd et. al., 1983).

Ion exchange properties of alginate are well documented. It is generally accepted that commercial cation-exchange resins have a maximum sorption capacity of approximately 5 X 10^{-3} kmol/kg resin. The maximum binding capacity of alginic acid gel particles (gelation by hydrogen ions) was evaluated as 3.78 X 10^{-3} kmol/kg dry gels (Konishi et. al., 1993). The maximum sorption capacity of sodium alginate (gelation by directly dispensing sodium alginate into copper solution) was 4.426 X 10^{-3} kmol/kg dry sodium alginate (Jang et. al., 1994). Thus, sodium alginate compares favorably with the

synthetic resins with respect to their maximum sorption capacity.

The low cost of sodium alginate (gel-forming biopolymer produced from kelp) makes it an attractive alternative to existing technologies for metal removal. Technical grade sodium alginate is roughly $7.00/Kg (Multi-Chem Corporation, New Jersey) (Lewandowski et. al., 1992).

Biopolymer Regeneration

For the biopolymer technology to work at a large scale, regeneration of metal saturated alginate needs to be addressed. Otherwise, disposal of metal saturated alginate will be a huge problem in applying this technology. Though many researchers have demonstrated and used alginate for metal removal, very little has been done to address the regeneration of metal saturated alginate. Concentrated HCl solution was used to regenerate alginic acid after collecting zinc, cadmium and lanthanum from aqueous solutions(Konishi et.al., 1993).

This paper presents a novel scheme for treating dilute copper solutions based on ion-exchange properties of biopolymer and electrowinning technologies. This system removes the copper from dilute aqueous solutions, recovers copper in a salable metallic form and regenerates the biopolymer for further use. The distribution ratios of copper between gel and liquid phases were measured in a constant temperature batch reactor. The equilibrium data were then analyzed to determine maximum sorption capacity of gel particles of alginic acid and calcium alginate. Based on maximum sorption capacities, calcium alginate gel beads were selected for further use for metal absorption and

regeneration. It was demonstrated that the calcium alginate beads can be fully regenerated and used a number of times.

THEORY

Ion Exchange

Ion exchange processes are used to remove undesirable ions from water and wastewater. The exchange medium consists of a solid phase of naturally occurring materials of a synthetic resin having a mobile ion attached to an immobile functional group. In the exchange process the mobile ions are exchanged with solute ions having a stronger affinity for the functional groups (e.g., Ca^{2+} replaces Na^{+} or Cu^{2+} replaces Ca^{2+}).

Selectivity

Affinity of ions for the functional groups, in general, is a function of charge and size. Ions with a larger ionic charge (e.g., Ca^{2+} versus Na^{+}) have greater affinity, and therefore, the equilibrium will favor the higher-charged ion in the solid phase. Affinity varies inversely with effective size. Therefore ions that are highly hydrated, and consequently have a larger effective size, have relatively less affinity for functional groups.

Alginate

Alginates are naturally occurring copolymers consisting of linear chains of 1,4 linked β-D-manuronic (M) and α-L-guluronic (G) acid residue. (Smisrød et. al., 1990). Their unbranched chains display acidic subunits of varying block lengths, proportions and

sequences depending on the organism from which the alginate was obtained. The monomers are arranged in a pattern of blocks along the chain, with homopolymeric regions (termed M and G blocks) interspersed with regions of alternating structure (MG blocks). The formulae for alginic acid, sodium alginate and uronic acid are $(C_6H_8O_6)_n$, $(C_6H_7O_6Na)_n$ and $C_6H_{10}O_7$ respectively (Jang, et. al., 1990). Each copper/calcium binding site involves two carboxyl groups on neighboring uronate residues and each hydrogen ion binding site involves one carboxyl group on uronate residue.

Alginate gels consist of chains of alginate cross-linked with monovalent or divalent ions. The strongest bonds with divalent metal ions are formed at G-block locations. The relative stability of metal alginate complexes decreases in the order: $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Co^{2+} = Ni^{2+} = Zn^{2+} > Mn^{2+}$ (Smisrød et. al., 1990). Metals higher in the affinity series can replace metals lower in the series, thus creating new metal alginate.

The affinity of alginic acid for homologous ions of the periodic table can be correlated with the size of the hydrated ionic radius and decreases in the following order: Ba > Sr > Ca > Mg = Cd > Zn (Konishi et. al., 1993). The factors affecting the capacity and affinity of a biopolymer to bind a metal from aqueous media include (1) the chemical nature of the metal ion (e.g., size, valence, electron orbital structure, and stable chemical forms in the nature) and the biopolymer (e.g., charge density and structure of the polymer chain, constituent sugar units and proteins, and functional groups), (2) environmental conditions (e.g., pH, temperature, ionic strength, and existence of competing organic or inorganic metal chelators), (3) morphology (e.g., orientation of metal binding groups,

sizes of the metal ion and metal binding groups, sizes of the metal ion and the metal-binding "cavity" formed by metal-binding groups, and the existence of stabilizing groups in the cavity), and the (4) thermodynamics of binding process (e.g., ordering effect that results in a decrease of entropy upon binding) (Jang, et. al., 1991).

Absorption

When the gel beads of calcium alginate or alginic acid act as a cation exchanger, the divalent cupric ion in the liquid phase exchanges with Ca^{2+} or $2H^{+}$ ions in the gel phase. The ion-exchange reaction is likely to be expressed as follows:

$$Cu^{2+} + \overline{CaX_2} \leftrightarrows \overline{CuX_2} + Ca^{2+} \qquad (1a)$$

or

$$Cu^{2+} + 2\overline{HX} \Leftrightarrow \overline{CuX_2} + 2H^{+} \qquad (1b)$$

where over scoring indicates that a species is present in the gel phase and X denotes functional groups(carboxyl groups). The equilibrium constants K_{cu} and K_{cu}^{1} for equations 1a and 1b are:

$$K_{Cu} = \frac{\overline{[CuX_2]}\ [Ca^{2+}]}{\overline{[CaX_2]}\ [Cu^{2+}]} \qquad (2a)$$

$$K_{Cu}^{1} = \frac{\overline{[CuX_2]}\ [H^+]^2}{\overline{[HX]^2}\ [Cu^{2+}]} \qquad (2b)$$

where square brackets indicate species concentration. The two equilibrium constants cannot be compared since the units are not the same. The distribution ratio D_{Cu} between the gel and liquid phases is defined as

$$D_{Cu} = \frac{\overline{[CuX_2]}}{[Cu^{2+}]} = \frac{(\ [Cu^{2+}]_{initial} - [Cu^{2+}]\ )\ V_L}{(W)\ [Cu^{2+}]} \qquad (3)$$

where W is the mass of dry sodium alginate used and V_L the volume of solution.

The combination of equations 2 and 3 gives

$$D_{Cu} = K_{Cu}\ \frac{\overline{[CaX_2]}}{[Ca^{2+}]} \qquad (4a)$$

$$D_{Cu} = K_{Cu}^{1}\ \frac{\overline{[HX]^2}}{[H^+]^2} \qquad (4b)$$

Since the functional groups in the gel phase are consumed for binding the cupric ions, the equilibrium concentration of free functional groups can be written using a mass balance on binding sites. For calcium alginate and alginic acid,

$$\overline{[CaX_2]} = \frac{Q_X}{2} - \overline{[CuX_2]} \tag{5a}$$

$$\overline{[HX]} = Q_X - 2\,\overline{[CuX_2]} \tag{5b}$$

where Q_X is the total concentration of functional groups in the gel phase, i.e., the maximum sorption capacity. Combining equations (4) and (5) gives

$$D_{Cu} = K_{Cu} \frac{\left(\frac{Q_X}{2} - \overline{[CuX_2]} \right)}{[Ca^{2+}]} \tag{6a}$$

$$D_{Cu} = K_{Cu}^{1} \frac{\left(Q_X - 2\,\overline{[CuX_2]} \right)^2}{[H^+]^2} \tag{6b}$$

The distribution ratios, D_{cu} in equations (6a) and (6b), are computed from the ratio of

copper concentration in the gel phase to copper concentration in solution at equilibrium. These concentrations are measured for each experiment separately. The unknown constant Q_X can be determined graphically by rearrangement of Eqn. (6) into the following form:

$$\overline{[CuX_2]} = -\left(\frac{1}{K_{Cu}}\right)\left(D_{Cu}\,[Ca^{2+}]\right) + \frac{Q_X}{2} \qquad (7a)$$

$$\overline{[CuX_2]} = -\frac{1}{2\left(K^1_{Cu}\right)^{(1/2)}}\left(D_{Cu}\right)^{(1/2)}[H^+] + \frac{Q_X}{2} \qquad (7b)$$

Thus, absorption of copper by calcium alginate should follow equation (7a), and a plot of $\overline{[CuX_2]}$ versus $D_{cu}[Ca^{2+}]$ should be linear with an intercept at $Q_X/2$ and a slope of $-(1/K_{Cu})$.

For copper absorption by alginic acid, equation (7b) applies, and a plot of $\overline{[CuX_2]}$ versus $D_{cu}^{(1/2)}[H^+]$ should be linear with an intercept at $Q_X/2$ and a slope of $-(1/2)(1/K^1_{Cu})^{(1/2)}$. The maximum sorption capacities (Q_x) of calcium alginate and alginic acid beads can thus be compared.

Desorption

Desorption follows the same ion exchange reactions as in (1a) and (1b). By driving these reactions in reverse, complete desorption can be obtained by increasing the concentration of free Ca^{2+} or H^{+} ions and/or simultaneously depleting the free Cu^{2+} ions in solution.

Substituting for D_{cu} from equation (3) into equation (7) we can get the copper concentration in gel beads of calcium alginate and alginic acid from equations 8a and 8b, respectively:

$$\overline{[CuX_2]} = \frac{Q_X}{2\left(1 + \frac{[Ca^{2+}]}{K_{Cu}\,[Cu^{2+}]}\right)} \tag{8a}$$

$$\left(\overline{[CuX_2]}\right)^2 + \left(\overline{[CuX_2]}\right)\frac{([H^{+}])^2}{4\,K^{1}{}_{Cu}\,([Cu^{2+}])} + \frac{(Q_X)^2}{4} = 0 \tag{8b}$$

Copper Electrowinning

Design and operation of electrochemical cells are based on classical reaction engineering. In fact, the modes of an electrochemical cell (EC) operations are very similar to those of simple batch, plug flow and continuously stirred tank reactors, with

respect to bulk solution. However, there are some notable differences in the way an EC is designed to overcome mass-transfer resistance between the bulk medium and electrode surface. In addition, the geometric arrangement of the anode and the cathode must be such that the EC can minimize the problems of non-uniform current distributions due to the generation of local potential differences on the electrode surface.

The chemical change occurring in an EC is determined by the oxidation reaction at the anode, the reduction reaction at the cathode, and the nature of the chemical species being reduced or oxidized.

At a molecular level, electron transfer is dependent on the local potential field at the electrode surface, driving the movement of the negatively charged electron across the electrode-solution interface. The field is controlled via the potential applied to the electrode. The potential for an electrode reaction

$$O + n\, e^{-} \leftrightharpoons R \qquad (9)$$

to occur at the desired rate depends on both thermodynamics and kinetics of the oxidant(O) and reductant(R) couple, both of which are related to the chemistry of O and R in the solution. Where as n, in the above equation is the number of electrons per molecule oxidized or reduced; Faraday per mole of substance electrolyzed. The equilibrium potential(E_e) for reaction (9) may be calculated from the Nernst equation:

$$E_e = E^0{}_e + [\frac{RT}{nF}] \ln(\frac{[O]}{[R]}) \quad (10)$$

where $E^0{}_e$ is the formal potential or standard potential for the couple O/R (tabulated by Bard, Parsons and Jordan, Des., 1985) and [O] and [R] are the activities and, in dilute solution, the molar concentrations of O and R in solution, and F is Faraday's constant (96500 coulombs/mole). At the equilibrium potential, there is no net conversion between O and R: above this potential, the oxidation of R to O is thermodynamically favorable, while below this potential, the reverse reaction is favorable. In practice, however, it is usually necessary to apply an overpotential, η (= E- E_e), to enhance the kinetics of the reaction, and this over potential can be thought to represent inefficiency in the cell. The rate of reaction commonly increases exponentially with overpotential, but the value of overpotential required varies greatly with electrode reactions (Pletcher and Weinberg, 1992).

For copper electrowinning, the reaction at the cathode is given by:

$$Cu^{2+} + 2e^- \rightarrow Cu^0 \quad (11)$$

The reaction at the anode for the test solution is given by:

$$H_2O \rightarrow \frac{1}{2} O_2(g) + 2\,H^+ + 2\,e^- \quad (12)$$

Current density is the current passing through the external circuit per unit area of the electrode. In order to maximize efficiency of electrolytic recovery (ratio of copper electroplated to initial copper in solution), the electrolytic cell should be operated at lower current density; to maximize the recovery rate, the cell should be operated at a very large current. To satisfy both these requirements, a very large cathodic area must be used. Further, when a large amount of current is delivered to a small cathodic area (operation at high current densities) a great deal of hydrogen can be generated, which will blanket the electrode and severely lower the efficiency of copper recovery.

Large cathodic area electrodes are often produced from expanded metallic mesh, stainless steel wool or metallized sponge. Under certain conditions the metallic deposit itself will increase cathodic area. (Hradil et. al., 1984)

The electrons must pass through an external circuit from the anode to the cathode. Measurement of the current, i, gives an immediate measure of the rate of chemical change at each electrode. In the absence of other cathodic reactions, since two moles of electrons (two Faraday) will reduce one mole of Cu^{2+} to Cu metal,
the rate of copper deposited on the cathode is given by,

$$\frac{dn_{Cu}}{dt} = \frac{i}{2\ F} \qquad (13)$$

where, i is the difference between the current recorded and the background current when equilibrium is reached, and n_{Cu} is the number of moles of copper electroplated.

Optimum Voltage for Electrowinning

The phenomenon of mass transport places a limitation on the current that can be transmitted to drive a particular electrode reaction. This is because a reactant cannot be oxidized or reduced at a rate faster than it is transported to the electrode surface. Transport occurs through diffusion, convection and migration. In most practical situations, convective transport is rapid, and diffusion and migration near the electrode surface limit the rate. The limiting current is given by

$$i_L = n\ F\ A\ k_m\ C \qquad (14)$$

A is the electrode area, k_m is an overall mass transfer coefficient which characterizes the mass-transport regime near the electrode surface, and C is the bulk concentration of species being oxidized or reduced. The value of k_m varies from $< 10^{-7}$ m/s in still solutions at room temperature to $> 10^{-4}$ m/s in highly stirred systems at 90^{0} C (Pletcher and Weinberg, 1992).

Simultaneous Desorption and Electrowinning

As can be seen from equation 1, desorption of copper from the gel phase can be driven by increasing the concentration of calcium and/or simultaneously depleting the aqueous concentration of copper. This can be achieved effectively by electrowinning copper in a high calcium ion background solution. Wiaux and Nguyen (1990) reported the advantages of combining electrolysis with ion exchange to electrolytically treat ion

exchange eluant to recover the metal and to avoid the production of heavy metal sludge. Kinetico Engineering Systems, Inc. has developed a treatment system for copper waste from printed circuit board industry based on ion exchange resin and electrowinning technologies (Fries and Chew, 1993).

MATERIALS AND METHODS

Experimental Design

Several batch experiments were conducted to observe the absorption behavior of copper by sodium alginate and alginic acid. Based on absorption experiments, distribution ratios for copper, between the gel and liquid phases, were measured. Comparing the experimental results with theoretical predictions, maximum sorption capacities of the two gel phases were calculated. Based on the maximum sorption capacity, calcium alginate gel beads were selected for copper recovery and alginate regeneration.

Batch experiments were conducted to evaluate regeneration of copper saturated alginic acid and calcium alginate gel beads by elution (ion exchange) with concentrated HCl or $CaCl_2$, respectively. When it was not sufficient to fully regenerate copper saturated gel beads by elution alone, the feasibility of regeneration by simultaneous desorption and electrowinning of copper from gel and liquid phases was studied. A Batch reactor for demonstration of the regeneration technology was designed. Experiments were conducted to know the optimum voltage to be applied for copper electrowinning in high calcium background. Experiments were conducted in duplicate to observe the regeneration process as a function of time. Two sets of experiments were conducted to study the resorption capacity of calcium alginate gel beads after repeated sorption-desorption-electrowinning cycling. Scale up of the technology was studied in a semi fluidized bed reactor designed for absorption of copper and regeneration of the

biopolymer.

Experimental Procedures

Batch Experiments

The overall reactor configuration is shown in Figure 1. All the reactions were carried out at a constant temperature of 25 ± 0.1 ^{0}C using water-jacketed beakers and a constant temperature water bath. Gel beads were kept in suspension during formation, absorption and regeneration experiments by stirring the solution with stirrer bar and plate.

Gel Bead Preparation. Beads of calcium alginate were formed in a batch reactor containing 750 ml solution of 0.5 M $CaCl_2 \cdot 2H_2O$ and 0.1 M nacl. Alginic acid beads were formed in a batch reactor containing 300 ml solution of 0.5M HCl and 0.1 M NaCl. When gels are formed in the presence of antigelling cations, such as Na^+ or Mg^{2+}, isogeneous alginate gel beads can be obtained. Such beads are mechanically stronger and have higher porosity than those formed in absence of antigelling ions (Smidsrød and Skjåk-Bræk, 1990). 0.1 M NaCl is added in all experiments to adjust the ionic strength. It also gives more mechanical strength to the beads.

A viscous solution of 3.2% sodium alginate (3.2 g of sodium alginate in 100 ml deionized water) (medium viscosity) was dispensed into the reactor fluid containing either calcium or hydrogen ions by using a dispenser (Figure 2). The dispenser was fabricated from a 200 ml plastic bottle and seven 200 µl pipette tips. The multi tip dispenser decreases the time of dispensing, significantly, when compared to the single tip dispenser. A compressed air source was used to force the viscous algin solution through

the tips at a constant rate in order to produce a uniform bead size. The dispensing rate was controlled by a clamp on the vent tube of the compressed air line connected to the dispenser (not shown in the figure). The alginate was allowed to equilibrate with either Ca^{2+} or H^{+} ions by constantly suspending the beads in a batch mode for four hours or more by a magnetic stirrer. The gel beads were removed from the solution by a strainer. Thorough washing with deionized water was required to remove the HCl or $CaCl_2$ that had penetrated into the gel phase. Deionized water was poured into the strainer containing the gel beads. The gel beads were then carefully dried with tissue paper from the back of the strainer.

Alginate dry mass within the gel beads was determined solely by monitoring the quantity of 3.2% alginate solution used in making beads. Once a batch of gel beads had been made, the entire batch was used in subsequent absorption, desorption and electrowinning experiments, save for occasional samples taken for analysis. Thus, all gel phase concentrations are reported on the basis of the quantity of alginate used at the bead preparation step.

Copper Absorption. Test solutions were aqueous solutions of $CuSO_4 \cdot 5H_2O$ with initial concentrations ranging from 1.5 mM to 9.7 mM and 0.1M NaCl. Gel beads of alginic acid or calcium alginate were carefully dropped into the 750 or 500 ml of test solution at time zero, and were suspended in the copper solution by a magnetic stirrer in a batch mode for four or more hours. Initial and equilibrium pH was measured with a pH meter (Cole Parmer Model # 05669-20). When calcium alginate beads were used for

absorption of copper, final equilibrium concentration of calcium was measured by Atomic Absorption Spectrophotometer (Perkin- Elmer model # 560). Solution samples were withdrawn periodically for analysis of copper. The gel phase concentration of copper was computed from the liquid phase mass balance.

The maximum sorption capacities of alginic acid and calcium alginate beads were compared to choose the type of alginate for further experiments. Experiments were carried out by a batch method and all the data were taken at 25^0C. A mixture of alginic acid gel beads or calcium alginate gel beads and the metal solution was shaken for four hours or more in a water-jacketed beaker. After sorption equilibrium was reached, the mixture was filtered and the filtrate was saved for analysis. In some runs the solution samples to be analyzed were periodically withdrawn from the beaker in order to investigate the sorption behavior as a function of time. The solution samples were analyzed for copper and calcium by atomic absorption spectrophotometry. Initial and equilibrium pH of the solution were measured by using a pH meter (Cole Parmer model# 05669-20). The concentration of metal in the gel phase was determined from the liquid phase mass balance. The distribution ratio (D_{cu}) of metal between the gel and liquid phases was calculated from the gel-phase concentration (number of moles per unit mass of dry Na-alginate used) divided by the liquid-phase concentration (the number of moles per unit volume of solution).

Copper Desorption by Ion Exchange. Desorption experiments were carried out to check whether complete regeneration can be achieved by increasing the concentration

of Ca^{2+} or H^+ ions alone without electrowinning. For desorption experiments, a mixture of copper saturated gel beads and the 0.5M $CaCl_2$ or 1M HCl solution was shaken for two hours or more in a water-jacketed beaker. The solution samples to be analyzed were periodically withdrawn from the beaker in order to investigate the desorption behavior as a function of time.

Design and Optimization of Electrowinning Cell. Good cell design is critical to the success of electrolytic processes. To obtain high conversion, a large ratio of electrode area to solution volume within the cell is required. This was achieved by using a stainless steel mesh as cathode. At the same time, it is important to minimize the inter electrode gap in order to minimize the potential drop across the cell (iR_{cell} drop) and hence the energy consumption of the cell. Even potential is possible if all points on the electrode surface are geometrically equidistant to the other electrode. With poor design, one ends up with totally inactive zones within the electrode or, a major loss in the current efficiency (when competing electrode reactions become important). The even distribution of potential was attained by using stainless steel mesh, in the form of a cylinder was used as cathode around a cylindrical carbon anode (EG & G). A saturated calomel electrode (SCE) was used as a reference electrode.

A linear polarization curve was generated to determine the range in which limiting current condition exists for copper reduction. The reactor solution was 0.5 M $CaCl_2$, 0.2 M NaCl and 15.737 mM $CuSO_4$. These conditions are similar to the conditions encountered in the regeneration process.

A linear polarization curve was also generated for a deoxygenated solution without aqueous copper. The reactor solution was 0.5 M $CaCl_2$ and 0.2 M NaCl.

Copper Desorption by Ion Exchange and Electrowinning. A schematic of the electrowinning cell is shown in Figure 3. The stainless steel mesh as cathode and carbon electrode as anode were inserted into the rubber stopper and were connected to the proper terminals of Potentiostat. Four hundred ml of 0.5M $CaCl_2$ solution were poured into the beaker. Copper saturated alginate beads were added to the solution. Simultaneously to addition of beads, predetermined voltage (with respect to SCE) was applied at the cathode. This was done to correlate the changes in copper concentration with the changes in current from the time the beads are added. Current was measured by Potentiostat and recorded continuously for four hours or more by EG&G software. The solution samples to be analyzed were withdrawn periodically from the reactor to know the copper concentration in solution with time. A specific number of beads were withdrawn periodically to measure the concentration of copper in the gel phase.

Multiple Cycles. Once all the cupric ions in the gel beads were exchanged by calcium ions, gel beads were removed from solution by a strainer. At this point the gel beads were completely regenerated to calcium alginate. Then, the gel beads were subjected to another sorption-desorption and electrowinning cycling. Two sets of experiments were conducted to study the resorption capacities of gel beads. In each set of experiments, gel beads were used for at least three absorption-desorption-electrowinning cycles.

Scale Up Experiments

A 2-liter continuous fluidized bed reactor was designed and used for scale up experiments. The reactor and the electrowinning cell used for regeneration experiments are shown in Figure 4. The reactor consists of a long transparent column. It has four ports at the bottom. Two ports were kept for influent copper solution and compressed air. The third port is for drainage of water at the end of the operation. In addition to the port on the side arm, the fourth port at the bottom was used to recirculate the reactor fluid through the electrowinning cell during the regeneration cycle. The reactor has an open arm at the top, which makes it easier for withdrawing or introducing the calcium alginate gel beads for absorption or sampling. The reactor along with the electrowinning cell was designed to operate as a continuous system during absorption of copper from solution and as a batch reactor during regeneration of copper saturated alginate gel beads.

Absorption. All tubing and the wetted portion of the fluidized bed reactor were cleaned initially by running with 5% HCl for three hours followed by deionized water for another three hours. Calcium alginate gel beads were formed and the amount of dry sodium alginate used was computed. The reactor was initially filled with an influent copper solution containing 1.57 mM $CuSO_4 \cdot 5H_2O$ and 0.1 M NaCl. Then, the flow rate was adjusted to 11 ml/min, which gave a residence time of approximately three hours. At time zero, the calcium alginate gel beads were added to the reactor from the open arm of the reactor at the top. The absorption process was monitored with time by taking effluent samples for copper analysis. The alginate gel beads were kept in suspension by

compressed air passed from the bottom of the column. This was continued for 15 hours in the first run and approximately 10 hours in the subsequent runs.

Desorption and Electrowinning. After each absorption cycle, the copper solution was drained, leaving the copper saturated calcium alginate gel beads in the reactor. A solution containing 0.5M $CaCl_2$ and 0.1 M NaCl (400 ml) was poured in the reactor and was run through the electrowinning cell in a closed loop (batch) mode, as shown in Figure 4. The solution volume was 400 ml. Because of the strainer placed at the ports in the reactor, the gel beads remained in suspension in the reactor itself. A potential of -0.5V (with respect to SCE) was applied to the cathode in the electrowinning cell. The current passing through the electrowinning cell was recorded with time and the desorption process was continued until steady current was recorded, typically for greater than four hours. In contrast to the batch system, mixing of solution was achieved by circulating the solution through the reactor. The reactor used was rectangular in the plan. Stainless steel coupons as cathode and carbon electrodes (EG & G) as anode were used. Saturated calomel electrode (SCE) was used as a reference electrode.

Analytical Methods, Equipment, and Reagents

Reagents

Algin (Keltone grade sodium alginate (medium viscosity) from kelp, courtesy of Kelco Co.) was used in this study. A 3.2% algin solution prepared by mixing 3.2 g algin with 100 ml deionized water was used as the absorbent in this work. Since the algin

powder was not readily dissolved in water, the solution was kept in a rotary shaker for 24 to 48 hours. The solution was then kept in a refrigerator until used. All chemicals used, including algin, were ACS reagents.

Potentiostat/Galvanostat

Model 273A Potentiostat from EG&G was used for applying a particular voltage between the electrodes determined previously by polarographic scans using the same instrument. "Model 352 Soft Corr TM" software from EG&G was used for collection of real time current and voltage data.

Analytical Methods

Copper concentration in solution was analyzed using Atomic Absorption Spectrophotometer (Perkin-Elmer model # 560). Copper concentration in the gel phase was computed from the liquid phase mass balance. In some regeneration runs, gel phase copper concentration was determined by taking small known portion of gel beads into an alumina crucible. The crucible is placed in an oven at 500^0 C for four hours. After the crucibles were cooled to room temperature, known volume of 6M HCl was used to extract copper ions left in the crucible. The HCl solution was then analyzed for copper. Based on the copper concentration and volume of 6M HCl used, the amount of copper in the gel phase was calculated. The ratio of number of beads used for analysis to the total number of beads gives the fraction of beads used for analysis. This fraction multiplied by the total dry weight of sodium alginate used for that experiment was taken as the dry weight of alginate used for that fraction. Based on the amount of copper in the fraction

and the dry weight of sodium alginate in that fraction, the gel phase concentration was computed.

RESULTS

Experiments were conducted leading to development of the technology for copper removal from aqueous solutions by alginate gel beads and bead regeneration for further use. The observed data are presented below. The raw data and figures for duplicate sets of data are given in appendices.

Absorption Behavior of Gel Beads of Calcium Alginate and Alginic Acid

Absorption studies were performed to collect equilibrium data on partitioning of copper ions between aqueous solution and the two gel phases. In general, three to five hours were required to reach equilibrium with both calcium alginate and alginic acid beads.

Figures 5 and 6 show typical absorption curves for copper absorption by gel beads of calcium alginate and alginic acid, respectively. The reactor fluid in absorption experiments with calcium alginate gel beads had final pH in the range of 4.39 to 4.89 and initial pH of 4.95 to 5.35. Initial pH in case of reactor fluids treated with alginic acid gel beads ranged from 5.47 to 5.7 and final pH from 2.72 to 4.94.

Maximum Sorption Capacity

As can be seen from Eq. (7a), the intercept of the plot $\overline{[CuX_2]}$ versus $D_{Cu}[Ca^{2+}]$ yields $Q_X / 2$ for calcium alginate beads. From the intercept in Figure 7, the maximum sorption capacity, Q_X, of calcium alginate gel beads was evaluated as 5.21 X

10^{-3} kmol/kg of dry sodium alginate. From Eq. (7b), the intercept

of the plot $\overline{[CuX_2]}$ vs. $D_{Cu}^{(1/2)}[H^+]$ yields $Q_X / 2$. From the intercept in Figure 8, the maximum sorption capacity, Q_X, of alginic acid was evaluated as 4.11×10^{-3} kmol/kg of dry sodium alginate, about 20% less than for calcium alginate gel beads. Based on higher maximum sorption capacity, calcium alginate gel beads were selected for further experiments of absorption and regeneration of biopolymer.

Desorption Without Electrowinning

Figure 9 shows the desorption behavior by copper saturated calcium alginate gel beads in 0.5 M Ca^{2+} solution. As can be seen from the Figure 9, complete desorption of copper was not possible, since (refer equation 1) equilibrium was established between the copper in aqueous and gel phase. However, assuming the change in calcium concentration (0.5M) to be negligible during the desorption process, the equilibrium copper concentration in the gel phase (equation 8a) was calculated to be 0.012 kmol/kg of dry sodium alginate. This does not correspond to the observed value of 0.208 kmol/kg.

Figure 10 shows the desorption behavior by copper saturated alginic acid gel beads. The copper was eluted using 1 M HCl solution. The theoretical value of equilibrium copper concentration in the gel phase, based on the parameter estimates from Figure 8, was calculated as 2.1×10^{-4} kmol/kg. As discussed with respect to elution with calcium, this gel phase copper concentration did not correspond to the observed value of 0.069 kmol/kg. The final equilibrium pH was 0.81.

Optimum Voltage for Copper Electrowinning

Figure 11 shows a linear polarization curve for copper with a background of 0.5 M $CaCl_2 \cdot 2H_2O$ and 0.2 M NaCl. The limiting current for copper was observed at -0.3 V (with respect to SCE). Based on the polarization curve, -0.5V (with respect to SCE) was chosen for regeneration experiments for electrowinning of copper.

Figure 12 shows the linear polarization curve for the background conditions, in a deoxygenated solution containing 0.5 M $CaCl_2$ and 0.2 M NaCl. These conditions are the same as those for Figure 11 except that there was no oxygen or copper in solution. This figure demonstrates that there was no interference due to the background ions.

Regeneration of Biopolymer (Simultaneous Desorption and Electrowinning)

Figure 13 shows data collected during the simultaneous desorption of copper from gel beads and electrowinning. It can be observed that the current recorded has the same trend as that of concentration of copper in solution. Copper desorption from biopolymer gel beads was effectively complete in 1.5 hours, as confirmed by direct measurement of gel phase concentration of copper. Initially the rate of desorption was faster than electrowinning, as can be seen from an increase in copper concentration in solution. If the background current is deducted, the net rate of charge transfer and rate of copper reduction may be estimated. The integral of the current versus time curve will give the total charge transferred. The net amount of copper reduced based on charge transferred was calculated to be 20% more than the initial amount in the beads. An even copper

deposit on the cathode was observed because of the arrangement of electrodes equidistant from each other in the form of concentric cylinders.

Figure 13 demonstrates that the alginate beads can be fully regenerated by a combination of electrowinning at -0.5V (with respect to SCE) and ion exchange with 0.5 M Ca^{2+} solution (the copper concentration in the gel phase was negligible after 1.5 hours of application of the technology).

Figure 14 shows duplicate set of data for solution concentration and current in the electrochemical cell, when regeneration of copper saturated alginate was in progress.

Absorption After Successive Regeneration Experiments

Figure 15 shows absorption kinetics of copper by a single batch of beads after successive regeneration by the combination of electrowinning and ion exchange with calcium ions. The reactor condition in these experiments was: initial copper concentration in solution was 1.574 mmol/l, and dry wt. of sodium alginate used was 0.3699 g. The equilibrium copper concentrations in the gel phase determined from liquid phase mass balance at the end of the first, second and third sorption tests were: 1.343, 1.117 and 1.085 kmol/kg, respectively. Figure 16 shows a duplicate set of experiments demonstrating the reuse of biopolymer after regeneration with electrowinning and ion exchange with calcium ions.

In both the experiments, it is to be noted that the sodium alginate dry weight was measured while making the calcium alginate beads, and any subsequent loss of biopolymer into the solution was not accounted for in the dry weight. In both the figures,

there was slight decrease in the maximum amount of copper absorbed in each successive absorption cycle after regeneration.

Scale Up of the Technology

Figure 17 shows the effluent copper concentration in the continuous fluidized bed reactor. Initially when the reactor is full of influent copper solution, without calcium alginate beads, the effluent concentration is equal to the influent copper concentration. At time zero, when the gel beads were added, the effluent copper concentration started decreasing as the copper was absorbed by the calcium alginate gel beads. As the gel beads were saturated with copper, the effluent copper concentration slowly increased. Continued operation would eventually have produced effluent concentrations that equaled the influent copper concentration. Experiments were **not** run till equilibrium conditions were reached. Each cycle consists of continuous absorption of copper by alginate gel beads, followed by the regeneration of copper saturated gel beads in a batch mode. Since, scale up experiments were carried out before optimizing the electrowinning cell, the data collected during regeneration process were erratic. This is partially due to the use of stainless steel coupons instead of stainless steel mesh as a cathode. Electrowinning of copper onto the coupon increased the cathodic area significantly. Due to the small cathodic area, the copper deposit was loose, leading to the detachment of deposited copper into the solution.

DISCUSSION

Absorption of Copper by Calcium Alginate and Alginic Acid

Comparison of Figures 5 and 6 shows that the equilibrium gel phase copper concentration in calcium alginate (Figure 5) is more than that in alginic acid (Figure 6). As can be seen from equations (3) and (4), copper concentration at equilibrium in the gel phase is dependent on equilibrium copper concentration in solution, concentration of free functional groups in the gel phase, and equilibrium solution concentration of calcium/hydrogen ions. One of the reasons for higher maximum gel phase concentration of copper in Figure 5 (calcium alginate) when compared to Figure 6(alginic acid), is due to the higher initial and equilibrium solution concentration of copper (2.46 mmol/l and 1.27 mmol/l compared to 1.63 mmol/l and 0.843 mmol/l). Affinity of copper ions for calcium alginate and alginic acid can quantitatively be described by the equilibrium constants K_{cu} and K_{cu}^{1}. Since, units of K_{cu} and K_{cu}^{1} are not the same [equation (2)], they **cannot** be compared to select the alginate which has higher affinity for copper ions. Equilibrium constants K_{cu} and K_{cu}^{1} can be calculated from the slopes of Figures 5 and 6 [refer Equations (7a) and (7b)]. Maximum sorption capacities of gel beads of calcium alginate and alginic acid, Q_X, per unit mass of dry sodium alginate used, can be compared [refer Eqns. (7a) and (7b)]. Ideally they should be the same, if all the functional groups maintain their integrity in the process of gel bead formation.

Concentrated HCl treatment destroys the structure of alginate chains and the hydrogen bonding capacity of the alginate (Kuyucak and Volesky, 1989). The lower

maximum sorption capacity of alginic acid compared to the calcium alginate (Figure 7 and Figure 8) is consistent with this observation.

pH Effect on Calcium Alginate

The formation of $Cu(OH)_2$ in the range of pH encountered in this work is known to be negligible. Below pH 6.5, free copper ion, Cu^{2+}, is the predominant copper containing species in natural water (Snoeyink and Jenkins, 1980). Since pK_A value of alginic acid [= 2.96 (Jang et. al., 1990)] was more than one unit below the pH of solution and copper has a strong affinity towards calcium alginate, the pH effect was not considered in this work for absorption experiments. Moreover, initial pH values in all experiments were higher than equilibrium pH values, suggesting that there is no absorption of H^+ ions by calcium alginate beads during copper absorption experiments. This observation also justifies neglecting the competition with H^+ ions during copper absorption experiments by calcium alginate. But, if initial pH of the reactor solution is very low, competition with

H^+ ions need to be considered.

Desorption Without Electrowinning

In both desorption experiments with calcium alginate and alginic acid gel beads, the theoretical predictions of equilibrium copper concentration in the gel phase (0.012 and 2.1×10^{-4} kmol/kg) were less than the observed equilibrium concentrations (0.208 and 0.069 kmol/kg). Further work must be done to explain discrepancy. At low gel

phase concentrations, kinetics of desorption might be limiting the desorption process.

Optimum Voltage for Copper Electrowinning

Pletcher and Weinberg (1992) presented a set of i-vs-E responses recorded at a rotating disc electrode for solutions of: (a) Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+} in a neutral chloride medium; (b) O_2 in the same solution; (c) a deoxygenated solution of the chloride medium. The limiting current for copper deposition was observed between -0.3 V and -0.6 V(with respect to SCE). These tests suggested that Cu^{2+} could be removed selectively without serious loss of current efficiency due to hydrogen evolution. Hydrogen evolution occurred at -1.1 V and below (with respect to SCE). Oxygen reduction need not interfere with Cu^{2+} removal. Limiting current for oxygen reduction occurred between -0.6V and -1.1V (with respect to SCE). The limiting current conditions for copper electrowinning observed in this study (-0.3 V with respect to SCE), (Figure 11) agree well with the literature values cited above. Further, the increase in current at -0.6 V (Figure 11) was probably due to the reduction of oxygen to water.

Regeneration of Biopolymer (Simultaneous Desorption and Electrowinning)

The net amount of copper reduced based on charge transferred was calculated to be 20% more than the initial amount in the beads. One reason might be due to the presence of copper in solution in interstitial voids of biopolymer. The solution concentration in interstitial voids is not accounted for in the mass balance. The gel phase concentration was calculated from the liquid phase mass balance at equilibrium during

absorption experiments. Considering the entire bead volume to be occupied with solution, the copper in interstitial volume alone did not explain for the 20% discrepancy.

Absorption After Successive Regeneration Experiments

As can be observed from Figures 15 and 16, equilibrium gel phase concentration in each subsequent absorption experiment was slightly less than the concentration in the previous absorption experiment. This is in contrast to the observation that the biopolymer is fully regenerated (refer to Figure 13). The decrease in gel phase concentration may be due to loss of alginate gel into the solution in each experiment due to agitation, straining etc. It is to be noted that the gel phase concentration is based on the dry weight of alginate used to prepare the batch of beads, and it is assumed to be constant in subsequent desorption and absorption experiments.

Scale Up of Technology

Figure 4 shows the fluidized bed reactor used to demonstrate the technology on a larger scale and under semi-continuous flow conditions. The fluidized bed reactor was designed in such a way that both absorption and regeneration took place in the same reactor column.

In Figure 17, it can be observed that the effluent copper concentration increased in each subsequent absorption run. In other words, the amount of copper absorbed decreased in each subsequent absorption into the gel phase. This can be explained by the loss of alginate gel into solution due to agitation of air bubbles etc. As in batch experiments, it

should be noted that the amount of dry alginate used for each experiment was measured only before the initial absorption run. This problem of loss of alginate may be partially alleviated by gentler agitation of beads to keep them in suspension. Continuous addition of small amounts of prepared beads is probably required.

CONCLUSIONS

The following conclusions were drawn from the work:

1) Full regeneration of the calcium alginate gel beads can be achieved by using a 0.5M solution of $CaCl_2$ and simultaneous electrowinning at -0.5V (with respect to SCE).

2) Full regeneration of the biopolymer(calcium alginate/alginic acid) was not possible with desorption using 0.5M $CaCl_2$/1 M HCl alone.

3)The resorption capacity of the calcium alginate gel beads does not decrease significantly during repeated sorption-desorption-electrowinning cycling. Calcium alginate gel beads were tested for up to three sorption-desorption-electrowinning cycles.

4)The gel beads of calcium alginate and alginic acid were found to have a maximum sorption capacity of 5.21 X 10^{-3} kmol carboxyl groups /kg of dry sodium alginate and 4.11 X 10^{-3} kmol carboxyl groups/kg of dry sodium alginate respectively.

REFERENCES CITED

Bard, A. J., Parsons, R., and Jordan, J., Des., " Standard potentials in aqueous solution", Narcel Dekker, New York, 1991

Charles Cooper, W., 1985. "Advances and future prospects in copper electrowinning" Journal of Applied Electrochemistry, 15, pp 789-805

Cozzi, D., et. al., 1969. "The mechanism of ion exchange with alginic acid" Journal of Chromatography, 40, pp 130-137

Farkas, J., 1985 " An ecologic and economic process for transition metal recovery". Journal of Metals, February 1985: pp 72-75

Fries, W. and Chew, D., 1993. " Get the metal out" Chemtech, February 1993, pp 32-35

Hassan, R. M., 1993. "Alginate polyelectrolyte ionotropic gels; part II Kinetics and mechanism of exchange of chelated nickel(II) by hydrogen ions in capillary ionotropic nickel alginate polymembrane gel complex" pp384-389

Hassan, R.M., 1991. " Alginate polyelectrolyte ionotropic gels"; part III Kinetics of exchange of chelated divalent transition metal ions especially cobalt(II) and copper(II) by hydrogen ions in capillary ionotropic metal alginate polymembrane gels" pp 5806-5810

Hradil, Edward F. And Hradil, George, 1984. "Electrolytic recovery of precious and common metals" Metal Finishing, November 1984, pp 85-88.

Hunt, S., 1986. "Diversity of biopolymer structure and its potential for ion-binding applications". In "Immobilization of ions by biosorption", Ellis Horwood Limited, West Sussex, England.

Jang, L. K. et. al., 1991. " Recovery of copper and cobalt by biopolymer gels" Biotechnology and bioengineering, 37, pp 266-273

Jang, L. K. et. al., 1990. "Use of gel-forming biopolymer directly dispensed into a loop fluidized bed reactor to recover dissolved copper". Wat. Res. Vol.24, No.7, pp 889-897

Jang, L. K., et. al.,1994. "Selectivity of alginate gel for Cu versus Co" Accepted for publication by Water Research.

Jang, L. K. et. al.,1994. "Effect of pH on the absorption of Cu(II) by alginate gel" Accepted for publication by Water Research.

Konishi, Y., Asai, S., Midoh, Y., and Oku, M. 1993 " Recovery of zinc, cadmium, and lanthanum by biopolymer gel particles of alginic acid" . Separation Science and Technology, 28(9), pp. 1691-1702

Konishi Y. et. al., 1992. "Recovery of neodymium and ytterbium by biopolymer gel particles of alginic acid" Ind. Eng. Chem. Res., 31, pp 2303-2311

Kyucak, N., and Volesky, B. 1989 "The mechanism of cobalt biosorption" Biotechnology and Bioengineering, Vol. 33, pp 823-831

Lewandowski, Z et. al., 1992 " Heavy metals removal from contaminated water solutions" Research proposal submitted by Center for Interfacial Microbial Process Engineering, Montana State University

Pletcher, D. and Weinberg, N. L., 1992. " The green potential of electrochemistry, part 1: The fundamentals" Chemical Engineering/ August 1992, pp 98-103

Randall, John M., 1977. " Variations in effectiveness of barks as scavengers for heavy metal ions" Forest Products Journal, Vol. 27, No. 11, pp 51-56

Schweiger, R.C., 1962. " Acetylation of alginic acid. II. Reaction of algin acetates with calcium and other divalent ions" Vol 27, pp 1789-1791

Scott, Charles D., 1992. " Removal of dissolved metals by plant tissue" Biotechnology and Bioengineering, Vol.39, Pp. 1064-1068

Smidsrød, Olav, 1968. " Dependence upon uronic acid composition of some ion-exchange properties of alginate" Acta Chem. Scand. 22, No 6, pp 1989-1997

Smidsrød, Olav and Skjåk-Bræk, Gudmund, 1990. " Alginate as immobilization matrix for cells" TIBTECH-MARCH 1990, vol 8, pp 71-78
Snoeyink, V. L. and Jenkins, D., 1980. " Water Chemistry" John Wiley and Sons, Inc. pp 220

Volesky, B., 1986. " Biosorbent materials" Biotechnology and bioengineering symposium. No. 16. pp 121-126

Wiaux, J. P. and Nguyen, T., 1990. "Recovered value from electroplating industry waste" Metal Finishing, June 1990, pp 85-92

Wong, P.K., et. al., 1993. "Removal and recovery of Cu(II) from industrial effluent by immobilized cells of *Pseudomonas putida* II-11" Appl. Microbiol. Biotechnol., 39, pp 127-131

Wong, P. K. And So, C. M., 1993. " Copper accumulation by a strain of *Pseudomonas putida*" Mirobios, 73, pp 113-121

Yang, T. C., et. al., 1984. " Absorption of metals by natural polymers generated from seafood processing wastes" Ind. Eng. Chem. Prod. Res. Dev., 23, pp 168-172

APPENDICES

Appendix A
Figures

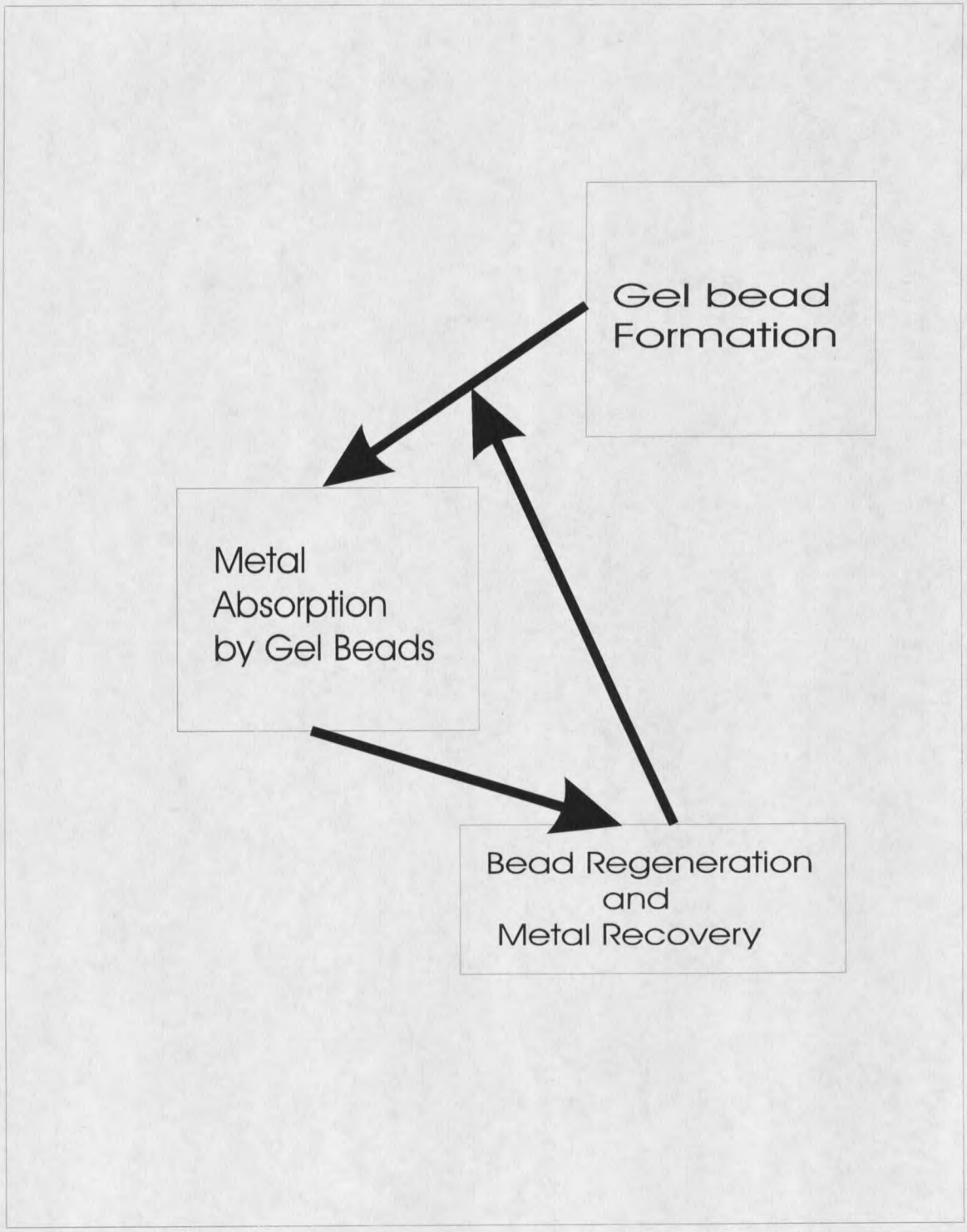


Figure 1- Schematic Diagram of Overall Reactor Configuration

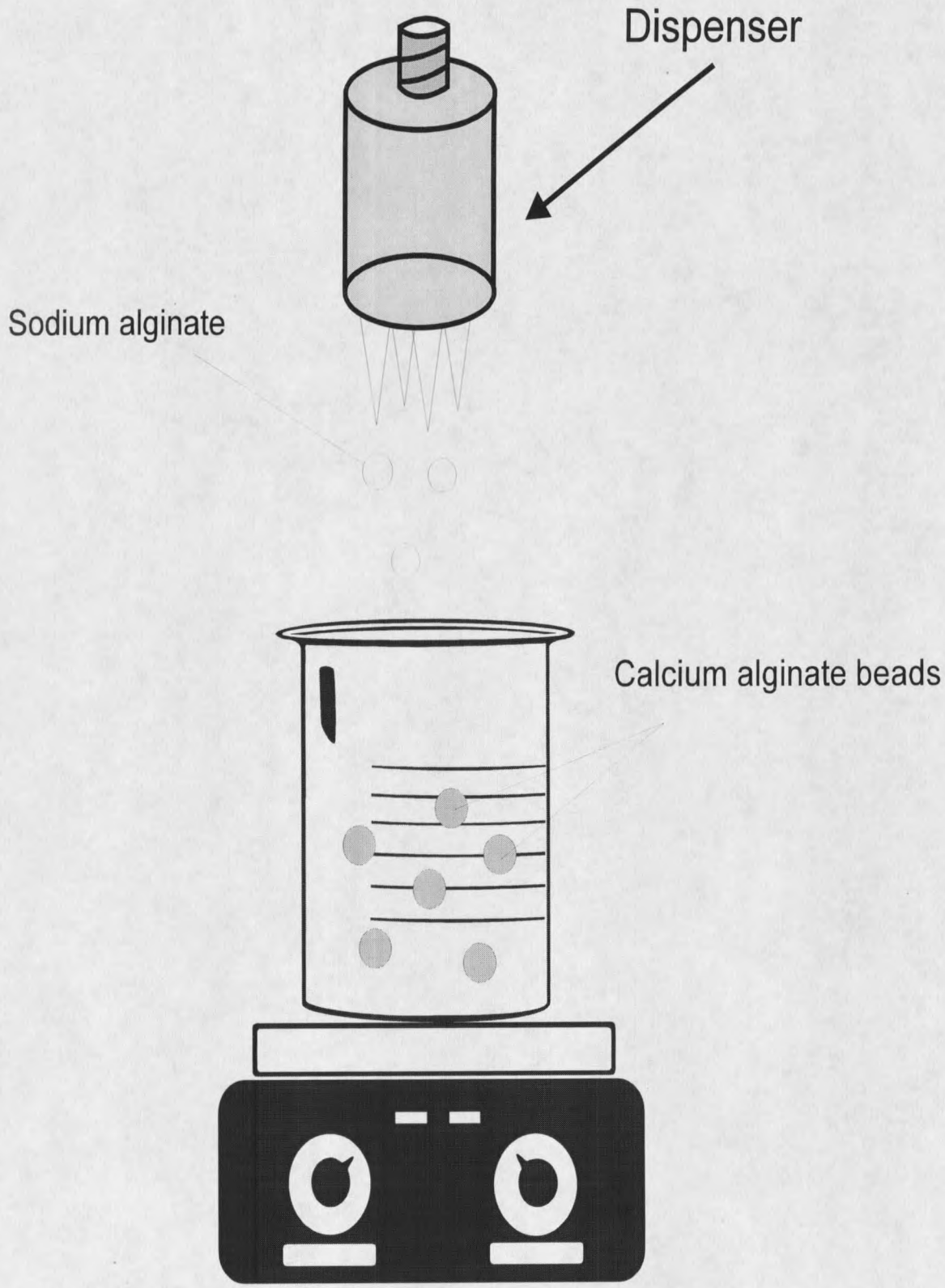


Figure 2- Schematic Diagram of Dispenser and Gel Bead Formation

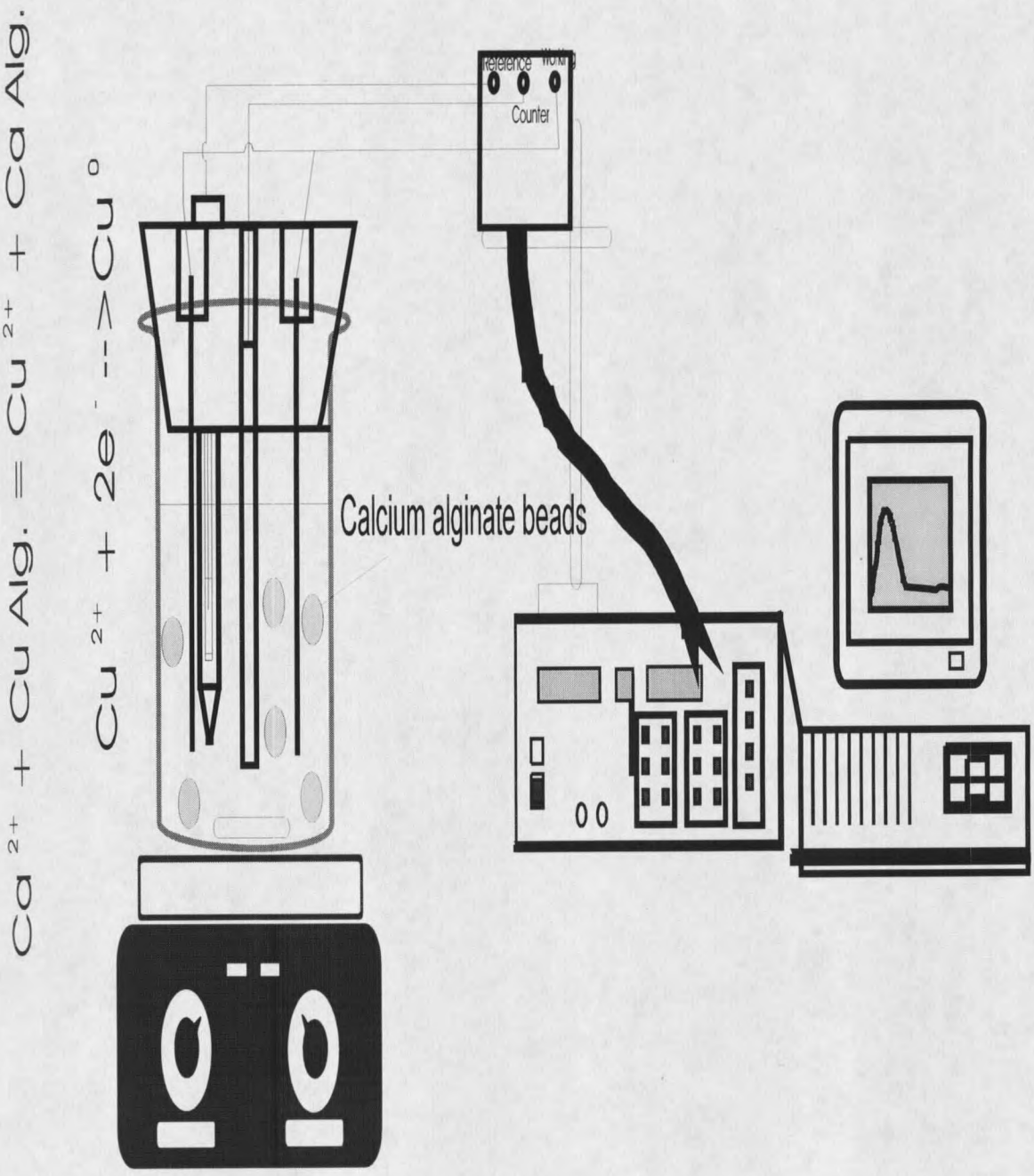


Figure 3-Schematic Diagram of Electrowinning Cell

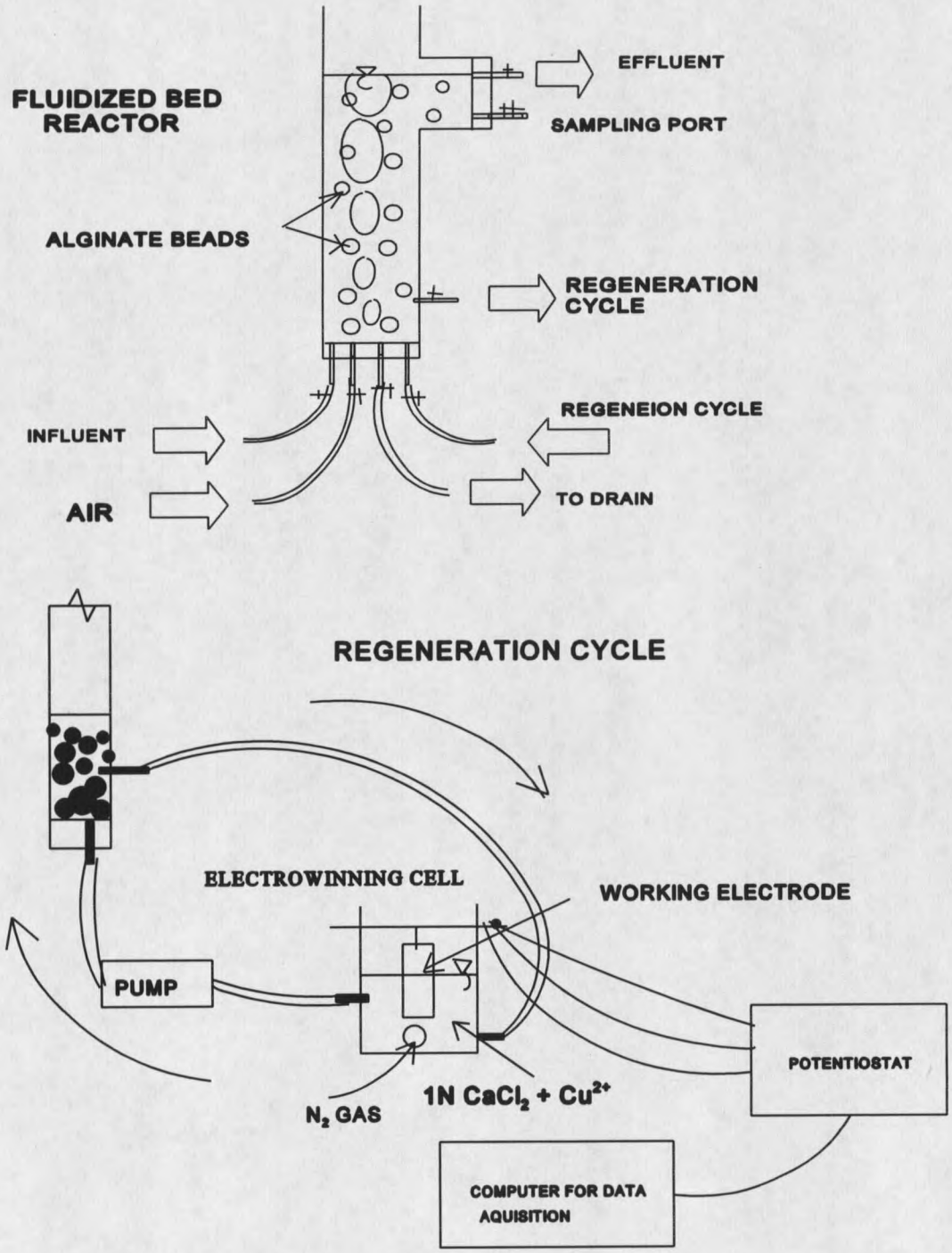


Figure 4-Semi Continuous Fluidized Bed Reactor Used for Absorption and Regeneration of Gel Beads in Scale Up Experiments

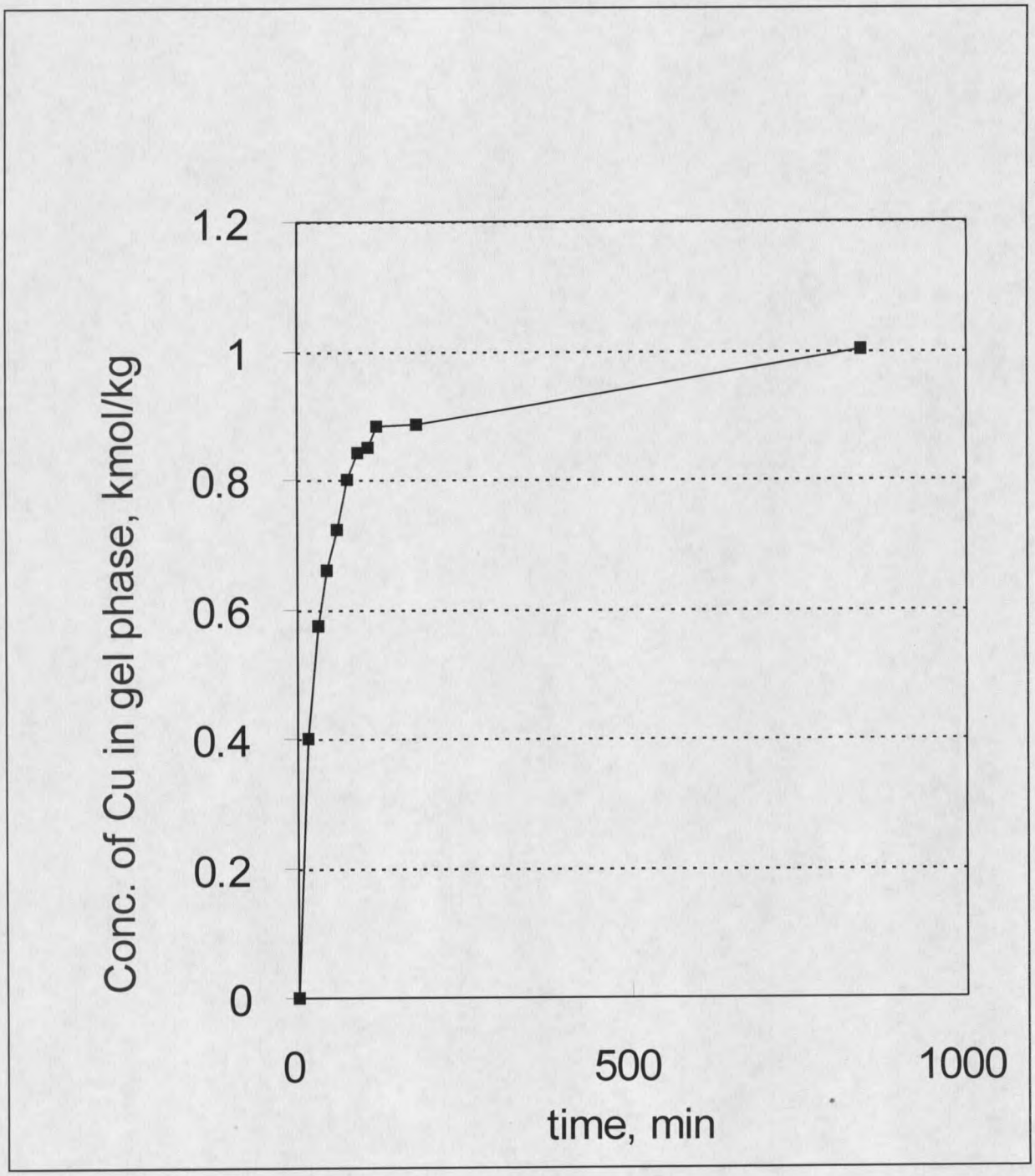


Figure 5-Typical Absorption Curve for Copper Absorption by Calcium Alginate Gel Beads. Reactor Condition: $[Cu]_{initial}$ = 2.36 mmol/l, Dry Weight of Sodium Alginate = 0.5907 g/ 500 ml Solution.

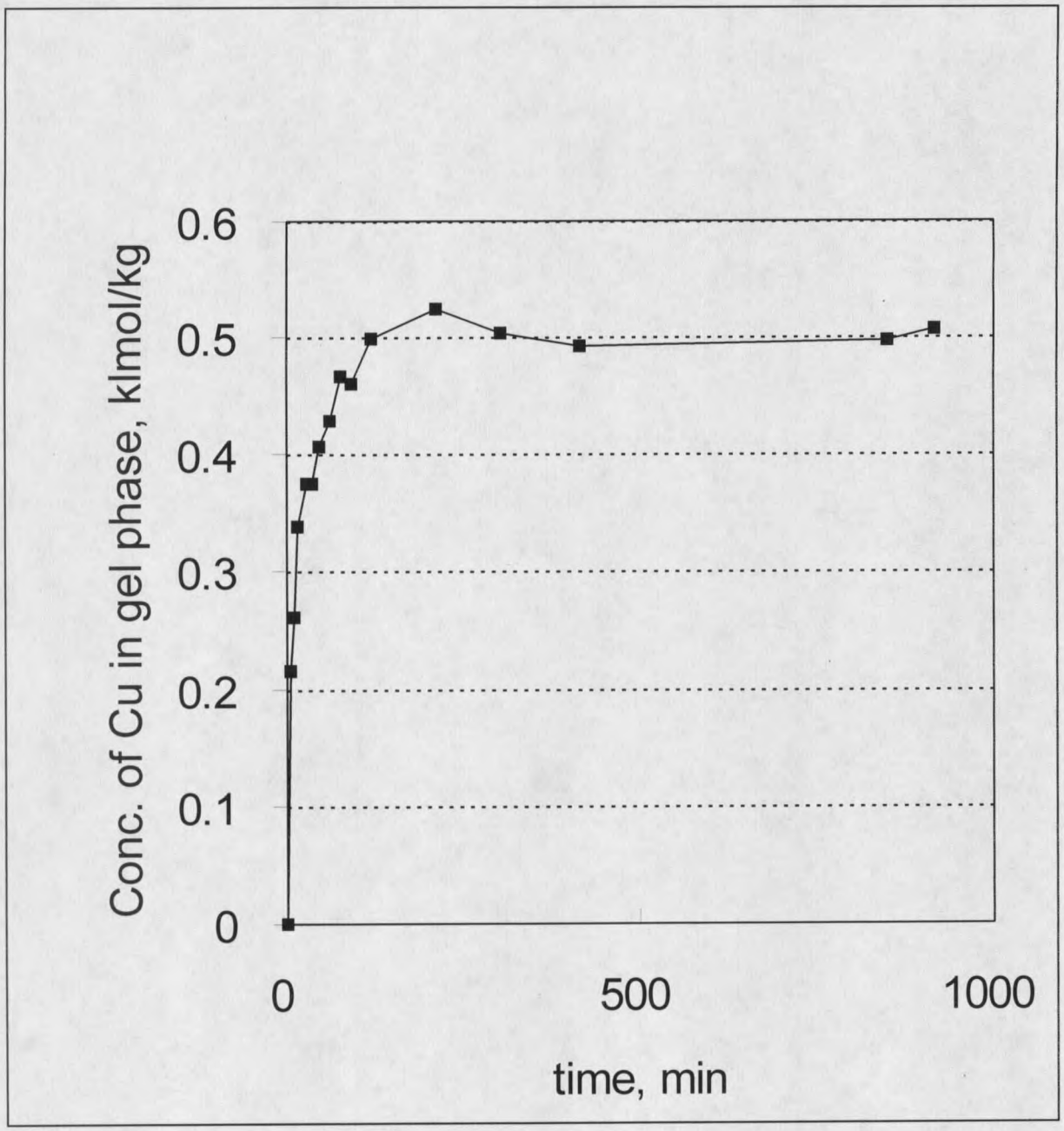


Figure 6- Typical Absorption Curve for Copper Absorption by Alginic Acid Gel Beads. Reactor Condition: $[Cu]_{initial}$ = 1.57 mmol/l, Dry Weight of Sodium Alginate = 0.7769 g/ 500 ml solution.

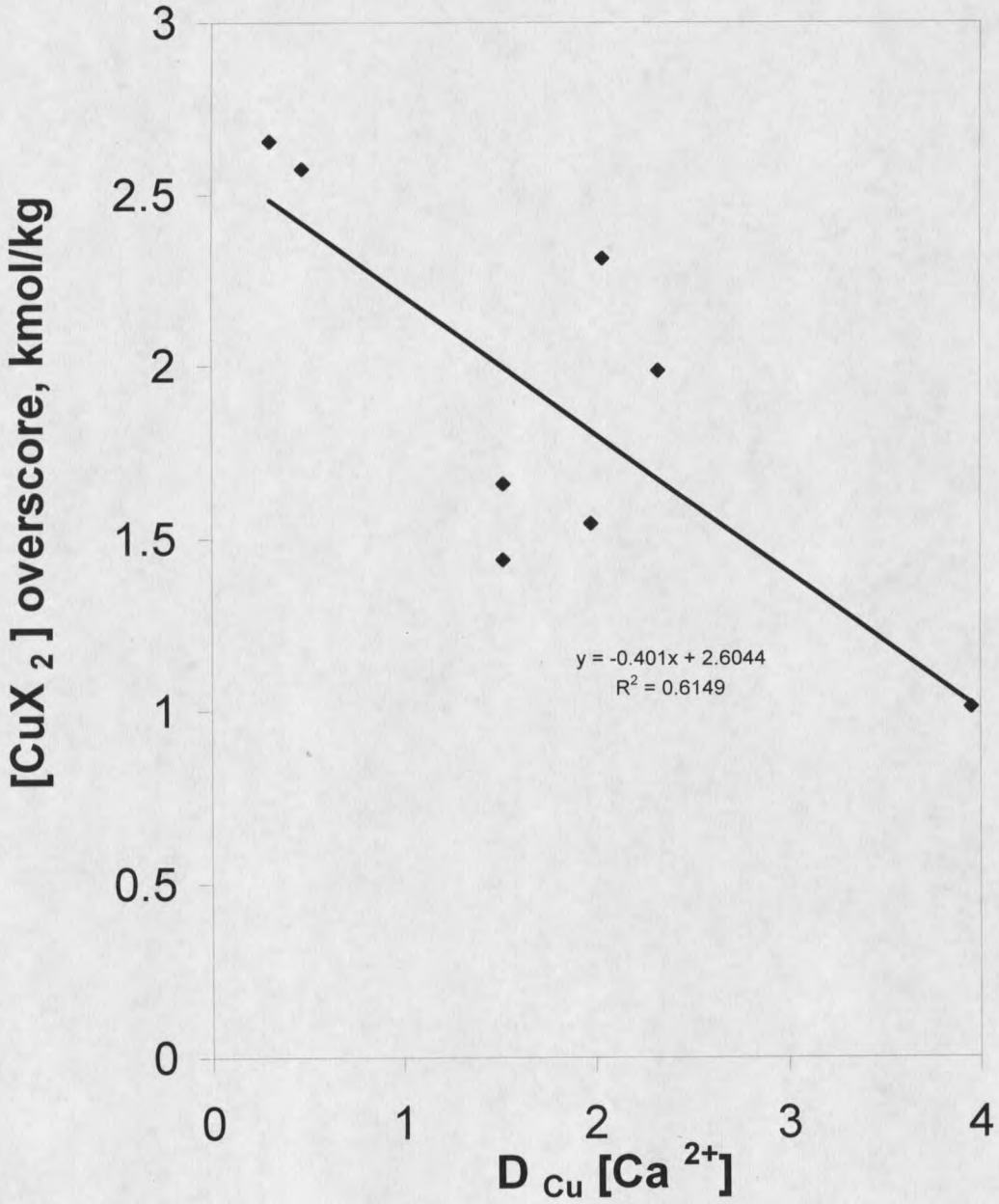


Figure 7-Maximum Sorption Capacity of Calcium Alginate Gel Beads

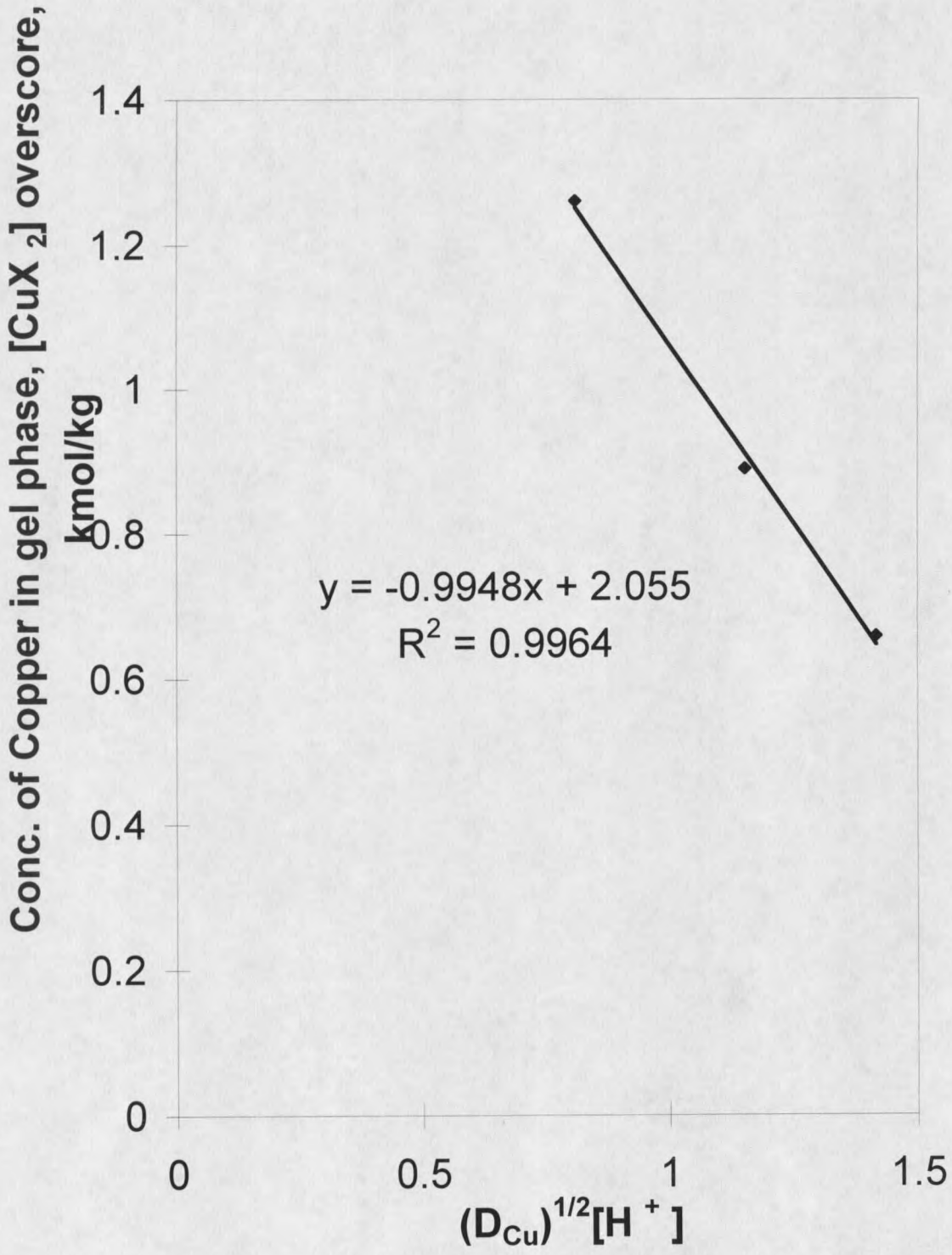


Figure 8- Maximum Sorption Capacity of Alginic Acid Gel Beads

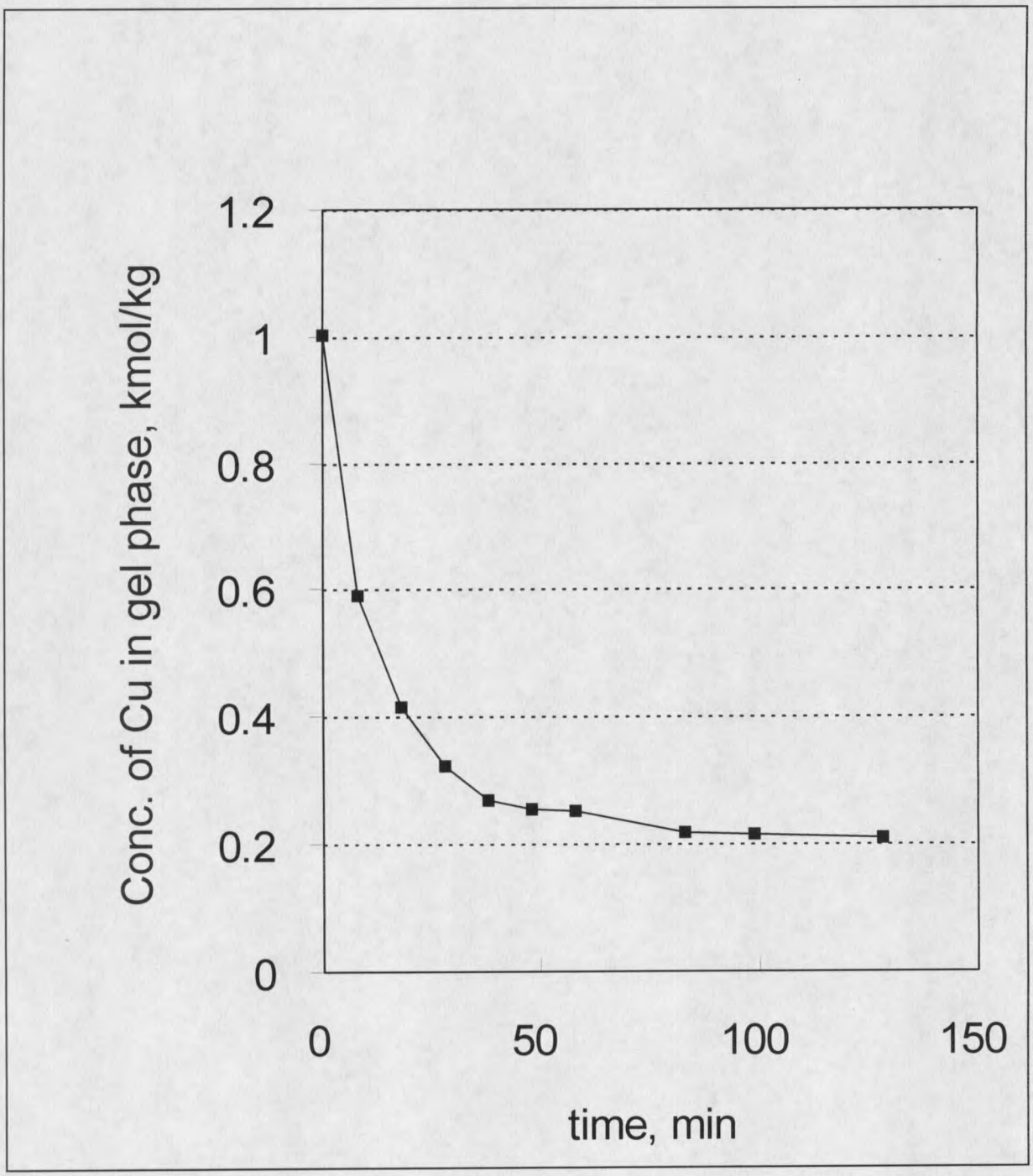


Figure 9 - Typical Copper Desorption Behaviour From Copper Saturataed Calcium Alginate Gel Beads in 0.5 M Ca^{2+} Solution.

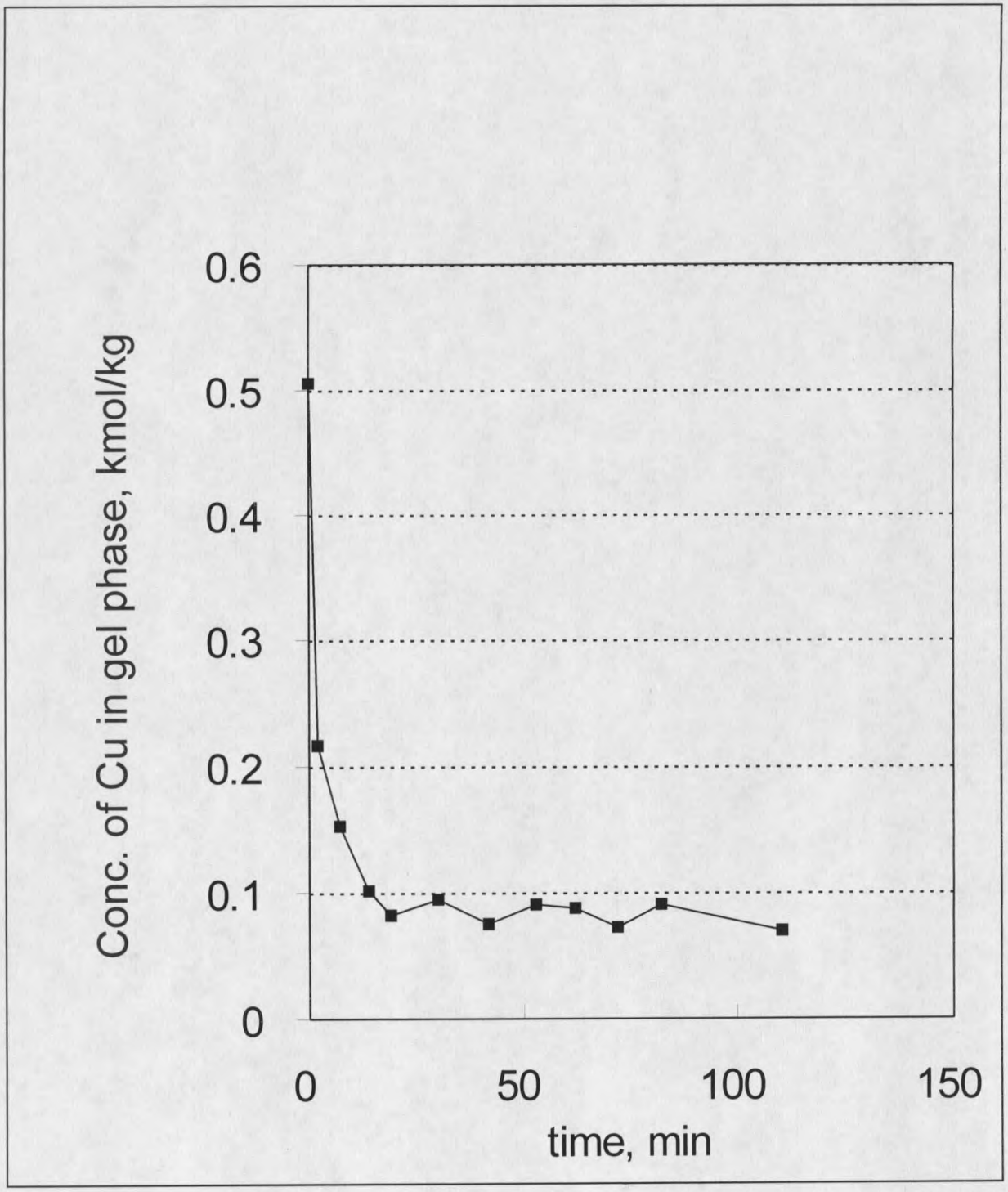


Figure 10 - Typical Copper Desorption Behaviour From Copper Saturated Alginic Acid Gel Beads in 1 M HCl.

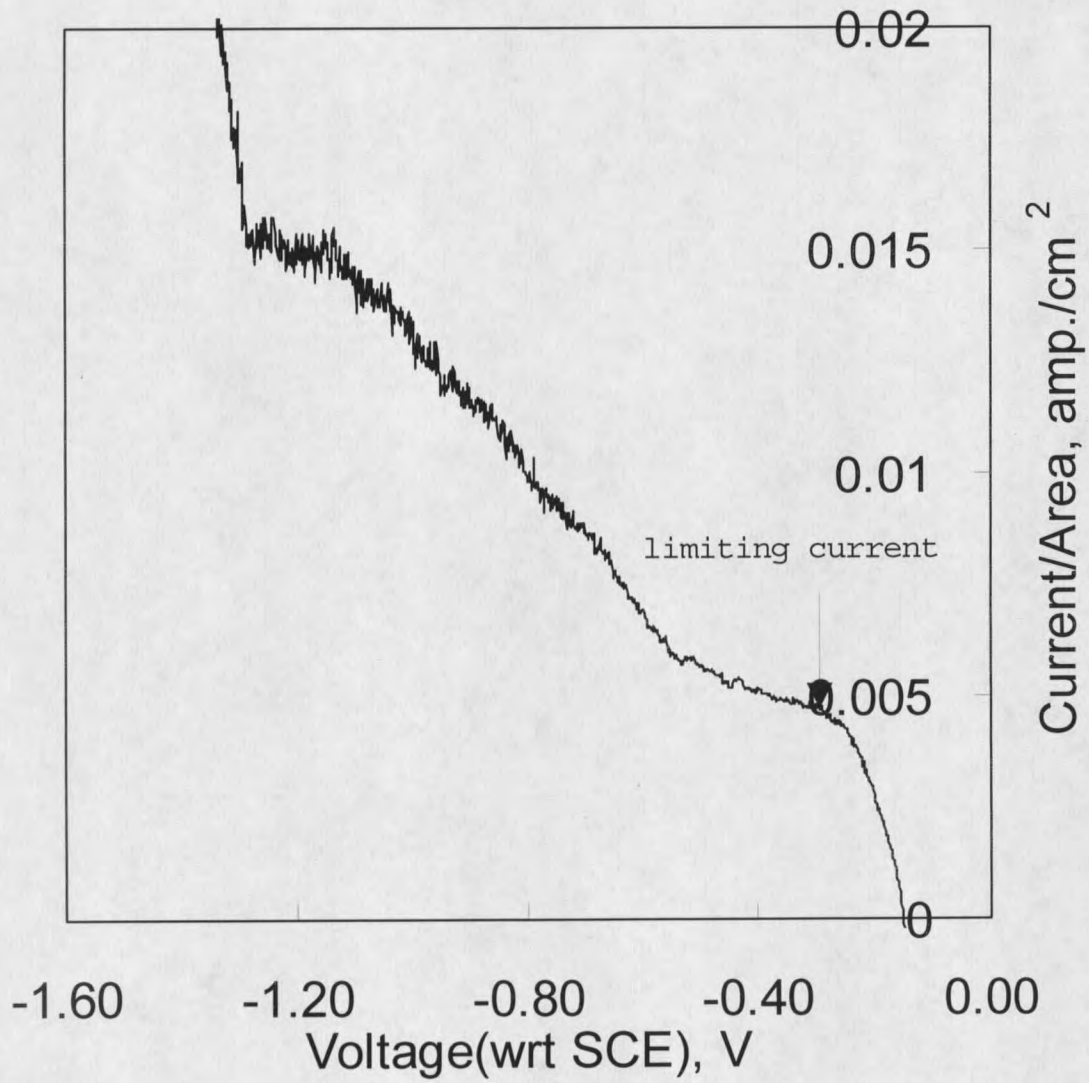


Figure 11 - Linear Polarization Curve for Copper With 0.5 M Calcium Chloride and 0.2 M Sodium Chloride Background.

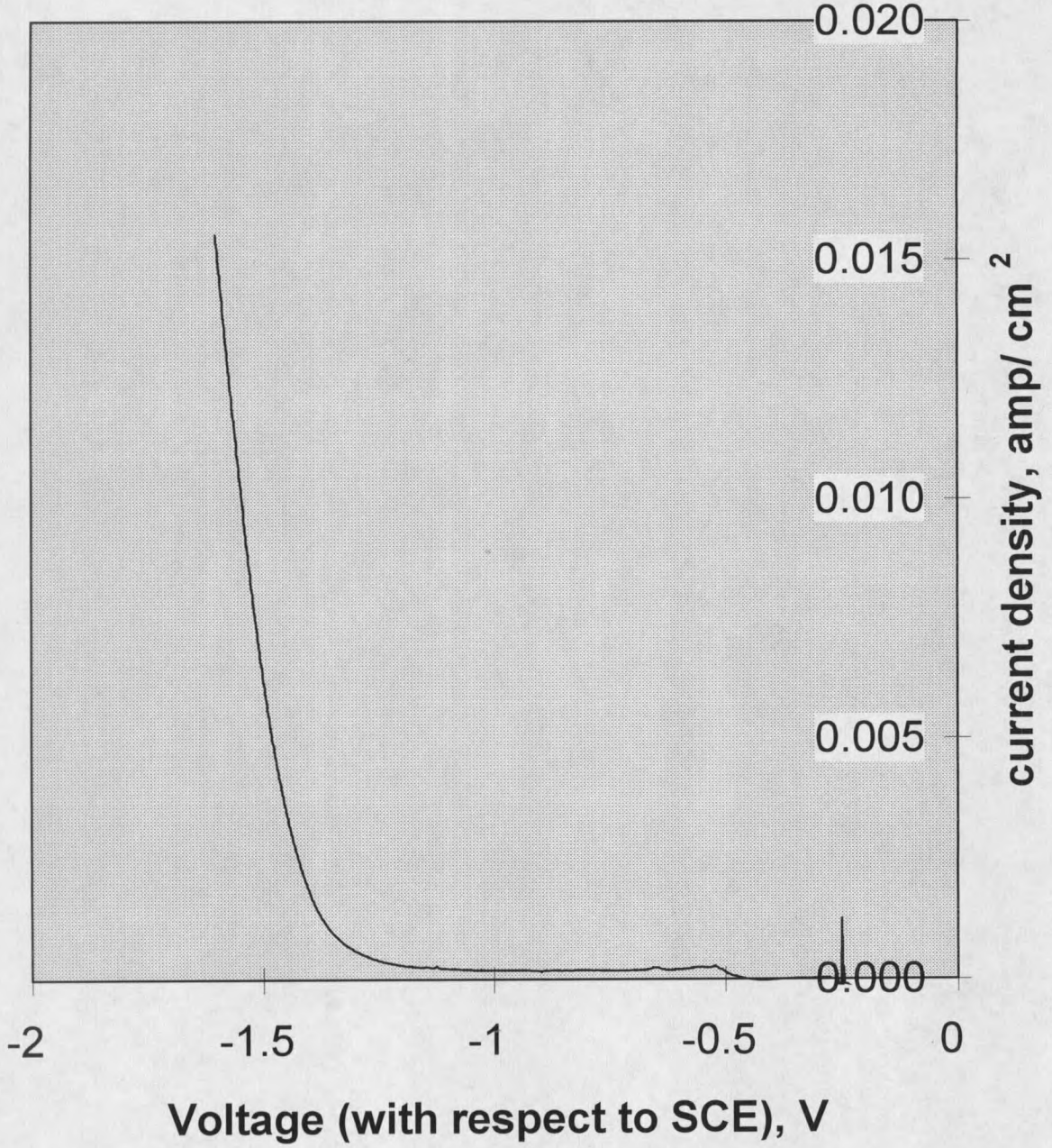


Figure 12- Linear Polarization Curve in a Deoxygenated Solution for Background Conditions.

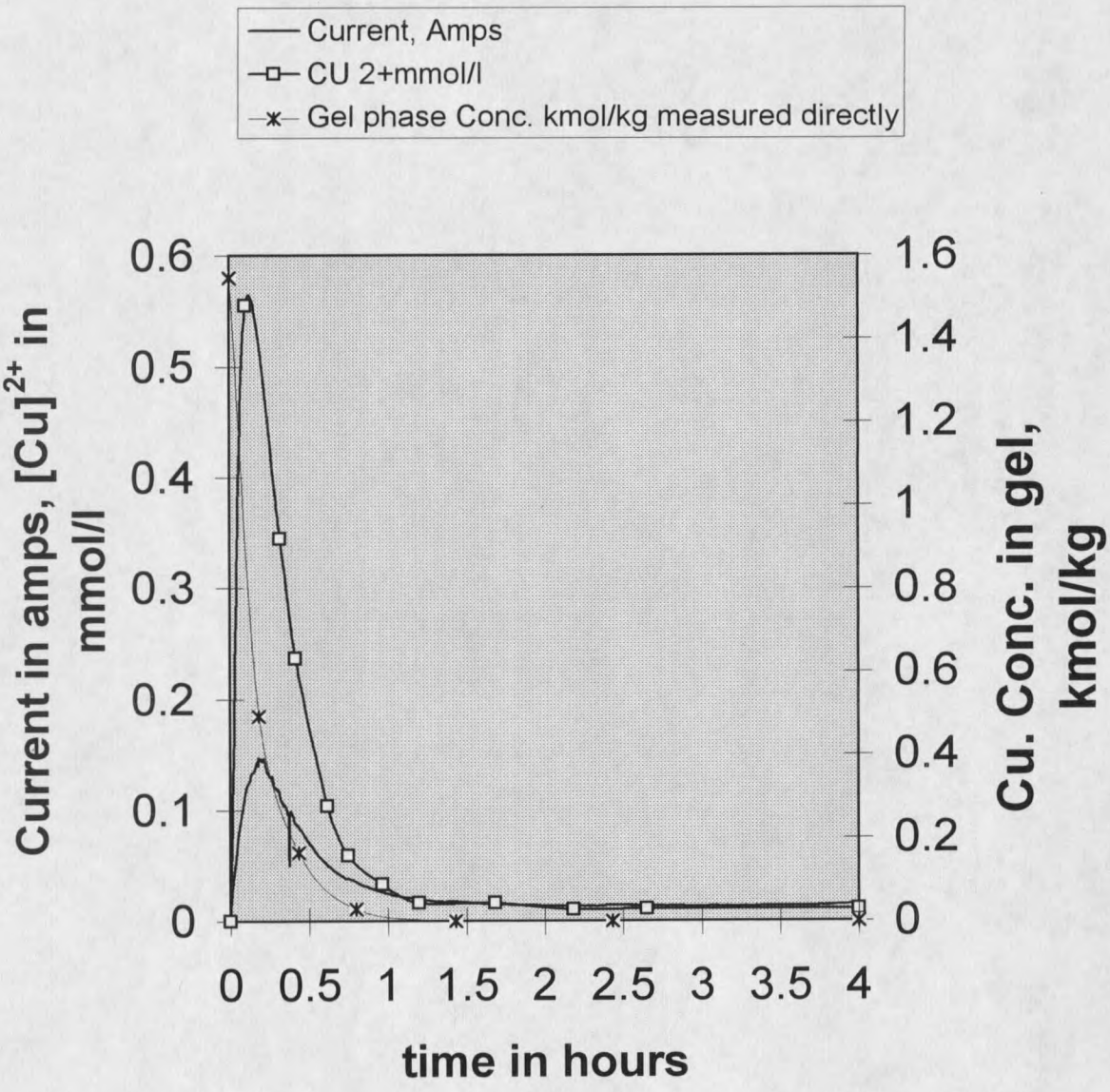


Figure 13 - Regeneration of Copper Saturated Calcium Alginate Gel by a Combination of Electrowinning at -0.5V (with respect to SCE) and Ion Exchange With 0.5 M Ca^{2+} Solution.

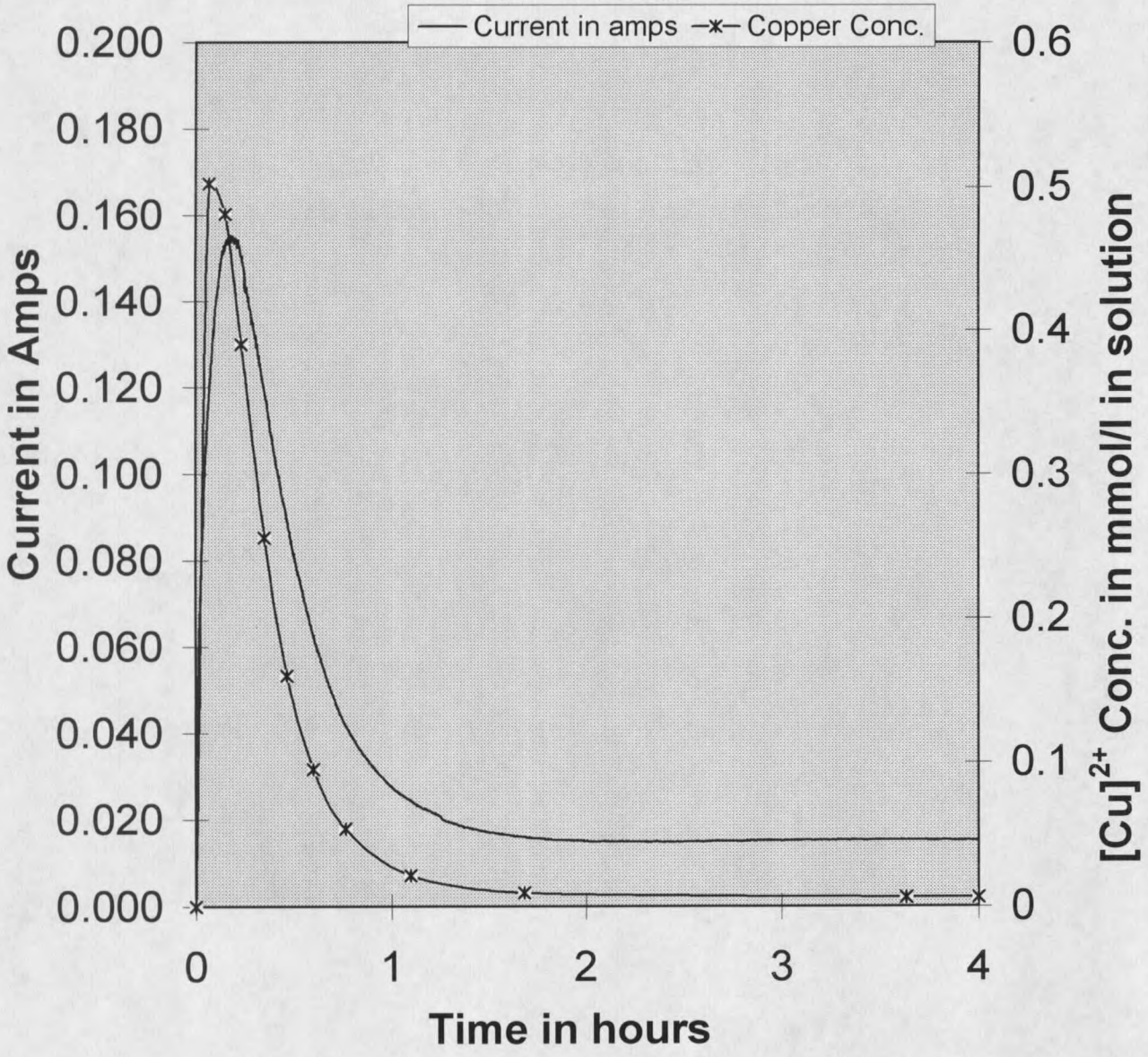


Figure 14 - Duplicate Set of Data During Regeneration of Copper Saturated Calcium Alginate Gel by a Combination of Electrowinning at -0.5 V (with respect to SCE) and Ion Exchange with 0.5 M Ca^{2+} Solution

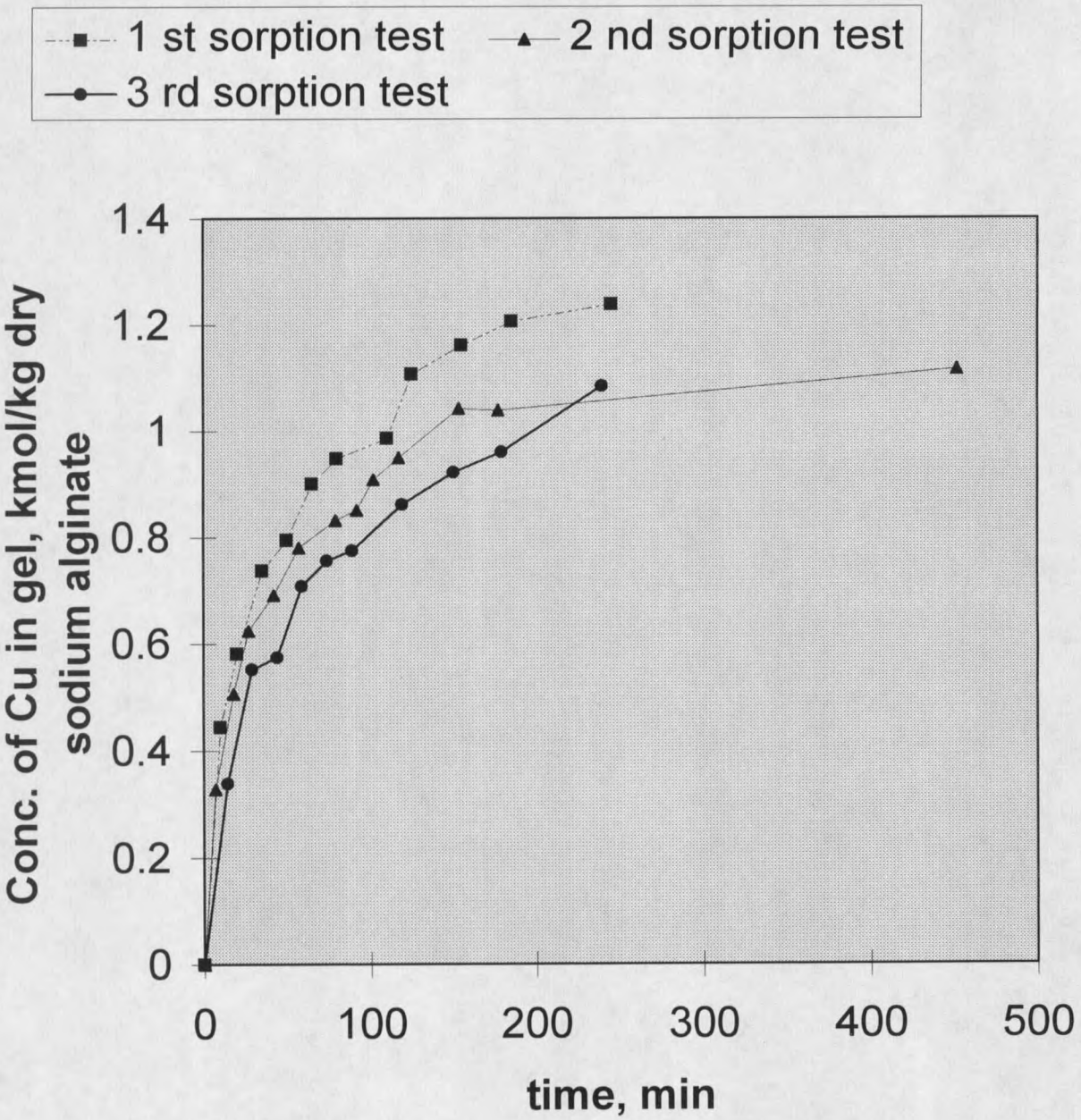


Figure 15 - Absorption Kinetics of Copper by a Single Batch of Beads After Successive Regeneration by The Combination of Electrowinning and Ion Exchange With Calcium Ions.

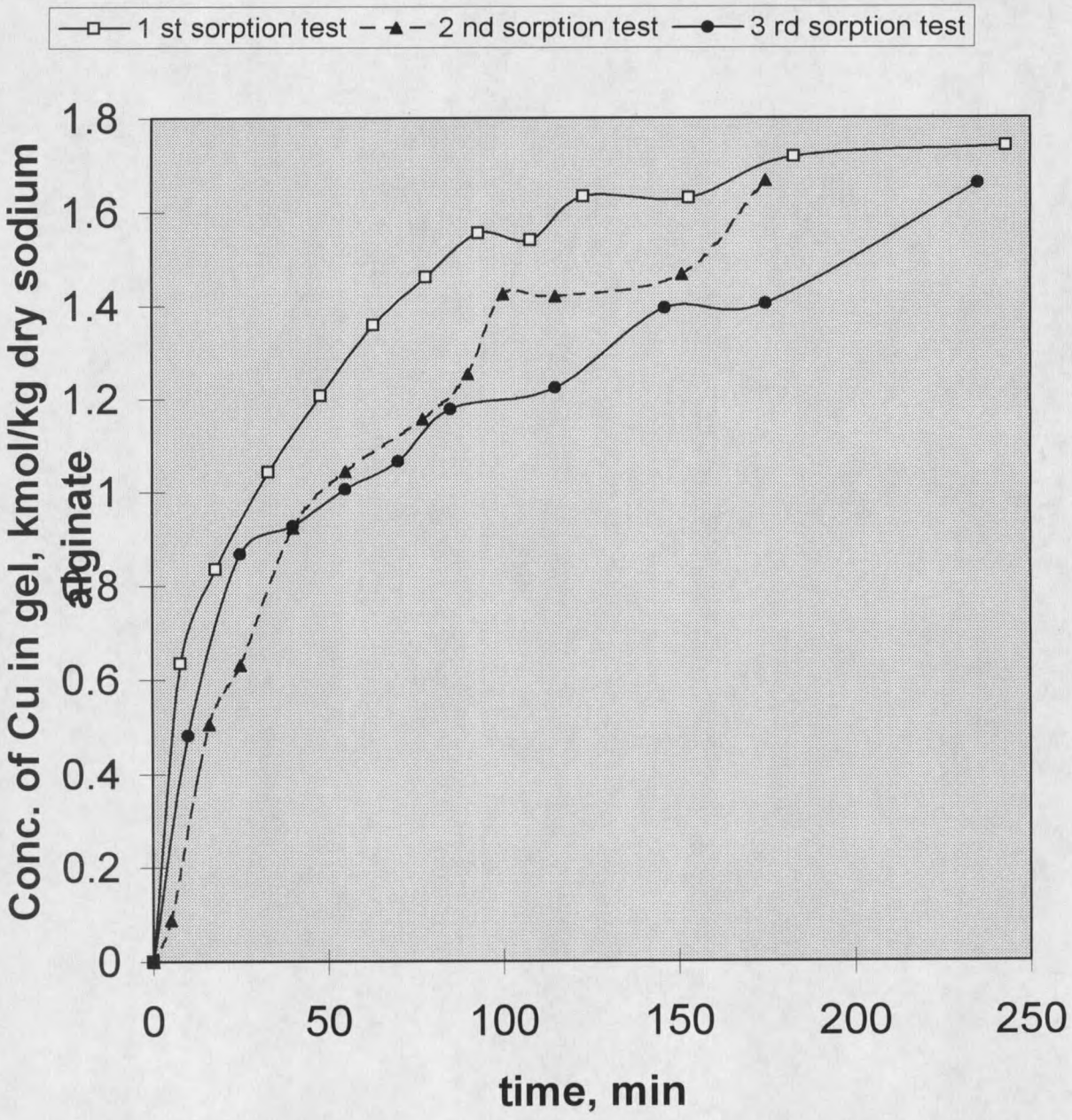


Figure 16- Duplicate Set of Data Showing Absorption Kinetics of Copper by a Single Batch of Beads After Successive Regeneration by The Combination of Electrowinning and Ion Exchange With Calcium Ions.

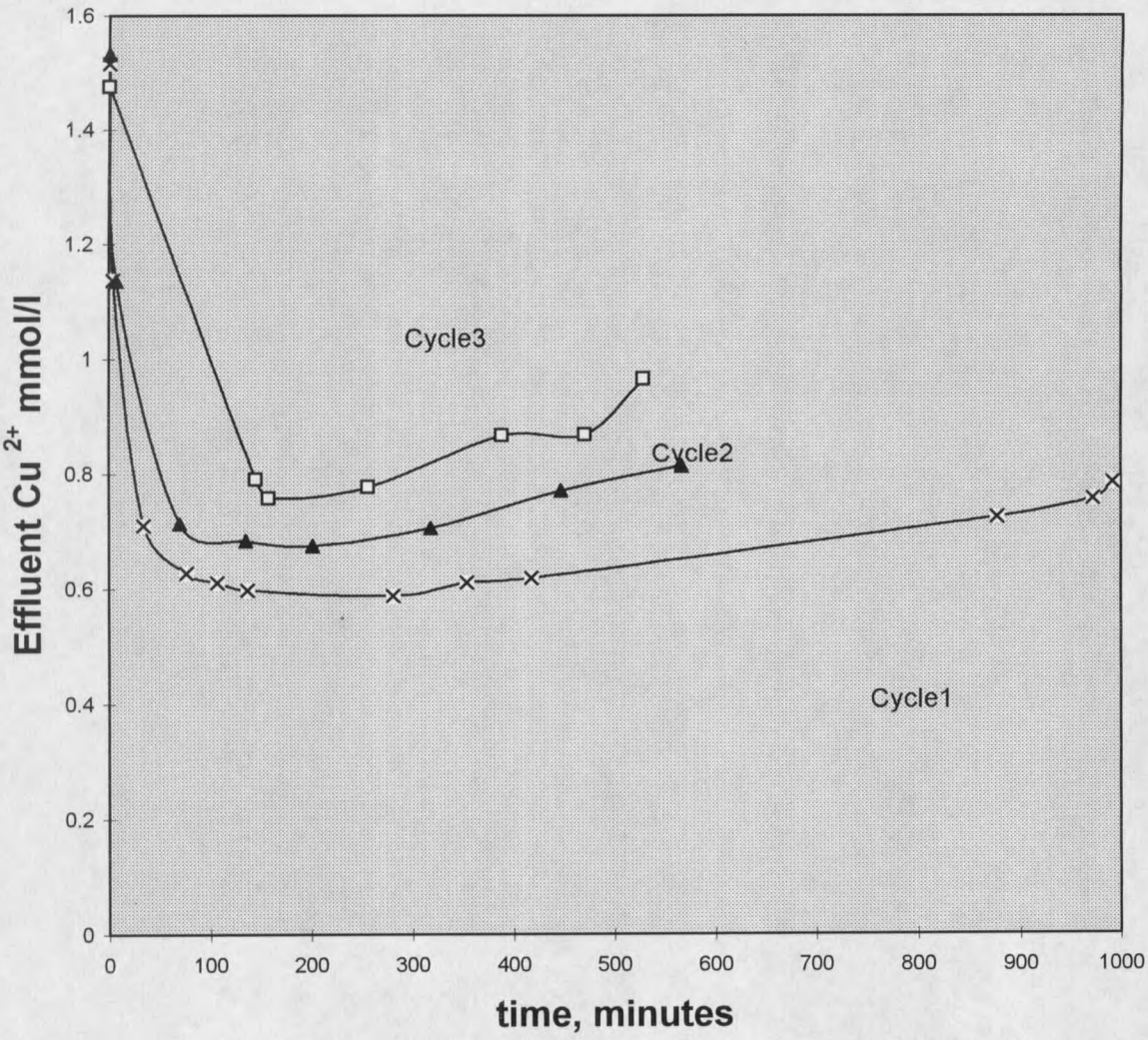


Figure 17 - Effluent Copper Concentration After Successive Regeneration by The Combination of Electrowinning and Ion Exchange With Calcium Ions in a Continuous Fluidized Bed Reactor.

Appendix B
Raw Data For Figures

		Table #1		
	Data for Figure # 5			
		Experiment # 77		
Time	$[Cu^{2+}]$	$[Cu^{2+}]$	$[CuX_2]$overscore	
min	mg/l	mmol/l	mmol/g	
0	156.59	2.4642	0	
15	126.41	1.98927	0.3996	
30	113.18	1.78107	0.57477	
45	106.87	1.68177	0.65831	
60	102.02	1.60545	0.72253	
75	96.23	1.51434	0.79919	
90	93.02	1.46382	0.84169	
105	92.4	1.45406	0.8499	
120	89.92	1.41504	0.88274	
180	89.61	1.41016	0.88684	
841	80.8967	1.27304	1.00221	

		Table # 2		
	Data for Figure # 6			
		Experiment # 42		
Time	$[Cu^{2+}]$	$[Cu^{2+}]$	$[CuX_2]$overscore	
min	mg/l	mmol/l	mmol/g	
0	103.8	1.63346	0	
6	82.4	1.2967	0.21544	
11	77.9	1.22588	0.26074	
16	70.2	1.10471	0.33825	
27	66.6	1.04806	0.37449	
36	66.5	1.04649	0.3755	
47	63.4	0.9977	0.40671	
61	61.2	0.96308	0.42886	
76	57.4	0.90328	0.46711	
91	58	0.91272	0.46107	
121	54.3	0.8545	0.49832	
213	51.8	0.81516	0.52349	
304	53.8	0.84663	0.50335	
416	54.9	0.86394	0.49228	
850	54.5	0.85765	0.49631	
916	53.55	0.8427	0.50587	

TABLE # 3

Data for Figure 7

Expt.# --->	#69	#70	#71	#77	#78	#79	#80	#81
Initial Conc., $[Cu^{2+}]_{initial}$, mmol/l	9.9625	5.016996	4.71095	2.464199	2.438758	4.84417	4.70436	8.03166
Fin Conc., $[Cu^{2+}]$ mmol/l	8.83	2.565	3.808	1.27304	1.948615	3.60159	3.722815	5.26443
dry wt. Na-alg. used, W in grams	0.2132	0.5305	0.1753	0.5907	0.1703	0.4026	0.29583	0.9762
total metal conc. in gel phase								
$[CuX_2]$ overscore, mmol/g	2.655957	2.311024	2.575442	1.008261	1.439058	1.543194	1.658968	1.984287
Distribution ratio, Dcu, l/g	0.300788	0.900984	0.676324	0.79201	0.738503	0.428476	0.445622	0.376923
Initial pH	4.95	5.19	5.21	5.35	5.35	5.11	5.16	5
Final pH	4.59	4.65	4.77	4.88	4.89	4.6	4.64	4.39
final $[Ca^{2+}]$, mmol/l	1.000175	2.264571	0.695559	4.991018	2.057884	4.61377	3.4145	6.181304
D_{Cu}*$[Ca^{2+}]$	0.300841	2.040342	0.470423	3.952937	1.519754	1.976889	1.521576	2.329878

			TABLE # 4			
			Data fro Figure 8			
Expt.# --->				#52	#53	#55
Initial Conc, $[Cu^{2+}]_{initial}$, mmol/l				1.5918	1.5831	3.27322
Fin Conc. $[Cu^{2+}]$,mmol/l				0.99062	1.0638	2.66815
dry wt. Na-alg. used, W in grams				0.4569	0.29205	0.23998
total metal conc. in gel phase, $[CuX_2]$ overscore						
mmol/g				0.65789	0.88906	1.260668
Distribution ratio, Dcu, l/g				0.66412	0.83574	0.472488
Initial pH				5.68	5.69	5.48
Final pH				2.76	2.9	2.93
initial $[H^+]$, mmol/l				0.002089	0.002042	0.003311
final $[H^+]$, mmol/l				1.737801	1.258925	1.174898
$[H^+]$ ions released from gel phase, mmol/g				1.899444	2.15183	2.441008
Dcu^(1/2)*$[H^+]$				1.416195	1.150895	0.807598

		Table #5		
	Data for Figure # 9			
Time	[Cu2+]	[Cu2+]	[CuX_2]overscore	
min	mg/l	mmol/l	mmol/g	
		Experiment 82		
0	0	0	1.00221	
8	31.01	0.48799	0.58915	
18	44.11	0.69414	0.41465	
28	51.13	0.80461	0.32114	
38	55.11	0.86725	0.26813	
48	56.16	0.88377	0.25414	
58	56.37	0.88707	0.25134	
83	58.99	0.9283	0.21644	
99	59.2	0.93161	0.21365	
128	59.61	0.93806	0.20819	
766	61.15	0.9623	0.18767	

		Table # 6		
	Data for Figure # 10			
		Experiment # 43		
Time	$[Cu^{2+}]$	$[Cu^{2+}]$	$[CuX_2]$overscore	
min	mg/l	mmol/l	mmol/g	
0	0	0	0.50587	
2	47.5	0.74749	0.21723	
7	58	0.91272	0.15342	
14	66.5	1.04649	0.10177	
19	69.8	1.09842	0.08172	
30	67.7	1.06537	0.09448	
42	71	1.1173	0.07442	
53	68.4	1.07639	0.09022	
62	68.9	1.08425	0.08719	
72	71.3	1.12202	0.0726	
82	68.4	1.07639	0.09022	
110	71.9	1.13146	0.06896	

Table # 7

Data for Figure # 15

Experiment # 112

Dry wt. of Na. alginate = 0.3699 g

Time min	[Cu2+] mg/l	[Cu2+] mmol/l	[CuX2] mmol/g
0	97.01	1.526611	0
10	83.1	1.307714	0.443829
20	78.8	1.240047	0.58103
35	73.9	1.162937	0.737375
50	72.1	1.134611	0.794808
65	68.8	1.08268	0.900102
80	67.3	1.059075	0.947963
110	66.1	1.040191	0.986252
125	62.3	0.980392	1.107499
155	60.6	0.95364	1.161741
185	59.2	0.931609	1.206411
245	58.2	0.915872	1.238318
1279	54.93	0.864413	1.342655

Experiment #122

Dry wt of Na. alginate= 0.3699

Time min	[Cu2+] mg/l	[Cu2+] mmol/l	[CuX2] mmol/g
0	100.7667	1.585728	0
7	90.5	1.424165	0.327581
18	84.9	1.33604	0.506261
27	81.2	1.277814	0.624318
42	79.1	1.244768	0.691323
57	76.3	1.200705	0.780663
79	74.7	1.175526	0.831714
92	74.1	1.166084	0.850859
102	72.3	1.137758	0.908292
117	71	1.117301	0.949771
153	68.1	1.071665	1.042302
177	68.2	1.073238	1.039111
451	65.76667	1.034946	1.116752

Experiment # 131

Dry wt. of Na. alginate = 0.3699 g

Time min	[Cu2+] mg/l	[Cu2+] mmol/l	[CuX2] mmol/g
0	97.73	1.537941	0
14	86.4	1.359645	0.338535
29	79.7	1.25421	0.552314
44	79	1.243194	0.574649
59	74.8	1.1771	0.708659
74	73.3	1.153495	0.75652
89	72.7	1.144053	0.775664
119	70	1.101564	0.861814
150	68.1	1.071665	0.922437
179	66.9	1.052781	0.960726
239	63	0.991408	1.085164

Table # 8

Data for Figure # 16

Experiment # 114

Dry wt. of Na. alginate = 0.5085 g

Time min	[Cu2+] mg/l	[Cu2+] mmol/l	[CuX2] mmol/g
0	286.98	4.516099	0
8	259.6	4.08523	0.6355
18	251	3.949895	0.835109
33	242	3.808265	1.044003
48	235	3.698108	1.206475
63	228.4	3.594247	1.359664
78	224	3.525006	1.461789
93	220	3.462059	1.554631
108	220.6	3.471501	1.540704
123	216.6	3.408554	1.633546
153	216.8	3.411702	1.628904
183	213	3.351903	1.717103
243	212	3.336166	1.740314

Experiment#124

Dry wt of Na. alginate= 0.5085

Time min	[Cu2+] mg/l	[Cu2+] mmol/l	[CuX2] mmol/g
0	299.4	4.711548	0
5	295.6	4.651748	0.088199
16	277.6	4.368489	0.505986
25	272.2	4.283511	0.631322
40	259.6	4.08523	0.923773
55	254.4	4.003399	1.044467
77	249.6	3.927863	1.155876
90	245.4	3.861769	1.25336
100	238	3.745318	1.425117
115	238.2	3.748466	1.420475
151	236.2	3.716992	1.466895
175	227.6	3.581657	1.666505

Experiment#133

Dry wt of Na. alginate= 0.5085

Time min	[Cu2+] mg/l	[Cu2+] mmol/l	[CuX2] mmol/g
0	292.13	4.597142	0
10	271.4	4.270922	0.481151
25	254.8	4.009694	0.866443
40	252.2	3.968779	0.92679
55	248.8	3.915274	1.005705
70	246.2	3.874359	1.066052
85	241.4	3.798823	1.177462
115	239.4	3.76735	1.223883
146	232	3.650899	1.39564
175	231.6	3.644604	1.404924
235	220.6	3.471501	1.660238

		Table# 9			
		Data for Figure # 17			
TIME	Cin	Cout	Cout	Cin-Cout	area
min	mM	mg/L	mM	mM	mM-min
		CYCLE 1			
0			1.517011		
4	1.517011	72.2	1.136185	0.380826	0.761653
34		45.1	0.709722	0.807289	17.82174
77		39.85	0.627105	0.889907	36.48971
107		38.85	0.611368	0.905643	26.93325
137		38	0.597992	0.919019	27.36994
281		37.35	0.587763	0.929248	133.0753
354		38.8	0.610581	0.90643	67.00225
418		39.3	0.61845	0.898562	57.75973
877		46.05	0.724672	0.792339	388.0618
972		48.05	0.756145	0.760866	73.77726
992		49.85	0.784471	0.73254	14.93406
		CYCLE 2			
0			1.532748		
7	1.532748	72.15	1.135398	0.39735	1.390725
70		45.3	0.712869	0.819879	38.3427
135		43.4	0.68297	0.849778	54.26384
201		42.9	0.675102	0.857646	56.34501
318		44.8	0.705001	0.827747	98.59551
447		48.95	0.770308	0.76244	102.567
566		51.65	0.812797	0.719951	88.20225
		CYCLE 3			
0	1.476096		1.476096		
145	1.476096	50.2	0.789979	0.686117	
158		48.1	0.756932	0.719164	
256		49.4	0.77739	0.698706	
389		55.1	0.867088	0.609008	
471		55.2	0.868662	0.607434	
529		61.3	0.964656	0.511441	

Appendix C
Figures for Duplicate Sets of Data

FIGURE 18
Absorption/Desorption behavior of Cu by Ca-alg
[Cu]initial=2.36 mmol/l, Na-alg=0.1703 g

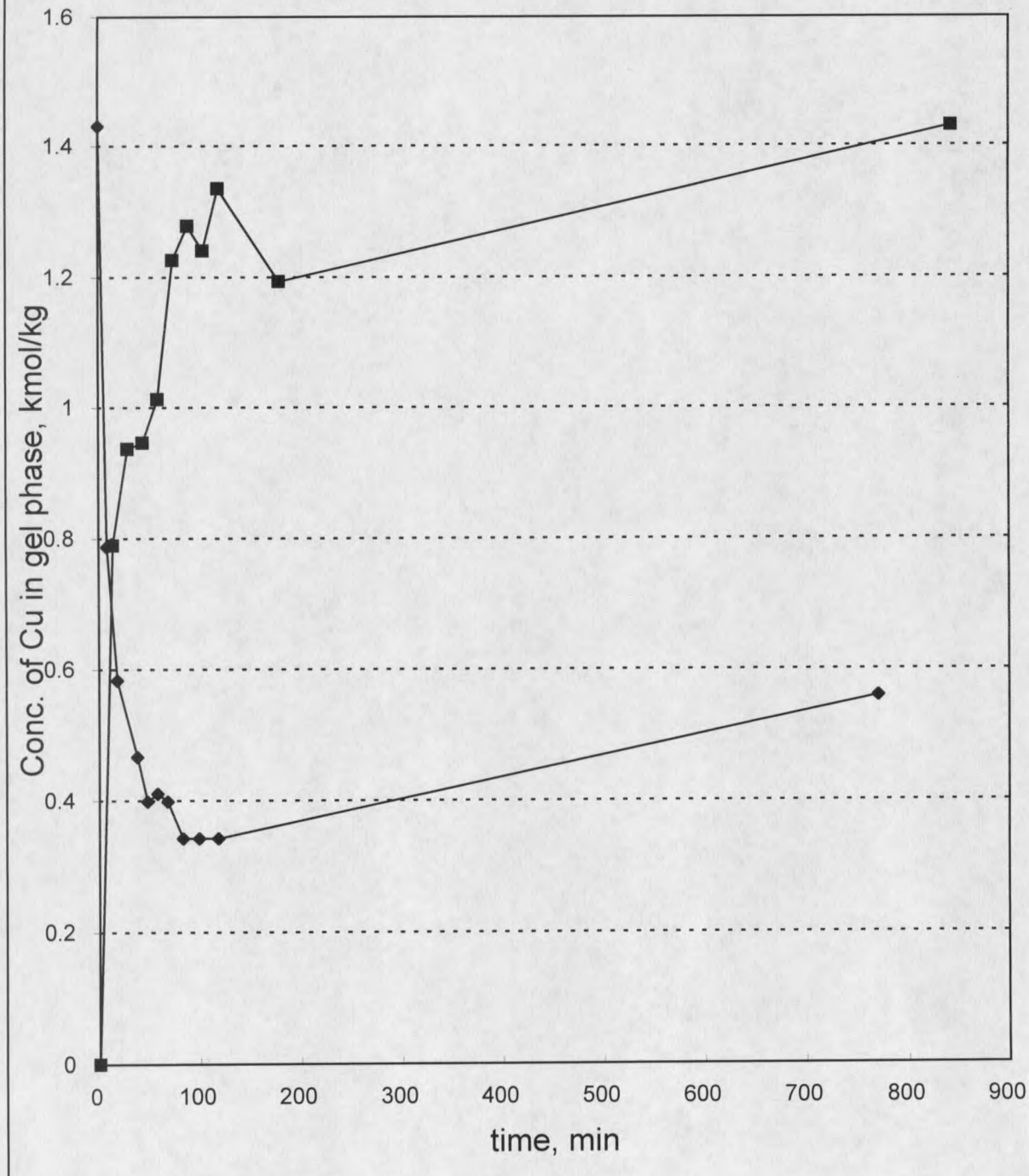


FIGURE 19
Absorption/Desorption behavior of Cu by Ca-alg
[Cu]initial=4.72mmol/l, Na-alg=0.4026g

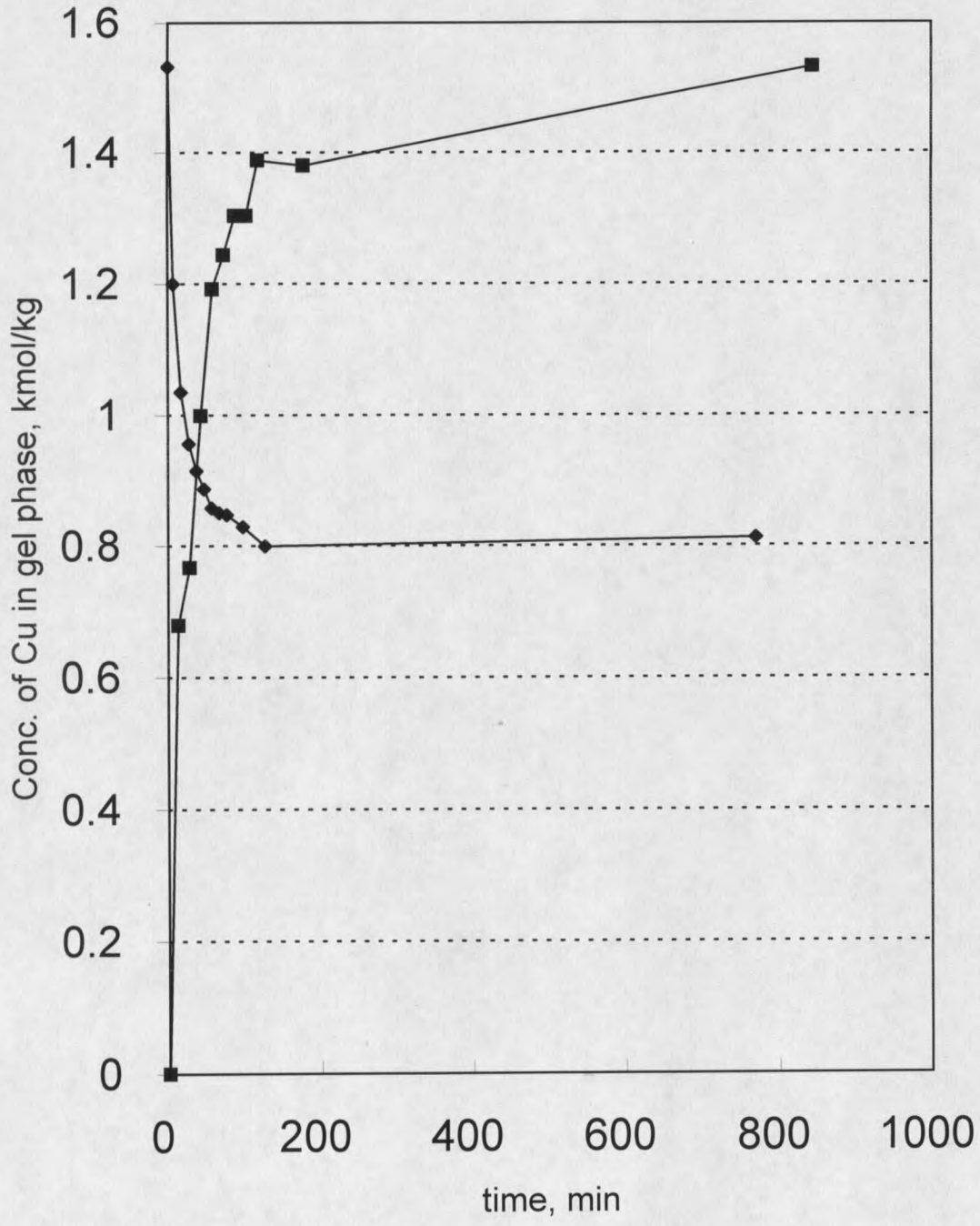


FIGURE 20
Absorption/Desorption behavior of Cu by Ca-alg
[Cu]initial=4.72mmol/l, Na-alg=0.2958g

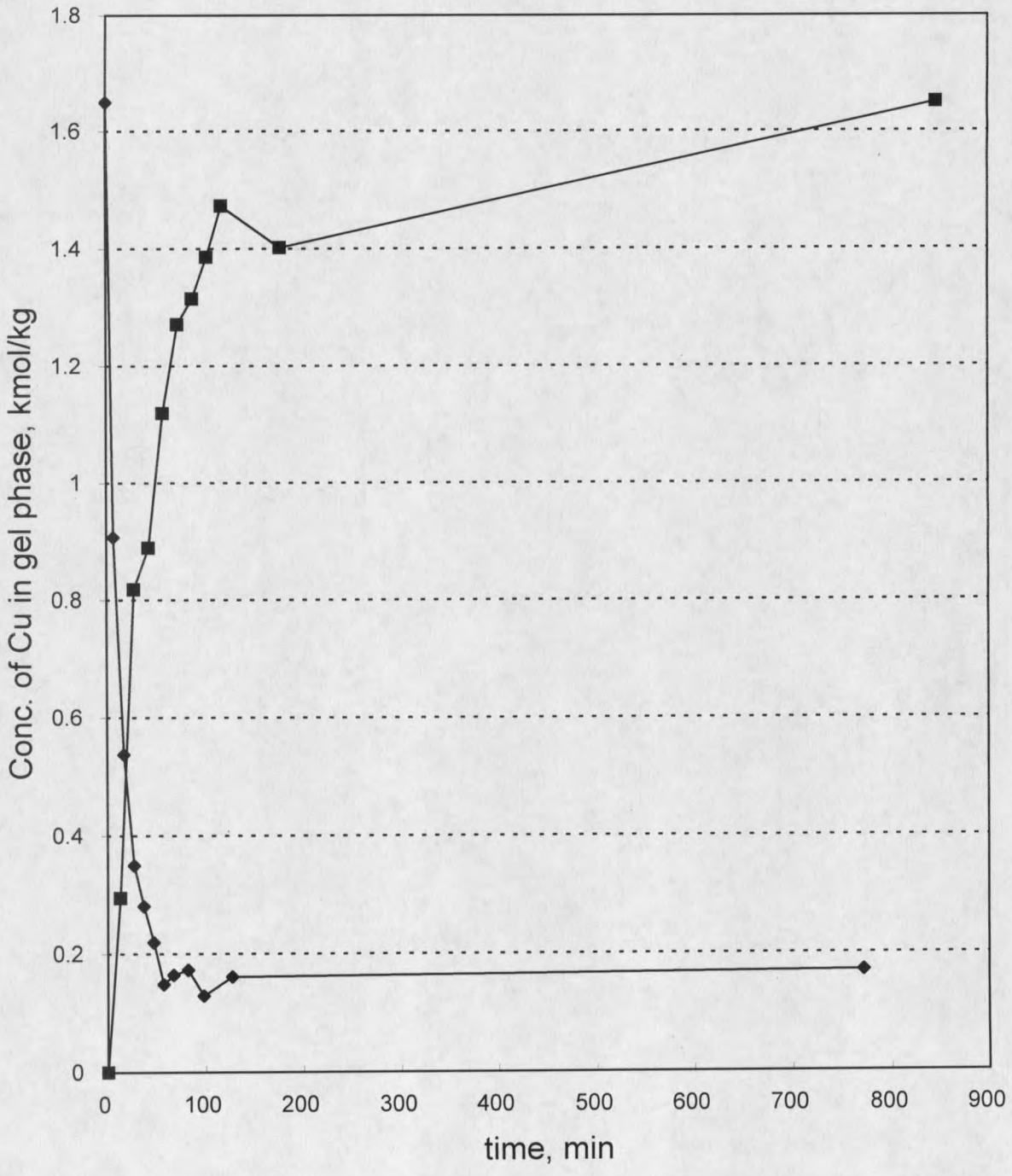
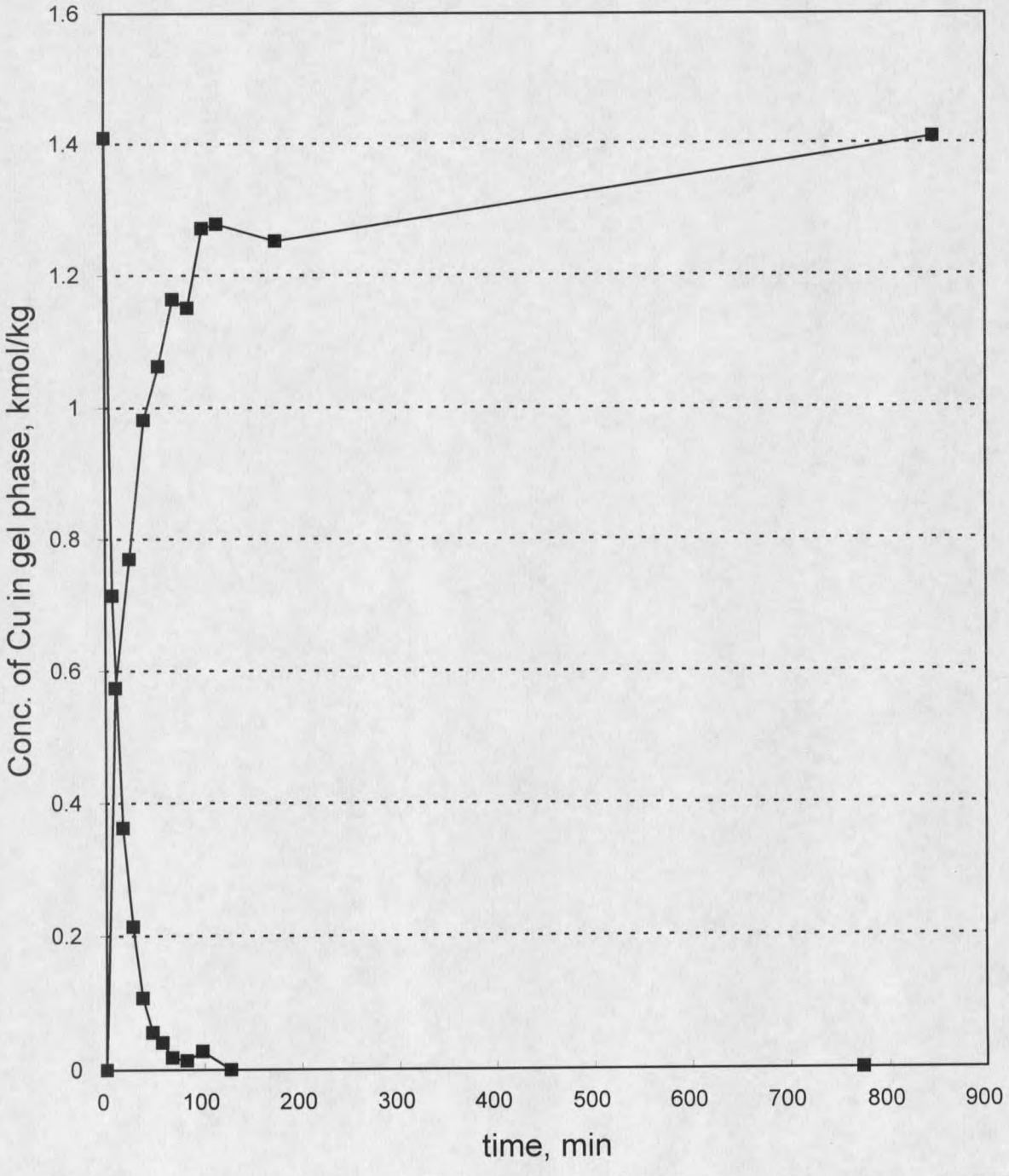


FIGURE 21
Absorption/Desorption behavior of Cu by Ca-alg
[Cu]initial=7.87mmol/l, Na-alg=0.9762g



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