Final Report

FEASIBILITY REPORT ON THE PURIFICATION, RECOVERY, AND REUSE OF METAL FINISHING SOLUTIONS

by

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EXECUTIVE SUMMARY

The Naval Civil Engineering Laboratory (NCEL) has been tasked by the Naval Facilities Engineering Command (NAVFAC) to reduce the hazardous waste generated from spent metal finishing solutions. The project focuses on purification, recovery and reuse of concentrated cadmium cyanide and chromium electroplating bath solutions, with an overall goal of total recycle. However, due to the highly toxic nature of the cadmium cyanide plating solution, priority was given for conducting laboratory studies on the purification and reuse of the cadmium cyanide plating solution.

An extensive literature review resulted in the selection of the following purification methods for detailed laboratory evaluations on reclamation and reuse of the concentrated cadmium cyanide plating bath:

- cementation
- solvent extraction
- crystallization
- electrolytic process (low-current dummying)
- sulfite reduction

The results of the cementation experiments showed that cementation of copper impurities with cadmium or magnesium was ineffective. The presence of cyanide in the plating solution lessens if not completely inhibits the ability of cadmium or magnesium to cement copper impurities. In addition, the presence of other metal ions in the cadmium cyanide plating bath interferes with the ability of magnesium turnings to cement copper, since copper, once cemented, acts as a sacrificial metal for cadmium and goes back into solution. A waste minimization strategy is recommended in order to reduce the metallic contaminants introduced into the plating bath.

The use of solvent extraction for removing oil and grease organic contaminants was found to contribute insignificant amounts of kerosene solvent in the aqueous phase. Only a small fraction of the organic constituents in the cadmium cyanide plating solution was co-extracted by kerosene. Kerosene extraction followed by filtration is recommended for removal of oil and grease contaminants. A fraction of the make-up brightener solution, along with the ligand sodium cyanide, will need to be added back to the plating bath after kerosene extraction.

A crystallization process, based on a U.S. patent, was found to effectively remove sodium carbonate contamination in the cadmium cyanide plating bath to levels below its threshold value of 70 g/L (i.e., 189 g/L as sodium carbonate decahydrate). A makeup solution of sodium hydroxide and sodium cyanide will need to be added to compensate for their loss during the carbonate removal process. Sodium sulfite satisfactorily controlled the minor anionic contaminant, chromate, to levels below its threshold level for reuse.

Electrolytic plating of cadmium solution was determined to be infeasible for removing copper contaminants. It was found that the process removed large quantities of cadmium, with little or no removal of copper contaminants. A small amount of magnesium turnings may be needed to control other minor cationic contaminants.

A batch treatment scheme utilizing the above processes, along with the practice of waste minimization, is recommended to reclaim a synthetic cadmium cyanide solution contaminated with cations, anions, oils and greases at concentrations found to impair the plating process. A Hull test cell would be used for monitoring the quality of the plated steel before and after treatment.

INTRODUCTION

The Naval Civil Engineering Laboratory (NCEL) has been tasked by the Naval Facilities Engineering Command (NAVFAC) to minimize hazardous waste volume and disposal costs from spent metal finishing solutions. Innovative and cost-effective technologies are to be researched for the purification, recovery and reuse of these solutions.

Electroplating is a metal finishing operation performed at shore-support activities. The electroplating process is used primarily to repair worn or damaged parts from aircraft and ships. Various metals are plated at these activities including: chromium, cadmium, copper, zinc, nickel, silver and gold. The parts are plated in solutions referred to as electroplating baths. Many of these baths (e.g., cadmium, silver, gold and zinc) contain cyanide which is added in the form of sodium or potassium cyanide. The cyanide is present in plating bath formulations as a complexing agent or ligand.

The objective of this project was to develop a closed-loop purification and recycling process for cadmium and chromium plating bath solutions. These two metals were selected for detailed analyses because they comprise the majority of the plating bath solutions in Navy electroplating operations, with cadmium a component in 30 percent of the solutions, and chromium a component in 60 percent of the solutions.[1]

In this Feasibility Report, several technologies on recovery, reclamation and reuse of contaminated cadmium cyanide baths have been evaluated based on literature reviews, discussions with vendors and professionals, and experimental results. Cementation, low-current dummying, solvent extraction, crystallization and sulfite reduction were selected as the most technically and economically feasible alternatives warranting further studies.

BACKGROUND

Electroplating is one of several types of processes within the broader category of metal finishing. Electroplating, as defined by the Environmental Protection Agency (EPA), is "the production of a thin surface coating of one metal upon another by electrodeposition".[2] An electroplating process includes cleaning, electroplating, rinsing and drying, with the electroplating operation being an oxidation-reduction reaction. In the electroplating solution, metal ions in either an acid, alkaline or neutral solution are reduced and deposited on cathodic surfaces. The cathodic surface is the part being plated. The metal ions in solution are usually replenished by the dissolution of metal from anodes or small pieces contained in inert wire or metal baskets, as well as from metal salts.[2] The two most common methods for plating are in barrels or on racks.

The basic plating operation involves immersing parts in a process solution, and then rinsing off the solution remaining on the part. Over time, the plating solution bath becomes contaminated with various organic and inorganic constituents. Once contaminated, the plating process is no longer effective and the solution is placed in one or more drums for disposal.

It has been estimated that over 500,000 gallons of spent plating and stripping baths are generated per year at naval facilities. Disposal costs of these wastes exceed $1,000,000 per year and are expected to escalate at least three-fold over the next five years as more stringent disposal regulations are implemented under amendments to the Resource Conservation and Recovery Act (RCRA) of 1976 (Public Law 94-580).[3] Waste minimization is already mandated in the 1984 Hazardous and Solid Waste Amendments (HSWA) to RCRA, and is defined as the reduction of any solid or hazardous waste that is generated or subsequently treated, stored or disposed. Reduction is considered to include volume reduction

as well as reduction in the quantity of toxic constituents or of waste toxicity.

Waste minimization efforts in the metal finishing industry consist primarily of methods designed to minimize consumption of rinse water, extend plating bath life, recover baths and rinses, and substitute less toxic raw materials. Whereas most of the efforts and technological advances have been devoted to in-plant reduction and recovery of rinse water, few advances have been made in in-situ recovery of spent plating baths.

Conventional treatment and disposal methods for plating bath wastes are considered unreliable, potentially unsafe, and costly. Innovative technologies attempted and discarded by NCEL in previous studies include freezing to precipitate carbonates using LICON or cold vapor processes, utilizing a gas membrane to recover cyanide, and using electrowinning for metal recovery. The current study may include some of these processes as alternatives, if appropriate.

TECHNICAL APPROACH

The objective of this study was to research and evaluate innovative purification and recycling technologies for concentrated plating bath solutions. Initially, a literature review was conducted in order to identify technologies which showed promise in extending bath life and/or recovering spent bath for reuse. The literature review was followed by preliminary laboratory evaluation of the most applicable treatment processes to reclaim synthetic spent cadmium cyanide baths or to maintain proper levels of the bath constituents for extended bath life. Since a complete closed-loop purification and recycling technique was the ultimate goal of this study, alternative coating technologies and raw material substitution were not considered.

Reclamation of spent baths usually involves destruction of certain bath components, such as cyanide, for recovery of valuable metals. Extending bath life involves methods to reduce plating bath contamination. The emphasis of this study was placed on the latter approach of extending bath life, although in some cases, methods to recover major bath constituents were also considered. Examples of practices which extend bath life include: use of purer anodes; improved rinsing and rack design, and extended drip time to reduce drag-in; use of deionized water to compensate for evaporative loss; and the use of treatment techniques to selectively remove contaminants. Examples of treatment methods include filtering to remove suspended solids, use of carbon adsorption or chemical oxidation to remove organic breakdown products, freezing to effect carbonate precipitation from cyanide solutions, and ion separation to selectively remove metal contaminants. Other treatment methods resulting in recovery of primary bath components (generally from rinses) include electrolytic recovery, ion exchange, reverse osmosis, evaporation and crystallization.

More than 90 percent of the Navy's plating facilities involve chromium (60 percent) and cadmium (30 percent) baths. Therefore, methods to extend the lives of these baths were given prime consideration. The approach was to first investigate methods for extending bath life of hard chrome plating due to both its larger usage volume at Navy installations, and the availability of innovative technologies on a commercial scale. This was followed by reviewing methods suitable for either extending bath life or recovering cadmium cyanide bath. The latter constituted the major effort in the laboratory evaluations. Both commercially available technologies and state-of-the-art research findings were investigated.

TECHNOLOGY ASSESSMENT

Literature Review

An extensive literature review was conducted utilizing the references listed below:

- *Journal of the Water Pollution Control Federation*, including the recent Literature Review issues of the Journal.
- *Plating and Surface Finishing*
- *Journal of Environmental Engineering, ASCE, EED*
- *Environmental Technology Letters*
- *Metal Finishing*
- *Solvent Extraction and Ion Exchange*
- *Process Engineering*
- *Water Research*
- *Proceedings of the Purdue Industrial Waste Conference*
- *Products Finishing*
- *Environmental Progress*
- *Journal of Metals*
- *Proceedings of the American Electroplater's Society Annual Technical Conference*
- Noyes Data Corporation (NDC) Publications
- Electroplating Reference Books
- Vendors' Brochures
- U.S. Patents

From these references, appropriate articles were reviewed for applicability and feasibility for purification and recovery of concentrated plating bath wastes.

Most of the methods reviewed were determined to be suitable for dilute waste streams only. Telephone calls placed to vendors, vendor's clients, and authors of the articles were used as guidelines for assessing whether further evaluation was warranted.

Preliminary Treatment Alternatives Evaluation

The generation of spent baths can be reduced by various approaches aimed at extending bath life or removing contaminants. A few of the more frequently used methods include filtration of bath solutions, crystallization of soluble salts with subsequent filtration, and oxidation of trivalent chromium. Contamination of baths can also be reduced by taking precautionary measures, such as thorough rinsing to reduce drag-in, rack maintenance to prevent contaminant build-up resulting from dissolution of rack materials, and using purer and more inert electrodes to minimize electrolytic dissolution or anodic oxidation of impurities from the electrodes. Below is a more specific evaluation of treatment technologies for chromium and cadmium plating bath solutions.

Chromium Plating Baths

Since various defects in chromium-plated deposits are attributed to metallic impurities, emphasis was focused on identifying technologies for removing metal impurities from chromium plating baths. Technologies for purifying chromium plating baths can be categorized into four major processes:

- Ion Exchange
- Electrolysis
- Electrodialysis
- Solvent Extraction

The functions or applications of these technologies can be divided into two groups: 1) removal or conversion of trivalent chromium (Cr^{3+}); and 2) removal of other metallic impurities (e.g., iron, copper, etc.). The build-up of organic impurities from degradation of brighteners, etc. was considered only when it posed severe problems. Table 1 lists the available bath purification technologies for removal of metal impurities, including Cr^{3+}, from hard chrome plating baths and/or rinses. With the exception of ion exchange, bath purification is a relatively slow process. Commercial purification units are not designed for rapid regeneration of highly contaminated baths. Rather, these technologies are intended more for continuous bath maintenance.

The selection of a bath purification unit should be based on the following:

- a target level of metal contaminants within the bath
- a reasonable time period for reaching the target level
- an estimate of the contaminants' build-up rate
- a current analysis of the bath
- the removal capacity of the technology
- the economics of the technology

Simple electrolysis (dummying) was not considered in this review. Although dummying remains a viable process for Cr^{3+} removal, there are many negative aspects. These negative aspects include requirements for tank shut-down, sharp fluctuations in Cr^{3+}, intensive labor efforts, inefficient Cr^{3+} removal, and most importantly, no effect on iron, copper and other tramp metals.

Cadmium Plating Baths

The build-up of both metallic and organic impurities is known to impair the quality of the plated parts. In addition, dragout of plating bath

TABLE 1

Available Chromium Bath Purification Technologies (In many instances, used in conjunction with recovery of rinse water)

TECHNOLOGY	VENDOR	BRIEF PROCESS DESCRIPTION	ECONOMICS
Ion Exchange	ECO-TECH[4] (Canada) Mr. M. Dejak (416-831-3400) (Contacted)	Short-bed ion exchange. Cationic and anionic contaminants are exchanged in separated cationic and anionic resins followed by regeneration with dilute acid and base. Chromate ions are recycled and deionized water is reused as rinse water. Sulfate removal is necessary. Only dilute rinse water is treated with potential for closed-loop treatment of bath.	Savings are high with chrome bath @ 4.34/ kg CrO_3 used. Pay back period 1.5 years. Capital $120,000
Electrolysis Porous Pot	CAI Engineering (Reference)[5]	Use of a porous ceramic to separate catholyte and anolyte. It is effective in reoxidizing Cr^{3+}, but is ineffective in removing metal contaminants. Large amounts of chromium-bearing waste generated.	
Membrane		An ion transfer membrane process employing a separate tank and power source. Uses a non-ion-selective membrane which differs from the electrodialytic process. Uses tank rectifier rather than separated power source with limited capacity.	
Electrodialytic Acid Catholyte	IONSEP Corp.[6] Dr. Dan Vaughan (302-764-7849) (Contacted)	Original design using ion-selective cationic membrane to separate catholyte and anolyte. Capacity is limited due to build up of cations and metal deposits on cathode. Generates acid wastes. Chrome carry-over due to poor design.	
Electrodialytic Caustic Catholyte	IONSEP Corp. Dr. Dan Vaughn (Contacted)	Newer and more advanced design. Metals are removed efficiently in separate compartments as hydroxide can be used directly in bath and indirectly in closed-loop recycling of rinse water and chromate.	Annual cost $6000 vs. $40,000 to change out a 5000 gal bath. Pay back 1 year. Capital $30,000
Extraction Extract Cr^{6+}	Cuer et al.[7] Japan Patent (Reference)	Chromate and dichromate ion extraction from acid solution by use of TBP or an amine extractant. 99% recovery of chromate from waste effluent. Additional organic solvent can be used to remove extracted impurities such as Fe and Cl.	
Extract Metal Impurities	MX Processor AB (Sweden) (Reference)[7]	Recovers spent chromium baths by extracting the impurities, thus regenerating the bath for reuse. A mixture of TBP and HDNNS extractants is used. Dilution of bath improves the operation. 5N H_2SO_4 or HCl is used for stripping chromate to yield 60 g/L bath.	Under Investigation. However, the economics look favorable as compared to a disposal cost of $5/gallon of spent bath.

constituents represents a loss of raw materials, as well as poses problems to disposal of contaminated rinse water. Although information on direct methods to extend bath life is scarce, several indirect methods to recover the plating constituents (mainly cadmium cyanide complex) from rinses for reuse with concomitant recycle of treated rinse water are available for review. These indirect methods for recovery of cadmium cyanide plating baths can be categorized into four major groups:

- Ion Exchange
- Solvent Extraction
- Low-Temperature Evaporation
- Reverse Osmosis

Several direct methods to recover cadmium from spent baths have been reviewed. They include freezing to precipitate cadmium carbonates and pH adjustment to precipitate cadmium hydroxide. These methods normally involve destruction of cyanide complexes by oxidants and recovery of metals by plating out (e.g., electrowinning). However, the purity of the cadmium recovered by these processes is sometimes undesirable for reuse. The ideal methods to extend bath life are to remove metallic impurities and organic contaminants. They are, however, unavailable from commercial sources. Results of a continual review of literature are presented in the following section on laboratory evaluation. The extensive literature review was conducted in order to fully explore the state-of-the-art technologies. Table 2 lists technologies which have shown potential for reuse and reclamation of cadmium cyanide baths, mainly through indirect methods.

TABLE 2

Cadmium Cyanide Bath Reuse/Reclamation Technologies

TECHNOLOGY	VENDOR	BRIEF PROCESSES DESCRIPTION	ECONOMICS
Solvent Extraction	F. L. Moore[8] U.S.Pat.4026790 1977 (Reference)	Quaternary amine halides (Aliquot 336, and Adogen 464) were used as a liquid ion exchanger (LIE) to concentrate cadmium. Cyanides from rinse water are subsequently stripped with NaOH to regenerate LIE and recycle $Zn(CN)_4$ and NaCN. Since this anionic LIE will not exchange with uncomplexed metal impurities, it serves to also purify cadmium cyanide bath with recovered Cd metal. For concentrated Cd solutions, the efficiency of Cd extracted decreased from 99.9% to 67% (at 8,000 ppm). Loss of LIE to rinse water requires carbon adsorption for its removal.	No commercial equipment for evaluation.
Anionic Ion Exchange		Based on principles of LIE solvent extraction, the use of strong base anionic exchange resins should be explored.	Cannot be assessed without additional information on laboratory studies.
Low Temperature Evaporation/ Recovery-Vapor Compression System	LICON [9] Pensacola, FL Mr. Williamson (904-477-0334) (Contacted)	Essentially involves low temperature evaporative recovery of rinse water with concomitant recovery of cyanide metal (Cd) plating solution in concentrated form. Therefore, it is a closed-loop system. Not applicable to extending bath life as no removal of impurities (especially metals) is accomplished. Studies were done under a DOE contract. Ken Chacey and Larry Mellichamp at Naval Facilities Eng. South Div., Charleston, SC should be contacted.	10 month pay back if compared to cost savings vs. the destructive chemical treatment process. Capital costs at $57,000 based on treating 12,000 gal spent $Cd(CN)_4$ bath. 2.5 year pay back on chemical costs.
Cold Vaporization	CALFRAN Intl. Inc. Mr. Val Partyka (413-325-4957) (Contacted)[10]	A low temperature evaporator used for concentrating $Cd(CN)_4^{2-}$ in rinse water for reuse and generation of condensate of superior quality for recycle. It suffers the same disadvantage as LICON's evaporator of being unable to purify baths.	$42,800 capital cost for 300 gpd unit. 90 KW
Crystallization Using Pellet Reactor	DHV Consulting Eng. The Netherlands Mr. Kiestra 0-11-31-33-689-111 (Contacted)[11]	Heavy metals can be removed from waste streams without sludge production. Carbonate is added to a fluidized bed containing sand grains as seeds. Metal carbonates (e.g., Zn, Ni, Cd, Cu) crystallize on the seed materials. The metals recovered are in their pure crystal form which can be reused. Recovery of Cd in an uncomplexed form should be excellent due to its larger pK_s. However, CN^- destruction is necessary.	$25,000 for a 22 gpm plant, operation cost @ $20/1000 gal.
Reverse Osmosis		Its low-temperature operation together with low energy consumption should be used in conjunction with either cold vaporization or low temperature evaporation. Again, it also suffers from being non-selective (i.e., no removal of impurity metals).	It can be used to pre-concentrate the dilute rinse water for final concentration with the evaporation processes in order to improve the economics.

Summary of Preliminary Evaluation

Based on the efforts of the literature search, the Ionsep Process appears to be the most promising technology for additional evaluation for direct purification of hard chrome plating baths. Although there are many successful cases of using this technology to indirectly remove metallic impurities in the hard chrome bath, only limited information is available for extending bath life by gradually purifying the plating bath to the desired contaminant level. A complete closed-loop purification and recycling of both plating bath and rinse water can be accomplished with the Ionsep method, and laboratory evaluation is warranted. Also, it is believed that with the experiences gained from these methods, comparable methods can be developed for extending bath life of cadmium cyanide plating solution. The inventor of the Ionsep Process, Dr. Daniel Vaughan, is willing to cooperate in this development.

Using low-temperature evaporation, cold vaporization and reverse osmosis for reuse of rinse water, with concomitant recovery of concentrated cadmium cyanide plating solution, appears to be a viable approach in recycling cadmium cyanide plating baths. The use of reverse osmosis, in conjunction with cold vaporization, should greatly improve the process economics. However, build-up of metallic and organic impurities utilizing these processes tends to impair this approach by requiring total change-out of the spent bath. Activated carbon has been used to remove organic contaminants in plating baths, although it is not applicable here due to its reducing power to destroy cyanide.

Although solvent extraction (i.e., liquid ion-exchange extraction) looks promising, the use of strong base anionic exchange resins appears to be a more practical approach in recovery of cadmium cyanide complex [$Cd(CN)_4^{2-}$] and cyanide. Therefore, $Cd(CN)_4^{2-}$ complex and cyanide exchange capacity data of

selected resins from synthetic and actual plating rinse waters need to be established to obtain preliminary process economics. $Cd(CN)_4^{2-}$ complexes can be stripped from the resins using concentrated sodium hydroxide (NaOH) or potassium thiocyanide (KSCN) for recovery of sodium cyanide (NaCN) and sodium cadmium cyanide [$Na_2Cd(CN)_4$] at concentrations suitable for recycling to plating baths.[12]

Selected Treatment Alternatives for Laboratory Evaluation

Due to the extensive development already existing or in progress for purification of chrome plating baths and the long-term need for the Navy to minimize the generation of the highly toxic cadmium cyanide spent baths, it was decided to restrict further evaluation to purification of cadmium cyanide plating baths. The following approaches were proposed at a contract review meeting held at NCEL in August 1989 in the order of the priority given below with respect to the ultimate fate of the cadmium cyanide bath.

1. Total recycle
2. Destruction of cyanide and recovery of cadmium
3. Destruction of cyanide and disposal of sludge
4. Contract hauling of spent baths with off-site reclamation

In the above approaches, the technical feasibilities were evaluated first. Economic analyses were performed for final process selection. The first two approaches contain several laboratory experiments performed according to priority. If an experiment was deemed successful, no further laboratory work was conducted for the ensuing approaches, which have a lower priority. These approaches are described in detail below.

Total Recycle - Removal of Impurities

Total recycle, being the ultimate goal of this project, was the most extensively analyzed. It requires either the removal of inorganic and organic impurities on a batch or continuous basis, or the recovery of major constituents on a batch basis. Table 3 outlines the priority for removal or recovery, as well as proposed methods to accomplish each. The investigation into the recovery of major constituents would only be required if laboratory experiments for the removal of impurities were not successful. In addition, experiments within each constituent to be removed are arranged according to their priority.

a) Removal of Inorganic Anions - Crystallization

Laboratory evaluation for the removal of inorganic anions initially focused on the removal of sodium carbonate (Na_2CO_3) by crystallization. The U.S. DOD Patent 4,365,481 was reviewed prior to laboratory work. The abstract of the patent and Reference [13] summarize the crystallization process. Basically, the process recovers and recycles cyanide from plating solutions containing excessive amounts of Na_2CO_3 (ratio of carbonate to cyanide > 2:1). The cyanide plating bath liquid is cooled via heat exchange with a cold surface (e.g., a tin box filled with dry ice and acetone inserted in the liquid) to initiate Na_2CO_3 crystal growth on the cold surface. With the removal from the solution of the cold surface upon which the crystals are grown, the Na_2CO_3 is reduced to a desirable level in the plating bath for reuse. The method does not involve addition of chemicals for removing carbonates. The precipitation methods listed in Table 3 will be evaluated only if the economics of this method are unfavorable.

TABLE 3

Sequence of Laboratory Experiments for Total Recycle

A. Removal of Impurities - Batch or Continuous
(treatment and recycle of plating bath)

Impurities	Proposed (Direct) Methods of Removal
i) Inorganics	
Anions: CO_3^{2-} (major) NO_3^-, CrO_4^{2-} (minor)	1. Crystallization and precipitation (ppt) of Na_2CO_3 2. ppt of $CaCO_3$ with $Ca(OH)_2$ 3. ppt of $CaCO_3$ with $CaSO_4$ followed by ppt of SO_4^{2-} with $Ba(CN)_2$ 4. ppt of $CaCO_3$ with $Ca(CN)_2$ 5. Reduction of CrO_4^{2-} with sodium hydrosulfite followed by removal of $Cr(OH)_3$ by filtration (Mostly for removing major anions) (Sludge reuse or disposal will be considered)
Cations: Ni, Cu, Pb (major) Sn, Sb, As, Ag (minor)	1. Cementation with cadmium 2. Cementation with zinc or magnesium with or without salt bridge 3. Low current dummying 4. Chelated ion-exchange weak acid resins in sodium form (may not be applicable to complexed transition metals)
ii) Organics	
Oils/Greases/ Chloroorganic solvents	1. Kerosene extraction without air purging 2. Hexane extraction followed by air purging for removing residual solvent and other volatile solvents (Solvents recovery or incineration will be considered)
Degradation Products of Brighteners	1. Coextraction of oil solubles, brighteners, and their degradation products with kerosene (makeup brighteners might be needed prior to reuse) 2. Removal of water soluble polar organics such as sugars, proteins, etc. and their degradation products (e.g., organic acids)

TABLE 3 (Continued)

B. Recovery of Major Constituents - Batch

Constituents	Proposed (Direct/Indirect) Methods of Recovery
i) Complexed Cadmium Cyanide	• Strong base resin using concentrated NaOH or NaSCN regenerants (complexed impurity metals may be coexchanged) [12]
ii) Complexed metal impurities and nitrate which may have accumulated in the eluant	• Solvent extraction (i.e., liquid ion exchange with quaternary ammonia salts in kerosene; complexed impurity metals may be coextracted) using NaOH as regenerant (Dilution of plating bath with rinse water may be needed and followed by concentration for reuse)

b) Removal of Inorganic Anions - Sulfite Reduction

Chromate, as an impurity, poses a serious effect on cadmium plating. Its presence results in poor coverage (insufficient electroplating) and a dark color (grey) at the high density end of the cathode. By conducting Hull Cell tests (as described in the Laboratory Experiments and Results section), a threshold value can be established. Above the threshold value, there will be no deposit at the low current density end of the cathode.

The lack of a deposit can be explained as a result of the depolarization of the cathode by chromate.[14][15] At the cathode, especially at low current density, the deposition of cadmium ions is interrupted due to the oxidizing property of such cathode depolarizers as chromate. Therefore, if chromate is introduced into the plating solution, it will be reduced preferentially prior to cadmium deposition (reduction) at the cathode, and thus will prevent the deposition of cadmium. This disappearance of overpotential (polarization) of the cathode results in a poor deposition of cadmium. In this case, chromate acts as a cathodic depolarizer, and the electrode is depolarized; it is as if electrons reacted with the depolarizer. This depolarization by chromate can be reduced by adding sodium sulfite (Na_2SO_3) or sodium hydrosulfite ($NaHSO_3$). The reactions are as follows:

- Using sodium sulfite,

$$2CrO_4^{=} + 3SO_3^{=} + 10\ H^{+} \rightarrow 2Cr^{3+} + 3SO_4^{=} + 5H_2O$$

$$Cr^{3+} + 3OH^{-} \rightarrow Cr(OH)_3 \downarrow$$

- Using sodium hydrosulfite,

$$2CrO_4^{=} + 3HSO_3^{-} + 7H^{+} \rightarrow 2Cr^{3+} + 3SO_4^{=} + 5H_2O$$

$$Cr^{3+} + 3OH^{-} \rightarrow Cr(OH)_3 \downarrow$$

When sodium sulfite is used, the amount of chromate removed per unit weight of sodium sulfite is as follows:

$$\frac{\text{weight of chromate}}{\text{weight of sodium sulfite}} = \frac{2 \times [52 + (16 \times 4)]}{3 \times [(23 \times 2) + 32 + (16 \times 3)]} = \frac{232}{378} = 0.61$$

c) Removal of Inorganic Cations - Cementation

The removal of inorganic cations (metal impurities) was first evaluated using cementation techniques. Cementation is a spontaneous electrochemical reaction which involves the reduction of more electropositive (noble) species, such as Ag^{+}, Cu^{2+} and Cd^{2+}, by more electronegative (sacrificial) metals, such as Fe, Zn and Mg. This process has been used in the industry for many years not only for the recovery of valuable noble metals, but also for the purification of process streams. The electrolytic potentials of the metal/ion couples at unit molal activity are given in Table 4 with the most electronegative metals located at the top of the left-hand column, and the most electropositive metals located at the bottom of the right-hand column.

In general, the cementation reaction can be written as:

$$mN^{n+} + nM \rightarrow nM^{m+} + mN \qquad (1)$$

The system can be described as a set of short-circuited electrolytic microcells, in which the noble species (N) is deposited at the cathodic site, and the sacrificial metal (M) dissolves from the anodic site. Electrons are conducted between the two metallic phases.

TABLE 4 ELECTROLYTIC POTENTIALS OF THE METALS. IONS AT UNIT MOLAL ACTIVITY *

Metal/Ion Couple	Standard Electrode Potential, E^0 (v), 25 C	Metal/Ion Couple	Standard Electrode Potential, E^0 (v), 25 C
Li/Li^+	−3.09	Cd/Cd^{++}	−0.403
Rb/Rb^+	−2.925	In/In^{+++}	−0.342
K/K^+	−2.925	Tl/Tl^+	−0.336
Cs/Cs^+	−2.923	Co/Co^{++}	−0.277
As/As^+	−2.923	Ni/Ni^{++}	−0.250
Sr/Sr^{++}	−2.89	Mo/Mo^{+++}	ca. −0.2
Ca/Ca^{++}	−2.87	Sn/Sn^{++}	−0.136
Na/Na^+	−2.714	Pb/Pb^{++}	−0.126
Mg/Mg^{++}	−2.37	Fe/Fe^{+++}	−0.036
Pu/Pu^{+++}	−2.07	$H_2/2H^+$	0.000
Be/Be^{++}	−1.85	Bi/Bi^{+++}	0.2
U/U^{+++}	−1.80	Sb/Sb^{+++}	0.2
Al/Al^{+++}	−1.66	As/As^{+++}	0.3
Ti/Ti^{++}	−1.63	Cu/Cu^{++}	0.337
Zr/Zr^{++}	−1.53	$2Hg/Hg_2^{++}$	0.789
Mn/Mn^{++}	−1.18	Ag/Ag^+	0.7991
V/V^{++}	ca. −1.18	Hg/Hg^{++}	0.854
Cb/Cb^{+++}	ca. −1.1	Pd/Pd^{++}	0.987
Zn/Zn^{++}	−0.763	Pt/Pt^{++}	ca. 1.2
Cr/Cr^{+++}	−0.74	Au/Au^{+++}	1.50
Ga/Ga^{+++}	−0.52	Au/Au^+	ca. 1.68
Fe/Fe^{++}	−0.440		

* The numerical values for the standard electrode potentials have been taken from *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions* by Wendell M. Latimer, Prentice-Hall, 1952, 2nd ed., with three exceptions. The values for trivalent bismuth, antimony, and arsenic were taken from *Theoretical and Applied Electrochemistry* by Maurice deKay Thompson, The MacMillan Co., 1939, 3rd ed. The sign convention used above is that of The Electrochemical Society.

The standard Gibbs free energy (ΔG°) is given by the equation:

$$\Delta G^\circ = -(n \times m)\ F\ (E^\circ_N - E^\circ_M) \qquad (2)$$

where (n x m) is the total number of electrons per mole of N, E°_N and E°_M are the standard potentials for N and M, respectively, and F is the Faraday constant (F = 96,500 coulombs/g·mole), since:

$$\Delta G^\circ = -RT\ \ell n\ K \qquad (3)$$

where R is the molar gas constant (R = 8.3 J mol^{-1} $^\circ K^{-1}$), T is temperature in Kelvin degrees and K is the equilibrium constant.

Combining Equations 2 and 3, the equilibrium constant of any reaction can be calculated as follows:

$$K = \exp\left[\frac{nm}{RT}\ F\ (E^\circ_N - E^\circ_M)\right] \qquad (4)$$

Table 5 gives the values of ΔG° and K for different typical cementation reactions. These values show that the reactions are spontaneous ($\Delta G^\circ < 0$) and theoretically, the noble ions can be removed from the aqueous phase. Although the more negative the value of ΔG°, the more the cementation process is favorable, in practice, the extent of the reaction is determined by kinetic rather than thermodynamic factors.

It has been suggested that the cementation reaction occurs in a series of three steps [16]:

TABLE 5

Cementation Reaction Thermodynamics

Reaction	ΔG° (Kcal/mole)	$\log K_{298}$*
$Cu^{+2} + Zn \rightarrow Cu + Zn^{+2}$	-50.7	37.19
$Cu^{+2} + Fe \rightarrow Cu + Fe^{+2}$	-35.83	26.27
$Cd^{+2} + Zn \rightarrow Cd + Zn^{+2}$	-16.60	12.18
$Cu^{+2} + Cd \rightarrow Cu + Cd^{+2}$	-34.11	25.01
$Cu^{+2} + Co \rightarrow Cu + Co^{+2}$	-28.33	20.77
$Cu^{+2} + Ni \rightarrow Cu + Ni^{+2}$	-27.06	19.84

*$\log K_{(298^\circ K)}$

Source: Strickland, P. H. and Lawson, F., "The Measurement and Interpretation of Cementation Rate Data," International Symposium on Hydrometallurgy, AIME, p. 293-330 (1973).

1. The transport of noble ions (N^{n+}) from the bulk solution to the surface of the sacrificial metal (M). (slow diffusion)
2. The electrode process at the interface resulting in precipitation of the noble metal (N) and dissolution of the sacrificial metal (M). (slow chemical)
3. The transport of the sacrificial metal ions (M^{m+}) to the bulk solution.

Either Step 1 or Step 2 is rate controlling. If the diffusion step is the rate controlling step, the kinetics of the reaction should be first order. However, many deviations from first order have been found. One researcher found that the cementation of cadmium on zinc followed half-order kinetics at low initial cadmium concentrations, and first-order kinetics at higher initial cadmium concentrations.[16]

The effect of pH on cementation appears to be highly system dependent. For cadmium cementation on zinc at low concentrations, the rate was found to be nearly independent of pH. At higher concentrations, the rate was found to decrease with increasing pH.[16]

It has been found that the kinetic rate increases as initial concentration of the noble metal increases, until a maximum rate is reached. The kinetic rate then decreases. It has been suggested that the increase in kinetic rate is due to increases in ionic activity. However, under conditions of constant ionic strength, the cementation of cadmium on zinc exhibited no change.[17]

From the literature review, most of the cementation experiments were conducted at low pH (mainly pH < 6) and used simple mixtures (one noble metal and one sacrificial metal). Most experiments did not use a ligand (e.g., cyanide) solution. References [16] through [20] address cadmium cementation.

In the paper dealing with the cementation of gold, the experiment was conducted in the pH range over 9.0.[19] However, the concentration of gold was only 5 mg/L, which was low as compared with cyanide plating solutions. In another paper, the authors used a mixture of mercury, silver and iron and studied the cementation of silver and mercury by iron.[21] However, the concentrations of mercury and silver were very low and did not involve systems using cyanide. In addition, cadmium cannot be separated from the other impurities using sacrificial zinc and magnesium except by possibly using cadmium as the sacrificial metal for cementation. The feasibility of using a cadmium sponge, granules or shavings to cement nickel, lead and copper metal impurities in cyanide plating bath solution was investigated in the laboratory. Nickel is actually used as an inorganic brightener at a very low level (e.g., 50 mg/L) in the plating solution, and is not considered an impurity. Cementation of iron with cadmium was not considered as iron is normally dissoluted into the ferrous form which is slightly more electronegative than cadmium. In addition, iron is not expected to be present in the cadmium cyanide bath unless it is from drag-in. The latter is unlikely to occur as acid pickling prior to electroplating is an uncommon practice in the cyanide process due to safety reasons. However, if it were used to clean iron base metals, an intermediate alkaline wash is normally incorporated to neutralize and precipitate the metal.

d) Removal of Inorganic Cations - Electrolytic Process (Low-Current Dummying)

Although there were no direct applications of this method to the cadmium plating bath, electrolytic recovery technology is one of the promising methods to remove and recover the impurities in the plating bath because of the relatively simple theory and operation. The electrolytic process has been used

for cleaning rinse water. However, in a research paper [22], a relatively high concentration was used to recover metals. By using this technique alone, cadmium cannot be separated from other metallic impurities. In addition, cyanide is destroyed at the anode, rendering the process less desirable over the approach of total recovery of cyanide plating bath.

e) Removal of Inorganic Cations - Chelating Resins

The use of chelating resins has been shown to successfully reduce the metal impurities in nickel and copper plating baths under a DOD Air Force research project [23]. However, it failed to remove metal impurities in chrome plating bath due to the highly acidic environment (very low pH).

Chelating resins behave similarly to weak acid cation resins, but are highly selective for heavy (transition) metal cations. This type of resin forms an essentially non-ionized complex with divalent metal ions. Consequently, once an exchange group is converted to the heavy metal form, it is relatively unreactive with other similarly charged ions (e.g., Ca^{2+}) in solution, regardless of concentration. Chelating resins come in both hydrogen (H^{+}) and sodium (Na^{+}) forms and will effectively and selectively remove heavy metal cations (Fe^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, etc.) from solutions of pH 4 and above. Several chelating resins are commercially available (e.g., Rohm & Haas Amberlite IRC-718).

The major disadvantages of a high degree of selectivity in an exchange resin is the reluctance of the resin to release the exchanged ion during regeneration. Therefore, the bed volumes required to completely elute divalent heavy metal from the chelating resin are more than those required to regenerate the weak acid cation resin (e.g., 7 versus 3 in regenerant Zn^{2+}).[12] This results in a diluted eluant for disposal/reuse. Also, more anion from the

regenerant may impair reuse of the eluant after reverse osmosis (RO) and/or evaporative concentration for possible reuse of the major cations in the plating bath.

The use of chelating resins for removal of metal impurities from cyanide baths has not been reported in the literature. Difficulties may be encountered in preferentially removing metal ions which are complexed with cyanide in anion forms. The affinity between the impurity metal ions to complex with cyanide and to chelate with the chelating group on the resins remains to be determined in laboratory experiments. **Table 6** gives the equilibrium constants of various salts and metal complexes in aqueous solutions. Another problem associated with the use of chelating resins is the use of regenerants. While hydrochloric acid (HCl) is an effective regenerant, the chelated resin is required to have a thorough rinsing prior to use of HCl as a regenerant due to potential generation of hydrogen cyanide (HCN) from resin contaminated with cyanide. The generation of a large amount of regenerated effluent may pose additional problems for disposal. Chelating resins will only be investigated in the future if cementation and low-current dummying are unsuccessful.

f) Removal of Organics - Solvent Extraction

The proposed methods for removing organic contaminants from plating baths include solvent extractions, stripping, and evaporation with or without solvent recovery. Organic contaminants come from both external and internal sources. External sources consist of drag in from oils, greases and emulsified solvents, as well as contamination such as lubricants and organic mists resulting from overhead tracks, busbars and other machinery. Emulsified solvents include chloroorganics and detergents. Examples of detergents are:

TABLE 6

Equilibrium Constants of Interest in Electroplating

$AgBr = Ag^+ + Br^-$	5.0×10^{-13}
$AgCl = Ag^+ + Cl^-$	2.8×10^{-10}
$AgCN = Ag^+ + CN^-$	1.6×10^{-14}
$Ag(CN)_2^- = Ag^+ + 2CN^-$	1.8×10^{-19}
$Ag_4Fe(CN)_6 = 4Ag^+ + Fe(CN)_6^{4-}$	1.55×10^{-41}
$AgI = Ag^+ + I^-$	8.5×10^{-17}
$Ag(NH_3)_2^+ = Ag^+ + 2NH_3$ (aq.)	5.9×10^{-8}
$AuCl_4^- = Au^{+++} + 4Cl^-$	5×10^{-22}
$Au(CN)_2^- = Au^+ + 2CN^-$	ca. 5×10^{-39}
$Cd(CN)_4^= = Cd^{++} + 4CN^-$	1.4×10^{-19}
$CdI_4^= = Cd^{++} + 4I^-$	ca. 5×10^{-7}
$Cd(NH_3)_4^{++} = Cd^{++} + 4NH_3$ (aq.)	7.5×10^{-8}
$Co(NH_3)_6^{++} = Co^{++} + 6NH_3$ (aq.)	1.25×10^{-5}
$Co(NH_3)_6^{+++} = Co^{+++} + 6NH_3$ (aq.)	2.2×10^{-34}
$Co(NH_3)_5 \cdot H_2O^{+++} = Co^{+++} + 5NH_3$ (aq.) + H_2O	1.6×10^{-35}
$CrCl_2^+ = Cr^{+++} + 2Cl^-$	1.26×10^{-2}
$HCrO_4^- = H^+ + CrO_4^=$	3.2×10^{-7}
$Cr_2O_7^= + H_2O = 2HCrO_4^-$	2.3×10^{-2}
$Cu + Cu^{++} = 2\,Cu^+$	6.3×10^{-7}
$Cu(CN)_2^- = Cu^+ + 2CN^-$	1×10^{-16}
$Cu(CN)_3^= = Cu^+ + 3CN^-$	5.6×10^{-28} [a]
$Cu(CNS) = Cu^+ + CNS^-$	4×10^{-14}
$Cu(NH_3)_2^+ = Cu^+ + 2NH_3$ (aq.)	1.35×10^{-11}
$Cu(NH_3)_6^{++} = Cu(NH_3)_4^{++} + NH_3$ (aq.)	2.8
$Cu(NH_3)_4^{++} = Cu^{++} + 4NH_3$ (aq.)	4.7×10^{-13}
$Fe(CN)_6^{4-} = Fe^{++} + 6CN^-$	ca. 10^{-24}
$Fe(CN)_6^= = Fe^{+++} + 6CN^-$	ca. 10^{-42}
$Fe_2(C_4H_4O_6)_3$ (aq.) $= 2Fe^{+++} + 3C_4H_4O_6^=$	10^{-20}
$In^{+++} + H_2O = In(OH)^{++} + H^+$	2×10^{-4}
$Mn(OH)_2 = Mn^{++} + 2OH^-$	2×10^{-13}
$Ni(CN)_4^= = Ni^{++} + 4CN^-$	1×10^{-22}
$Ni(NH_3)_4^{++} = Ni^{++} + 4NH_3$ (aq.)	1×10^{-8}
$Ni(NH_3)_6^{++} = Ni^{++} + 6NH_3$ (aq.)	1.8×10^{-9}
$PbBr_2 = Pb^{++} + 2Br^-$	4.6×10^{-6}
$PbBr^+ = Pb^{++} + Br^-$	7.1×10^{-3}
$PbCl_2 = Pb^{++} + 2Cl^-$	1.6×10^{-5}
$PbF_2 = Pb^{++} + 2F^-$	4×10^{-8}
$PbI_2 = Pb^{++} + 2I^-$	8.3×10^{-9}
$PbI^+ = Pb^{++} + I^-$	3.45×10^{-2}
$PdCl_4^= = Pd^{++} + 4Cl^-$	5×10^{-13}
$PtCl_4^= = Pt^{++} + 4Cl^-$	ca. 1×10^{-16}
$PtBr_4^= = Pt^{++} + 4Br^-$	ca. 3×10^{-21}
$Sn(OH)_4 = Sn^{+4} + 4OH^-$	ca. 1×10^{-57}
$Zn(CN)_4^= = Zn^{++} + 4CN^-$	1.3×10^{-17}
$Zn(NH_3)_4^{++} = Zn^{++} + 4NH_3$ (aq.)	3.4×10^{-10}

[a] These values have been taken from *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions* by Wendell M. Latimer, Prentice-Hall, 1952, 2nd ed.

[b] Ernst and Mann, *Trans. Electrochem. Soc.*, **61**, 363 (1932).

- linear alkyl sulfonate - anionic
- aromatic sulfonate - anionic
- phenols - nonionic

Internal sources of organic contaminants consist of brighteners and degradation products of brighteners. Components of each are as follows:

Brighteners

- Carbohydrates - sugar
- Proteins - gelatin

} These are for viscosity control and are not used in the formulas used for laboratory study. They may not be needed at all in cadmium plating.

- Aromatic hydrocarbons - coumarin
  - aldehydes
- Sulfonic acid detergents

Degradation products of brighteners

- Amino acids - polypeptides
- Simple sugars - aldehydes
- Organic acids - low molecular weight; volatile acids
- Aromatics - mainly benzene/toluene

A study on the solubilities of the above organic contaminants indicates that they can be classified into three major classes according to the solvents used. These solvents are identified as aqueous, polar organic and nonpolar organic. Table 7 lists the various organics soluble in these solvent classes.

All of the organic contaminants from external sources require removal. From internal sources, only the degradation products of organic brighteners are considered for removal. The organic constituents from the brighteners should be retained as much as possible. In the event that removal occurs simultaneously with other undesirable organic contaminants, these organic brighteners are to be added back to the plating solution. Due to the proprietary nature of the plating solutions, the composition of these organic brighteners is normally unknown. Commonly known organic brighteners (e.g., gelatin, sugars, coumarin, etc.) can be used to supplement the solution. This is done only on the basis

TABLE 7

Organics Soluble in Aqueous and Organic Solvents

Aqueous Solvent	Organic Solvent	
	Polar	Nonpolar
Sugars (mono-, poly-)	Chloroorganics Aromatics Alcohols* Ether* Coumarin	Alkanes Oils Greases Lubricants Aromatics Hydrocarbons Alkanes Alkenes Polyaromatic hydrocarbons (PAHs)
Organic acids (esp. in basic solution)	Aromatic aldehydes	
Proteins (polypeptides)	Phenols (esp. in acid solution)	
Sulfonic acids (alkyl or aromatic derivatives esp. in basic solution)	Organic acid RCOOH (esp. in acid solution)	
Detergents, Others	Detergents - alkyl, aromatic linear alkyl sulfonates (LAS) (esp. in base solution)	

*Not applicable due to their solubility in H_2O

Source: Lowenheim, Frederick A., Electroplating, McGraw-Hill Book Company: New York, NY, 1978.

of need. For example, if the plated parts from the recycle/reclaimed baths lose their luster, a fractional amount of the commonly known or proprietary organic brighteners (such as ROHCO^{R} 20XL) is added to the recycled baths and checked for improved brightness using a Hull Cell.

In order to balance the amount of organic contaminants to be removed from the plating solution and the amount of organic brighteners needed for plating processes, the organics may be partially removed using a single-stage solvent extraction with a mainly nonpolar solvent (e.g., kerosene or hexane for oil/grease removal) followed by stripping (on a need basis) the residual extraction solvent and other volatile organic solvent contaminants (such as trichloroethylene). A TOC analyzer is used to determine the fraction of organics removed by kerosene and the solubility of extraction solvent (i.e., kerosene) in the water blank and in the plating solutions. It is generally assumed that all non-polar organic contaminants (such as oil, greases, lubricants, etc.) are removed quantitatively by kerosene extraction. Therefore, only the amount of carbonaceous materials from plating solutions that are co-extracted with kerosene are of concern in the laboratory extraction experiments. This information is necessary in order to determine the amount of plating solution constituents to be added back to the solution after solvent extraction is performed using kerosene.

Total Recycle - Recovery of Major Constituents

The strong base ion-exchange resins can be used for removal of complexed $Cd(CN)_4^{2-}$ from the spent bath, and the complexed $Cd(CN)_4^{2-}$ can be recovered using concentrated sodium hydroxide (NaOH) or NaSCN as regenerants. Complexed metal impurities may be coexchanged and thus coextracted using NaOH as the regenerant,

as described in Table 3. Dilution of the spent plating bath with rinse water may be necessary for extending the life of the ion-exchange resins. It appears to be an indirect method of recovery which involves dilution of the plating bath. This may not be acceptable to the Navy due to the ongoing research conducted elsewhere in the NCEL.

Destruction of Cyanide and Recovery of Cadmium

If the total recycle experiments are unsuccessful, cyanide can be destroyed and cadmium recovered with mainly commercially available processes. For the plating bath, cyanide is destroyed using either alkaline chlorination or wet oxidation. Cadmium is then recovered by precipitating cadmium hydroxide [$Cd(OH)_2$] and cadmium carbonate ($CdCO_3$), dewatering the resulting precipitate, and recovering the cadmium by using a smeltering or electrolytic process. The recovered cadmium's purity may not be acceptable for plating processes when the electrowinning process is employed to plate out cadmium. It can, however, be purified by secondary smeltering processes.

In the still dragout tank, anodic cyanide destruction and cathodic cadmium (and other impurities) recovery by deposition can be accomplished using a commercially available electrolytic process.[24] The still dragout tank can be reconstituted by diluting the spent bath with the first-stage rinse water, if it is needed for laboratory study. The first-stage rinse water is treated using alkaline chlorination followed by hydrogen peroxide, ultraviolet or ozone, and ion exchange polishing for final discharge into the receiving water.

Destruction of Cyanide and Disposal of Sludge

This alternative is considered only if the economics of recovery for pure cadmium are unfavorable due to a limited quantity of cadmium involved. Cyanide is destroyed using alkaline chlorination. Cadmium and other impurities are precipitated as metal hydroxides or carbonates. The precipitates are then prepared for final disposal by solidification with cement and other materials.

Contract Hauling of Spent Baths

This is the current practice and is included only for future cost comparison purposes. Increasingly stringent regulations with correspondingly higher disposal costs and liabilities in the future necessitate the implementation of recovery and reuse procedures wherever possible.

Laboratory Experiments and Results

A concentrated cadmium cyanide plating solution (CAD-SOL) was obtained from McGean-Rohco, Inc. for use during the laboratory experiments.[25] CAD-SOL is composed of the following:

Cadmium Metal	180 g/L (24 oz/gal)
Sodium Cyanide	360 g/L (48 oz/gal)
Caustic Soda	129 g/L (17.2 oz/gal)

CAD-SOL, along with other ingredients, is added to the laboratory plating tank and diluted to 100 liters with water. The composition of the plating solution is given below:

CAD-SOL	10 L
Sodium Cyanide	9.35 kg
Caustic Soda	0.95 kg

McGean-Rohco 20XL 1 L

Water to make 100 L ----

Brightener (20XL) was also obtained from McGean-Rohco, Inc. It is a proprietary product and no information, other than that it contains 1% nickel sulfate, is available on its composition.

The plating solution was spiked with metal impurities, carbonates and brightener in order to simulate actual conditions occurring during plating operations. Different experiments designed to remove these contaminants or recover the cadmium cyanide were then conducted on the baths.

Laboratory experiments involving cyanide require strict adherence to safety procedures. Appendix A contains first aid and medical treatment information for cyanide poisoning obtained from the manufacturer. First aid and medical treatment information is also provided for ROHCO® 20XL. Appendix B contains outlines of safety procedures followed during the different experiments.[25][26]

Procedures for the laboratory experiments performed are given in Appendix C.[27] A summary of the results for each experiment is presented below.

Hull Cell Test

The Hull Cell test can be most useful for monitoring additive and contaminant levels, as well as overall performance characteristics, if the test is conducted on a regular basis and the results are correlated with production experiences. The experimental procedure for conducting the Hull Cell test is given in detail in Appendix C.

The Hull Cell, described and patented by R. O. Hull in 1939, is a trapezoidal box of nonconducting material. An anode is laid against the right-angle side and a 100 x 70-mm cathode is laid against the sloping side, connected

to a current source with clips. When a current is passed through the solution sample contained in the cell, the current density along the sloping cathode varies in a known manner, so that the character of the plate at a range of current densities is determined in one experiment. The standard Hull Cell contains 267 mL, a volume selected because 2 g of material added to the sample corresponds to a 1-oz/gal (7.5-g/L) addition to the main plating bath. Hull Cells are usually of polymethyl methacrylate, which allows observation of the cathode during plating. Cathodes of the proper size are supplied by makers of the cells. They are usually of zinc-plated sheet steel, from which the zinc deposit is stripped just before use by immersion in hydrochloric acid (wiping off any smut). Current used in the cell varies from 1 to 3 amps, and time varies from 2 to 10 minutes, depending on the type of solution being tested.

The appearance of the Hull Cell cathode after plating can offer considerable information about the condition of the solution. The bright range, coverage, appearance of the plate, and other factors, as influenced by current density, all appear from one Hull Cell test. The interpretation of the appearance of a Hull Cell cathode is largely a matter of experience, although much has been published concerning specific solutions. Vendors' technical brochures are good sources of information. But the best source is a collection of Hull Cell cathodes accumulated over time by the operator. The collection of cathodes should include those representing satisfactory conditions, and those representing various specific problems which were satisfactorily resolved. If a Hull Cell panel displays a particular problem, appropriate additions or adjustments are made to the sample solution and the test is repeated. When the panel is finally satisfactory, the necessary adjustments made to the bath should be included with those methods of correction previously known and documented by manufacturers.

The results of the Hull Cell test showed that above the threshold concentration of each contaminant added to the cadmium cyanide bath, the effect of the contaminant on electroplating was as follows:

Contaminant	Effect
Lead (5 mg/L)	Obtained a dark deposit, especially at the high current density end of the cathode.
Chromium (500 mg/L)	Obtained a dark color (grey) at the high current density end of the cathode. No deposit was obtained at the low current density end of the cathode.
Copper (8,000 mg/L)	Obtained a dull and grey deposit at the low current density end of the cathode.

Cementation

The effects of cyanide on the cementation of copper contaminant onto cadmium were studied in completely mixed glass batch reactors at room temperature and cadmium plating solution pH. Cadmium powder and pellets were used as the sacrificial metal. The effects of mixing time, mixing speed, and initial cadmium concentration in cadmium plating solutions containing varied amounts of cyanide were investigated. The cementation of copper in the absence of cyanide at a pH of 2.3 in deionized water was also studied.[28]

The presence of excess cyanide completely inhibited the ability of cadmium metal to cement cupric ions. Experiments conducted in deionized water at a pH of 2.3 supported calculations which showed that cadmium had the ability to cement copper in the cupric form. Experiments conducted with varied concentrations of cyanide in the plating solution showed that the cuprous ion, Cu^{+}, was formed in the presence of excess cyanide instead of the cupric ion, Cu^{2+}. Calculations of the electrode potential of copper were thus performed again using constants

appropriate for the cuprous ion. These calculations showed that thermodynamically, Cu^+ ions could not be cemented by cadmium in the presence of an excess amount of cyanide.

Magnesium turnings were also used to cement Cu^+. Experiments showed that magnesium could cement approximately 5% of copper contaminant (i.e., 500 ppm Cu^+) with five minutes of mixing at 300 rpm. The remaining magnesium, however, and the cemented copper, also cemented approximately 500 ppm Cd^{2+}. Thus, magnesium was determined infeasible for use as a sacrificial metal to cement copper impurities from a cadmium cyanide plating bath. In addition, the cementation of copper and cadmium were occurring simultaneously, so that mixing could not be terminated to take advantage of copper cementation while Cd^{2+} ion was still in solution. Detailed descriptions and results of the cementation experiments are provided in Reference [28], which is presented in its entirety in **Appendix D**.

Solvent Extraction

Solvent extraction was used to remove nonpolar organic contaminants from the cadmium cyanide bath. Kerosene was selected as the solvent. The purposes for employing solvent extraction using kerosene are two-fold: 1) removal of nonpolar organic contaminants (such as oils, greases and lubricants) from plating solutions; and 2) collection of preliminary information for future liquid ion-exchange extraction using kerosene as a carrier for the water-immiscible phase.

Since oil and grease contaminants can be easily extracted with kerosene from the plating solution, the main objectives were to determine the solubility of kerosene in the cyanide plating solution, as well as the solubilities of the organic constituents in the brighteners and those in the cadmium plating solution

into the kerosene phase. The experimental procedures designed to evaluate solvent extraction using kerosene are given in detail in Appendix C.

The deionized water blank extraction with kerosene provided information on the solubility of kerosene in water. This was determined by the increase in total organic carbon (TOC) in the deionized water after being extracted with 1/10 of the volume of kerosene in a separatory funnel. The same principles apply to the extraction of the brightener and CAD-SOL solutions with kerosene. The results of the TOC analyses are given in Table 8.

It is seen from Table 8 that the solubility of kerosene in deionized water is 17 mg/L TOC, which is equivalent to approximately 20 mg/L of kerosene by assuming that the carbon content in kerosene is 85% (computed value for saturated C_{10} hydrocarbons). Therefore, the solubility of kerosene in water (17 mg/L TOC) is negligible as compared to the TOC found in the brightener (317 mg/L TOC) and cadmium plating bath (8840 mg/L TOC). Based on the results shown in Table 8, the losses in TOC from the brightener and the plating solution are 13 percent and 12 percent, respectively, after extraction with three portions of kerosene. These losses are reasonable, and make-up brightener and plating solution can be added back to the bath after kerosene extraction of spent bath for removal of oil and grease contaminants.

An inspection of the TOC data for the 10 percent CAD-SOL solution shows that the amount of TOC found is exactly equal to that of NaCN present in the concentrated cadmium plating solution (360 g/L), as given in the data sheet from the manufacturer (McGean-Rohco, Inc.). Since the TOC of carbon in cyanide is on a one-to-one basis, the amount of NaCN in the original concentrated cadmium plating solution can be computed as follows:

TABLE 8

Solubilities of 1% ROHCO® Brightener and 10% CAD-SOL in Kerosene and Kerosene in Water Blank

Sample	Total Carbon (TC) mg/L	Total Inorganic Carbon (TIC) mg/L	Total Organic Carbon (TOC) mg/L
1% Brightener			
Before Extraction	319	2	317
After First Extraction	242	2	240
After Second Extraction	319	18	301
After Third Extraction**	297	22	275
10% CAD-SOL*			
Before Extraction	8850	10	8840
After First Extraction	7950	10	7940
After Second Extraction	7790	0	7790
After Third Extraction**	7790	0	7790
Water Blank	19	2	17

*Since cyanide will also contribute to TOC, separate tests with NaCN standards (52 mg/L carbon as in CN) indicated that a TOC of 50 mg/L was obtained with the standard.

**The loss of TOC with kerosene extraction:

For Brightener $1 - \frac{\text{TOC remaining after extraction}}{\text{TOC before extraction}} = 1 - \frac{275}{317} = 0.13$ or 13%

For CAD-SOL $1 - \frac{7790}{8840} = 0.12$ or 12%

$$8{,}840 \text{ (mg/L)} \times \frac{49}{12} \frac{\text{(MW of NaCN)}}{\text{(MW of C)}} \times 10 \text{ (dilution factor)}$$

$$= 361{,}000 \text{ mg/L or } 361 \text{ g/L}$$

This is nearly identical to what is given in the manufacturer's data sheet of 360 g/L. Therefore, the 12 percent loss of TOC in the plating solution after kerosene extraction is likely contributed by the loss of NaCN into kerosene. This unexpectedly high solubility of NaCN in kerosene at high pH ($\geq$ 12) will need to be confirmed.

In conclusion, it appears that kerosene can be used for the removal of oil and grease contaminants from spent bath. Although the removal of organics in the ROHCO^{R} 20XL brightener and that of NaCN in the CAD-SOL cadmium plating solution can be supplemented after kerosene extraction, the ability of kerosene to remove the degradation organic products in the plating bath remains to be investigated. Also, due to its relative insolubility in water (approximately 20 mg/L), kerosene can be used as a carrier for the liquid ion-exchange solvent extraction process in a future study.

Crystallization for Removing Sodium Carbonate

Sodium carbonate is known to build up very slowly in alkaline-cyanide plating baths as a result of absorption of carbon dioxide (CO_2) from the surrounding air and cyanide decomposition at the anode of the plating bath system. When excessive carbonates (e.g., 100 g/L and above) build up in the plating baths, rough or dull deposits on the plated surface may result. Also, at carbonate concentrations above 60 g/L, the top current density is lower than the optimum level.[25]

The conventional method of removing sodium carbonate from spent plating baths is to transfer the plating bath solution outdoors to drums or to another tank during the winter, and to crystallize the carbonates at near freezing temperatures (e.g., 4°C). There are disadvantages to the conventional method resulting from poor control of temperature which may cause a loss of desirable bath constituents. Additional costs are incurred due to the extra tanks and drums needed for the crystallization operation. In addition, not all naval plating operations can utilize this method as many naval facilities are not located in cold weather climates.

The addition of barium and/or calcium salts is another method used for removing carbonate compounds. In this method, the carbonate compounds are precipitated. Additional tanks are required, and the method is troublesome in both operations and sludge disposal. Chemical precipitation may change the plating bath composition if the barium or calcium salts are not added with proper anions or in proper quantities.

The method evaluated in the laboratory study is based on crystallizing the sodium carbonate onto a surface at freezing temperature (i.e., 0°C). A simple and yet innovative apparatus was employed in this study according to a U.S. Patent (No. 4,365,481) assigned to the U.S. Army.[29] This method involves the use of a bundle of three, 1.9-cm diameter, copper tubes filled with dry ice in aqueous solution of acetone or water alone which produces a temperature of approximately 0°-1°C inside the tubes. The excess sodium carbonate is precipitated as a crystalline deposit on the chilled surface. Only the plating solution adjacent to the exterior of the copper tubes was cooled while the plating bath temperature was maintained at only a few degrees below room temperature. A modified version of the apparatus and experimental method is

described in Appendix C.

It should be noted that only sodium-based cyanide plating bath solutions can be precipitated by cooling methods. The potassium plating bath solutions produce soluble carbonates which can only be removed by the chemical precipitation methods described in ROHCO's technical data sheets. The solubility of potassium carbonate in water at 0°C is 1,070 g/L as compared to 80 g/L for sodium carbonate [i.e., 215 g/L as sal soda (decahydrate $Na_2CO_3 \cdot 10H_2O$)].

A modified commercial ROHCO® cadmium plating solution was employed in this study. According to the formulas of typical cadmium plating solutions as given in Table 9, as much as 75 g/L of sodium carbonate can be tolerated in cadmium plating solutions. Therefore, approximately 40 percent of sodium carbonate in excess of 75 g/L (i.e., 106 g/L) was added to the commercial cadmium plating bath for crystallization study. By assuming that all carbonate in the plating bath resulted from oxidation of cyanide, an equivalent amount of sodium cyanide (i.e., 49 g/L) was eliminated in the plating solution formula. The modified plating solution for the crystallization study is given in Appendix C.

The 600-mL plating solution was agitated initially by gently moving the tubes inside the 1-L beaker in order to promote crystal growth. Many needle shaped crystals (i.e., decahydrate sodium carbonate) formed outside of the copper tubes. The crystals that formed tended to slough off from the tubes and fall down into a perforated metal dish welded to the bottom of the copper tube bundle. Some crystals tended to redissolve due to the higher plating solution temperature (18-19°C). While the temperature inside the metal tube could be maintained constant at 1°C by continuously adding dry ice, the temperature of the plating bath, which was placed at a room temperature of 20°C during the experiment, fluctuated slightly (18-19°C).

TABLE 9

Representative Compositions and Operating Conditions for Cadmium Plating Baths

Solution	Composition, grams/liter					Current Density Range,[a] amp/sq cm	Operating Temperature, °C	Remarks
	Cadmium Oxide	Cadmium Metal	Sodium Cyanide	Sodium Hydroxide	Sodium Carbonate			
					Cyanide Solutions			
1	22.5	19.7	78.0	14.3	30-75	0.005-0.065	27-32	Used for still plating; good efficiency, fair throwing power; also used in bright barrel plating
2	22.5	19.7	138	14.3	30-45	0.011-0.086	27-32	Used for still and automatic plating; high throwing power; uniform deposits, fair efficiency; not for barrel plating
3	26.3	23.0	115	16.4	30-60	0.005-0.097	24-30	Use mostly for still plating, but can be used for barrel and automated plating; high efficiency, good throwing power and deposit uniformity
4	41.3	36.2	163	25.8	30-45	0.005-0.162	27-32	Used for high speed-high efficiency plating; used for plating on cast iron
					Fluoborate Solution			
	Cadmium Fluoborate	Cadmium Metal	Ammonium Cyanide	Boric Acid	Licorice			
5	242	94.5	60.0	27.0	1.0	0.032-0.65	21-32	Used mostly for barrel plating; adaptable to plating of strip and wire

[a] For good uniform deposits from the cyanide solutions a current density of 0.022 to 0.043 amp/sq cm is recommended.

Source: Hallowell, J. B., et al. (Battelle Columbus Laboratories), "Assessment of Industrial Waste Practices - Electroplating and Metal Finishing Industries - Job Shops," Report PB-264 349, Springfield, VA, National Tech. Information Service (September 1976).

Although the concentration of carbonate in the plating solution fluctuated due to the continuous dissolution of sodium carbonate crystals, the amount of crystal attached to the copper tubes remained constant at approximately 1.5-cm thick along a 5-cm length of the tubes immersed in the solution. A total of 70 g of sal soda crystal collected around the tubes and inside the perforated metal dish. This is equivalent to the removal of 25.9 g of anhydrous sodium carbonate from a 600-mL plating solution. Therefore, the concentration of sodium carbonate remaining in the solution was estimated to be 62.8 g/L [106 g/L - (25.9 g/0.6 L)] which is equivalent to 169 g/L of decahydrate sodium carbonate (sal soda), and is below the solubility of 215 g/L of sal soda at 0°C. This agrees with crystallization theory, in that the concentration of salts could be reduced to levels lower than that of the saturation level due to the presence of the growing crystal nuclei.

In conclusion, the advantages of this patented apparatus for the removal of sodium carbonate from cyanide plating baths are numerous. It is simple in design and easy to operate. It can be used to continuously maintain the carbonate in plating baths at appropriate levels without having to rely on winter weather. In addition, both the capital and the operating costs are reasonably low since a refrigeration system is not required, and the liquid to be chilled to near freezing temperatures is limited to the water (as described in the patent) inside the submerged container. This volume of the chilled water is a fraction [< 20 percent (see Appendix C for calculations)] of the plating bath solution. The plating bath solution can be maintained at room temperature without the need for cooling the entire bath.

The sodium carbonate crystal recovered is relatively pure and contains less than 0.05 percent sodium cyanide, and even less for toxic metals (according to

the patent). With a simple staging rinsing step using the chilled water from the cooling apparatus to further purify the precipitates, the resulting sodium carbonate crystal can be either recovered for sale or disposed of in a sanitary landfill as a pH modifier.

Electrolytic Process (Low-Current Dummying)

As an alternative to cementation, low-current dummying was conducted according to Reference [30]. The low-current dummying technique is similar to ordinary electroplating. Insoluble anodes, e.g., platinum, platinized titanium, graphite or stainless steel are employed. It is an electrolytic recovery process in which there is electrochemical reduction of metal ions (impurities, including cadmium) at the cathode, where these ions are reduced to elemental metal. At the same time, there is evolution of oxygen at the anode. This technique is used primarily to remove metal ions from solutions. For example, if there is lead in the plating solution, the following reaction will take place at the cathode:

$$Pb^{2+} + 2e^- \rightarrow Pb$$

and at the anode:

$$2OH^- \rightarrow H_2O + \tfrac{1}{2}O_2 + 2e^-$$

A total of six experimental runs were conducted using variations in applied current. Type 316 stainless steel was used as the anode. The conditions of each run are given in Table 10.

TABLE 10

Electrolytic Process Experimental Conditions

Run	Current (Ampere)	Voltage (volts)
1	0.2	2.0
2	0.4	2.2
3	0.6	2.5
4	0.8	2.7
5	1.0	3.0
6	3.0	5.7

For each run, one sample was collected during the electrolytic process at time intervals of 0, 5, 15 and 60 minutes. Each sample was analyzed to determine concentrations of cadmium and copper remaining in solution. **Table 11** summarizes the results of the analyses. **Figure 1** graphically depicts the reduction of cadmium concentration in the plating solutions as the applied current was increased. **Figure 2** shows the relatively little change in copper concentrations with increasing current. The standard electrode potentials of copper and cadmium from the electromotive (Emf) series are +0.337 V and -0.403 V, respectively. In general, copper in solution is in the cupric form. However, if copper is complexed with cyanide, cupric copper changes to cuprous copper, and the standard electrode potential becomes +0.52 V. Since the electrode potential of copper (whether it is cupric or cuprous) is much greater than that of cadmium, copper ions will be preferentially reduced to copper metal at the cathode during the electrolytic process if there is no complexation with cyanide. However, if cyanide is present, copper and cadmium are complexed with cyanide and their electrode potentials are changed.

During this experiment, 10,000 mg/L of copper were added into the plating solution as an impurity. The concentration of cadmium in solution was 18,000 mg/L. The electrode potentials of copper (cuprous) and cadmium were calculated to be -1.36 V and -1.00 V, respectively. The calculations are presentation in Section 2.1 of Appendix D. Therefore, when complexation with cyanide occurs, preferential reduction of cadmium is expected during the electrolytic process. This was verified experimentally.

Figures 1 and 2 also show the variations of cadmium and copper concentrations with time. For copper, there was a reduction in concentration during the starting stage. However, with increasing time, the copper redissolved

TABLE 11

Concentrations* of Copper and Cadmium at Various Applied Currents and Time Intervals

Current (Ampere)	Cd (mg/L)				Cu (mg/L)			
	C_0	C_5	C_{15}	C_{60}	C_0	C_5	C_{15}	C_{60}
0.2	19690	19320	17470	16730	9419	9419	9191	9292
0.4	20060	19875	17470	12290	9140	9114	9064	9064
0.6	18395	18025	16360	11180	9089	9038	8912	8962
0.8	18580	18025	16730	10255	9191	9114	9165	9191
1.0	18765	18765	17100	9145	9191	9191	9140	9165
3.0	18395	17470	12845	---	9317	9216	9089	9191

*C_0 = concentration at time t = 0

C_5 = concentration at time t = 5 minutes

C_{15} = concentration at time t = 15 minutes

C_{60} = concentration at time t = 60 minutes

FIGURE 1

Cadmium Concentrations at Various Applied Currents and Time Intervals

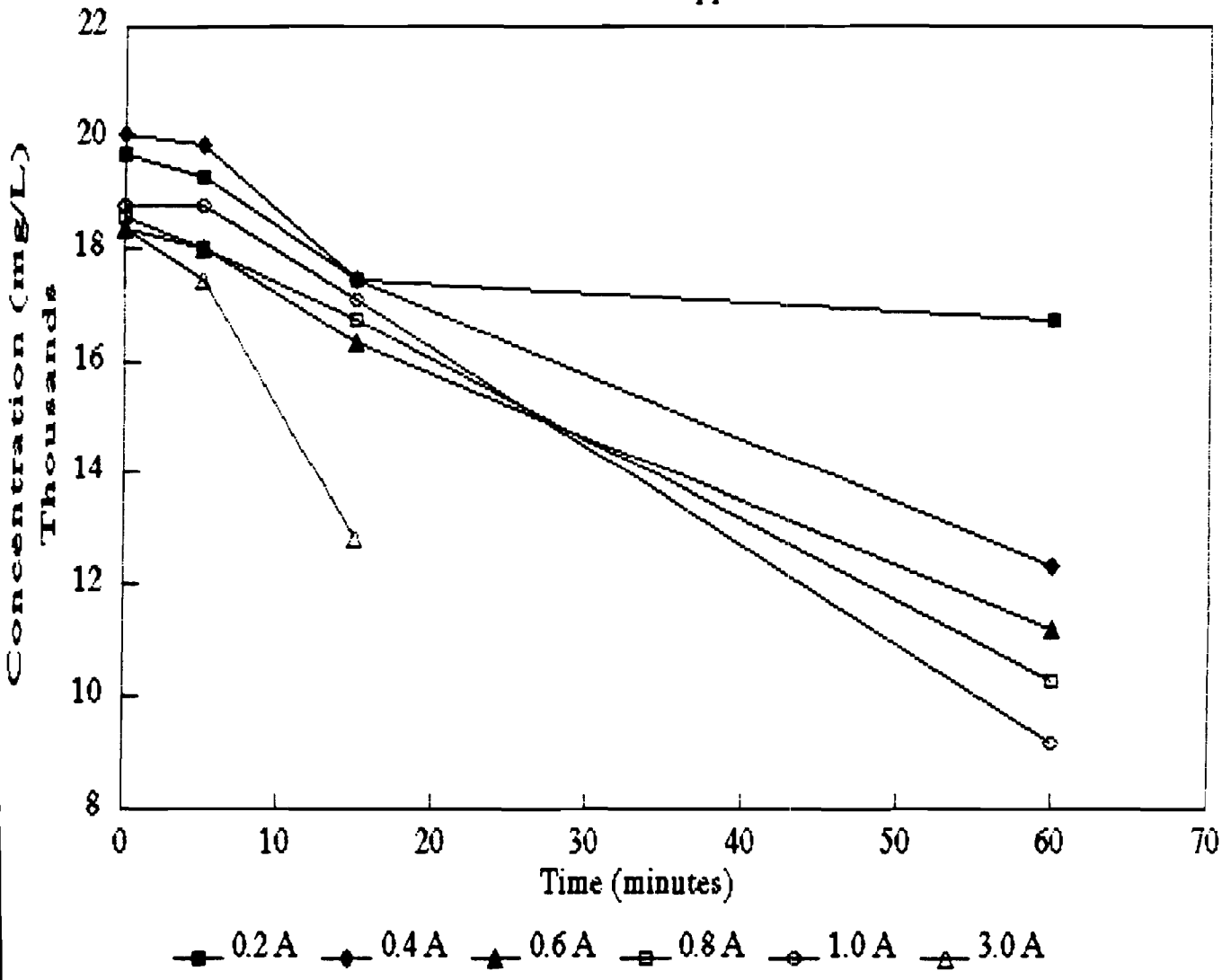
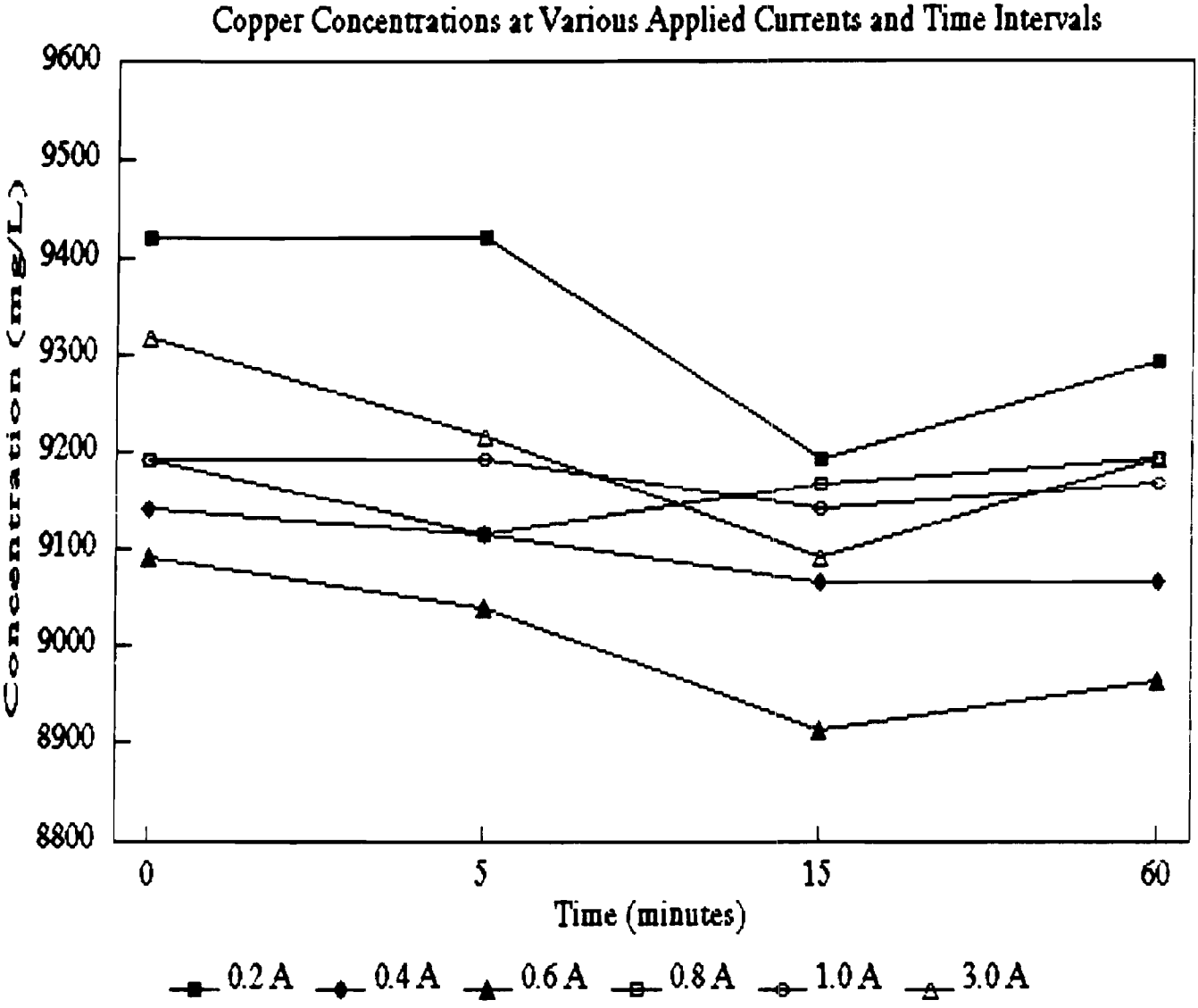


FIGURE 2


Copper Concentrations at Various Applied Currents and Time Intervals
9600
9500
9400
9300
9200
9100
9000
8900
8800
Concentration (mg/L)
0
5
15
60
Time (minutes)
0.2 A
0.4 A
0.6 A
0.8 A
1.0 A
3.0 A

due to the more electronegative property of copper which occurs when it complexes with cyanide.

The current efficiency was calculated in order to compare expected versus actual cadmium deposited. Since the concentrations of copper remained relatively constant during the electrolytic process, the amount of copper deposited was neglected. Faraday's Law equation was used for the calculations, and is given below:

$$w = \frac{I \cdot t \cdot A}{z \cdot F}$$

where w = weight of cadmium (g)

I = current (amperes)

t = time (seconds)

A = atomic weight of cadmium (112 g/mole)

z = valency of cadmium in solution (2)

F = Faraday's constant (96,500 coulomb/mole).

The electrolytic process was conducted for one hour at various applied currents (w = 2.1 x I). The results of expected and actual cadmium deposition values are given in Table 12.

Sulfite Reduction

Through Hull Cell tests, it was found that the threshold concentration of chromate for poor coverage is 500 mg/L (i.e., above 500 mg/L, no deposit occurred at the low current density end of the cathode). When the concentration of chromate was 900 mg/L, the poor coverage problem was solved with the first addition of 75 mg/L of sodium sulfite crystals; however, the dark color (grey) was not removed with more additions of sodium sulfite.

TABLE 12

Expected and Actual Deposited Weights of Cadmium

Current I (Ampere)	Expected Value (g)	Actual Value* (g)
0.2	0.42	0.79
0.4	0.84	2.07
0.6	1.26	1.93
0.8	1.68	2.22
1.0	2.10	2.57
3.0	6.30	--

*Actual value = $(C_0 - C_{60})$ mg/L x 267 mL x $\frac{1\ L}{1000\ mL}$ x $\frac{1\ g}{1000\ mg}$

Treatment of Spent Plating Solution

Treatment of the wastewater from the cadmium cyanide plating solution process involved destruction of cyanide by chlorination and recovery of cadmium and copper by precipitation utilizing pH changes. These procedures are described in detail in Appendix C.

Chlorination is the most common process used to destroy cyanide. Cyanide in plating solutions can be destroyed by oxidation with chlorine or hypochlorite prior to precipitation of the metals. This method is simple, effective, and economically feasible, even for small volume installations. Two factors in determining how quickly cyanide is destroyed are how strongly the cyanide is complexed to metal ions and how rapidly the complex can then be broken.

In the laboratory experiments, chlorination was conducted using commercial Clorox^{R}. The following are proposed reactions for oxidation by hypochlorite:

$$CN^- + NaOCl + H_2O \rightarrow CNCl + NaOH + OH^- \rightarrow NaCNO + Cl^- + H_2O$$

$$CN^- : NaOCl = 26 : 74.5 \text{ (by weight)}$$

Since Clorox^{R}, which contains 5.25% sodium hypochlorite by weight, was used, the amount of Clorox^{R} to oxidize cyanide is 1/0.0525, or 19 times that of cyanide. For example, if 1 kg of cyanide was used, then the following calculation shows the amount of Clorox^{R} needed:

$$\text{Clorox}^{R} = \frac{74.5}{26} \times (1 \text{ kg}) \times (19) = 55 \text{ kg} \simeq 55 \text{ L}$$

Since the plating solution, which was made with a known composition, contains 70 g/L of cyanide, 3.85 L of Clorox^{R} was needed to react with one liter

of plating solution. Approximately 20 L of plating solution was made and, therefore, the theoretical amount of Clorox^{R} needed was 20 gallons. However, in actuality, approximately 32 gallons of Clorox^{R} were consumed when safety factors were incorporated.

After the cyanides in the plating solution were oxidized, the soluble metallic contents of the effluent were recovered. The most efficient way of achieving this was to precipitate the metallic contents as insoluble compounds which could then be removed as a semi-solid sludge. The most commonly used method is to change the pH of the effluent so that metal hydroxides are produced. In this laboratory experiment, cadmium and copper were the selected metals desired for recovery. Sodium hydroxide was used as the reagent for changing the pH because it reacts rapidly and is readily soluble. The optimum pH values for removal of cadmium and copper were found to be 11.0 and 12.5, respectively. Since the pH of the effluent after adding Clorox^{R} to the plating solution was below 11.0, cadmium and copper were precipitated stepwise by increasing the pH.

CONCLUSIONS

The objective of this study was to identify and evaluate the innovative technologies which can be used to reclaim and recycle spent cadmium cyanide plating baths. This was accomplished by selecting treatment techniques, based on an extensive literature search, which are capable of preferentially removing the major contaminants commonly found in spent cadmium cyanide baths without introducing undesirable constituents into the reclaimed plating bath.

The technologies evaluated in this laboratory study included cementation and electrolytic process (low-current dummying) for removing metallic impurities, crystallization for removing the major anionic contaminant (carbonate), sulfite

reduction for removing the minor anionic contaminant (chromate), and solvent extraction for removing organic contaminants. Based on the results of this laboratory study, which used a commercially available cadmium cyanide solution spiked with known impurities, the following conclusions can be drawn:

1) Cementation of metallic impurities with magnesium turnings was found to be effective in removing lead contaminant to levels below the threshold value of 0.01 g/L (see Appendix D), and ineffective in removing copper contaminant to below the threshold value of 6 g/L. It was found that cadmium was removed efficiently, instead of the copper contaminant, due to its forming a weaker complex with cyanide than copper. In addition, magnesium should be able to control other contaminant metals which are more electropositive than cadmium and are more weakly complexed with cyanide or hydroxide than cadmium cyanide complex (such as Ag, As, Sb).

2) The initial results indicated that the metallic brightener nickel was not removed significantly during magnesium cementation due to its strong complexation with cyanide.

3) Electrolytic (low-current dummying) plating of cadmium solution resulted in an undesirable reduction of large quantities of cadmium with little or no removal of copper contaminants. Therefore, it cannot be used for controlling copper.

4) The use of an innovative U.S. patent to crystallize sodium carbonate onto a freezing surface was found to effectively control the major anionic contaminant to levels below its threshold value of 70 g/L (i.e., corresponding to 189 g/L of decahydrate sodium carbonate), which is below the solubility of decahydrate sodium carbonate (sal soda) at 0°C (i.e., 215 g/L).

5) The use of sodium sulfite for reducing chromate, Cr (VI), was found to satisfactorily control the minor anionic contaminant, chromate, to levels below its threshold level for reuse.

6) The use of solvent extraction for removing organic contaminants of oil and grease was found to contribute insignificant amounts of kerosene solvent dissolved in the aqueous phase. Only a small fraction (approximately 12 to 13 percent) of the organic constituents from the brightener (i.e., ROHCO^{R} 20XL) in the cadmium cyanide plating solution was found to be co-extracted by kerosene.

RECOMMENDATIONS

Based on the conclusions of this laboratory study, the following strategy and treatment technologies are recommended to control the contaminants in the cadmium cyanide plating bath by selectively removing them for reuse.

1) It is recommended that the strategy of waste minimization be implemented in order to greatly reduce the amount of metallic contaminants introduced into the plating bath. This can be accomplished by modifying the electrical supply system to the plating bath. For example, the electrical conductor (busbar) could be installed on the sides of the plating bath instead of above, so as to prevent the copper dust from falling into the bath. Another method could involve the installation of trays to catch the metallic dust generated from the busbar and the overhead tracks by moving the barrels and racks back and forth across the plating and cleaning tanks.

2) It is recommended that the design of the apparatus described in U.S. Patent No. 4,365,481 be used to control sodium carbonate contamination of the cadmium cyanide bath. The advantages of using this

crystallization apparatus are that it is simple in both design and operation, and that it can be used in all weather conditions. However, a make-up solution of sodium hydroxide and sodium cyanide should be added to compensate for sodium hydroxide and cyanide ions lost through the formation of sodium carbonate.

3) It is recommended that kerosene extraction be used to remove grease and oil contaminants from the plating solution. A fraction of the make-up brightener solution, along with the ligand sodium cyanide, should be added to compensate for their loss during the kerosene extraction process.

4) It is recommended that sodium sulfite crystals be added to control chromate contamination.

5) If necessary, a small amount of magnesium turnings should be added to control other minor cationic contaminants.

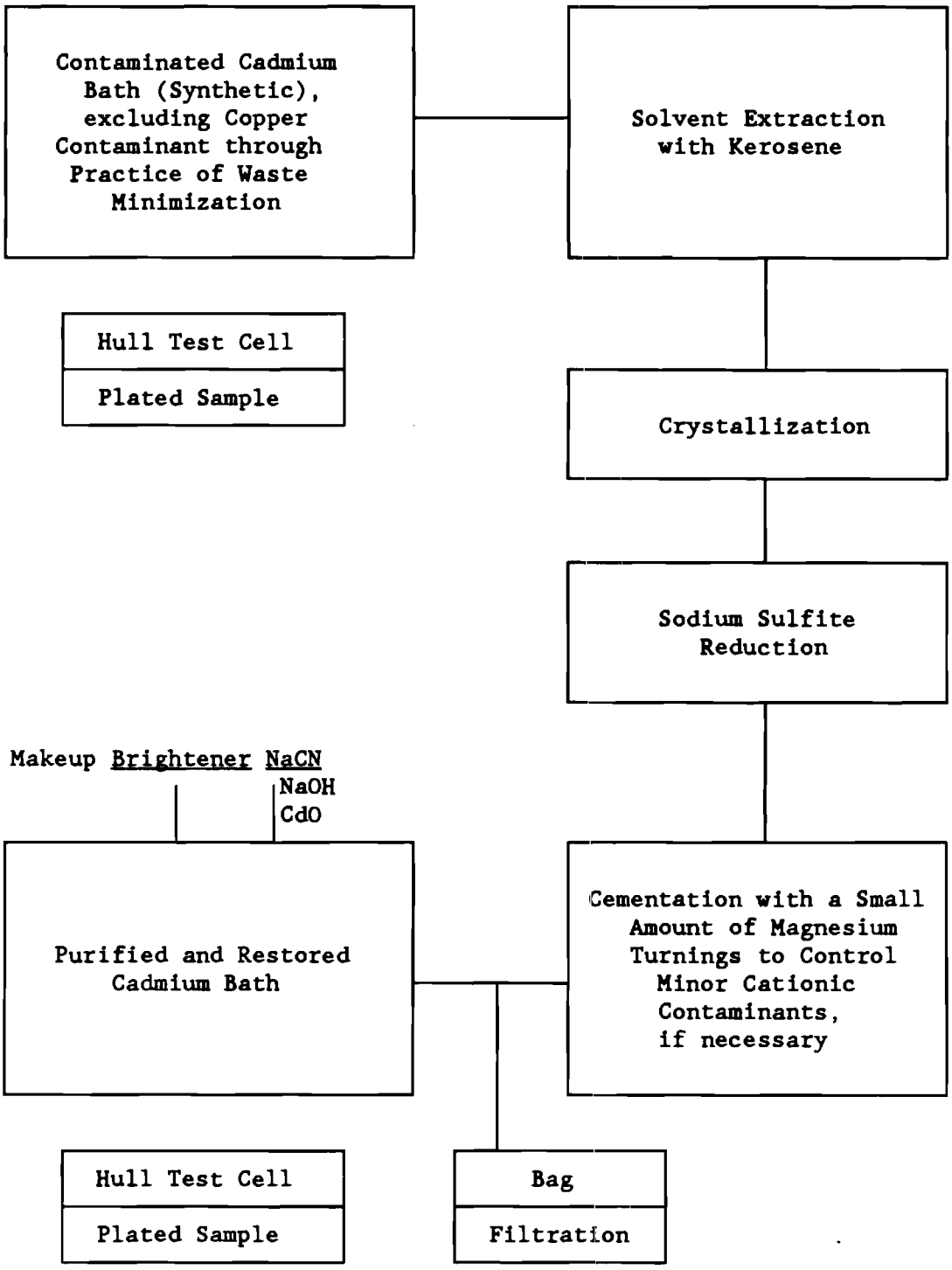
6) It is recommended that a batch treatment scheme, as shown in Figure 3, be evaluated to reclaim a synthetic cadmium cyanide solution contaminated with minor cations, anions, oil and grease at levels found to impair the plating process. A Hull Cell test should be used to monitor the quality of the plated steel before and after such treatment.

FUTURE/PROPOSED WORK

1) A plant survey of cadmium plating operations at various Navy installations should be conducted to assess the feasibility of modifying the existing electroplating equipment to eliminate the introduction of metallic contaminants from sources other than the parts being plated.

FIGURE 3

BATCH TREATMENT SCHEMATIC



2) A detailed laboratory study on the operating costs of the proposed sulfite reduction, cementation (if necessary), crystallization, solvent extraction, and bag filtration processes should be carried out to establish the economics of the treatment costs.

3) A more detailed study on kerosene extraction of organic impurities, along with an evaluation of the appropriate extraction devices required for efficient operation, needs to be performed in order to establish its efficiency in removing organic degradation products in the plating baths.

4) Upon obtaining favorable cost estimates on the above processes, a pilot-scale treatment system should be fabricated to fully assess the technical and economic merits of the proposed treatment system in the field (i.e., at various Navy plating installations).

5) An extensive data bank on Hull Cell platings of various contaminated cadmium cyanide baths needs to be established in order to identify problems associated with plating in the field.

6) Lastly, chelating resins for removal of metal impurities from the cadmium cyanide plating baths should be investigated, if necessary. In addition, appropriate regenerants and disposal options for the regenerated effluent should be evaluated.

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APPENDIX A

First Aid and Medical Treatment Procedures

June 6, 1984

McGean-Rohco, Inc.
2910 Harvard Avenue. P.O. Box 09087. Cleveland, OH 44109. 216/441-4900

CYANIDE TREATMENT

HEALTH HAZARD INFORMATION:

First Aid & Medical Treatment:

In case of contact with cyanide, start treatment immediately. Call a physician.

A. Introduction:

In first aid and medical treatment of persons exposed to cyanide, the following points are important:

(1) The treatment of cyanide poisoning is properly divided into two parts: First Aid and Medical Treatment. First Aid is the prompt action taken to prevent further harm or death and to put the victim of the accident in the best condition for later treatment. First Aid is generally given by the layman before a doctor arrives. Medical Treatment is administered by a physician.

(2) A key to treatment of cyanide poisoning is the administering of antidotes. Always have on hand for immediate use a supply of the materials given in Sections (B) and (C) below.

(3) Actions to be taken in case of exposure to cyanide should be studied and planned before beginning work with this class of chemicals.

B. First Aid Supplies:

Always have on hand a conveniently located "First Aid Kit" containing the following supplies, which should be checked at regular intervals by a responsible person:

(1) Two boxes (2 dozen) of amyl nitrite pearls. CAUTION!!!! UNSTABLE -- REPLACE ANNUALLY! Store in a cool, dark location.

(2) Two one-pint bottles of 1% sodium thiosulfate solution.

(3) A set of instructions on First Aid Treatment.

C. Medical Supplies (for use ONLY by a physician!):

Always have on hand a conveniently-located "Medical Supplies Kit" containing the following supplies, which should be checked at regular intervals by a responsible person.

C. Medical Supplies (continued):

(1) Two boxes (2 dozen) of amyl nitrite pearls. CAUTION!!!! UNSTABLE -- REPLACE ANNUALLY! Store in a cool, dark location.

(2) Two sterile ampules of sodium nitrite solution (10 mL of a 3% solution in each).

(3) Two sterile ampules of sodium thiosulfate solution (50 mL of 25% solution in each).

(4) Two one-pint bottles of 1% sodium thiosulfate solution.

(5) One 10 mL sterile syringe and one 50 mL sterile syringe. Two sterile intravenous needles. One tourniquet.

(6) One stomach tube.

(7) One dozen gauze pads.

(8) A set of instructions on Medical Treatment.

D. First Aid -- Directions for Giving Antidote:

(1) If patient is conscious and breathing:

Break an amyl nitrite pearl* in a cloth and hold lightly under the patient's nose for 15 seconds, repeating 5 times at about 15 second intervals. If necessary, repeat this procedure every 5 minutes with fresh pearls until 3 or 4 pearls have been given.

(2) If patient is unconscious but breathing:

Break an amyl nitrite pearl* in a cloth and hold lightly under the patient's nose for 15 seconds, repeating 5 times at about 15 second intervals. If necessary, repeat this procedure every 5 minutes with fresh pearls until 3 or 4 pearls have been given. If recovery is not forthcoming, give oxygen from an inhalator.

(3) If patient has stopped breathing:

Give artificial respiration until breathing starts. Break an amyl nitrite pearl* in a cloth and hold lightly under the patient's nose for 15 seconds, repeating 5 times at about 15 second intervals. If necessary, repeat this procedure every 5 minutes with fresh pearls until 3 or 4 pearls have been given.

*WARNING!!!!

Any person giving First Aid should be careful to keep the broken pearls away from his/her own mouth and nose; otherwise, he/she may inhale sufficient amyl nitrite to become dizzy and be incompetent to give proper assistance. Since amyl nitrite is flammable, be careful to remove all sources of ignition, such as open flames or cigarettes, before breaking the pearls.

McGean-Rohco, Inc
1250 Terminal Tower, Cleveland, Ohio 44113, 216/621-6425

MATERIAL SAFETY DATA SHEET

Product Name: CAD-SOL		Emergency Phone No.: 216/441-4900
Plant Address: 2910 Harvard Ave., Cleveland, OH 44109		Chemtrec Phone No. 800/424-9300
Prepared By: TSCA Coordinator	Issue Date: 1/80	Revised Date: 5/85

INGREDIENTS AND HAZARDOUS COMPONENTS

Material	%	TLV	C.A.S. #	Suspect Carcinogen
Cadmium* Cyanide SARA 313 Chemical	20	0.05	542-83-6	X
Sodium Cyanide**	16	5	143-33-9	NA
Sodium Hydroxide	10	2	1310-73-2	NA
		Mg/M3		
* TLV for cadmium ** TLV for cyanide				

PHYSICAL DATA

Boiling Point:	Freezing Point:	Specific Gravity:	pH:
UK	UK	1.35	~ 12
Vapor Pressure at 20° C:	**Vapor Density (Air = 1):**	**% Volatiles by Volume:**	**Odor:**
UK	UK	80	slight
Evaporation Rate (Butyl Acetate = 1)		**Solubility in Water:**	
<1		complete	

Appearance and Form: clear liquid

FIRE AND EXPLOSION HAZARD DATA

Flash Point:	Flammable Limits in Air:
NA	Upper:
Test Method: NA	% By Volume Lower: NA

Extinguishing Media: NA

Special Fire Fighting Procedures: NA

Unusual Fire and Explosion Hazards: If involved in a fire, cadmium oxide fumes could form.

DOT Classification: Poison & Corrosive UN-1689

Note: UK = Unknown NA = Not Applicable

CAD-SOL

HEALTH HAZARD DATA

Effects of Overexposure and Primary Entries to Body:

Primary entry thru skin and inhalation.
Poison - contains cyanide. Cadmium is suspect carcinogen.
Highly corrosive to skin and eyes.

Emergency and First Aid Procedures:

Flush skin and eyes with water for at least 15 minutes. Get medical attention.

Cyanide poisoning - see attachment.

REACTIVITY DATA

☒ Stable ☐ Unstable **Conditions to Avoid:**

Incompatability — Materials to Avoid:

Acids release HCN gas

Hazardous Decomposition Products:

NA

Hazardous Polymerization:

☐ May Occur ☒ Will Not Occur

SPILL OR LEAK PROCEDURES

Spills:

Absorb on suitable material. Place in compatible container for transfer to waste treating dept.

Waste Disposal Methods:

Standard cyanide destruction along with removal of cadmium - - or - - send to an EPA approved T/S/D facility. Follow all local, state and federal regulations

SPECIAL PROTECTION INFORMATION

Respirator: Required only if TLV's are exceeded. They then must be NIOSH or MSHA approved.

Ventilation:

Mechanical

Gloves:	Eye and Face:	Other:
Rubber	Chemical goggles & face shield	Sufficient to prevent skin contact

Handling and Storage:

Do not store near any type of acid.

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McGean-Rohco, Inc.
1250 Terminal Tower, Cleveland, Ohio 44113, 216/621-6425

MATERIAL SAFETY DATA SHEET

Product Name: 20 XL			Emergency Phone No.: 216/441-4900
Plant Address: 2910 Harvard Avenue	Cleveland, OH 44109		Chemtrec Phone No. 800/424-9300
Prepared By: TSCA Coordinator		Issue Date: 2/82	Revised Date: 2nd 2/87

INGREDIENTS AND HAZARDOUS COMPONENTS

Material	%	TLV	C.A.S. #	Suspect Carcinogen
Nickel Sulfate	1	0.1*	7786-81-4	NO
		mg/M^3		
*As Ni				

PHYSICAL DATA

Boiling Point: >100°C	Freezing Point: UK	Specific Gravity: 1.04	pH: 5-6
Vapor Pressure at 20° C: UK	Vapor Density (Air = 1): UK	% Volatiles by Volume: 90	Odor: None
Evaporation Rate (Butyl Acetate = 1) <1		Solubility in Water: Complete	
Appearance and Form: Viscous blue liquid			

FIRE AND EXPLOSION HAZARD DATA

Flash Point: NA	Flammable Limits in Air:
Test Method: NA	% By Volume Upper: NA Lower:
Extinguishing Media: NA	
Special Fire Fighting Procedures: NA	
Unusual Fire and Explosion Hazards: None	
DOT Classification: NA	Note: UK = Unknown NA = Not Applicable

HEALTH HAZARD DATA

Effects of Overexposure and Primary Entries to Body:

Primary entry through cuts.
May irritate skin or eyes.

Emergency and First Aid Procedures:

Wash skin with soap and water.
Flush eyes with water for at least 15 minutes.
If any irritation persists, see a physician.

REACTIVITY DATA

☒ Stable ☐ Unstable **Conditions to Avoid:**

Incompatability — Materials to Avoid:

None known

Hazardous Decomposition Products:

None known

Hazardous Polymerization:

☐ May Occur ☒ Will Not Occur

SPILL OR LEAK PROCEDURES

Spills:

Flush with water.

Waste Disposal Methods:

Remove nickel by best method.
Take to an EPA approved disposal facility.
Remaining solution can be sewered.

Follow all Local, State and Federal regulations.

SPECIAL PROTECTION INFORMATION

Respirator:

Not normally required.

Ventilation:

Mechanical

Gloves:	**Eye and Face:**	**Other:**
Rubber	Chemical goggles	Sufficient to prevent skin contact.

Handling and Storage:

Normal handling and storing.

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Date

APPENDIX B

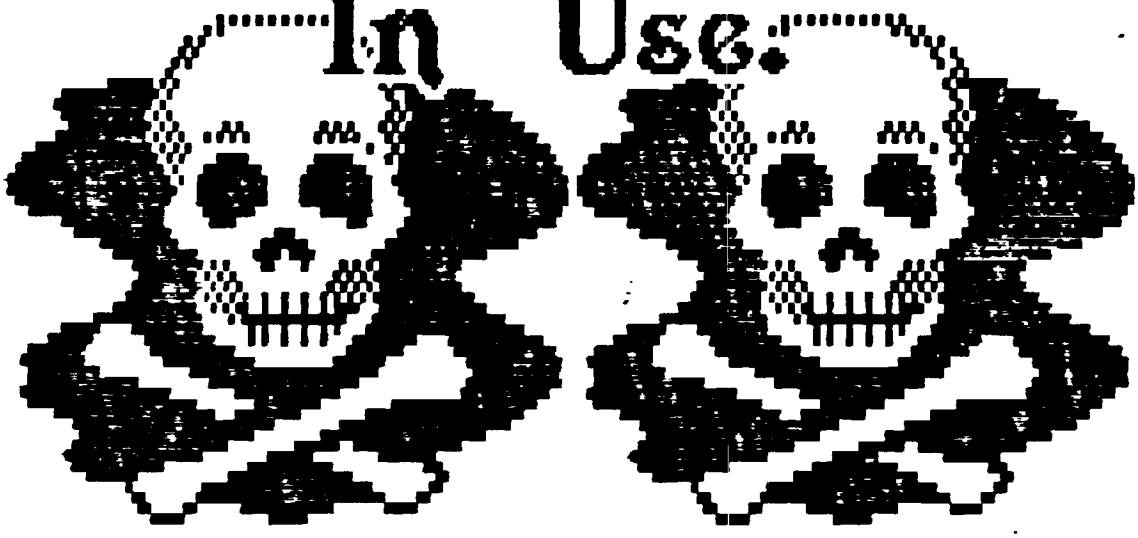
Laboratory Safety Procedures

Laboratory Safety Procedures for Cyanide-Containing Solutions and Materials

- All operations were conducted under a hood due to the toxicity of cyanide.
- Safety glasses, laboratory clothes, latex gloves and respirator were used.
- Contaminants, including Cu^{++}, Pb^{++} and Fe^{++}, were prepared away from the plating bath stock solution to prevent the possible generation of HCN gas.
- Paper and trash were disposed of in a specifically labelled container designated for separate disposal.
- All used glassware was soaked in a Clorox^{R} solution and then rinsed thoroughly with tap water.
- All used plastic containers were soaked in a Clorox^{R} solution prior to disposal.
- All countertops of laboratory tables were wiped several times with Clorox^{R} and then wiped clean with water.
- Ventilation apparatus (fan) and hood were operated during the experiment.
- Danger notices, as attached, were posted on several places in the laboratory to prevent possible accidents.
- First aid instructions, along with telephone numbers for the infirmary, campus police and Poison Control Center of Atlanta, were posted in all areas where laboratory work was conducted.
- A pH meter was used at all times during the experiment to prevent the solution from dropping below pH 11.5. If the pH did decrease, NaOH was used to increase it to above 11.5.

CAUTION!!

Alkaline Cyanide Solutions In Use.



APPENDIX C

Laboratory Procedures

EXPERIMENTAL PROCEDURE FOR THE HULL CELL TEST

A. Preparation of a Plating Solution

1. Pour approximately 600 mL of deionized (DI) water into a 1-L volumetric flask.
2. Add 9.5 g of NaOH into the flask and let stand for 10 minutes.
3. Add 93.5 g of NaCN into the flask.
4. Using a magnetic stirrer, mix the contents of the flask completely.
5. After mixing, pour the solution into a 1-L plastic bottle.
6. Using a pipette, add 100 mL of CAD-SOL into the plastic bottle.
7. Using a pipette, add 10 mL of 20XL Brightener.
8. Add DI water to bring the volume to 1 liter.

B. Hull Cell Test

1. Prepare a plating solution as described above.
2. Place a cadmium anode into an empty Hull Cell.
3. Place a cathode panel into approximately 800 mL of diluted HCl solution (HCl: DI water = 1:1) for about 5 seconds, until the bubbling from the panel surface stops. Then remove the cathode panel from the solution.
4. Wash a panel with DI water and clean paper.
5. Place a cathode into an empty Hull Cell.
6. Pour plating solution up to the indicated line.
7. Connect both electrodes with the rectifier [anode with (+) charge (red), cathode with (-) charge (black)].
8. Turn on the switch of the rectifier (5 minutes of electroplating time and 2 amps of current are recommended).
9. During electroplating, mix the solution continuously and gently with a glass rod.
10. After electroplating is completed, turn off the rectifier switch.
11. Dip the electroplated cathode panel into 3-step rinse water bottles.
12. Rinse the panel with tap water.

13. Dry the panel on paper towels.

14. Collect the electroplated cathode panels and retain for comparison.

EXPERIMENTAL PROCEDURES FOR CEMENTATION

A. Preparation of the Plating Solution

1. 9.5 g NaOH and 93.5 g NaCN were added into approximately 600 mL of deionized (DI) water in a 1-L bottle and mixed completely using a magnetic stirrer.

2. 100 mL of CAD-SOL and 10 mL of 20XL Brightener were added.

3. The resulting solution was adjusted to 1 L with DI water and thoroughly mixed by hand.

B. Preparation of the Contaminants

1. 100 mg/mL Cu was prepared by dissolving 26.9 g $CuCl_2 \cdot 2H_2O$ in 100 mL of DI water.

2. 100 mg/mL Pb was prepared by dissolving 16 g $Pb(NO_3)_2$ in 100 mL of DI water.

C. Calculation of the Least Amount of Cadmium Metal Required for Cementation

1. For Cu/Pb = 1000/500 mg/L:

$$1000 \text{ mg/L Cu} = \frac{1000 \text{ mg/L}}{64 \text{ mg/mmoles}} = 15.6 \text{ mM}$$

$$500 \text{ mg/L Pb} = \frac{500 \text{ mg/L}}{207 \text{ mg/mmoles}} = 2.4 \text{ mM}$$

Total = 15.6 + 2.4 = 18 mM

Therefore, 18 mM Cd (2 g/L) is required.

2. For Cu/Pb = 2000/1000 mg/L:

36 mM Cd (4 g/L) is required.

3. For Cu/Pb = 500/250 mg/L:

9 mM Cd (1 g/L) is required.

D. Calculation of the Surface Area of Cadmium Granules

1. 1 g of cadmium was found to contain 270 pieces (by counting).

2. Using an average diameter of 0.076 cm for the leading end of the comet-shaped cadmium granules, the surface area was calculated as 0.0046 cm^2.

3. Assuming a 200% total surface area due to the comet shape factor having a tail length four times the diameter of the leading end, one piece of cadmium granule was calculated to occupy 0.01 cm^2.

4. The surface area per gram of cadmium was then obtained from:

$$\frac{270}{g\ Cd} \times 0.01\ cm^2 = 2.7\ \frac{cm^2}{g\ Cd}$$

5. 20 cm^2/L of surface area was selected and calculated as equivalent to 7.4 g/L Cd, which is more than the minimum amount required for cementing the contaminant metals added into the solutions for this study.

E. Experimental Runs

Refer to Appendix D.

EXPERIMENTAL PROCEDURES FOR TOTAL METALS DIGESTION

1. Each 10-mL sample was transferred to a 150-mL (or appropriate size) beaker. Each vial was rinsed with deionized (DI) water approximately 4 times to ensure all the sample was transferred to the beaker. This rinse volume was approximately 40 mL.

2. Approximately 10 mL of concentrated nitric acid (10 M HNO_3) were added to each sample to ensure that all the cyanide was converted to HCN gas and thus removed from each sample. The samples were placed on the hot plate with glass covers and boiled for 15 minutes.

3. After cooling slightly, 4 mL more of concentrated nitric acid were added to each beaker. A glass cover was then placed over each beaker.

4. The beakers were placed again on the hot plate and the sample mixture allowed to boil down to approximately 10 mL.

5. The beakers were removed from the hot plate and the mixture allowed to cool slightly. Then 4 mL more of concentrated nitric acid were added.

6. The beakers were placed on a hot plate and the sample mixture allowed to again boil down to approximately 10 mL.

7. The beakers were removed from the hot plate and allowed to cool slightly. Then 1 mL of a 1:1 nitric acid solution (1 part DI water and 1 part nitric acid), and 3 mL of hydrogen peroxide (H_2O_2) were added.

8. The beakers were placed back on the hot plate and heated until the effervescing due to the hydrogen peroxide stopped.

9. The beakers were removed from the hot plate and cooled slightly. Then 1 to 1.5 mL H_2O_2 were added and the beakers were placed back on the hot plate until the effervescing stopped and another 1 to 1.5 mL H_2O_2 were added. The beakers were kept on the hot plate until the effervescing stopped.

10. 1 mL of the 1:1 nitric acid solution was added and warmed for 10 minutes.

11. The beakers were removed from the hot plate and allowed to cool completely.

12. The sample was poured into an appropriate volumetric flask and diluted. The beaker was rinsed with DI water and poured into the volumetric flask to ensure all the digested sample was transferred. A record of this dilution was kept for future dilutions.

EXPERIMENTAL PROCEDURES FOR SOLVENT EXTRACTION

(Removal of Nonpolar Organics)

A. Determination of the Solubility of Kerosene in Water

1. ACS certified-grade kerosene was obtained from the Georgia Institute of Technology School of Chemistry in Atlanta, Georgia.

2. A Beckman Total Organic Carbon (TOC) Analyzer was used to measure the TOC in a deionized water blank.

3. 25 mL of kerosene were added to a 500-mL separatory funnel containing a 250 mL deionized water blank.

4. The mixture was shaken vigorously by hand.

5. The TOC analyzer was used to measure the increase in TOC in the deionized water blank after extraction with kerosene.

B. Extraction of ROHCO^R 20XL Brightener (1% solution)

1. 2.5 mL of ROHCO^R 20XL Brightener were added to deionized water. The final solution volume was adjusted to 250 mL.

2. Three volumes of kerosene (25, 15 and 15 mL) were used to repeatedly extract and separate the aqueous solution in 500-mL separatory funnels.

3. The TOC analyzer was used to measure the aqueous phase TOC before and after each step of extraction with kerosene.

C. Extraction of ROHCO^R CAD-SOL Cadmium Plating Solution (10% solution)

1. 25 mL of concentrated ROHCO^R CAD-SOL cadmium plating solution were added to deionized water. The final solution volume was adjusted to 250 mL.

2. Three volumes of kerosene (25, 15 and 15 mL) were used to repeatedly extract and separate the aqueous solution in 500-mL separatory funnels.

3. The TOC analyzer was used to measure the aqueous phase TOC before and after each step of extraction with kerosene.

EXPERIMENTAL PROCEDURES FOR CRYSTALLIZATION

A. Preparation of Plating Solution

A modified commercial ROHCO^R cadmium plating solution was prepared as given below:

ROHCO^R CAD-SOL	100 mL
ROHCO^R 20XL Brightener	10 mL
Na_2CO_3	106 g
NaOH	95 g
NaCN*	44.5 g
Deionized Water to 1000 mL	---

*93.5 g - 49 g (converted to CO_3)

A 600-mL solution was placed in a 1-L graduated beaker and used in the crystallization study.

B. Modified U.S. Patent No. 4,365,481 Crystallization Procedure

1. A bundle of three 1.9-cm diameter copper tubes welded at the bottom onto a 10-cm diameter perforated metal dish was used as the metal container described in the patent. After immersing it into the 600-mL plating solution, the final solution volume was 710 mL. The total surface area of the copper tubes in contact with the solution was calculated to be 230 cm^2. The volume of chilled acetone/water mixture was approximately 18.3% [i.e., (710 - 600) ÷ 600].

2. The coolant used was an aqueous solution of acetone, having a water/acetone ratio of 2:1. (The U.S. Patent suggested water instead of the acetone solution.) The temperature of the coolant was maintained at 0-1°C throughout the experiment.

3. The temperature of the coolant with dry ice and the plating bath were monitored constantly.

4. The plating solution was agitated initially by gently moving the copper tubes inside the beaker in order to promote crystal growth.

5. Excess sodium carbonate was precipitated as a crystalline deposit on the chilled surface, and fell from the exterior surface of the copper tubes into the perforated metal dish below, due to its own weight.

6. The crystals were collected around the copper tubes and inside the metal dish.

EXPERIMENTAL PROCEDURES FOR CHLORINATION OF CYANIDE AND PRECIPITATION OF CADMIUM AND COPPER

1. Approximately 0.5 gallon of cyanide-containing wastewater was slowly transferred into a 5-gallon bucket using a syphon.

2. Under the hood, approximately 2 gallons of Clorox^{R} were added into a 5-gallon bucket. The Clorox^{R} was added slowly in order to avoid sudden effervescing (it usually took about 30 to 60 minutes to transfer 2 gallons of Clorox^{R}).

3. The solution was stirred with a rod for 2 to 3 hours until the reaction was complete and particles had precipitated.

4. A spot test on the wastewater was performed to ensure that no cyanide remained in the wastewater (less than 50 μg CN^{-}/L). See the procedure on spot testing for further details.

5. If less than 50 μg CN^{-}/L were present, sodium hydroxide was added to increase the pH of the wastewater to 11.0. Precipitation of cadmium occurred approximately 4 to 5 hours later.

6. The supernatant was transferred to another bucket, and the residual cadmium sludge was poured in a beaker dried in a 103°C oven.

7. Sodium hydroxide was added to the supernatant and the pH was increased to 12.5. Copper precipitation occurred after 4 to 5 hours.

8. The supernatant was then disposed of and the copper sludge was poured in the beaker with the residual cadmium sludge from Step 6, and dried in a 103°C oven.

9. The procedure was repeated until all of the wastewater was treated.

10. If more than 50 μg CN^{-}/L were present after the spot test, more Clorox^{R} was added and the procedure repeated from Steps 2 through 8.

SPOT TEST FOR SAMPLE SCREENING OF CYANIDE

A. Reagents

1. Chloramine-T solution: 1.0 g of white, water-soluble powder was dissolved in 100 mL of deionized (DI) water.

2. Stock cyanide solution: Approximately 1.6 g of NaOH and 2.51 g of KCN were dissolved in 1-L of DI water (1 mL = 1 mg CN^-).

3. Pyridine-barbituric acid reagent: 15 g of barbituric acid were placed in a 250-mL volumetric flask. Just enough water was added to wash the sides of the flask and wet the barbituric acid. Seventy-five (75) mL of pyridine were added and thoroughly mixed. Fifteen (15) mL of concentrated hydrochloric acid (HCl) were then added and mixed thoroughly. The solution was allowed to cool to room temperature. DI water was added to obtain a 250-mL solution. The solution was thoroughly mixed.

4. Hydrochloric acid ($HCl:H_2O$ = 1:9).

5. Phenolphthalein indicator aqueous solution.

6. Anhydrous sodium carbonate (Na_2CO_3).

B. Spot Test Procedure

1. A 20- to 25-mL sample of wastewater was collected and neutralized with acid.

2. Approximately 250 mg of Na_2CO_3 were added and swirled until dissolution occurred.

3. One (1) drop of phenolphthalein indicator was then added.

4. 1:9 $HCl:H_2O$ were added as droplets with constant swirling until the solution became colorless.

5. Three (3) drops of the wastewater sample, 3 drops of standard solution containing 50 μg CN^-/L, and 3 drops of DI water (blank) were placed in separate bottles.

6. In each bottle, 1 drop of chloramine-T solution was added and mixed thoroughly by shaking.

7. One (1) drop of pyridine-barbituric acid solution was then added to each bottle. The bottles were shaken thoroughly.

8. After 1 minute, the sample spot color would turn from pink to red if 50 $\mu g/L$ or more of CN^- were present.

Note: The blank spot is faint yellow due to the color of the reagents.

APPENDIX D

Factors Influencing the Cementation of Copper from Cadmium-Cyanide Electroplating Baths

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ABSTRACT

The effects of cyanide on the cementation of copper contaminant onto cadmium were studied in completely mixed glass batch reactors at room temperature and cadmium plating solution pH. Cadmium powder and pellets were used as the sacrificial metal. The effect of mixing time, mixing speed, and initial cadmium concentration in cadmium plating solutions containing varied amounts of cyanide were investigated. The cementation of copper in the absence of cyanide at pH = 2.3 in deionized water was also studied.

The presence of excess cyanide completely inhibited the ability of cadmium metal to cement cupric ions. Experiments conducted in deionized water at pH =2.3, supported calculations which showed that cadmium had the ability to cement copper in the cupric form. Experiments conducted with varied concentrations of cyanide in the plating solution showed that the cuprous ion, Cu^{+}, was formed in the presence of excess cyanide instead of the cupric ion, Cu^{2+}. Calculations of the electrode potential of copper were thus performed again using constants appropriate for the cuprous ion. These calculations showed that thermodynamically Cu^{+} ions could not be cemented by cadmium in the presence of an excess amount of cyanide.

Magnesium shavings were also used to cement Cu^{+}. Experiments showed that Mg could cement approximately 5% of copper contaminant, i.e. 500 ppm Cu^{+} with five minutes of mixing at 300 RPM. The

concentration of Cu^{+} increased after five minutes, apparently because it began to cement Cd^{2+}. In addition, Cd^{2+} was being cemented by Mg. A third ion, Pb^{2+} was introduced into the system to determine if the three ions, Cu^{+}, Cd^{2+}, and Pb^{2+}, were being cemented in any particular order, thus enabling the cementation process to be terminated at optimum Cu^{+} removal and least Cd^{2+} removal. There was no distinct time period where one ion was being removed more quickly than another.

INTRODUCTION

Electroplating, as defined by the Environmental Protection Agency, is "the production of a thin surface coating of one metal upon another by electrodeposition."(1) Electroplating facilities and the metal finishing industry as a whole have long had a comparatively inexpensive and easy means of discarding the toxic wastes they generate: land disposal. Less than a decade ago, toxic waste could be transported to a landfill for as little as $5 per ton.(2) Congress began to limit the amount and nature of toxic wastes disposed in landfills with the enactment of the 1984 Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act of 1976. In 1985, metal finishing companies were required to certify that the volume and/or toxicity of their waste had been reduced to the maximum degree economically practical. In 1987, wastes containing more than 100 mg/L of cadmium were banned from landfills.

The Naval Civil Engineering Laboratory has been given the task by the Naval Facilities Engineering Command to reduce the hazardous waste generated from spent metal finishing solutions. It has been estimated that over 500,000 gallons of spent plating and stripping baths are generated per year at naval facilities. Disposal costs of these wastes exceed $1,000,000 per year and are expected to increase in the future.

1.1 Cadmium

Cadmium is a rare element and is strongly chalcophilic, i.e. concentrated in sulfide minerals such as zinc and mercury, and to a lesser extent, lead and copper.(3)

The plating of metals with cadmium on a commercial scale was not accomplished until the early 1900's. Using cadmium metal to coat steel, iron, copper, brass, and other metals increases resistance to corrosion. Properties of cadmium metal that have led to its use in electroplating include (a) low contact resistance, (b) ready deposition on intricately shaped objects, and (c) good corrosion resistance to alkali and seawater, to name a few. (3)

Cadmium is highly toxic to human beings and is included in the EPA list of priority pollutants.(4) Lethal doses range from 350 mg to 9 g cadmium. Table 1 below shows the lethal doses of various chemical forms of cadmium listed by the National Institute of Occupational Health and Safety (NIOSH).

Table 1. Lethal Doses of Various Chemical Forms of Cadmium

Substance	Toxic Concentration or Dose (exposure for 10 minutes)
Cadmium (fume)	9 mg/m^3
Cadmium chloride	88 mg/kg
Cadmium lactate	13.9 mg/kg
Cadmium oxide	50 mg/m^3 or 72 mg/kg
Cadmium phosphate	650 mg/m^3
Cadmium stearate	1225 mg/kg
Cadmium succinate	660 mg/kg

Acute cadmium poisoning can result from inhalation of cadmium fumes or dust, or ingestion of contaminated food or water. Inhalation of cadmium dust may result in anosmia, dyspnea, and emphysema, and cadmium poisoning through ingestion may cause chronic renal failure, hypertension, and osteomalacia.(3)

1.2 Cyanide

Cyanide is commonly used as a buffer in electroplating because it forms complexes with other impurities which will impair the quality of plated parts. Also, cyanide helps with the dissolution of metals. A major disadvantage of using cyanide in the metal finishing process is that it will form toxic hydrocyanic gas (HCN) at pH's approaching the pKa of HCN (9.21). Other electroplating buffers include chloride, fluoride, boric acid, and EDTA. These, however, are not without disadvantages either. Chloride, for example, has to be used in such high concentrations that it quickly becomes uneconomical. Fluoride does not form good complexes with the impurities and its use requires that four times the amount of cadmium be used as is used with cyanide. This is also uneconomical. EDTA breaks down far too quickly for it to be considered a feasible option.

It is estimated that approximately 20 million pounds of aqueous cyanides are discharged each year by the electroplating industry in the United States.(5) Cyanide effluent from industrial processes usually does not escape in any appreciable amounts into

the environment due to proper waste management procedures which degrade cyanide before it is discharged.

Cyanide is highly toxic to living cells. The lethal effects of cyanide result directly from inhibition of respiration, or more specifically, the binding and inactivation by cyanide of cytochrome oxidase, the terminal component of the mitochondrial electron transport chain. Gettler and St. George (6) have described the signs and symptoms of cyanide poisoning and divided them into three stages. In the first stage, there is headache, vertigo, weak and rapid pulse, nausea and vomiting, and a staggering gait. In the second stage, there are convulsions, the victim falls, pupils dilate, the skin is cold, clammy, and moist, and the pulse becomes weaker and more rapid. In the final stage, the heartbeat becomes irregular and slow, the body temperature falls, the victim sinks into coma and subsequent death.

1.3 Cementation Process

The build-up of metallic impurities such as copper and lead is known to impair the quality of plated parts. The removal of these impurities was first evaluated using cementation techniques. Cementation is a spontaneous electrochemical process that involves the reduction of more electronegative (noble) species, e.g., Cu^{2+}/Cu^{+}, Ni^{2+}, and Cd^{2+}, by more electropositive (sacrificial) metals such as Fe, Zn, and Mg. This process can be used for the treatment of wastewaters, leachates, and sludges bearing heavy metals.

1.4 Objectives of Research

The objective of this research was to use cementation as a means for the purification, recovery, and reuse of concentrated cadmium cyanide electroplating bath solutions by removing the metal contaminants. Initially, cadmium metal was chosen as the reductant metal to cement copper impurities. Magnesium metal was then used when it became apparent that cadmium metal would not cement copper when cyanide was present in the solution containing the copper impurities. Several conditions were studied to determine the effects of cyanide on the cementation of copper on to cadmium and magnesium. These conditions were:

1. Cd-Cu^{2+}/Cu^{+} cementation tests in the presence of cyanide at varied concentration of cyanide;
2. Cd-Cu^{2+}/Cu^{+} cementation tests in the absence of cyanide;
3. Mg-$Cu^{2+}/Cu^{+}/Cd^{2+}$ cementation tests in the presence of cyanide; and
4. Mg-$Cu^{2+}/Cu^{+}/Cd^{2+}/Pb^{2+}$ cementation tests in the presence of cyanide.

CHAPTER II

REVIEW OF LITERATURE

2.1 Thermodynamics of Cementation

The general reaction for a cementation process is given by:

$$mN^{n+} + nM = nM^{m+} + mN \qquad (1)$$

where N represents the noble metal and M denotes the reductant or sacrificial metal. This is an electrochemical process in which the noble metal ion is precipitated from solution and replaced in solution by a metal higher in the electromotive series.(7)

The reaction for copper cementation by cadmium can be written as:

$$Cd^{\circ} \text{ ------> } Cd^{2+} + 2e^{-} \qquad E^{\circ} = 0.403 \text{ V} \qquad (2)$$

$$Cu^{2+} + 2e^{-} \text{ ------> } Cu^{\circ} \qquad E^{\circ} = 0.337 \text{ V} \qquad (3)$$

The standard Gibbs free energy (dG) is given by the equation:

$$dG^{\circ} = -(n)\ F\ (E_N^{\circ} - E_M^{\circ}) \qquad (4)$$

where:

(n) = total number of electrons per mole of N
E_N° = standard potential of the noble metal
E_M° = standard potential of the sacrificial metal
F = Faraday constant (9.648×10^4 coulombs/mole)

or by the equation:

$$dG = -RT \ln K \qquad (5)$$

where:

R = molar gas constant (8.31 J mol^{-1} K^{-1})
T = temperature (Kelvin)
K = equilibrium constant

Combining equations 4 and 5 yields:

$$E = E^{\circ} + \frac{0.059}{n} \log_{10} K_{eq} \qquad (6)$$

At equilibrium, E = 0, K_{eq} = 8.22×10^{-26} and dG = -140 kjoules/mole and the cementation of copper by cadmium is thermodynamically favorable. In practice, equilibrium conditions are rarely approached. The extent of the reaction is determined by the reaction rate rather than by equilibrium thermodynamics.

When the cuprous ion, Cu^{+}, is used instead of the cupric ion, Cu^{2+}, E° = 0.52 V, K_{eq} = 5.15×10^{-32}, and dG = 2.3 kjoules/mole. The cementation reaction is not thermodynamically favorable under these conditions.

$Cd(CN)_2$ and $Cd(CN)_4^{2-}$ are formed as a white precipitate when CN^- ions are added to a Cd^{2+} solution.(8) When cyanide is introduced into the system, the potential, E, for the half reaction for cadmium changes as follows:

$$Cd^{2+} + 4CN^- \text{ -----> } Cd(CN)_4^{2-} \qquad (7)$$

and equation 6 becomes

$$E = E^{\circ} - \frac{0.059}{n} \log_{10} K_f + \frac{0.059}{n} \log_{10} \frac{[Cd(CN)_4^{2-}]}{[CN^-]^4} \qquad (8)$$

where:

E = potential of half reaction, V
E° = 0.403 V
K_f = formation constant = 1.4×10^{-18}
$[Cd(CN)_4^{2-}]$ = 0.16 M
$[CN^-]$ = 1.5 M

The composition of the plating solution is given in Table 2.

Table 2. Composition of Plating Solution

Cad-Sol Solution	10 L		
Sodium Cyanide	9.35 kg		
20-XL Brightener	1 L		
DI Water to Make	100 L		
Cad-Sol contains:		Cadmium Metal	180 g/L
		Sodium Cyanide	360 g/L
		Caustic Soda	129 g/L

Total Cd^{2+} in plating solution = 18 g/L or 0.16 M Cd
Total NaCN in plating solution = 129.5 g/L or 2.64 M NaCN
Total NaOH in plating solution = 22.4 g/L or 0.56 M

Recall from equation 7 that the Cd^{2+} to CN^- ratio is 1:4. Therefore, 4 times the CN^- concentration of Cd^{2+} (0.16 M) is used up by the $[Cd(CN)_4^{2-}]$ complex. Also, some of the CN^- will be used up by $[Cu(CN)_4^{3-}]$ complexes. This amount is calculated in equations 11 and 13 below. The amount of CN^- left in solution to react with other components of the plating solution is:

$$2.64\ M - 0.64\ M - 0.50 = 1.5\ M\ CN^- \qquad (9)$$

Substituting these values for $[Cd(CN)_4^{2-}]$ and $[CN^-]$ in equation 8 yields:

$$E = -0.403 - \frac{0.059}{2} \log_{10} \frac{1}{1.4 \times 10^{-19}} + \frac{0.059}{2} \log_{10} \frac{0.16}{(1.50)^4} \quad (10)$$

$$E = -1.00 \text{ V.}$$

Substituting this value in equation 6 yields $K_{eq} = 1.22 \times 10^{-21}$, And substituting K_{eq} in equation 5 yields dG = 120 kjoules/mole. These values are for the half reaction of Cd and CN^-. Additional calculations determining the effect of cyanide on copper must also be evaluated before a comparison between CN^- containing and CN^- free systems can be made. These calculations are shown below.

The addition of CN^- ions to a Cu^{2+} solution causes the precipitation of $Cu(CN)_2$ as a brownish-yellow solid.(8) This solid is very unstable and rapidly decomposes to cuprous-cupric cyanide or pure cuprous cyanide when heated. Also, the addition of CN^- ions to a solution containing Cu^{2+} ions causes the precipitation of $Cu(CN)_2$ which rapidly decomposes into CuCN and cyanogen. The white CuCN is soluble in excess CN^- to form solutions of complex cyanides.(8) The tendency to complex formation is so strong in copper that the metal will dissolve in excess CN^- solution with evolution of hydrogen.(8) The complexes of Cu(I) are extremely stable and in aqueous solutions there is practically no free Cu^+ present.(8) Because Cu^{2+} is changed to Cu^+, the following calculations will be based on the cuprous ion. The potential of

the half reaction for Cu^+ also changes when CN^- is introduced into the system. Equation 2 becomes:

$$Cu^+ + 4CN^- \text{ -----> } Cu(CN)_4^{3-} \quad (11)$$

and

$$E = E^\circ - \frac{0.059}{n} \log_{10} K_f + \frac{0.059}{n} \log_{10} \frac{[Cu(CN)_4^{3-}]}{[CN^-]^4} \quad (12)$$

where:

$E^\circ = 0.522$ V
$Kf = 5.01 \times 10^{-31}$
$[Cu(CN)_4^{3-}] = 0.126$ M
$[CN^-] = 1.5$ M

Recall from equation 11 that the Cu^+ to CN^- ratio is 1:4. Therefore 4 times the CN^- concentration of Cu^+ (0.50 M) is used up by $[Cu(CN)_4^{3-}]$ complexes, in addition to the CN^- that was used up by $[Cd(CN)_4^{2-}]$ complexes.

$$2.64 \text{ M} - 0.64 \text{ M} - 0.50 \text{ M} = 1.5 \text{ M } CN^- \quad (13)$$

Substituting these values in equation 12 gives:

$$E = 0.344 - \frac{0.059}{1} \log_{10} \frac{1}{5.01 \times 10^{-31}} + \frac{0.059}{1} \log_{10} \frac{0.126}{(1.5)^4} \quad (14)$$

$E = -1.36$ V.

These values, when substituted into equations 5 and 6 above, yield dG = 35 kjoules/mole. These values indicate that copper in

the cuprous form will not be cemented by cadmium in the presence of cyanide. Recall that only if the Gibbs Free energy is negative, is the reaction spontaneous. Also, the electrode potential for Cu^{+} which equals -1.36 V is more negative than the electrode potential for cadmium which equals -1.02 V. This indicates that cadmium does not have the ability to cement Cu^{2+}/Cu^{+} in the presence of cyanide.

A metal which has an electrode potential which is more negative than Cu^{+} must be used in order to cement copper. One such metal is magnesium, Mg.

Magnesium forms a precipitate with hydroxide and the electrode potential can be calculated as follows:

$$Mg + 2OH^{-} \text{ -----> } Mg(OH)_2 + 2e^{-} \qquad E^{\circ} = -2.37 \text{ V} \qquad (15)$$

and

$$E = E^{\circ} - \frac{0.059}{n} \log_{10} K_f + \frac{0.059}{n} \log_{10} \frac{[Mg(OH)_2]}{[NaOH]^2} \qquad (16)$$

where:

$E^{\circ} = -2.67$ V
$K_f = 380.2$
$[Mg(OH)_2] = 0.041$ M
$[NaOH] = 0.478$ M

Recall from equation 15 that the Mg^{2+} to OH^{-} ratio is 1:2. Therefore 2 times the magnesium concentration of OH^{-} (0.082 M) is used up by the $[Mg(OH)_2]$ precipitate.

0.56 M - 0.082 M = 0.478 M NaOH. (17)

Substituting these values in equation 16 gives:

$$E = -2.67 - \frac{0.059}{2} \log_{10} 380.2 + \frac{0.059}{2} \log_{10} \frac{0.041}{(0.478)^2} \qquad (18)$$

$E = -2.77$ V.

Using this potential for Mg and the potential obtained for Cu^+ in the presence of cyanide in equations 5 and 6 yields $dG = -136$ kjoules/mole. Therefore, the reaction is spontaneous, and Mg can cement Cu^+. The electrode potential for Cu^+ is -1.36 V and can therefore be cemented by magnesium which has a more negative electrode potential of -2.27 V.

2.2 Cementation Mechanisms

Cementation is a heterogeneous physicochemical process that involves a number of interdependent transport and chemical or electrochemical steps (10). Several researchers (4,11,12,13) have found cementation kinetics to be diffusion controlled. Cementation kinetics usually follow a general first-order rate equation. For Cu^{2+} this expression is:

$$\frac{d[Cu^{2+}]}{dt} = \frac{-k.A}{V} [Cu^{2+}] \qquad (19)$$

where $[Cu^{2+}]$ is the copper ion concentration, t is time, V is volume

of solution, A is surface area of the sacrificial metal, and k_o is rate constant.

Strickland and Lawson (14) have described cementation as a diffusional process as follows:

1. Transport of ions of the depositing metal N^{n+} from the bulk of the solution to the deposit-solution interface.
2. Conductance of electrons from the dissolving metal M through the deposit.
3. Incorporation of the atoms of deposited metal N into a crystal lattice.
4. Release of M^{m+} ions into the solution.
5. Transfer of M^{m+} ions to the deposit-solution interface through the deposit layer.
6. Transport of M^{m+} ions into the bulk of the solution.

These steps are shown diagrammatically in Figure 1.(14)

Studies of copper cementation kinetics by Nadkarni et.al.(15), Nadkarni and Wadsworth (16), and Rickard and Fuerstenau (17), have shown that the rate controlling step to be the diffusion of the cupric ions to the reaction surface. Strickland and Lawson (11) found that in a large number of cementation reactions using a rotating disc technique, nearly all of the reactions showed similar kinetic behavior and were under diffusion control.

Studies on the codeposition of copper and cadmium onto zinc by Lee, et.al.(18) have shown that cementation in the early stages is controlled by a diffusion mechanism and as deposits grow, the reaction controlling mechanism changes to a mixed control.

If a reaction is diffusion controlled, the kinetics should be first order.(14,19) While many researches have found the cementation process to be diffusion controlled, others have

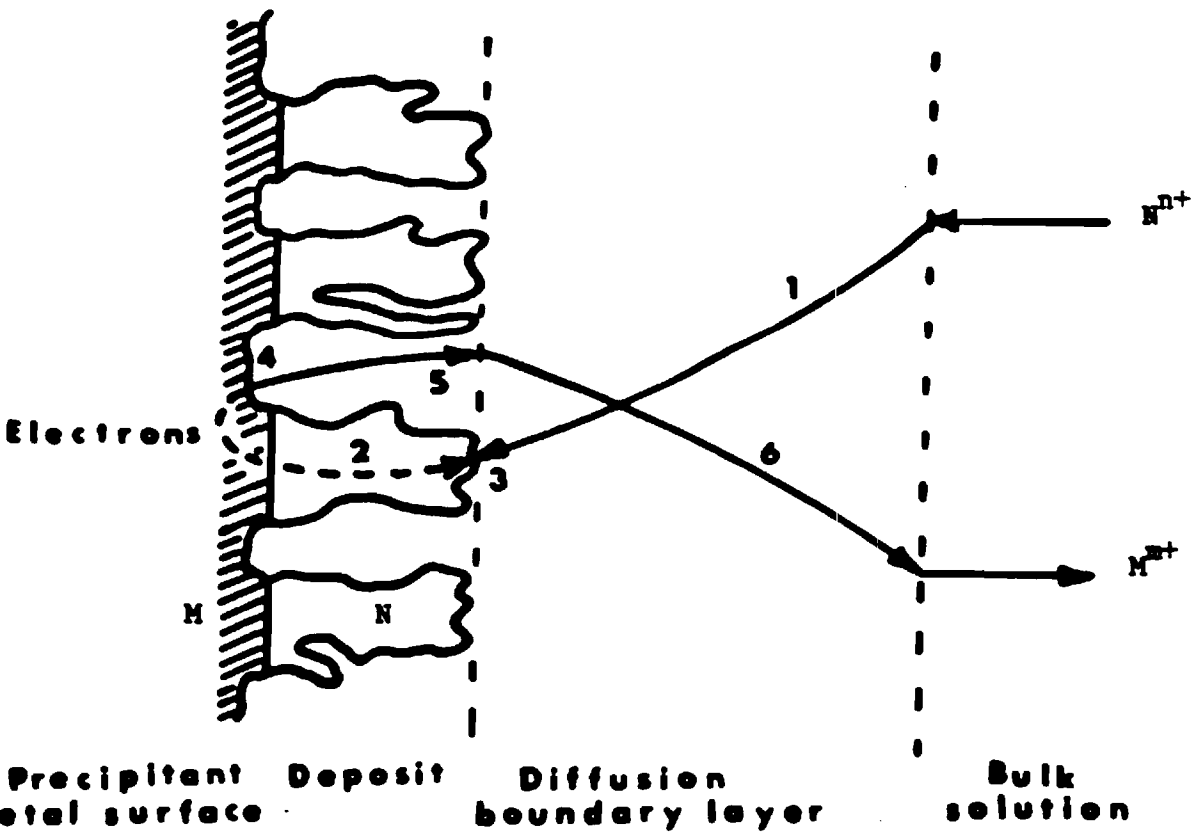

Figure 1. Steps involved in the cementation reaction.

reported deviations from the first order model. These deviations have been attributed to changes in the morphology of the deposit that results in an increase in the surface area.

Power and Ritchie (12) found that when the deposit of mercury (II) onto a rotating copper disc became thick enough, the kinetic rate was suddenly enhanced. A study by Annamalai and Hiskey (20) found the cementation of copper onto a rotating aluminum disc to follow a mixed control mechanism. At high temperatures, the rate was diffusion controlled, while at low temperatures, it was chemically controlled .

2.3 Kinetics of Cementation - Previous Studies

Lee, et.al.(18) found that increasing the mixing rate in oxygen free systems increased the cementation rate of both cadmium and copper onto zinc. Still other researchers (8,21) found that increased mixing rate yields increased rate constants. Annamalai and Hiskey (20) showed that the cementation rate of copper onto aluminum increased with the rotational speed of the disc. At values of 1000 RPM and higher, however, the rate remained constant.

In a cementation study of copper on iron, Agrawal and Kapoor (22) found that there exists an optimum value for the initial concentration of copper ions in solution for which the rate of cementation is highest. Several studies (20,23,24) have shown the reaction rate to increase with increasing noble ion concentrations up to some maximum concentration, and then decrease. Morrison, et.al.(21) studied the effects of initial silver ion concentration

at four different volumes in a system that used rotating discs of copper and lead to cement silver. They found the cementation rate to decrease more quickly for smaller solution volumes than for the larger volumes, but the concentration decreases were much more dramatic for the smaller volumes. Also, Mathes, et.al.(13) have shown that in a silver-zinc/ferrous alloys system, the increase of silver ion concentration from 10 g/L to 100 g/L caused the cementation rate to decrease.

The effect of temperature on the cementation rate has been studied to determine the activation energy of the process. The activation energy is given by the slope of the straight line in an Arrhenius plot, which is the logarithm of the rate constant versus the inverse of the absolute temperature. Several studies (20,22) have shown that increases in temperature enhance the cementation rate of the noble ion onto the sacrificial metal. On the other hand, a study by Blaser and O'Keefe (25) on cementation of cadmium onto zinc and manganese powder, found that temperature had little effect on the reaction rate.

CHAPTER 3

EXPERIMENTAL MATERIALS AND METHODS

3.1 Experimental Apparatus

Cementation experiments were conducted in 250 milliliter (mL) completely mixed glass batch reactors (screwtop Erlenmeyer flasks). The total solution volume for each experiment was 200 mL. Mixing was provided by a Sybron-Thermodyne Big Bill SE Rotator/Shaker (Dubuque, Iowa) which could be varied in speed up to 550 RPM. The mixing rate was controlled by the RPM control on the shaker.

Experiments were conducted at room temperature. Because the first experiments conducted were for range finding, the temperature of the room was not measured. As the experiments continued and cementation was found not to occur, the effects of temperature on the cementation rate were not studied. Gibb's Free Energy was calculated using higher temperatures than room temperature, and they showed that the cementation of Cu^{2+}/Cu^{+} onto Cd was not favorable even at higher temperatures. Another test, test C, showed that the cementation of Cu^{2+}/Cu^{+} onto Cd did occur at room temperature. Details of that experiment are discussed later. The pH of the solution remained above 12.5 due to the excess NaOH used when the plating solution was prepared. It was desirable to maintain the pH at these high levels due to the presence of cyanide in the plating solution. If the pH were to

approach the pKa of HCN, 9.21, then toxic HCN gas would have been formed.

The plating solution was prepared by adding 9.5 g of NaOH, 93.5 g of NaCN, 100 mL of Cad-Sol, and ten mL of 20XL Brightener, to approximately 600 mL of deionized water, and the resulting solution was diluted to one liter with deionized water. Cad-Sol was provided by McGean-Rohco, Incorporated. Cad-Sol is used in making new cadmium bath solutions or for maintaining bath solutions. The composition of Cad-Sol includes 180 g/L cadmium metal, 360 g/L sodium cyanide, and 129 g/L caustic soda. Prior to the addition of the NaCN, the NaOH was completely dissolved by stirring with a magnetic stirrer. This was desirable in order to adjust the pH to very alkaline levels. If the solution was not alkaline, and below the pKa of HCN, then toxic HCN would have been produced.

The Cu^{2+} contaminant and spiking solution was prepared by adding 26.8 g of $CuCl_2.2H_2O$ to approximately 30 mL of deionized water and diluting to 100 mL. This yielded a solution which contained 100 mg Cu^{2+} per one mL of solution.

The Cd^{2+} spiking solution was prepared by adding 81.5 g of $CdCl_2$ to approximately 30 mL of deionized water and diluting to 100 mL. This yielded a solution which contained 500 mg Cd^{2+} per one mL of solution.

A Fisher-Scientific (Fair Lawn, New Jersey) Ni^{2+} Standard Solution of one mg per one mL was used as the Ni^{2+} spiking solution.

The Pb^{2+} contaminant solution was prepared by dissolving 0.67 g of $PbCl_2$ to approximately 30 mL deionized water and diluting to 100 mL. This yielded a solution which contained 5 mg Pb^{2+} per one mL solution.

3.2 Standard Test Conditions

Ten-mL samples were collected at fixed time intervals determined specifically for each experiment. The initial sample, C_0, was taken immediately after the sacrificial metal, Cd powder or granules, was added to the solution in the reactor. In retrospect, it would have been better to take the initial sample before the addition of the sacrificial metal. Mixing was interrupted during sampling, however the time required to take a sample was small compared with the total mixing time. The first experiments conducted were for range finding, and no corrections were made in the results of the analysis for the changes in volume which occurred during sampling. Most probably, the decrease in volume during the experimental period would cause an increase in the ratio of sacrificial metal to noble metal in the reactor. Therefore, it would be expected that the cementation rate would increase. Because cementation was not enhanced by the decrease in volume in the reactor, no volume corrections were made during the course of this study. Also, a larger proportion of the literature supports that decreasing solution volume will increase the cementation rate. The samples were stored for no more than two days before they were analyzed. It was possible

that a cementation reaction could continue after mixing ceased, i.e. during storage. The samples were then filtered through either a Whatman #4, #1, or #40 filter and into a 150 mL beaker. The filters were rinsed thoroughly with deionized water to make sure all ten mL of the sample passed through the filter. The rinse volume was approximately 40 mL. The filtered sample was then digested according to the procedure recommended in Standard Methods.(26) The procedure was as follows:

> Approximately ten mL of concentrated nitric acid (HNO_3 - 69%- 71%, Reagent A.C.S., Fisher Scientific) were added to each sample to ensure that all the cyanide was converted to HCN gas and thus removed from sample. The samples were placed on the hot plate with glass covers and boiled for 15 minutes
>
> An additional four mL of concentrated nitric acid were added to each beaker and the sample was allowed to boil down to approximately 20 mL.
>
> An additional four mL of concentrated nitric acid were added and the sample was allowed to boil down again to approximately 20 mL.
>
> The beakers were removed from the hot plate and allowed to cool slightly. Then one mL of a 1:1 nitric acid solution (1 part deionized water and 1 part concentrated nitric acid) and 3 mL of hydrogen peroxides (H_2O_2 - 31.4%, Fisher Scientific) were added.
>
> The beakers were placed back on the hot plate and heated until the effervescence due to the hydrogen peroxide stopped.
>
> The beakers were removed from the hot plate and cooled slightly. Then 1 to 1.5 mL of H_2O_2 were added and the beakers were placed back on the hot plate until the effervescence stopped.
>
> Again, the beakers were removed from the hot plate and cooled slightly. Then 1 to 1.5 mL of H_2O_2 were added and the beakers were placed back on the hot plate until the effervescence stopped.

One mL of the 1:1 nitric acid solution was added and warmed for approximately ten minutes.

The beakers were removed from the hot plate and allowed to cool completely.

The sample was transferred to a 50-mL volumetric flask. The beaker was rinsed with deionized water and the rinse water was transferred to the 50-mL volumetric flask to ensure all the digested sample was transferred. The solution contained in this 50-mL volumetric flask represented a five fold dilution of the original ten mL sample. Five hundred fold and 5000 fold dilutions were also prepared.

The appropriate dilution of these digested samples was analyzed for Cu^{2+}/Cu^{+}, Cd^{2+}, and Ni^{2+}. The samples were analyzed by atomic absorption spectroscopy using a Perkin-Elmer Atomic Absorption Spectrophotometer, Model 303 (Norwalk, Connecticut).

The Cu^{2+}/Cu^{+} analyses were conducted using a Cu hollow-cathode lamp (Fisher-Scientific Type 4536024) and an air-acetylene flame. The sensitivity of the chart recorder could be adjusted by changing the path length of the flame through which the light beam passed. The path length could be shortened or lengthened by using either a 10 cm burner or a 5 cm burner. The 5 cm burner could be turned at three different angles shortening the path length further. A specific burner orientation was used to obtain the proper sensitivity for which the samples could be analyzed. The instrument was calibrated using at least four different concentrations of standard Cu^{2+}. Cu^{2+} standards were prepared from a stock solution (1,000 mg/L, Fisher-Scientific SC194-500) and diluted to an appropriate concentration. A typical calibration curve is shown in Figure 2.

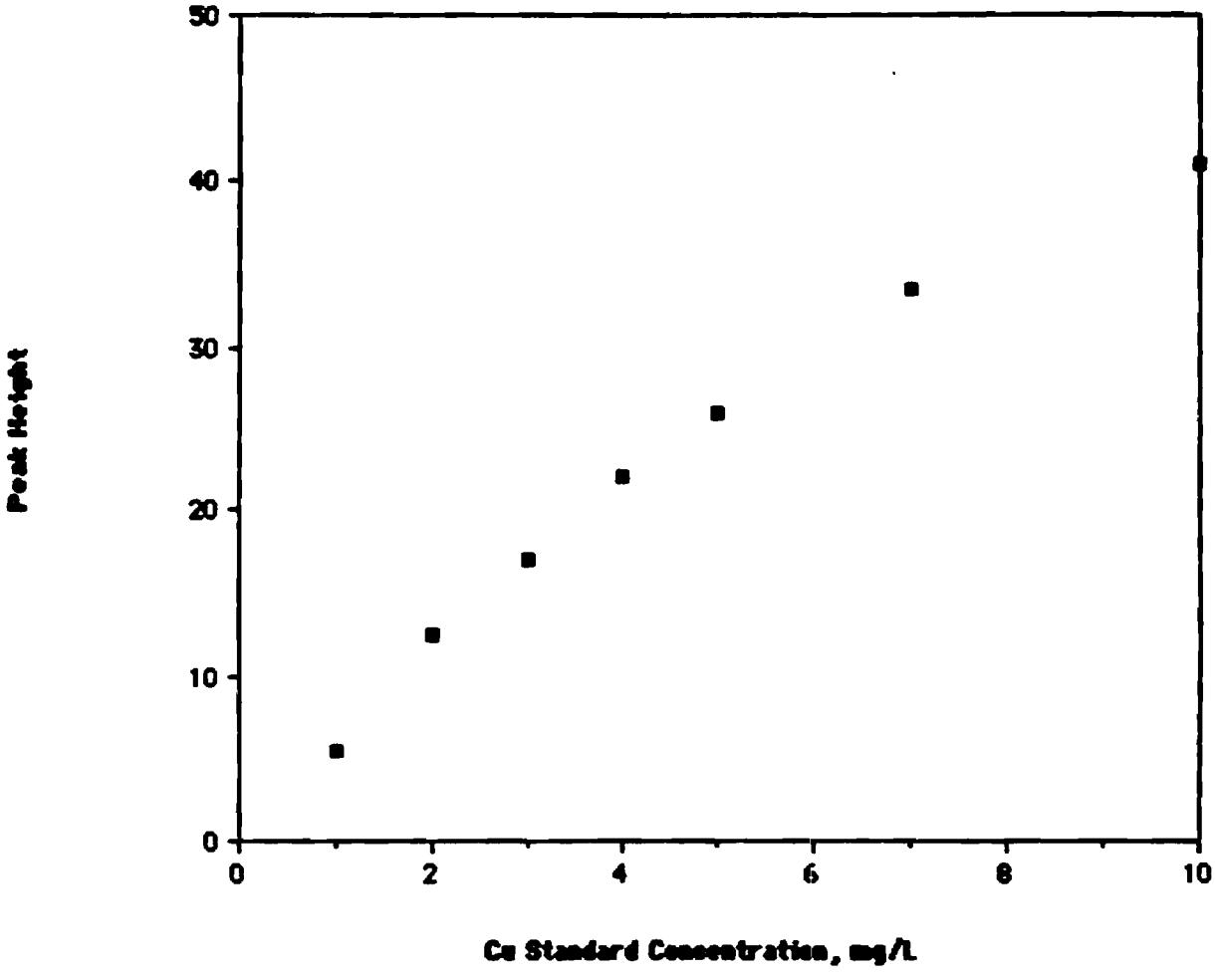

Figure 2. Typical Cu Standard Calibration Curve

The Cd^{2+} analyses were conducted using a Cd hollow-cathode lamp (Fisher-Scientific Type 45-36016) and an air-acetylene flame. A specific burner orientation was used to obtain the proper sensitivity for which the samples were to be analyzed. The instrument was calibrated using at least four different concentrations of standard Cd^{2+}. Cd^{2+} standards were prepared from a stock solution (1,000 mg/l, Fisher-Scientific SC118-500) and diluted to an appropriate concentration. A typical calibration curve is shown in Figure 3.

The Ni^{2+} analyses were conducted using a Ni hollow-cathode lamp (Fisher-Scientific Type 14-386-106C) in an air-acetylene flame. A specific burner orientation was used to obtain the proper sensitivity for which the samples were to be analyzed. The instrument was calibrated using at least four different concentrations of standard Ni^{2+} . Ni^{2+} standards were prepared from a stock solution (1,000 mg/l, Fisher-Scientific SN70-500) and diluted to an appropriate concentration. A typical calibration curve is shown in Figure 4.

The Pb^{2+} analyses were conducted using a Pb hollow-cathode lamp (Fisher-Scientific Type 14 386 1054) in an air-acetylene flame. A specific burner orientation was used to obtain the proper sensitivity for which the samples were to be analyzed. The instrument was calibrated using at least four different concentrations of standard Pb^{2+}. Pb^{2+} standards were prepared from a stock solution (1,000 mg/l, Fisher-Scientific SL21-500)

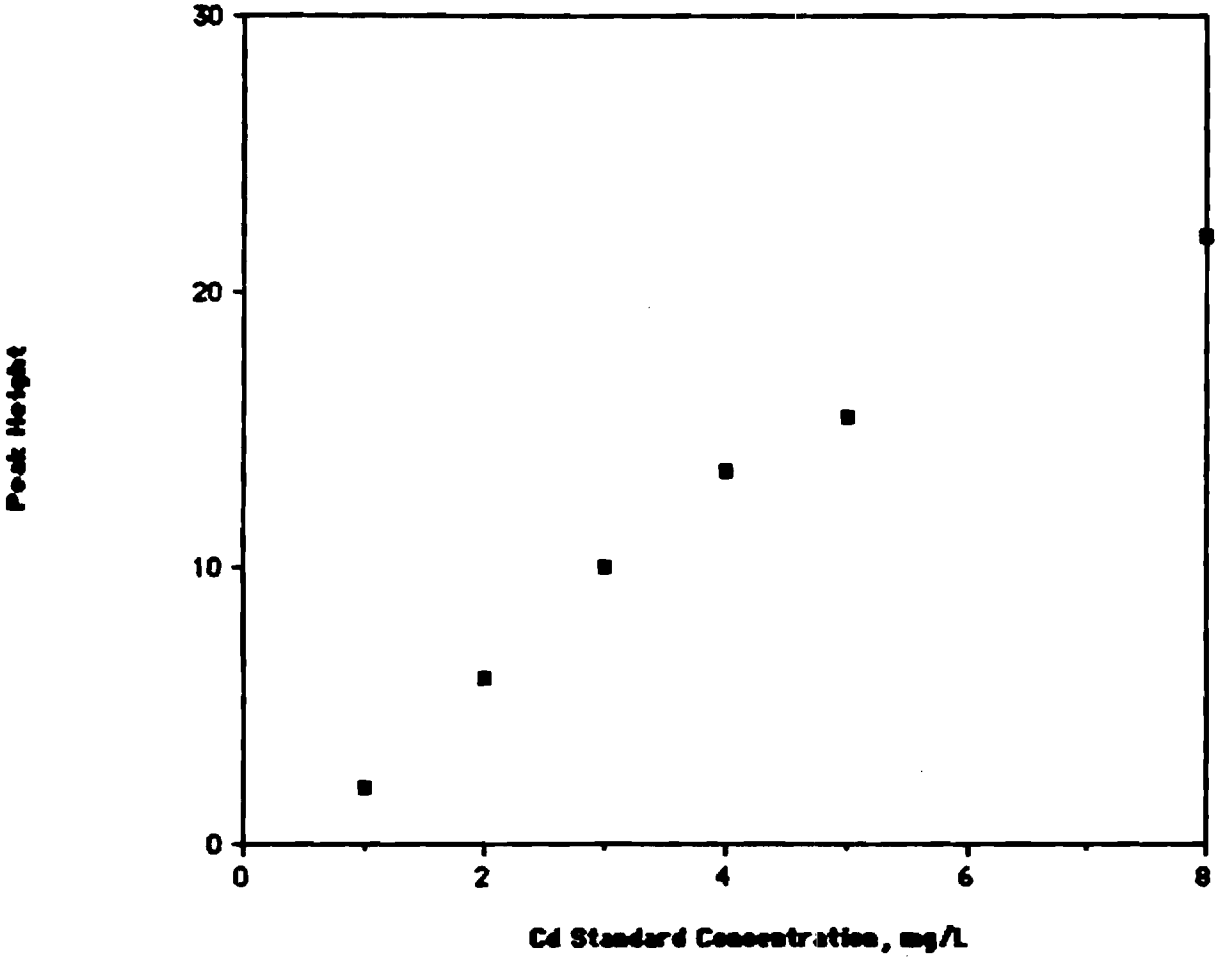

Figure 3. Typical Cd Standard Calibration Curve

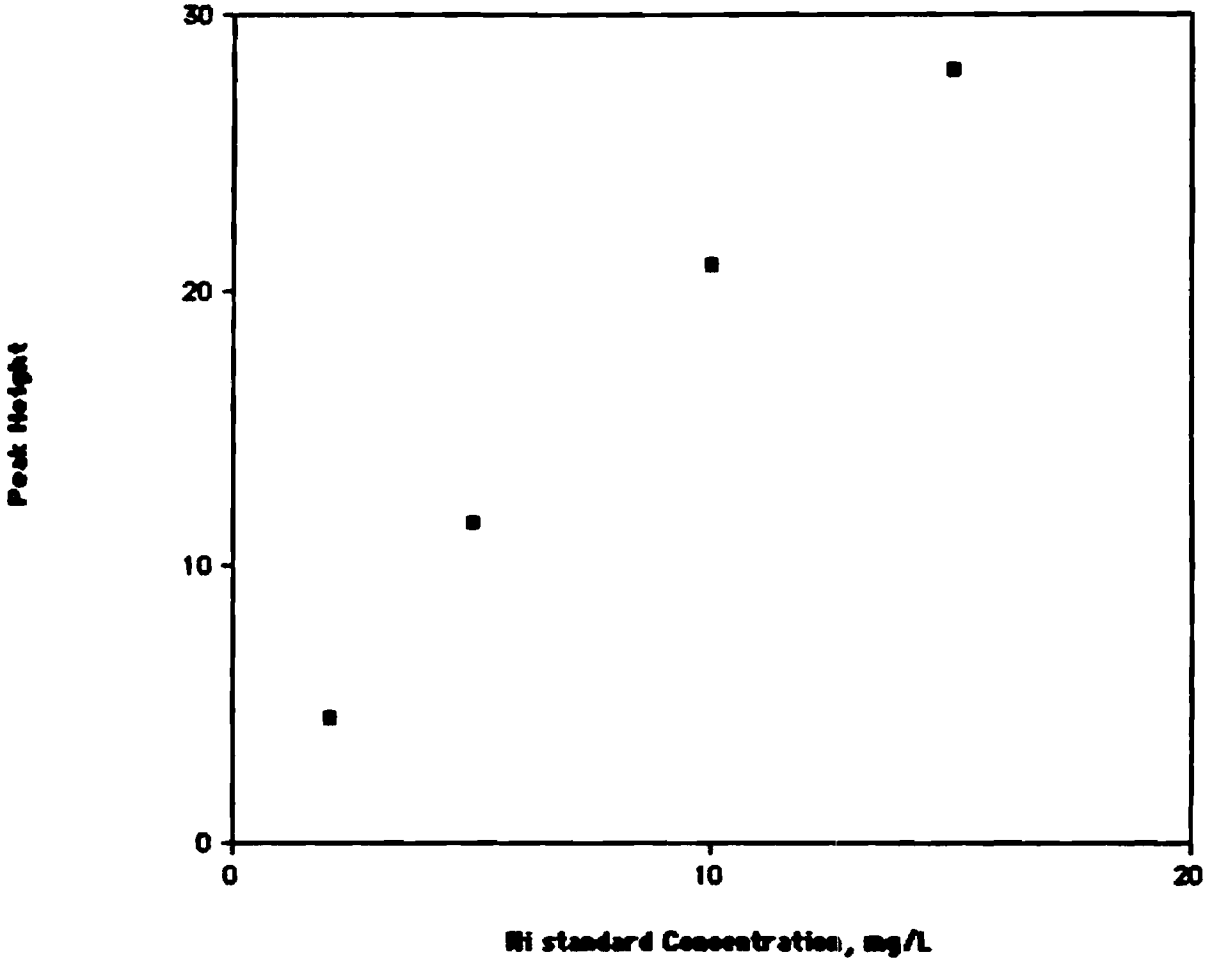

Figure 4. Typical Ni Standard Calibration Curve

and diluted to an appropriate concentration. A typical calibration curve is shown in Figure 5.

The Mg analyses were conducted using a Mg hollow-cathode lamp (Fisher-Scientific Type 4536042) in an air-acetylene flame. A specific burner orientation was used to obtain the proper sensitivity for which the samples were to be analyzed. The instrument was calibrated using at least four different concentrations of standard Mg^{2+}. Mg standards were prepared from a stock solution (1,000 mg/l, Fisher-Scientific SM51-500) and diluted to an appropriate concentration. A typical calibration curve is shown in Figure 6.

3.3 Reproducibility of the Experiments

Duplicate reactors were set up under identical conditions for each experiment to establish the reproducibility and validity of the research methodology. The results of most experiments were reproducible.

Quality assurance and quality control (QA/QC) tests were conducted to establish accuracy and validity of analytical techniques. QA/QC tests were conducted on four metals including Cu^{2+}/Cu^{+}, Cd^{2+}, Ni^{2+}, and Pb^{2+}. Matrix (plating) solutions and deionized water were spiked with solutions of known concentrations of the above mentioned metals. Cd^{2+} and Pb^{2+} solutions were spiked into deionized water, only. Average concentrations and standard deviations were based on four data values. The larger the standard deviation, the larger the spread

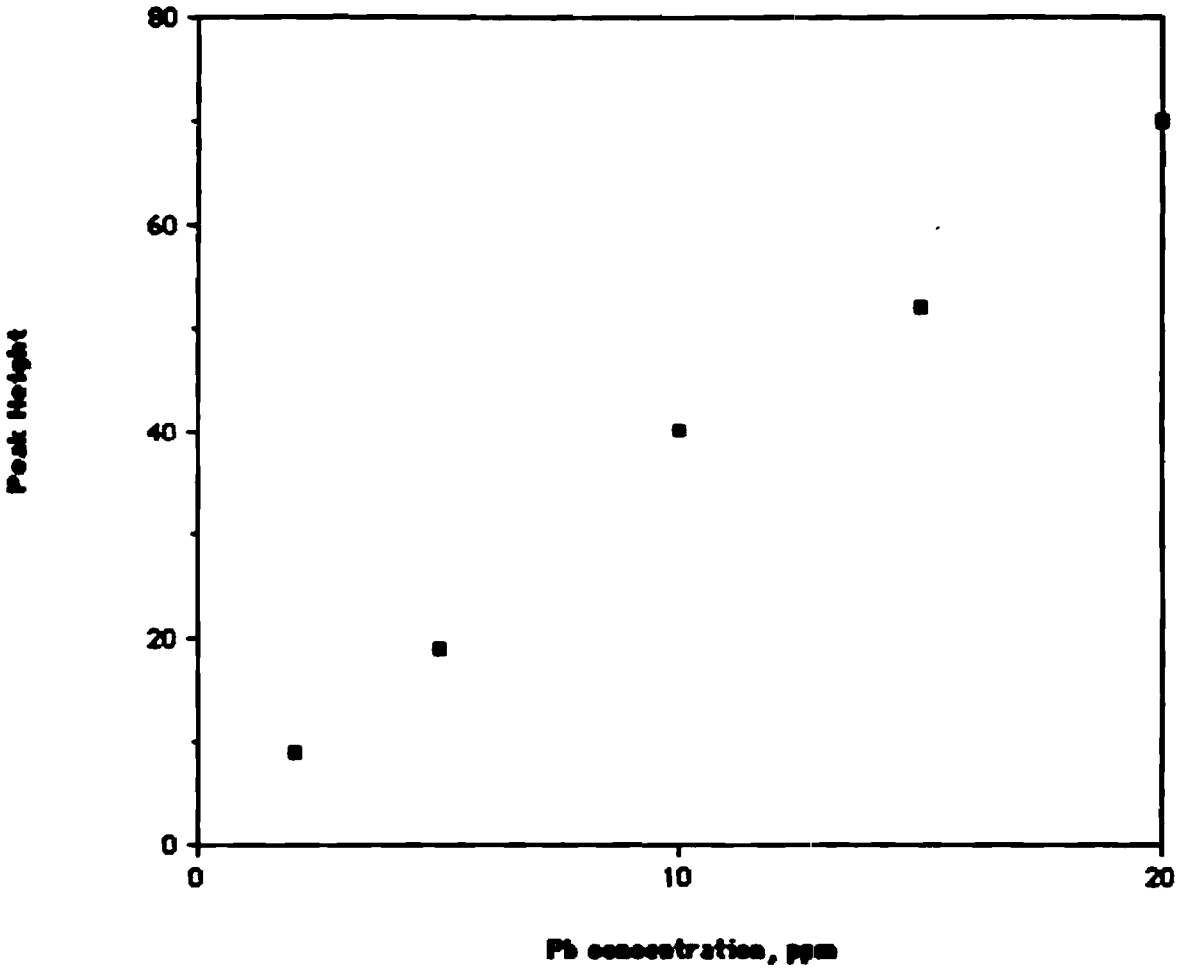

Figure 5. Typical Pb Standard Calibration Curve

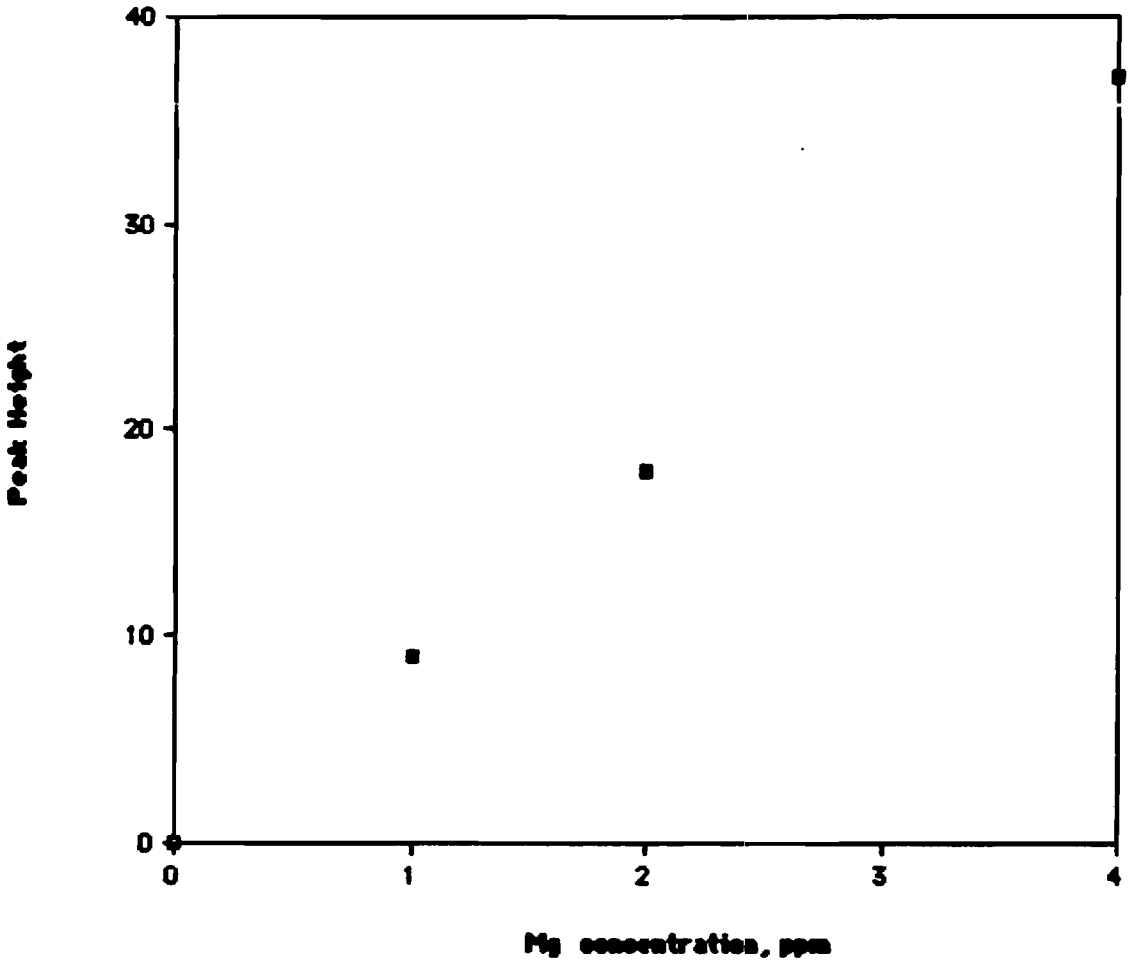

Fig 6. Typical Mg Standard Calibration Curve

of the data. The coeffificient of variation (CV) represents the average deviation about the mean. At threshold concentrations, the CV for Ni^{2+}, Cu^{2+}, and Cd^{2+} in deionized water are 3%, 3%, and 0.9%, respectively. The CV for Ni^{2+} and Cu^{2+} were 1.4% and 1.8%, respectively. The CV was not calculated for Cd^{2+} in the matrix samples because the Cd^{2+} concentration was not measured in these samples.

The parameters and results of these deionized water spiked samples (WS) and matrix spiked samples (MS) may be found in Tables 3 - 5 below. Recoveries of contaminant spikes in deionized water ranged from 95 - 100 %. Note that the matrix solution contained 20,000 ppm Cd^{2+} and 38 ppm Ni^{2+} prior to any contaminant spiking. The percent recovered for any contaminant represents a percentage of the total metal ion present in the plating solution. The concentrations of Cd^{2+} and Ni^{2+} in the matrix were analyzed and corresponded with the values mentioned above.

Table 3. Parameters and Results of QA/QC Experiments for Threshold Concentrations.

Metal	Water Spike (WS) ppm	Matrix Spike (MS) ppm	Average WS conc. % recovery ppm	Average MS conc. % recovery ppm	Standard Deviation WS	Standard Deviation MS
Cu^{2+}	8,000	8,000	7,170 (90%)	7,440 (93%)	208	138
Cd^{2+}	20,000	0	16,500 (82%)	NA*	144	NA
Ni^{2+}	40	40	44 (110%)	64 (82%)	1.3	0.89
Pb^{2+}	100	0	92.5 (92%)	NA	0.72	NA

*NA - Not Applicable

Table 4. Parameters and Results of QA/QC Experiments for Low Range Concentrations.

Metal	Water Spike (WS) ppm	Matrix Spike (MS) ppm	Average WS conc. % recovery ppm	Average MS conc. % recovery ppm	Standard Deviation WS	Standard Deviation MS
Cu^{2+}	4,000	4,000	3,620 (90%)	3,750 (94%)	45.0	45.0
Cd^{2+}	16,000	0	14,400 (90%)	NA	378	NA
Ni^{2+}	20	20	22 (110%)	40 (70%)	1.3	1.8

Table 5. Parameters and Results of QA/QC Experiments for High Range Concentrations.

Metal	Water Spike (WS) ppm	Matrix Spike (MS) ppm	Average WS conc. & recovery ppm	Average MS conc. & recovery ppm	Standard Deviation WS	Standard Deviation MS
Cu^{2+}	12,000	12,000	10,400 (87%)	10,800 (90%)	200	262
Cd^{2+}	24,000	0	20,600 (86%)	NA	0	NA
Ni^{2+}	60	60	67 (110%)	39 (39%)	0.65	1.6

Digestion blanks were also analyzed to determine the concentrations of Cu^{2+}/Cu^{+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, and Mg^{2+} which might be made by HNO_3 and H_2O_2. No appreciable concentrations of any of these metals were found.

The coefficient of variance describes in terms of percentage, the amount the data points vary from the mean.

3.4 Laboratory Methods

In the first laboratory experiment, Test A, the sacrificial metal used to cement copper was cadmium in the powder form (100 mesh, Alfa Products, Danvers, Massachusetts). The initial concentrations of Cd^{2+} and Ni^{2+} in the plating solution were 20,000 ppm and 40 ppm, respectively. There was no Cu^{2+}/Cu^{+} in the plating solution, originally. Twenty mL of the copper contaminant solution were added to 165 mL of the plating solution. One point two grams Cd powder were added to the

solution in a slurry form. The slurry contained Cd powder and dilute HCl solution used to depassivate the powder. The Cd powder was depassivated with approximately 15 mL of a dilute HCl solution (10 mL of concentrated HCl diluted to 1 liter with deionized water) in order to remove any oxide films which could have interfered in the cementation process. This made the total solution volume in the reactor 200 mL. The reactors were then agitated at 350 RPM for 6 days. Ten-mL samples were taken at 0, 4, 8, 48, 86, and 144 hours. Samples were taken from all reactors and digested and analyzed for Cu^{2+}/Cu^{+}, Cd^{2+}, and Ni^{2+}. The dilution factor (DF) used to determine Cu^{2+}/Cu^{+} concentration was 5000X and 1000X. The dilution factor used for Cd^{2+} analysis was 5000X, and the dilution factor used for Ni^{2+} analysis was 5X. Other test conditions may be found in Table 6 below.

When the Cu^{2+} contaminant solution first came into contact with the plating solution, fluffy solids were formed. These solids appeared to have dissolved with a few seconds of vigorous agitation by hand.

The Cd powder formed pellets after approximately 4 hours, thus greatly reducing the surface area for cementation to occur. After the first 4 samples (0,4,8,24, & 48 hours) were taken, the Cd pellets began to break up and dissolve and the solution, initially clear, became cloudy. Thus, the remaining samples (96 & 144 hours) were filtered in order to remove any suspended Cd powder which might skew results. Also, they were filtered to remove any Cu which might have been cemented. To determine if

any Cu had indeed been cemented, a dilute nitric acid solution (1 part of concentrated nitric acid to 1 part of deionized water) was rinsed through the filter in order to dissolve any copper which may have been retained on the filter. These samples were digested and analyzed for Cu^{2+}/Cu^{+}.

Table 6. Test Conditions for Experiments Test A through E.

Test	Number of Reactors	Mass in g and form of Cd Cementing Agent Added per liter of solution	Initial Cu^{2+} conc. ppm	Grams NaCN Added	Time Span	Mixing Speed RPM	Metals Analyzed
A	1	6 powder	10,000	93.5	6 days	350	$Cu^{2+}/Cu^{+}, Cd^{2+}, Ni^{2+}$
	1	6 powder	10,000	93.5	6 days	350	$Cu^{2+}/Cu^{+}, Cd^{2+}, Ni^{2+}$
B	1	15 granules	10,000	93.5	6 days	350	$Cu^{2+}/Cu^{+}, Cd^{2+}, Ni^{2+}$
	1	30 granules	10,000	93.5	6 days	350	$Cu^{2+}/Cu^{+}, Cd^{2+}, Ni^{2+}$
C	2	30 granules*	10,000*	93.5	20 hrs	300	$Cu^{2+}/Cu^{+}, Cd^{2+}$
D	2	0	10,000	93.5	72 hrs	300	$Cu^{2+}/Cu^{+}, Cd^{2+}, Ni^{2+}$
	2	37.5 granules	10,000	93.5	72 hrs	300	$Cu^{2+}/Cu^{+}, Cd^{2+}, Ni^{2+}$
E	1	30 granules	10,000	0	42 hrs	300	$Cu^{2+}/Cu^{+}, Cd^{2+}$
	1	30 granules	10,000	28.5	42 hrs	300	$Cu^{2+}/Cu^{+}, Cd^{2+}$
	1	30 granules	10,000	93.5	42 hrs	300	$Cu^{2+}/Cu^{+}, Cd^{2+}$

*In deionized water, pH=2.3

The second experiment, Test B, used Cd granules (Fisher Scientific, C3-500, Fair Lawn, New Jersey) instead of powder to overcome the pellet formation problem presented when Cd powder was used. Also, the mass of Cd granules was increased in order to provide sufficient surface area for cementation to occur, and to determine the effects of the surface area of Cd on the cementation rate of Cu^{2+}/Cu^{+}. Twenty mL of copper contaminant solution were added to 165 mL of the plating solution. Three grams Cd were added to one reactor and 6 grams Cd were added to another reactor. The Cd granules were cleaned with hexane and acetone, and then depassivated with dilute HCl before adding to the plating solution. The reactors were agitated at 350 RPM for 6 days. Ten-mL samples were taken from each reactor at 0, 12, 24, 48, and 144 hours. All samples collected were filtered through Whatman #4 filter paper. The latter samples were filtered immediately and the earlier samples were filtered after four days of storage. Samples from all reactors were digested and analyzed for Cu^{2+}/Cu^{+}, Cd^{2+}, and Ni^{2+}. The dilution factor used to determine Cu^{2+}/Cu^{+} and Cd^{2+} concentrations was 5000X, and for Ni^{2+} was 5X. A lower dilution factor was later used for Cu^{2+}/Cu^{+} analysis, and Cu^{2+}/Cu^{+} was reanalyzed at a 500X dilution.

To make sure that Cd would indeed cement Cu^{2+}/Cu^{+} as was determined earlier on a theoretical basis, another experiment, Test C, was performed. In this experiment, 20 mL of Cu^{2+} contaminant solution were added to 165 mL of deionized water. Six grams of depassivated Cd granules were added to the reactor.

The pH was brought to 2.3 using concentrated HCl. Deionized water was used instead of the plating solution because under the acidic conditions used, cyanide would form toxic HCN gas. The total solution volume in the reactors was 200 mL. Four identical reactors were used. The reactors were agitated at 300 RPM for 20 hours. Ten-mL samples were taken from each reactor at 0, 2, 4, and 20 hours and analyzed for Cu^{2+}/Cu^{+} and Cd^{2+}. The last three samples from two reactors were filtered through Whatman #1 filter paper before analysis after storage for 24 hours. None of the samples from the other two reactors were filtered. The samples were digested and analyzed for Cu^{2+}/Cu^{+} and Cd^{2+}. The dilution factor used for Cu^{2+}/Cu^{+} analysis was 5X, and for Cd^{2+} was 5000X. Other conditions for this experiment may be found in Table 6 above.

A reddish-brown deposit formed on the Cd granules immediately during Test C. After 2 hours of mixing, solid copper colored granules were seen on the Cd granules. The solution in the reactor was clear. After 4 hours of mixing, the copper colored, granular deposits had broken up and the entire solution was copper colored. The solution in the reactor was allowed to settle approximately 5 to 10 minutes before samples were taken.

The next experiment, Test D, was performed to determine the effects of Cd on the cementation process. Twenty mL of Cu^{2+} contaminant were added to all reactors. One reactor had no Cd granules added to it, and the other reactor had 7.5 g of Cd granules added. The Cd granules were depassivated prior to

addition to reactors. The reactors were then agitated at 300 RPM for 72 hours. Ten-mL samples were taken at 0, 24, and 72 hours. Other test conditions may be found in Table 6 above. All samples were filtered through Whatman #1 filter paper prior to analysis. These samples had been stored for approximately three days. Samples from all reactors were digested and analyzed for the concentrations of Cu^{2+}/Cu^{+} and Cd^{2+}. The dilution factor used to analyze Cu^{2+}/Cu^{+} was 500X and for Cd^{2+} was 5000X.

The effects of cyanide ion (CN^{-}) were then investigated. An experiment, Test E, was performed using different amounts of NaCN in the plating solution. The masses of NaCN added per liter of plating solution in this experiment were 0, 28.5, and 93.5 g. Other components used to make up the plating solution were the same as those used in previous experiments. Twenty mL of Cu^{2+} contaminant were added to 165 mL of each plating solution in the reactors. Six grams of depassivated Cd granules were added to each reactor. Other parameters for this experiment may be found in Table 6 above. When the Cu^{2+} solution was added to the reactor in which 0 g of NaCN was added, a light blue, fluffy solid was formed. The solids did not dissolve regardless of the intensity or time of mixing. When the Cu^{2+} solution was added to the reactor in which 28.5 g of NaCN was added, a light grey, fluffy solid was formed. Again, the solids would not dissolve. When the Cu^{2+} solution was added to the reactor in which the usual 98.5 g of NaCN was adde to the plating solution, fluffy solids were formed, and dissolved when shaken vigorously for a

few seconds. None of the samples were filtered because the solids in two of the reactors did not dissolve. The Cu^{2+}/Cu^{+} samples were analyzed at a dilution factor of 500X, Cd^{2+} analyzed at 5000X, and Ni^{2+} at 5X.

The next set of experiments, Runs 1 through 4, used magnesium (Mg) shavings (Fisher Scientific, Lot # 790651) to cement Cu^{2+}/Cu^{+}. The plating solution used was the same as in the previous experiments. Twenty mL of Cu^{2+} contaminant solution were added to 165 mL of plating solution. The Mg shavings were cleaned and depassivated using acetone and approximately 15 mL of very dilute HCl solution (1 mL of concentrated HCl diluted to 1 liter with deionized water). The total solution volume in the reactors was 200 mL.

Ten-mL sample volumes were taken at pre-determined time intervals. Samples taken at time zero were taken prior to the addition of Mg shavings except in experiment Run 1. All samples were filtered through Whatman #40 filter paper prior to digestion and analysis. These samples were stored for less than 24 hours. Filters were rinsed with approximately 30 mL of deionized water to make sure all the 10-mL sample passed through the filter. The dilution factors used to analyze for Mg^{2+}, Cu^{2+}/Cu^{+}, and Cd^{2+} were 5X, 500X, and 5000X, respectively. Other test conditions for these experiments may be found in Table 7 below.

Table 7. Test Conditions for Experiments Run 1 through 4.

Run Number	Reactor Number	Number of Reactors	Mass of Cementing Agent Added per liter of solution	Initial Cu^{2+} conc. ppm	Total Time Span	Mixing Speed RPM	Metals Analyzed
1	1	1	2 Mg	10,000	21 hrs	300	$Cu^{2+}/Cu^{+}, Cd^{2+}, Mg^{2+}$
	2	1	4 Mg	10,000	21 hrs	300	$Cu^{2+}/Cu^{+}, Cd^{2+}, Mg^{2+}$
	3	1	8 Mg	10,000	21 hrs	300	$Cu^{2+}/Cu^{+}, Cd^{2+}, Mg^{2+}$
2	1	1	2 Mg	10,000	120 min	300	$Cu^{2+}/Cu^{+}, Cd^{2+}$
	2	1	4 Mg	10,000	120 min	300	$Cu^{2+}/Cu^{+}, Cd^{2+}$
3	1	2	2 Mg	10,000	60 min	175	$Cu^{2+}/Cu^{+}, Cd^{2+}$
4	1	2	2 Mg	10,000	30 min	250	$Cu^{2+}/Cu^{+}, Cd^{2+}$
	2	2	2 Mg	10,000	30 min	400	$Cu^{2+}/Cu^{+}, Cd^{2+}$

In the first experiment, Run 1, 0.4 g, 0.8 g, and 1.6 g of Mg shavings were added to 165 mL of plating solution in reactors 1, 2, and 3, respectively. Samples were taken at 0, 1, 2, 4, and 21 hours. Mixing was stopped during sampling.

Run 2 was performed under the same conditions as Run 1, except the time span was shortened from 21 hours to 120 minutes. 0.4 g and 0.8 g of Mg shavings were added to reactors 1 and 2, respectively. Samples were taken at 0, 5, 15, 40, 60, 90, and 120 minutes. Mixing was stopped during sampling.

The mixing speed in Run 3 was reduced from 300 RPM to 175 RPM and the mixing time was shortened from 120 minutes to 60 minutes. Four-tenths of a gram of Mg shavings were added to reactor 1. As mentioned previously, duplicate reactors were set up. In this experiment, the purpose of the duplicate reactor was twofold; first to test reproducibilty of methodology and analytical techniques, and second to allow some samples to be taken from it so the total solution volume in the first reactor did not drop significantly. Samples from the first reactor were taken at 0, 5, 15, 20, 25, and 30 minutes, and samples from the duplicate reactor were taken at 0, 25, 30, 45, and 60 minutes. The mixing speed was temporarily reduced to 75 RPM during sampling. This was done because the cementation of Cu^{2+}/Cu+ and Cd^{2+} was occurring within 2.5 minutes, and stopping the mixing for the 45 second required to take the samples might have retarded or stopped the cementation process

In Run 4, the mixing time was reduced from 60 minutes to 30

minutes, and the sampling frequency increased. Also, two additional mixing speeds were used, 250 RPM and 400 RPM. Four-tenths of a gram of Mg shavings were added to reactors 1 and 2. Samples were taken at 0, 2.5, 5, 10, 15, 20, and 30 minutes. Duplicate samples from another reactor were taken at 0, 5, 15, and 30 minutes. The mixing speed was temporarily reduced to 75 RPM during sampling.

The next set of experiments, Runs 5 and 6, (Table 8), were similar to Runs 1 through 4 with the exception that 4 mL of Pb^{2+} contaminant solution were added to the solution in the reactors. Four tenths of a gram of Mg shavings were added to all reactors, with the exception of the reactor in Run 5-4, where 1.2 grams of Cu wire were added to the reactor. Ten-mL samples were taken at 0, 2.5, 5, 10, and 20 minutes in all Runs. Duplicate samples were taken at 0, 5, and 20 minutes from a second reactor. Test conditions for these experiments may be found in Table 8 below.

Table 8. Test Conditions for Experiments Runs 5 and 6.

Run Number	Number of Reactors	Mass in g of Cementing Agent Added per liter of solution	Initial Cu^{2+} conc. ppm	Initial Pb^{2+} conc. ppm	Time Span	Mixing Speed RPM	Metals Analyzed
5-1	2	2 Mg	10,000	100	20 min	300	$Cu^{2+}/Cu^{+}, Cd^{2+}, Pb^{2+}$
5-2	2	2 Mg	0	100	20 min	300	Cd^{2+}, Pb^{2+}
5-3*	2	2 Mg	10,000	100	20 min	300	$Cu^{2+}/Cu^{+}, Pb^{2+}$
5-4	2	6 Cu	0	100	20 min	300	$Cu^{2+}/Cu^{+}, Cd^{2+}, Pb^{2+}$
6	1	2 Mg	10,000	100	20 min	300	$Cu^{2+}/Cu^{+}, Cd^{2+}, Pb^{2+}$
	1	2 Mg	10,000	100	20 min	300	$Cu^{2+}/Cu^{+}, Cd^{2+}, Pb^{2+}$

*No Cad-Sol solution was added

In Run 5, four experiments were conducted using either Mg shavings or Cu wire (code 1625, Allied Chemical, Morristown, New Jersey) as the sacrificial metals. In the first series, 5-1, Mg was the sacrificial metal and Cu^{2+}/Cu^{+}, Cd^{2+}, and Pb^{2+} were present in solution. In series 5-2, Mg was the sacrificial metal and no Cu^{2+} contaminant was added to the solution in the reactor. However, the total solution volume in the reactor remained 200 mL by using 185 mL of the plating solution instead of the 165 mL used in earlier experiments. In series 5-3, Mg was the sacrificial metal, and the 100 mL of Cad-Sol solution used to make up the plating solution was not added, thus no Cd^{2+} was present in solution. In series 5-4, the sacrificial metal used was Cu wire and Pb^{2+} and Cd^{2+} were present in solution. The Cu wire was cleaned and depassivated using acetone and very dilute HCl solution.

Run 6 was identical to Run 5-1. However, one set of samples was not filtered in order to determine the effects of filtration on sample analysis.

CHAPTER 4

RESULTS AND DISCUSSION

4 Cadmium/Copper Cementation

With the exception of the cyanide free system (Test C), none of the parameters investigated in these experiments had a beneficial effect on the cementation of Cu^{2+}/Cu^{+} onto Cd. Neither increased mixing time and rates nor increased surface area, were found to render the cementation process more favorable.

As shown in Table 6, the metals analyzed in Test A were Cu^{2+}/Cu^{+}, Cd^{2+}, and Ni^{2+}. Two dilution factors were used for metal analysis, 1000X and 5000X. It was expected that the concentration of Cu^{2+}/Cu^{+} for each dilution factor would be different because of error introduced in diluting samples (Figure 7a). The values represented by the 1000X dilution factor were more accurate because the error in dilution becomes greater as the dilution factor becomes larger.

The Cu^{2+}/Cu^{+} concentration did not decrease over the testing period of 2 days (Figure 7a). In fact, the Cu^{2+}/Cu^{+} concentrations increased. It is most likely that this initial increase and later equilibrium in Cu^{2+}/Cu^{+} concentrations was due to reactions which probably occurred when Cd powder was first added to the reactor. Possibly, small quantities of Cu^{2+}/Cu^{+} were being cemented very quickly, and then the cemented Cu slowly went back into solution. The initial sample was taken after the sacrificial metal had been added. Therefore, this sample would

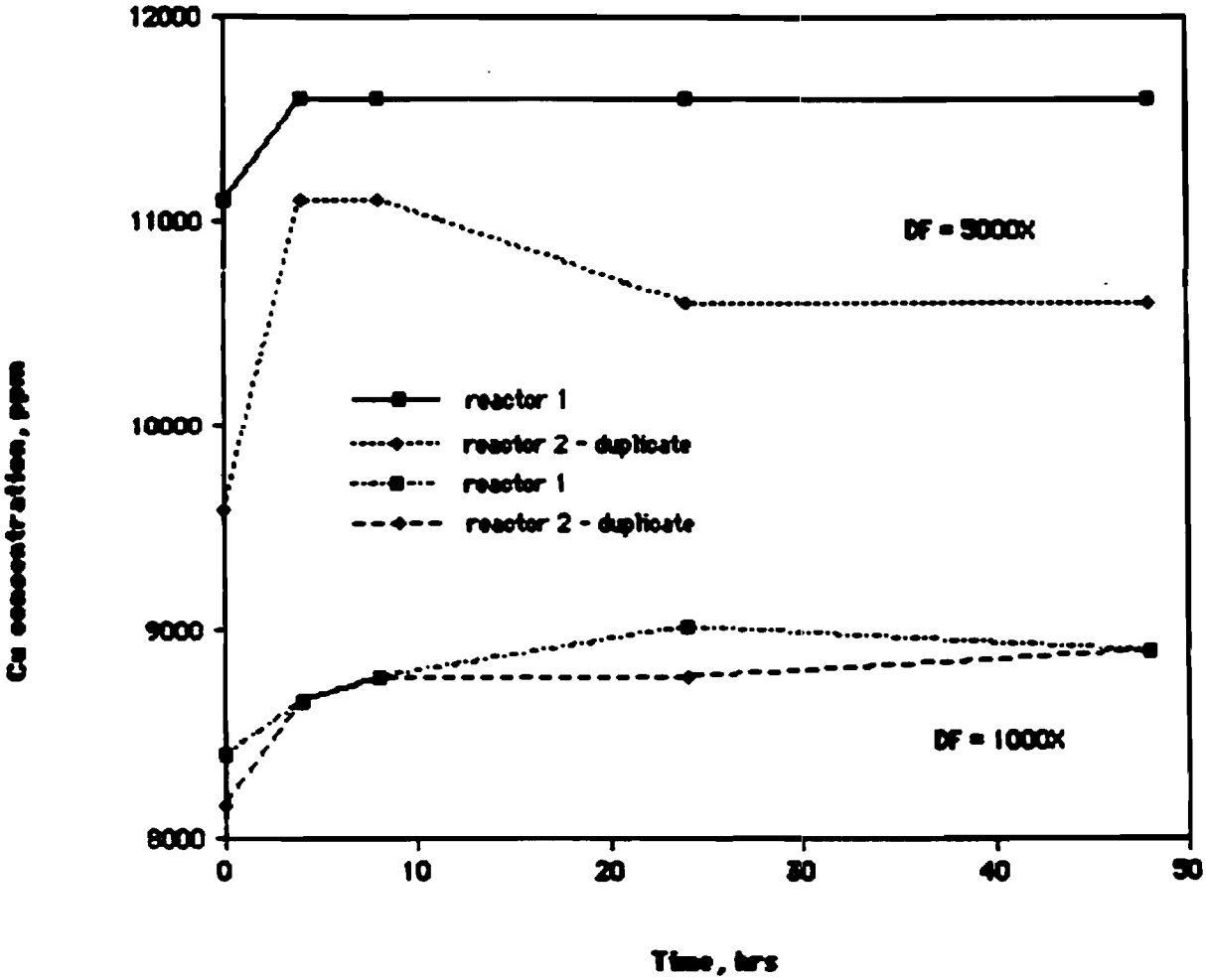

Figure 7a. Variation of Cu Concentration with Time

(6 g/L Cd powder, RPM=350)

represent the solution in the reactor while cementation was occurring. Subsequent samples represented the solution after the Cu went back into solution. Another possible explanation for this initial increase in Cu^{2+}/Cu^{+} concentration may be due to the solids which formed when the Cu^{2+} contaminant spiking solution first came into contact with the plating solution. While it appeared as if these solids dissolved completely within a few seconds of vigorous agitation, it is possible that these solids did not dissolve completely by the time the first samples were taken. The solids probably dissolved completely after 8 hours of continuous agitation, when the latter samples had been taken. This would explain the increase in Cu^{2+} concentration because part of the Cu^{2+} would have been in the solid phase and therefore the 10-mL samples taken at the beginning of the experiment would not have represented a completely mixed solution. A total of four samples were filtered prior to analysis to determine if Cu^{2+}/Cu^{+} was either being cemented or if it was suspended in the solids which formed upon contact between CN^{-} and Cu^{2+} contaminant. Analyses showed no Cu^{2+}/Cu^{+} was being retained on the filters.

During the course of the first experiment the Cd powder agglomerated and formed Cd pellets very quickly (within 4 hours) thus greatly reducing the surface area for which cementation could occur. In a Zn,Mn-Cd^{2+} system, where Zn and Mn were the sacrificial metals and Cd^{2+} was the noble metal, Blaser and O'Keefe (21) found that particle agglomeration of Zn and Mn powder occurred whenever a two-dimensional, leaf type, dendritic

growth structure of Cd was observed on the Zn and Mn powders. It was possible that small quantities of Ni^{2+} were being cemented and thus causing the agglomeration of the Cd powder.

The Cd^{2+} concentration increased with time (Figure 7b) indicating that a metal was being oxidized by O_2 in the presence of CN^-. The reaction would be as follows:

$$H_2O + Cd + 1/2O_2 + 4CN^- \text{ -----> } Cd(CN)_4^{2-} + 2OH^-.$$

The difference in concentration for the duplicate samples was within three standard deviations (98 % confidence limit) as determined in the QA/QC tests performed earlier. Figure 7c shows the concentration of Ni^{2+} over time. The Ni^{2+} concentration remained within the error limits of the analysis throughout the sampling period.

Because suspended particulates were observed in the reactors, 4 and 6 day samples were analyzed. These samples were filtered through Whatman #4 filter paper prior to digestion and analysis. Figures 7d and 7e show the concentrations of Cu^{2+}/Cu^+ and Cd^{+2} after 6 days in the reactor vessel. The Cu^{2+}/Cu^+ concentration remained constant after 4 hours indicating that Cd was not cementing Cu^{2+}/Cu^+. The concentration of Cd^{2+} continued to increase at 4 and 6 days, which indicates that it was being oxidized, as shown by the reaction presented on page 45.

Test B showed that increased Cd surface area did not affect the cementation of Cu^{2+}/Cu^+ onto Cd (Figure 8a). The Cu^{2+}/Cu^+

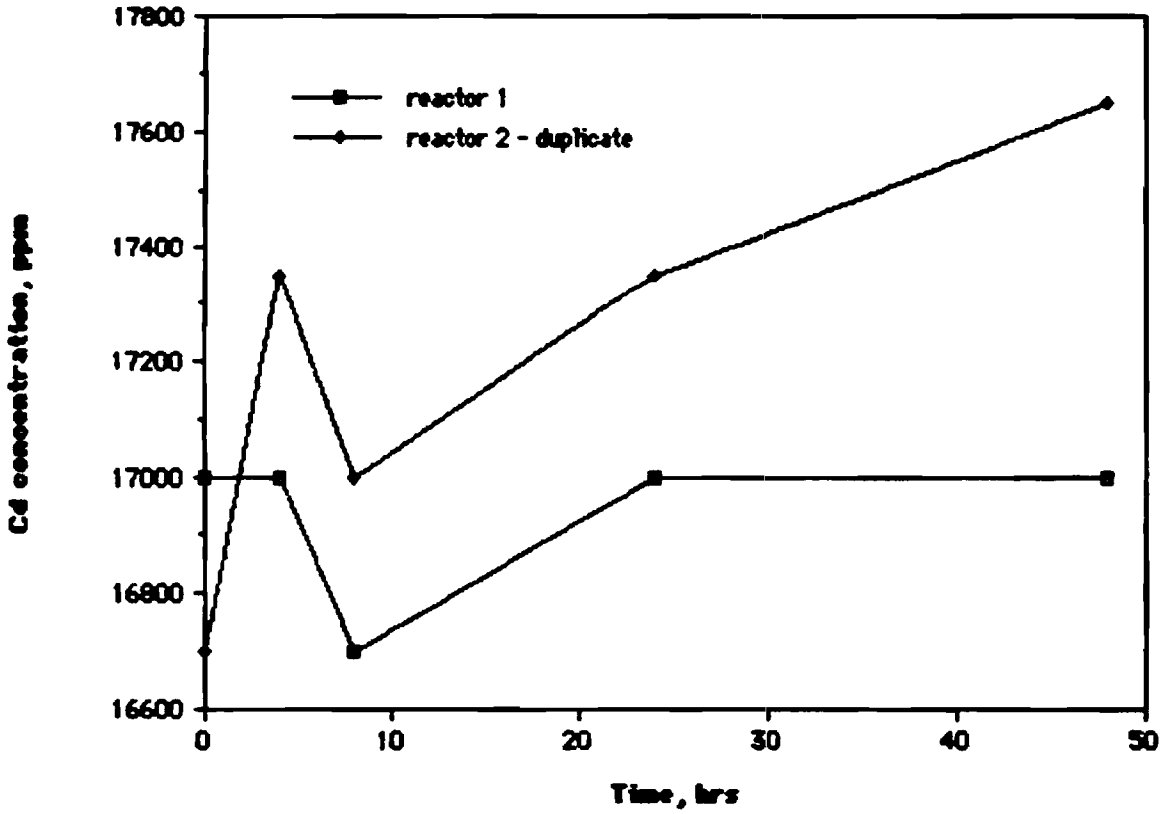

Figure 7b. Variation of Cd Concentration with Time
(6 g/L Cd powder, RPM=350, DF = 5000X)

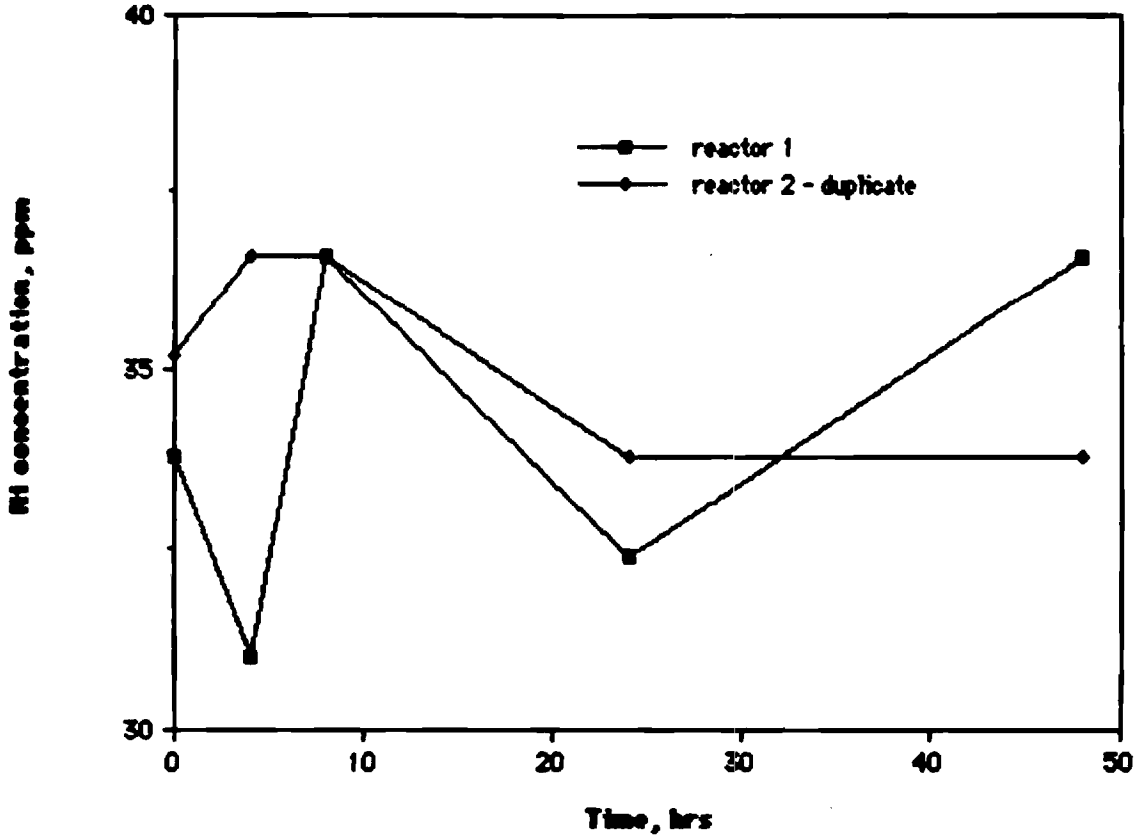

Figure 7c. Variation of Ni Concentration with Time
(6 g/L Cd powder, RPM=350, DF=5X)

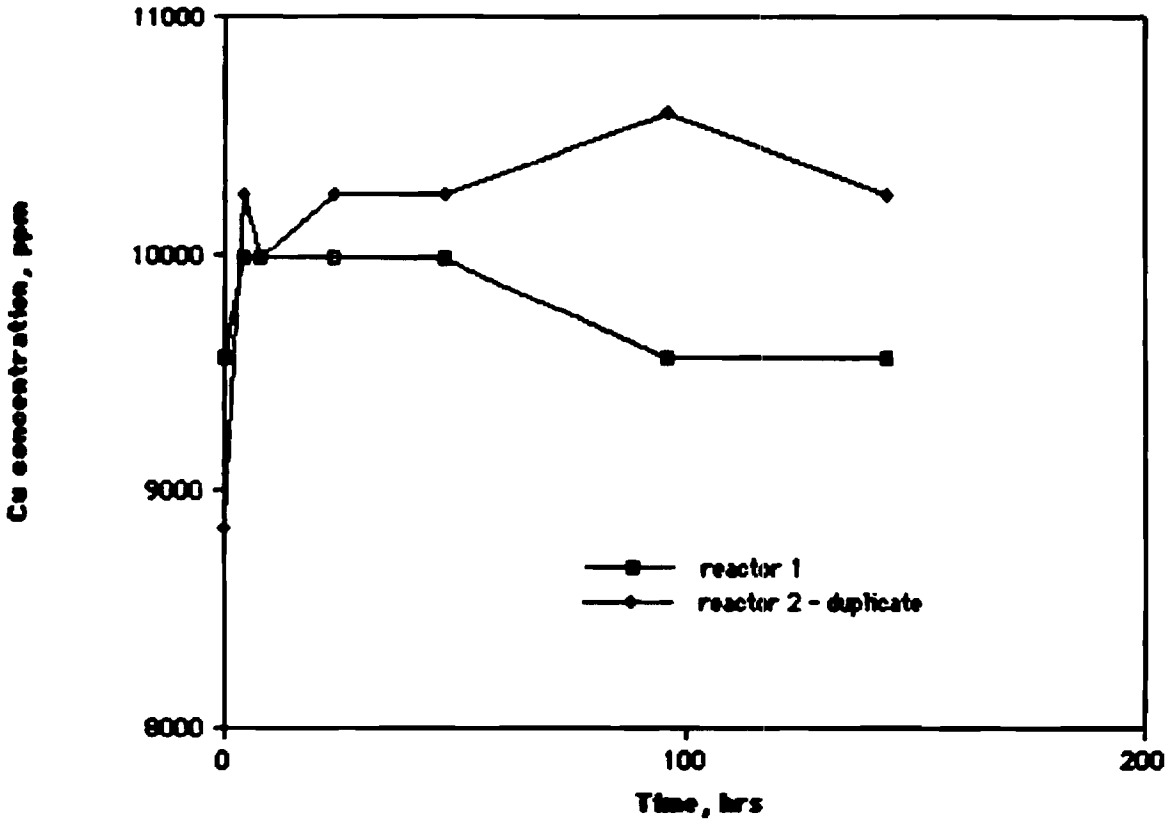

Figure 7d. Variation of Cu Concentration with Time
(6 g/L Cd powder, RPM=350, DF=5000X)

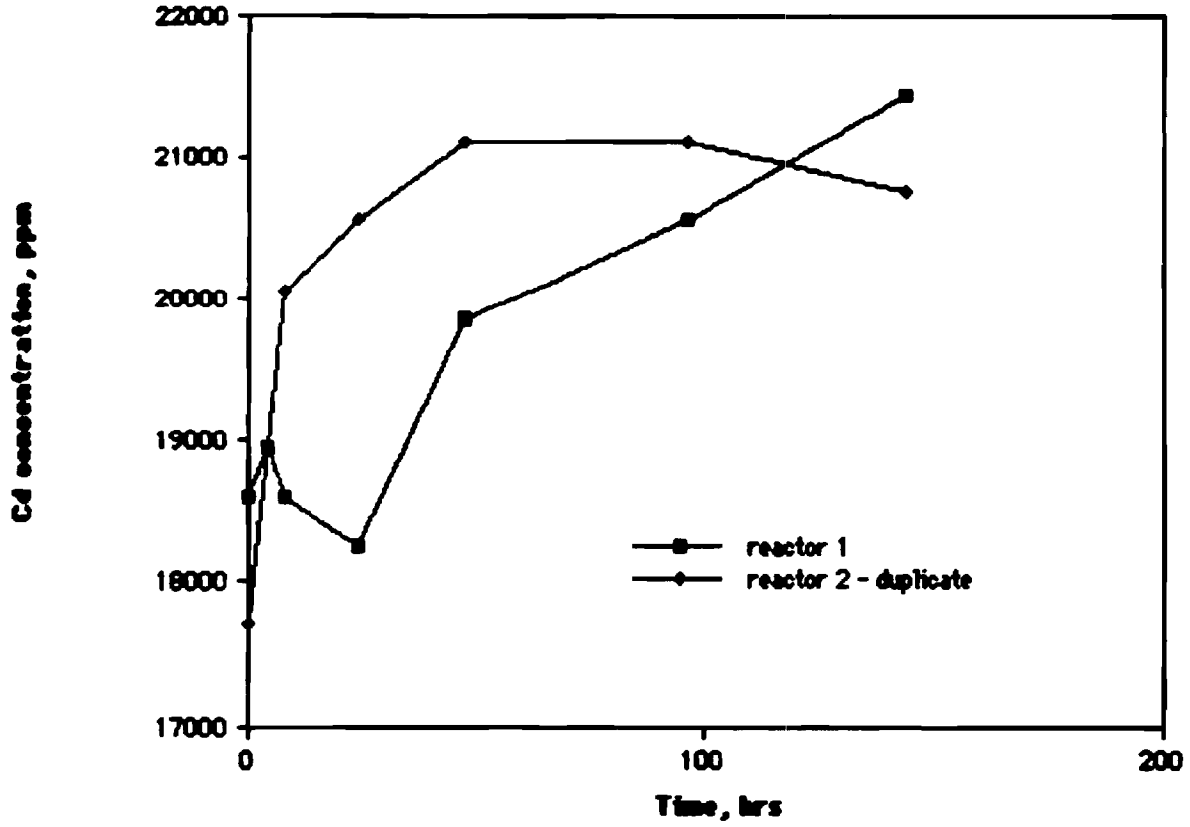

Figure 7e. Variation of Cd Concentraion with Time
(6 g/L Cd powder, RPM=350, DF=5000X)

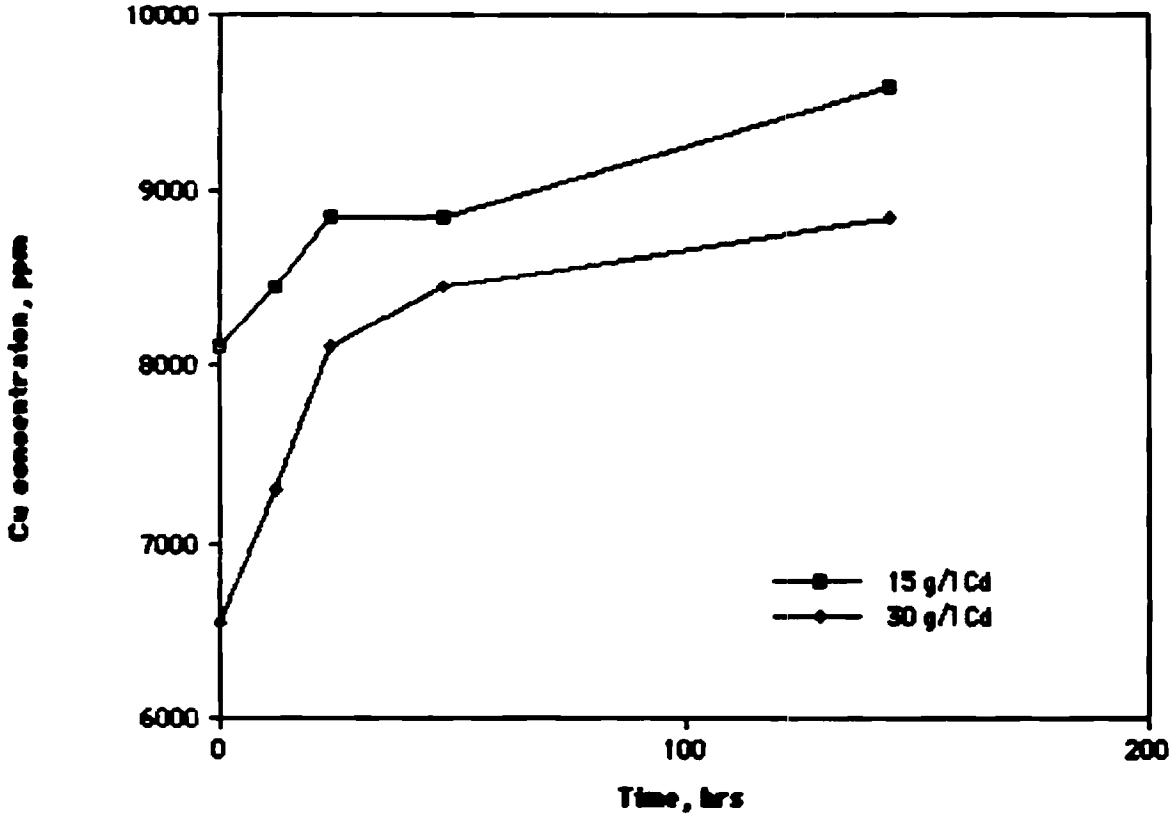

Figure 8a. Variation of Cu Concentration with Time
(15 & 30 g/L Cd granules, RPM=350, DF = 5000X)

concentration again increased with time. The most reasonable explanation for this increase in Cu^{2+}/Cu^{+} concentration is the same as mentioned earlier in Test A; cementation of Cu^{2+}/Cu^{+} by Cd which probably occurred when Cd powder was first added to the reactor. The initial sample was taken while other reactions may have been occurring. Possibly, some Cu^{2+}/Cu^{+} was being cemented and then slowly went back into solution. Thus the Cu^{2+}/Cu^{+} concentration at time zero was misrepresented. The Cu^{2+}/Cu^{+} concentration increased approximately 25%. Apparently, Cu^{2+}/Cu^{+} was not cemented by Cd. Figure 8b shows that the Cd^{2+} concentrations fluctuated considerably, but, after 6 days, the concentrations of Cd^{2+} had generally increased. Again, this was due to the oxidation of Cd metal. Figure 8c shows that the concentration of Ni^{2+} decreased over the 6 day experimental period. This decrease in concentration in these reactors was within the error limits of the analysis.

Because the Cd^{2+} concentration increased and the Ni^{2+} concentration decreased, Cd was probably cementing Ni^{2+} (Figure 8c). In test A, the Cd powder formed pellets and the Ni^{2+} concentration remained constant. No change in the Ni^{2+} concentration was detected because the surface area of the sacrificial metal was greatly reduced, therefore no noticeable quantities, if any, were being cemented. However, in Test B, there was sufficient surface area for Cd to cement Ni^{2+} and therefore the change in Ni^{2+} concentration was noticeable. The cementation of Ni^{2+}, however, was not the purpose of the

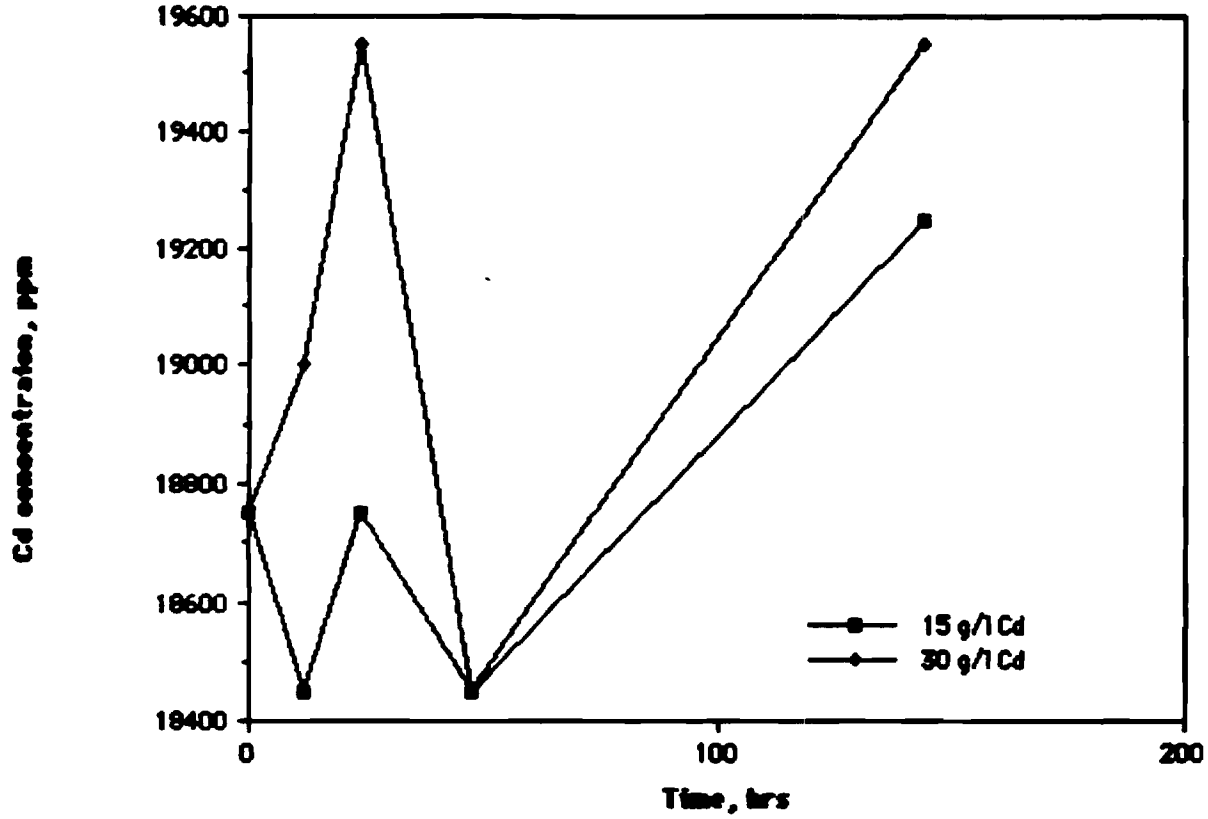

Figure 8b. Variation in Cd Concentration with Time
(15 & 30 g/L Cd granules, RPM=350, BF = 3000X)

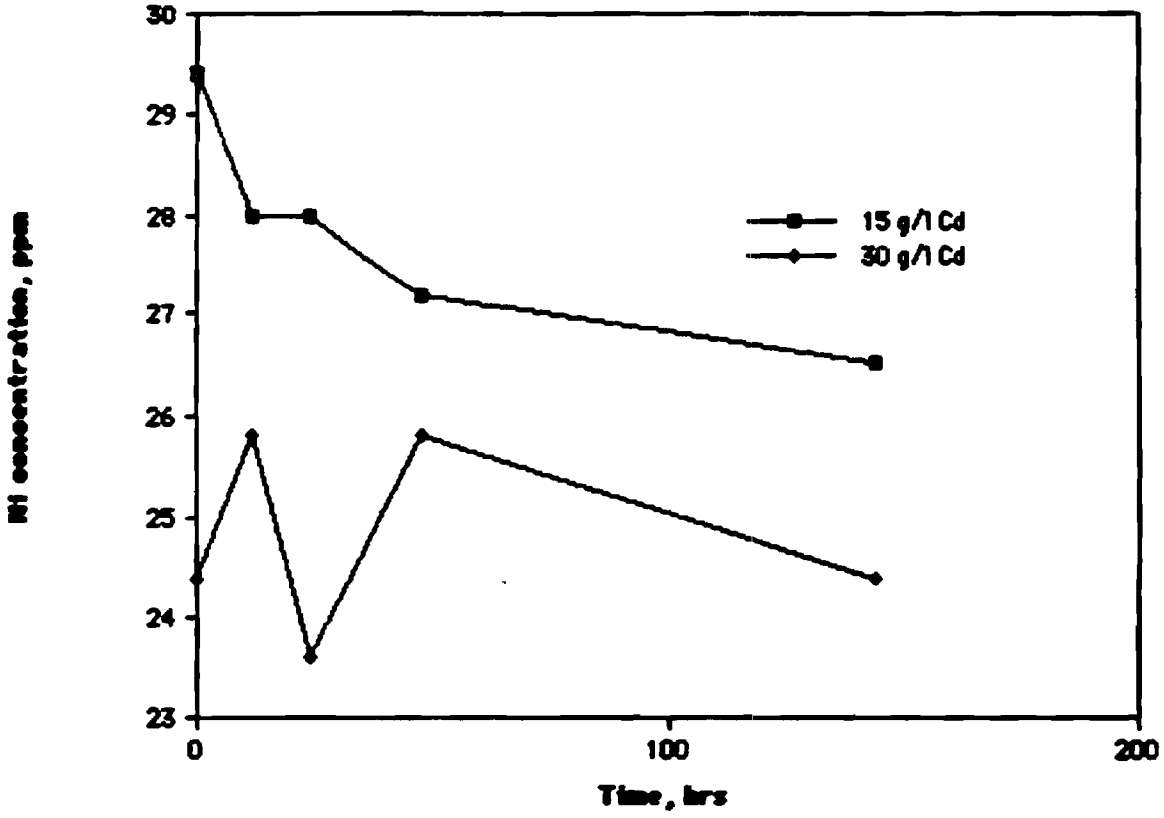

Figure 6c. Variation of Ni Concentration with Time
(15 & 30 g/L Cd granules, RPM=350, DF = 5X)

experiment nor was it a desired outcome because Ni^{2+} is used as a brightener in the electroplating process.

In the absence of the plating solution and under acidic conditions, Cd did cement Cu^{2+}/Cu^{+} rapidly (Figure 9a). One of the non-filtered samples and two of the C_0 samples taken were not analyzed. This was because the samples were lost during the digestion process. The initial concentration of Cu^{2+}/Cu^{+} in all cases was less than 60 ppm, which yielded better than 99.5% decrease from the initial Cu^{2+}/Cu^{+} concentration. Recall that the initial sample was taken after the cadmium pellets had been added, within one minute. Therefore, measurement of Cu^{2+}/Cu^{+} concentration at time zero was misrepresented. The low concentrations of Cu^{2+}/Cu^{+} indicated that cementation of Cu^{2+}/Cu^{+} onto Cd was taking place immediately. The filtered samples had higher Cu^{2+}/Cu^{+} concentrations, when in fact, it was expected that the non-filtered samples would have the higher Cu^{2+}/Cu^{+} concentrations. This would be expected because the Cu^{2+}/Cu^{+} which was cemented would have been retained on the filter. However, the differences in the filtered and non-filtered samples cannot be rigorously interpreted because the difference in values was within the error limits of the analysis for Cu^{2+}/Cu^{+}. Also, the QA/QC experiments were performed at a 1250X dilution while these Cu^{2+}/Cu^{+} analyses were performed at a 5X dilution. The standard deviation would be smaller for lower dilutions, because more error was introduced in larger dilutions.

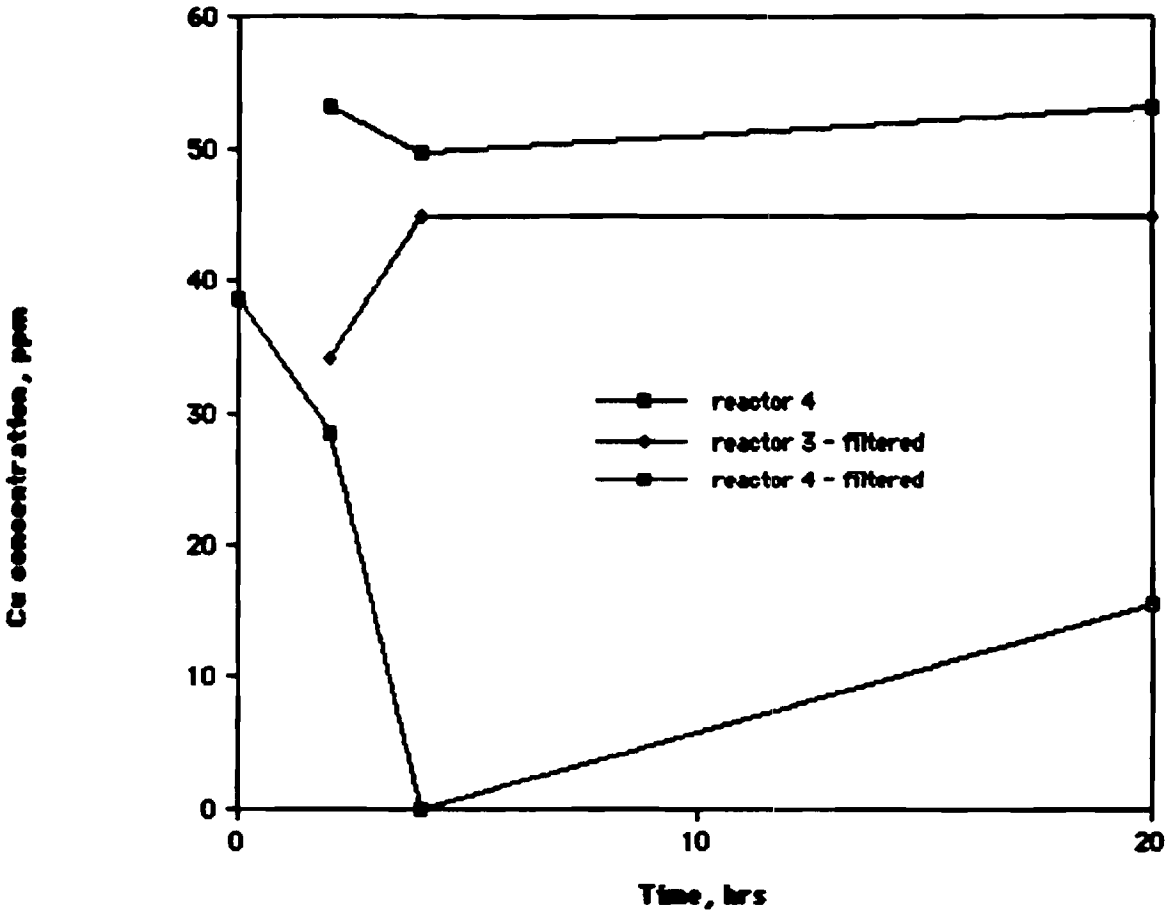

Figure 9a. Variation of Cu concentration with Time

(pH=2.3, RPM=300, DF=500X, 10,000 ppm Cu
30 g/L Cd granules, no plating solution)

Figure 9b shows the Cd^{2+} concentration over time for the non-filtered samples. The filtered samples were lost during the digestion process. The initial Cd^{2+} concentration was 0 ppm. This was not expected, however, because the Cu^{2+}/Cu^{+} concentration in the initial sample had dropped significantly. It was expected that Cd2+ be present when the initial sample was taken. The transport of Cd^{2+} into the bulk solution was probably limited by the Cu deposit which formed on the Cd granules. It was possible that a smooth Cu deposit formed on the Cd granules which would have retarded the transport of the Cd^{2+} ions.

The Cd^{2+} concentration had increased significantly by 2 hours, indicating that Cd was going into solution and that Cu^{2+}/Cu^{+} was being cemented. Although the samples at 4 and 20 hours are not shown for one of the reactors, the 2-hour sample was sufficient to show cementation of Cu^{2+}/Cu^{+} onto Cd did occur and was essentially completed by 2 hours.

Figure 10a shows the Cu^{2+}/Cu^{+} concentration over a 72-hour time period. Two samples contained cadmium granules and the other two samples did not. Some of the samples were lost during digestion and therefore those data points are not shown on the figure. The data shown for the reactor which contained no Cd granules covers only a 24-hour time period. These data show that the Cu^{2+}/Cu^{+} concentration was constant for this time, and it can be concluded that the Cu^{2+}/Cu^{+} concentration would remain constant when no Cd granules were present. Further samples were not collected because it had already been shown in the QA/QC

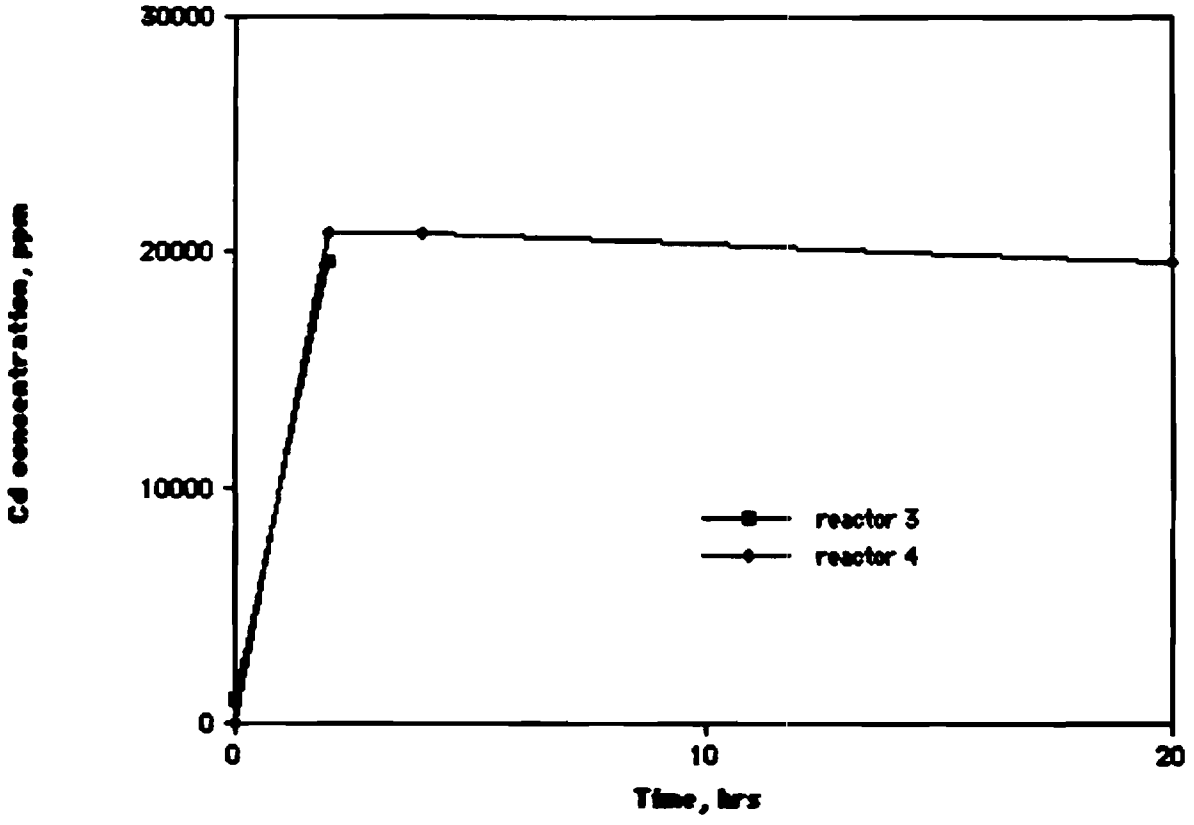

Figure 9b. Variation of Cd Concentration with Time
(pH=2.3, no plating solution, RPM=300, DF=5000X, 30 g/l Cd granules)

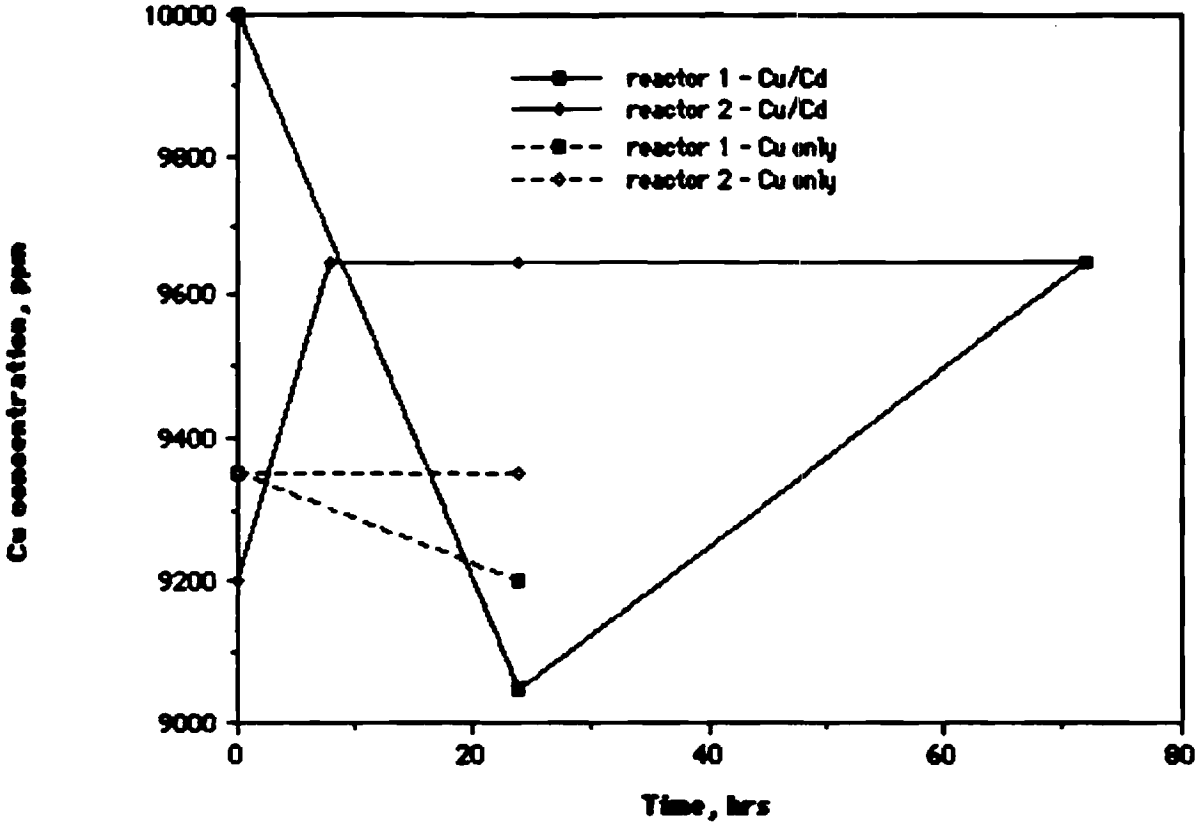

Figure 10a. Variation of Cu Concentration with Time
(37.5 g/L Cd granules, RPM=300, DF=500X)

experiments for Cu^{2+}/Cu^{+} that the Cu^{2+}/Cu^{+} concentration would remain constant. The Cu^{2+}/Cu^{+} concentration in the reactors which contained the Cd granules was erratic. The duplicate data collected for reactors which contained Cd granules were not reproducible. The duplicate sample which shows the sharp decrease in Cu^{2+}/Cu^{+} concentration was probably inaccurate because earlier tests showed that Cu^{2+}/Cu^{+} concentrations increase with time as the other reactor containing Cd granules on this figure shows. Overall, it was apparent that Cu^{2+}/Cu^{+} was not being cemented by Cd.

Figure 10b shows the concentration of Cd^{2+} over the 72 hour time period in the reactors containing Cd granules. No data were collected for the reactors not containing Cd granules. The Cd^{2+} concentration generally increased with time. This was consistent with data in the other experiments. The concentration of Cd^{2+} in one reactor was significantly higher than that in the other reactor. This difference may have been due to errors made in the amount of Cd granules added. More Cd granules may have been added to one reactor than the other. This however, was unlikely because a significantly larger amount of Cd would have had to have been added to increase the Cd^{2+} concentration to almost one and a half times the normal findings. Experimental error during analysis was not likely due the good reproducibility shown during other experiments and QA/QC experiments.

Figure 10c shows the concentration of Ni^{2+} over time. In the reactors containing Cd granules, the Ni^{2+} concentration

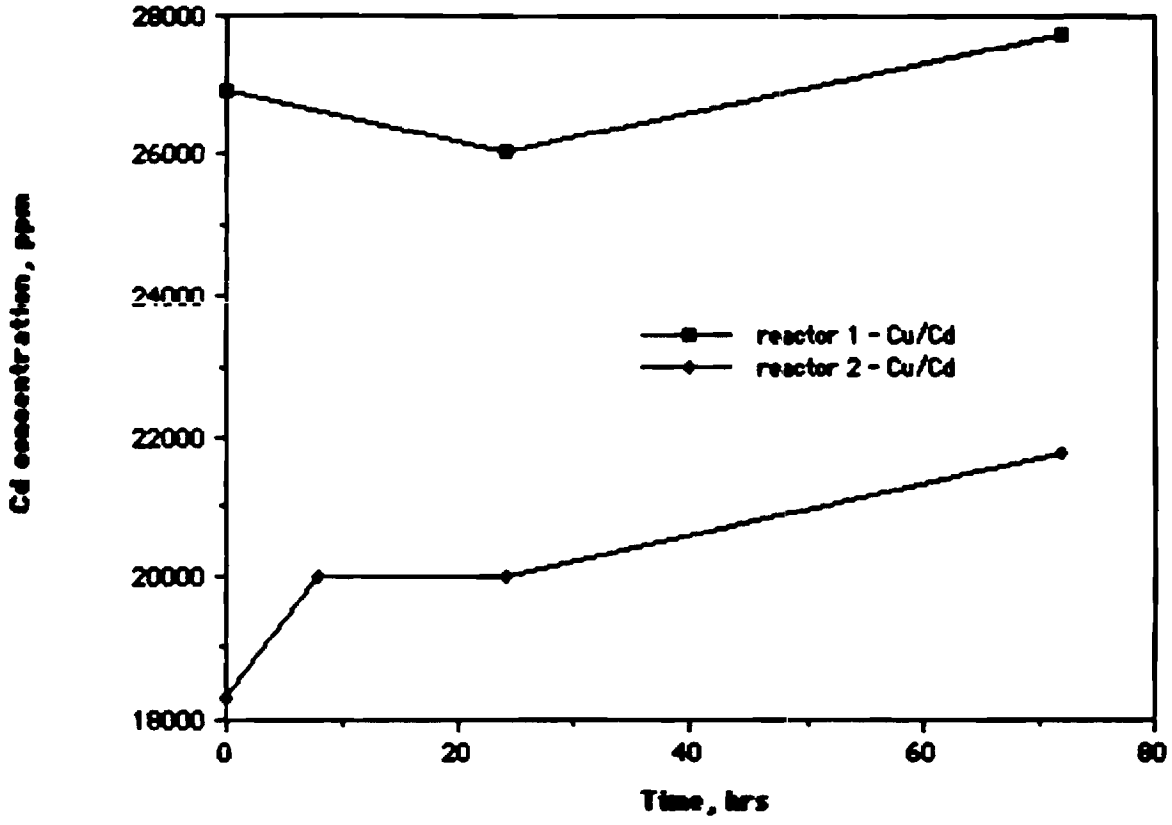

Figure 10b. Variation of Cd Concentration with Time
(37.5 g/L Cd granules, RPM=200, DF=5000X)

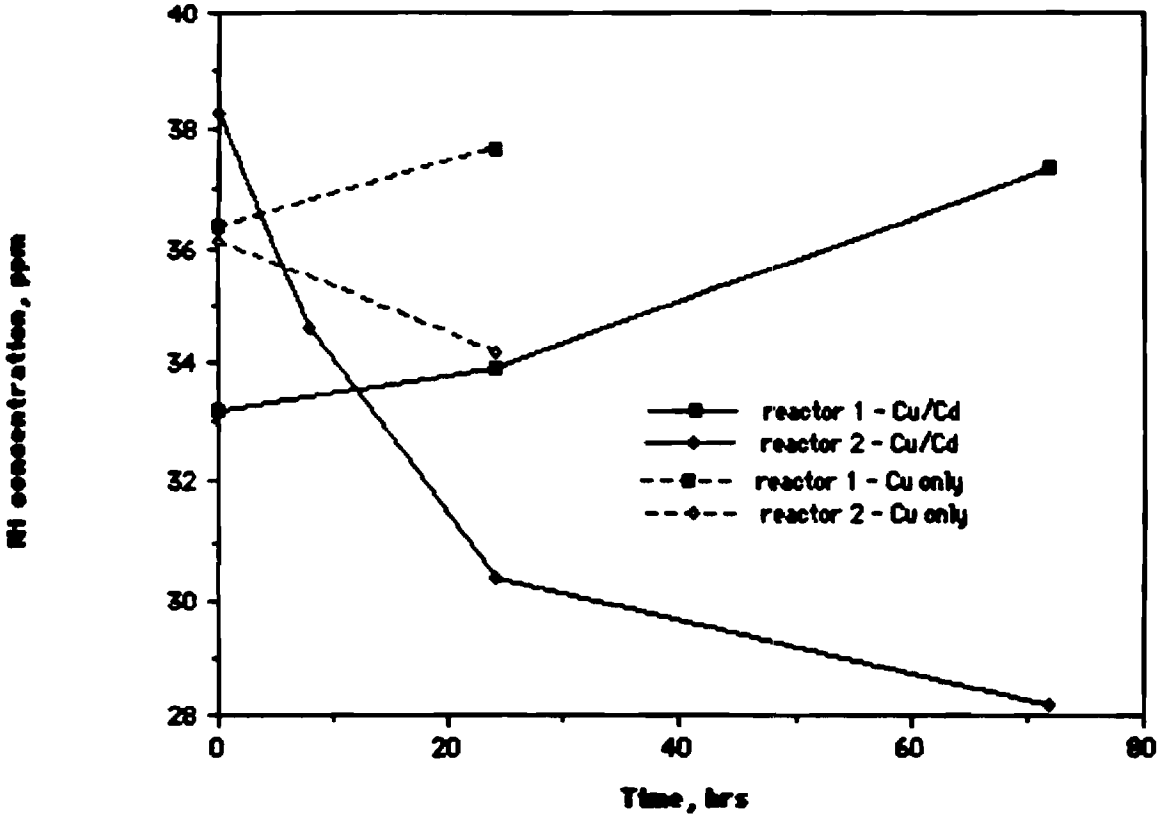

Figure 10c. Variation of Ni Concentration with Time
(37.5 g/L Cd granules, RPM=300, DF=5X)

decreased significantly in one case and increased in the other. The opposite reactions in two supposedly identical reactors may be attributed most probably to analytical error; however it was unlikely that the Ni^{2+} concentration increased over time, but rather more likely that Ni^{2+} was being cemented out by Cd. The other two curves represent the Ni^{2+} concentration in the reactors which contained no Cd granules. Data for these reactors were collected over a 24-time period only.

In all three graphs for Cu^{2+}/Cu^{+}, Cd^{2+}, and Ni^{2+}, it was the same reactor which showed the unusual and not reproducible results. It may therefore be concluded that something was awry in that reactor. Thus it may be concluded that the presence of Cd pellets did have an effect on the Ni^{2+} concentration. Ni^{2+} was probably cemented by Cd in small quantities. However, the effect of the presence of Cd pellets in the plating solution on Cu^{2+}/Cu^{+} was not discernable.

4.2 The Effect of Cyanide on the Cementation Process

Decreasing the amount of NaCN added to the plating solution from 93.5 g to 28.5 g to 0 g had no appreciable effect on Cu^{2+}/Cu^{+} cementation onto Cd (Figure 11a). However, it must be noted that the Cad-Sol contained approximately 36 g/L NaCN. Therefore, when no NaCN was added to make up the plating solution, it did not mean that no cyanide was present in the plating solution because 100 mL of Cad-Sol was still used.

The light blue, fluffy, solid which was formed when the NaCN

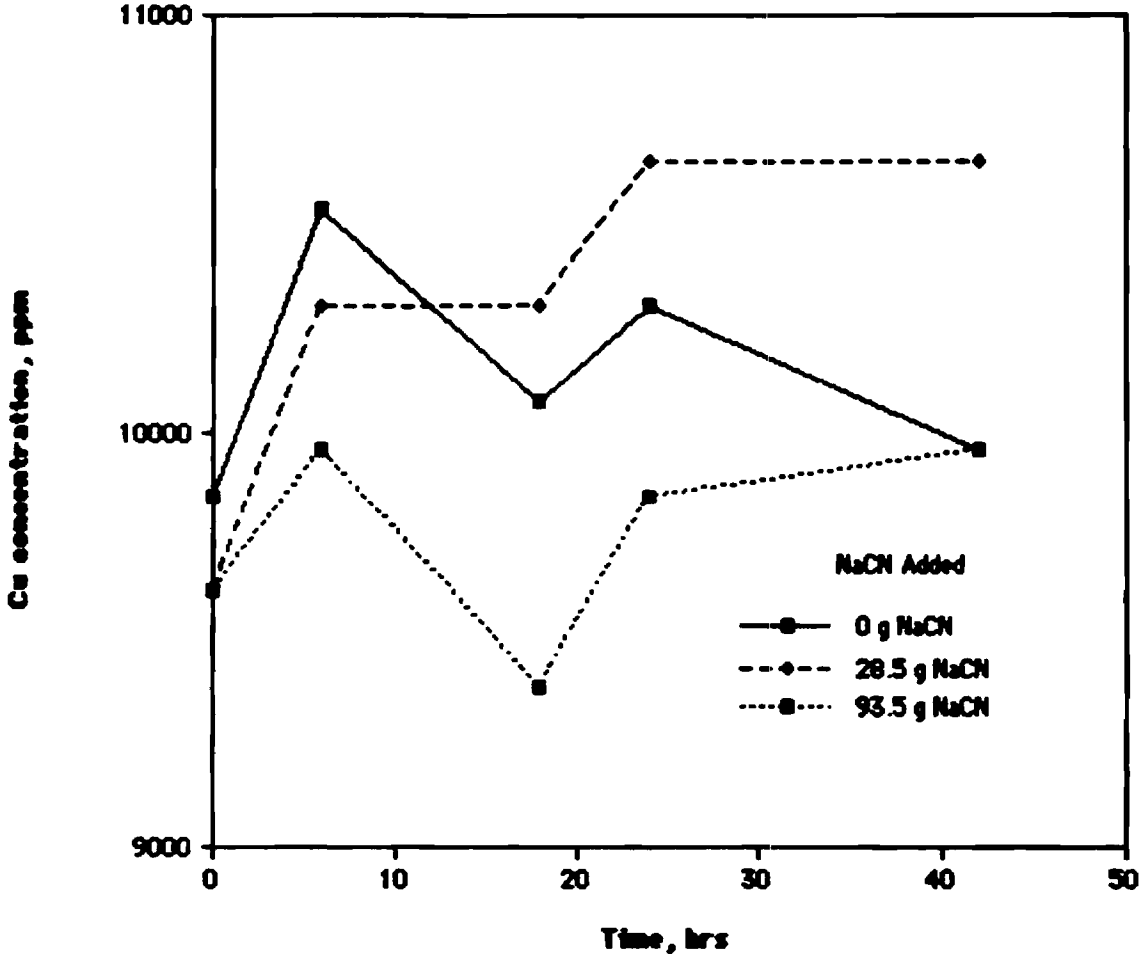

Figure 11a. Variation of Cu Concentration with Time

(30 g/L Cd granules, RPM=300, BF=500X
original NaCN concentration = 36 g/L)

addition was reduced to zero most probably contained cupric ion, Cu^{2+}. The grey, fluffy solid which was formed when the amount of NaCN added was reduced to 28.5 g most probably contained cuprous ion, Cu^{+}. The concentration of Cu^{2+}/Cu^{+} in the reactors containing additional NaCN generally increased, while the concentration of Cu^{2+}/Cu^{+} in the reactor with no NaCN addition generally decreased, but only slightly. The reactor with the addition of 93.5 g of NaCN had a lower overall Cu^{2+}/Cu^{+} concentration than the other two reactors. This difference in Cu^{2+}/Cu^{+} concentration probably occurred during sampling. The two reactors containing 0 and 28.5 grams NaCN had large amounts of undissolved solids. These solids most probably contained Cu^{2+}/Cu^{+}. A uniform sample of these solids were not necessarily sampled when the 10-mL samples were taken. A large amount of solids was probably sampled. Whatever solids were sampled dissolved completely during digestion, thus a higher Cu^{2+}/Cu^{+} concentration was found. The reactor containing 93.5 grams NaCN did not have any noticeable undissolved solids, and therefore it was more likely that a very uniform solution was sampled, i.e. no large flocs of solids. Figure 11b shows that the concentration of Cd^{2+} increased over time for all three reactors. The addition of NaCN appeared to have no effect on the changes of the Cd^{2+} concentrations.

Because the solids, most probably containing Cu^{2+}/Cu^{+}, dissolved completely in the reactor with 93.5 g of NaCN added, it may be said that Cu^{2+}/Cu^{+} and CN^{-} were fully complexing, thus

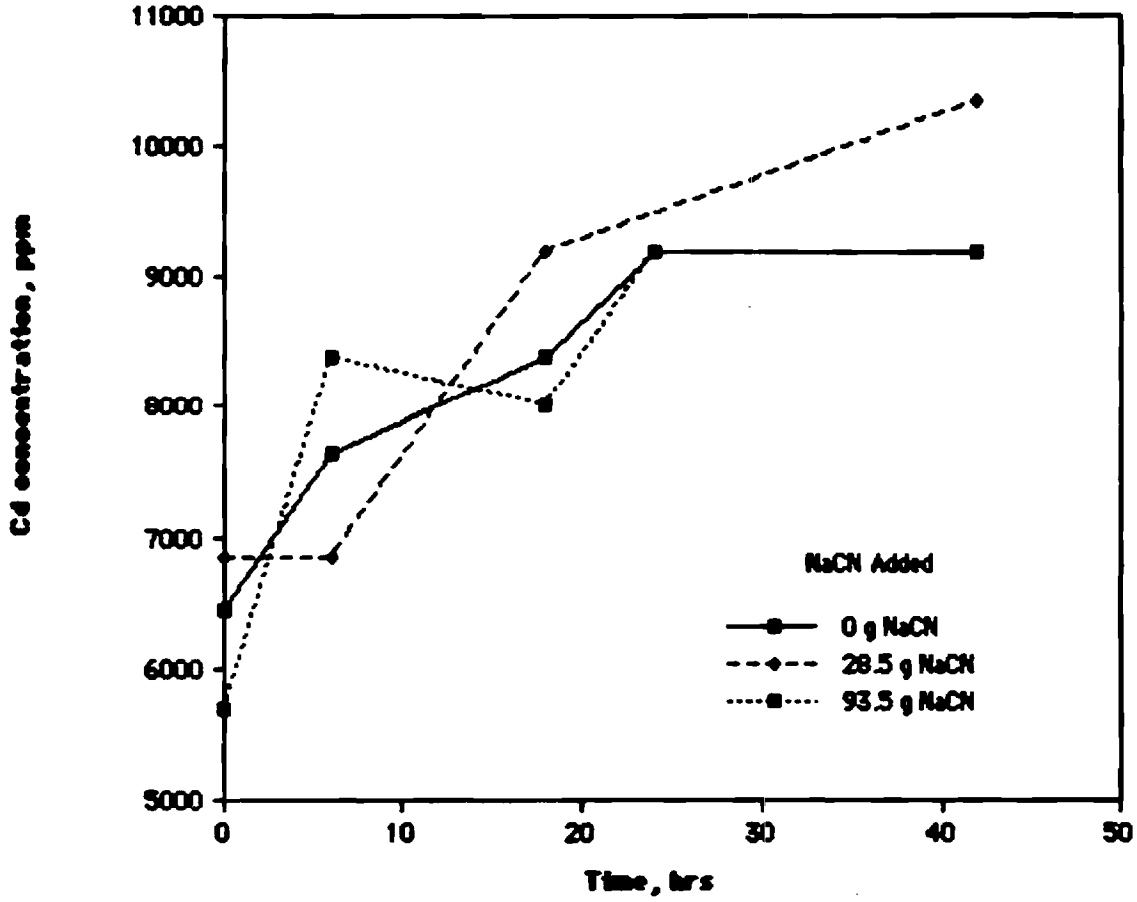

Figure 11b. Variation of Cd Concentration with Time

(30 g/L Cd granules, RPM=300, DF=5000X
original NaCN concentration = 36 g/L)

allowing Cu^{2+}/Cu^{+} to go back into solution, while in the other reactors, there was not enough CN^{-} for the Cu^{2+}/Cu^{+} to complex with and therefore at least a portion of the precipitate remained in solid form. When the Cu^{2+}/Cu^{+} went back into solution, it was complexed with CN^{-} and therefore could not be cemented.

4.3 Magnesium/Copper Cementation

Gas production, most probably hydrogen gas (H_2), was noticed immediately upon contact between the Mg shavings and the plating solution. In Run 1, after 4 to 6 hours of mixing, dark particles formed on the Mg shavings in the reactor. After 21 hours, the solution in the reactor was grey and full of particles. These particles were probably Cd particles which had been cemented by Mg. A small portion of these particles may have been Cu. Also, the Cu^{2+}/Cu^{+} concentration decreased after one hour of mixing by approximately 1,000 ppm, but began to increase during the second hour of mixing back to the concentration found at time zero (Figure 12a). At this time, the Cu^{2+}/Cu^{+} concentration began decreasing again and after 21 hours, the overall decrease in Cu^{2+}/Cu^{+} concentration was approximately 500 ppm.

The effect of increased Mg surface area was not significant on the change in Cu^{2+}/Cu^{+} concentrations. While reactor 1 showed Cu^{2+}/Cu^{+} concentrations averaging about 1,000 ppm higher than reactor 2, the difference in concentrations in the initial samples also varied by 1,000 ppm. The Cu^{2+} contaminant solution had probably been added in a slightly greater quantity to reactor

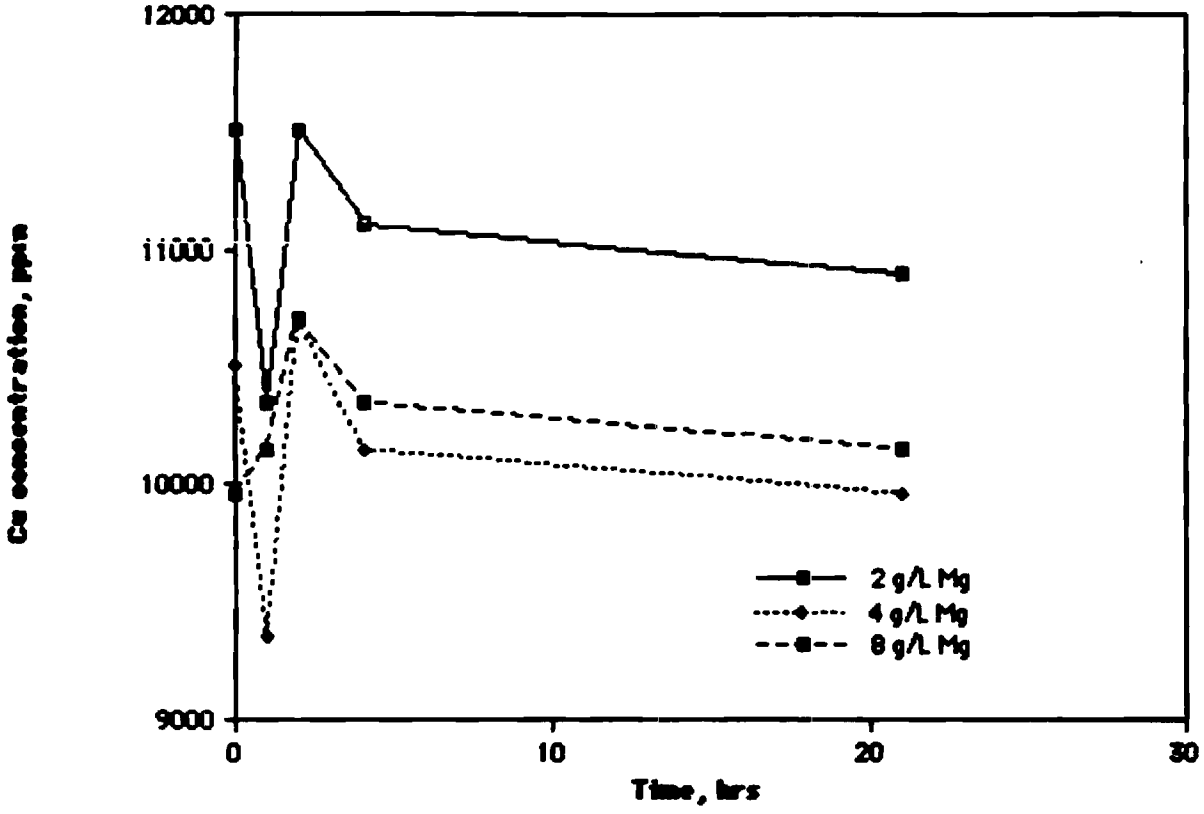

Figure 12a. Variation of Cu Concentration with Time
(Mg shavings, RPM=300, DF=500X)

1. The trends in the changes in Cu^{2+}/Cu^{+} concentrations were identical for these reactors. Reactor 3 exhibited a slightly different change in Cu^{2+}/Cu^{+} concentration. This occurred after one hour of mixing. The Cu^{2+}/Cu^{+} concentration did not decrease as expected, instead it increased by 100 ppm. However, this increase was not significant because it was within one standard deviation (i.e. 68 % confidence limit) obtained from the QA/QC results shown earlier in Table 3. The changes in Cu^{2+}/Cu^{+} concentration over the remaining mixing period were identical to reactors 1 and 2.

Initially, the changes in Cd^{2+} concentration followed the same trends as the changes in Cu^{2+}/Cu^{+} concentration (Figure 12b). However, after 21 hours of mixing, the Cd^{2+} concentration dropped off significantly in reactors 1 and 2, and completely in reactor 3.

Initially, Mg was cementing Cd2+ and Cu^{2+} Cu^{+}. However, Mg was cementing Cd^{2+} more quickly than Cu^{2+}/Cu^{+}. The reason for the increase in Cu^{2+}/Cu^{+} concentration at 2 hours as shown in Figure 12a, was once it was cemented by Mg becoming Cu°, it acted as a sacrificial metal for the more noble metal Cd. Similarly, the increase in the Cd^{2+} concentration at 2 hours was probably because it was cementing a more electropositive metal. However, the effect of Mg and Cu° was strong enough to cement Cd^{2+} more quickly than Cd could cement another metal, thus explaining the continual decrease in Cd^{2+} concentration. The increased surface area in reactor 3 probably allowed the Cu^{2+}/Cu^{+} and Cd^{2+}

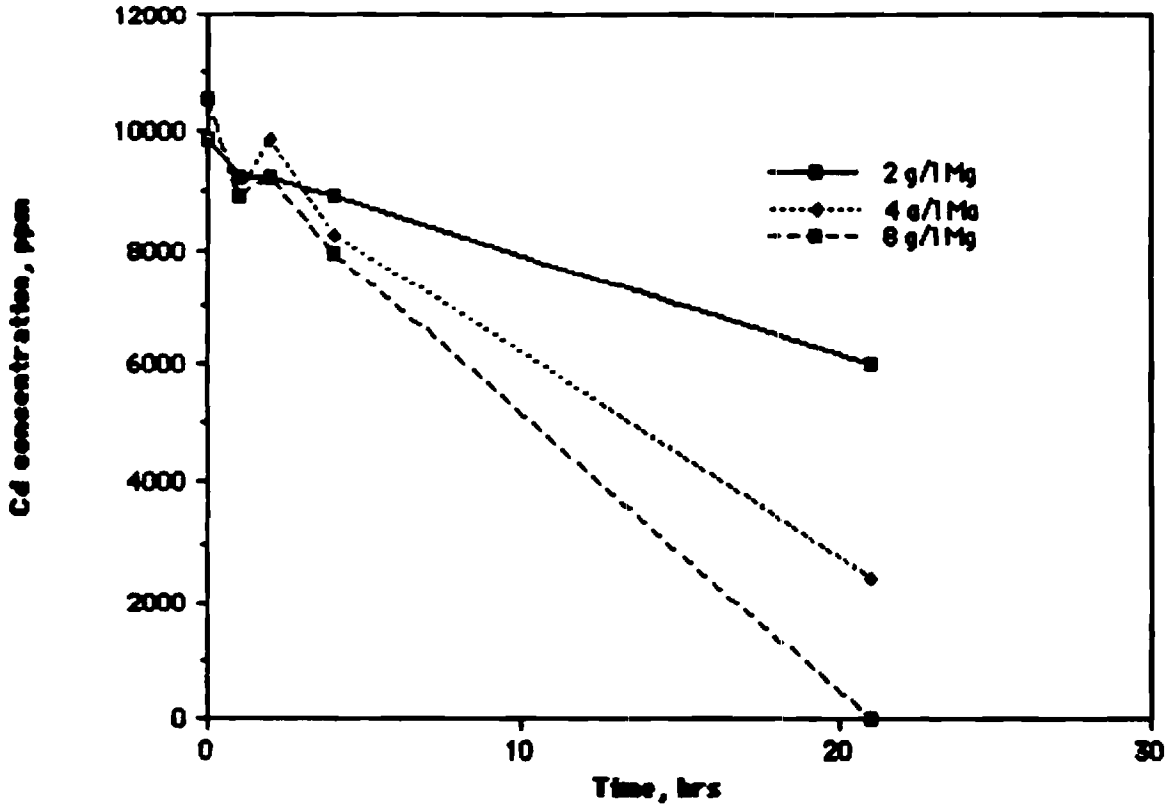

Figure 12b. Variation of Cd Concentration with Time
(Mg shavings, RPM=300, DF=5000X)

cementation processes to occur quickly enough so that the initial decrease in Cu^{2+}/Cu^{+} was not detected.

Figure 12c shows the concentration of Mg^{2+} maintains the solubility of $Mg(OH)_2$, 9.8 mg/L at this pH. The reason the sample taken at time 0 shows Mg concentrations was because in this Run, Run 1, the initial samples were taken after the Mg shavings had been added to the reactors.

Because Mg had the effect of removing Cd^{2+} completely after 21 hours of mixing, the time of mixing was shortened to 120 minutes in Run 2. The Cu^{2+}/Cu^{+} concentration decreased by 1,000 ppm during the first 5 minutes of mixing (Figure 13a). It remained at that concentration for approximately 10 minutes and then began to increase back to the concentration at time 0. The concentration of Cu^{2+}/Cu^{+} in reactor 2 decreased more than it did in reactor 1. This was possibly due to the increased surface area of Mg shavings in reactor 2.

Figure 13b shows that the Cd^{2+} concentration also decreased within the first 5 minutes of mixing. The overall Cd^{2+} concentrations in reactors 1 and 2 were different, but the trends were the same. This difference may be attributed to experimental error. The decrease in the Cd^{2+} concentration in reactor 2 was larger than in reactor 1. Again, this was possibly due to the increased surface area of the Mg shavings.

The shortened mixing time and more frequent sampling times made it possible to determine more precisely when the Cu^{2+}/Cu^{+} and

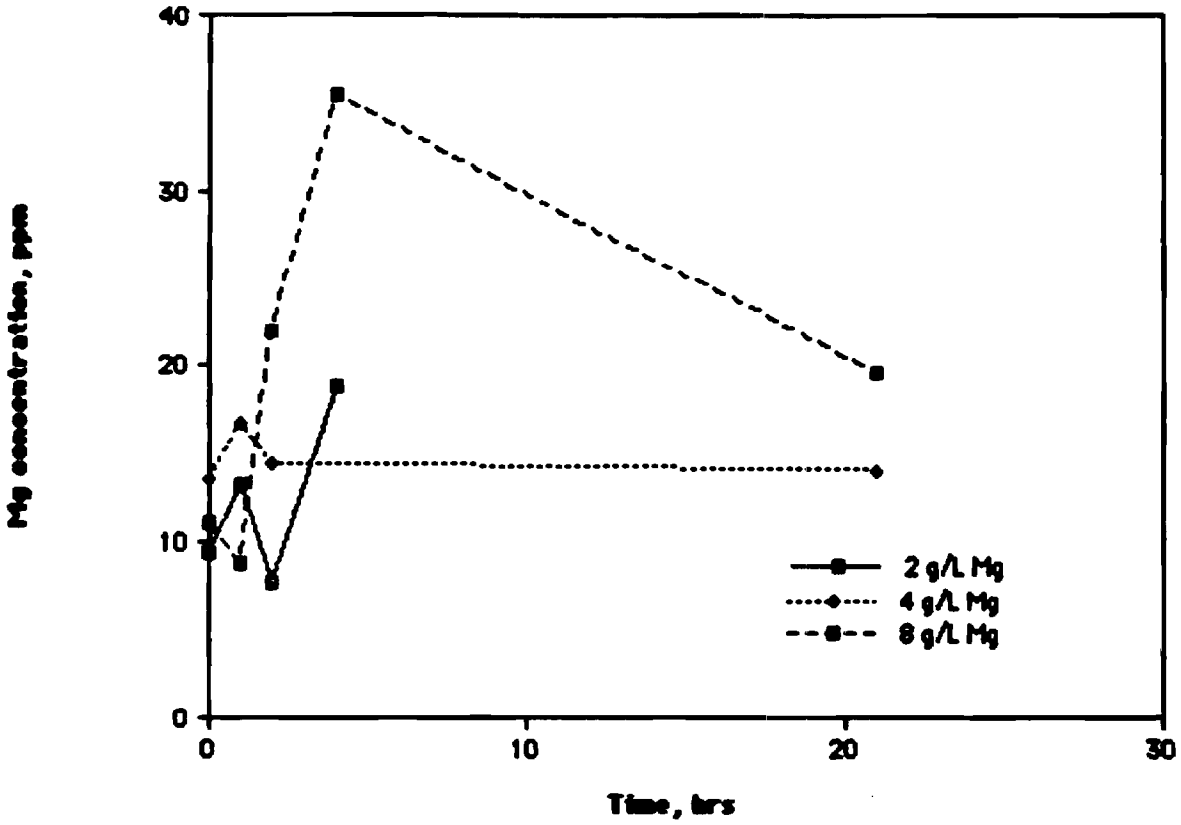

Figure 12c. Variation of Mg Concentration with Time
(Mg shavings, RPM=300, DF=5X)

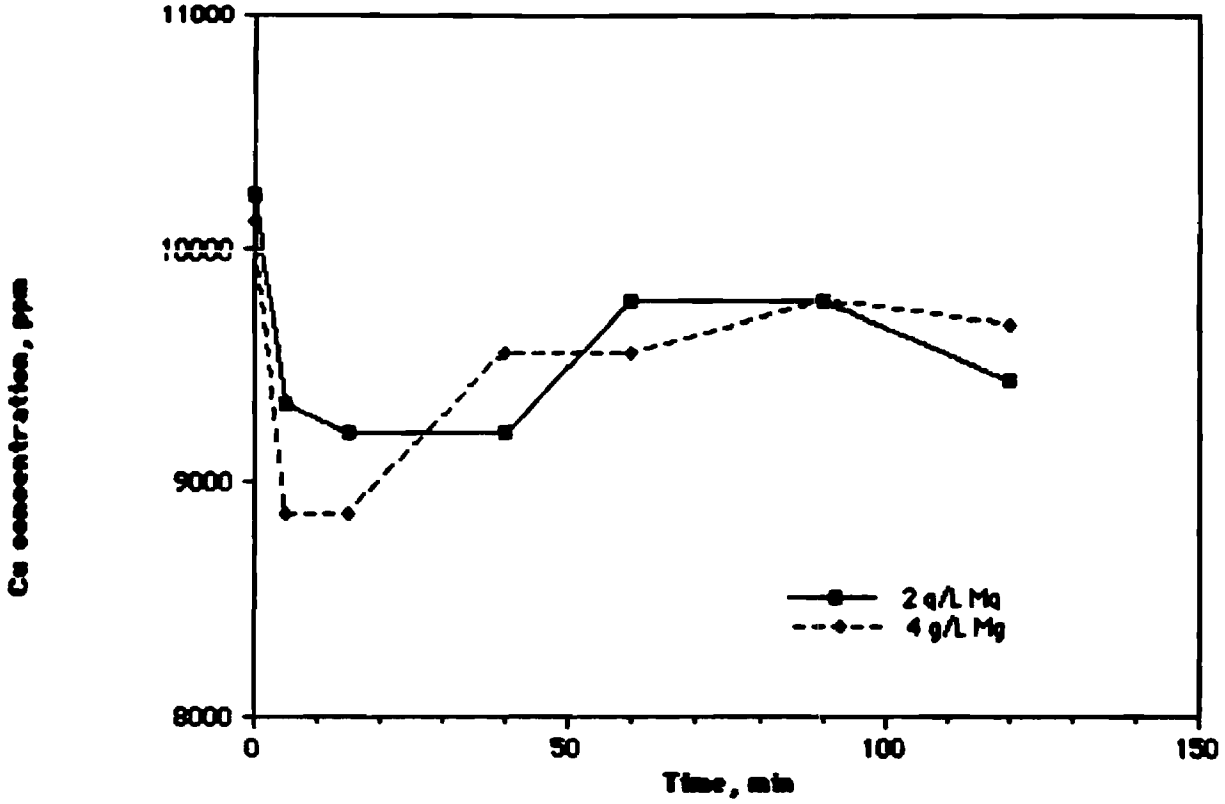

Figure 13a. Variation of Cu Concentration with Time
(Mg shavings, RPM=300, DF=500X)

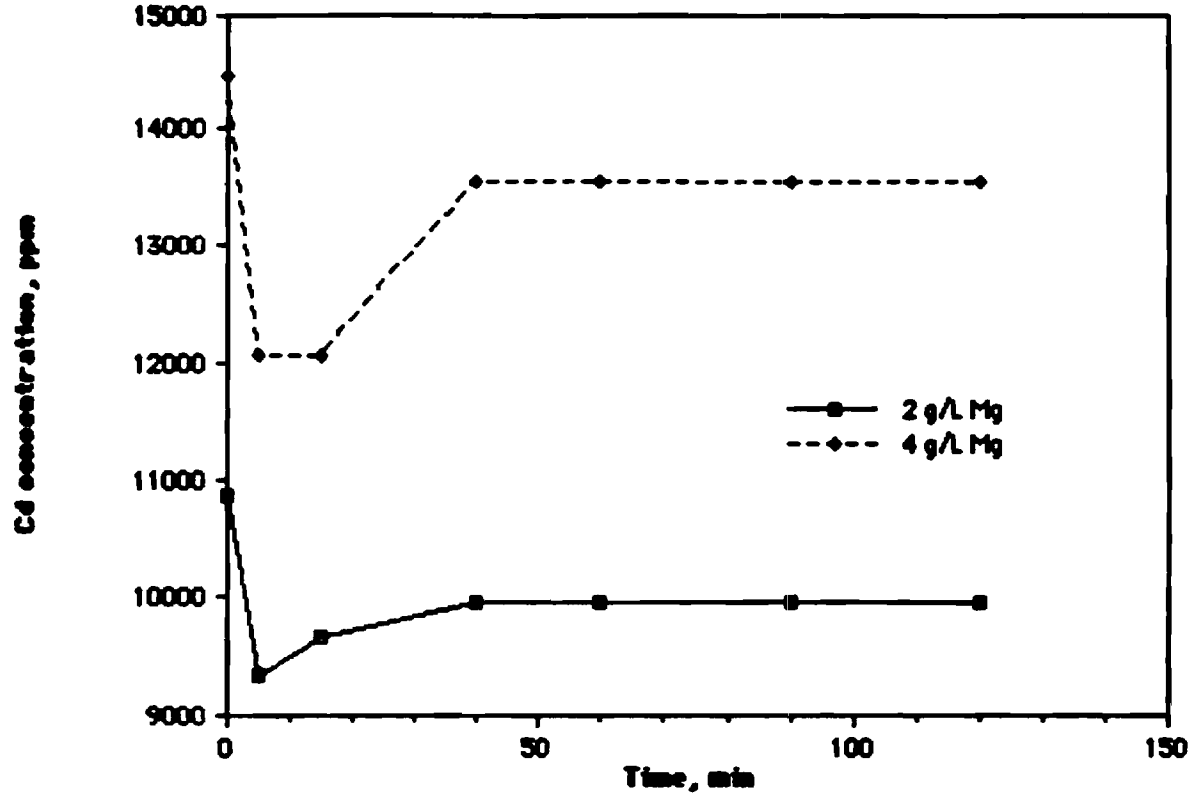

Figure 13b. Variation of Cd Concentration with Time
(Mg Shavings, RPM=300, DF=5000X)

Cd^{2+} concentrations decreased. Both metals were cemented within the first 10 minutes of mixing.

If the sampling intervals became even more frequent during the first 10 minutes of sampling, and if the mixing rate was slowed from 300 RPM to 175 RPM, it would have perhaps been possible to determine exactly when Cu^{2+}/Cu^{+} reached its lowest concentration. These parameters were evaluated in Run 3. Figure 14a shows that Cu^{2+}/Cu^{+} reached its lowest concentration at 5 minutes and began to increase thereafter. At 25 minutes, the Cu^{2+}/Cu^{+} concentration again decreased to the same concentration at 5 minutes. However, it was possible that the Cu^{2+}/Cu^{+} concentration was lower before 5 minutes of mixing. Figure 14b shows that the Cd^{2+} concentration also reaches a low concentration at 5 minutes and then again at 20 minutes.

The figures show that the decreases in Cu^{2+}/Cu^{+} and Cd^{2+} concentrations occurred at the same time as in Run 2. These figures also show that the initial decreases in concentrations occurred at the same time.

Figures 15a and 15b show the effects of the rate of mixing on cementation of Cu^{2+}/Cu^{+} on Mg in Run 4. Increasing the mixing rate from 300 RPM to 400 RPM did not enhance the cementation rate of either Cu^{2+}/Cu^{+} nor Cd^{2+}. The drops in Cu^{2+}/Cu^{+} and Cd^{2+} concentrations occurred at the same times as in previous experiments. However, decreasing the mixing rate from 300 RPM to 250 RPM slowed the cementation rate of both Cu^{2+}/Cu^{+} and Cd^{2+} by 5 minutes and also the amount of Cu^{2+}/Cu^{+} cemented. The trends in

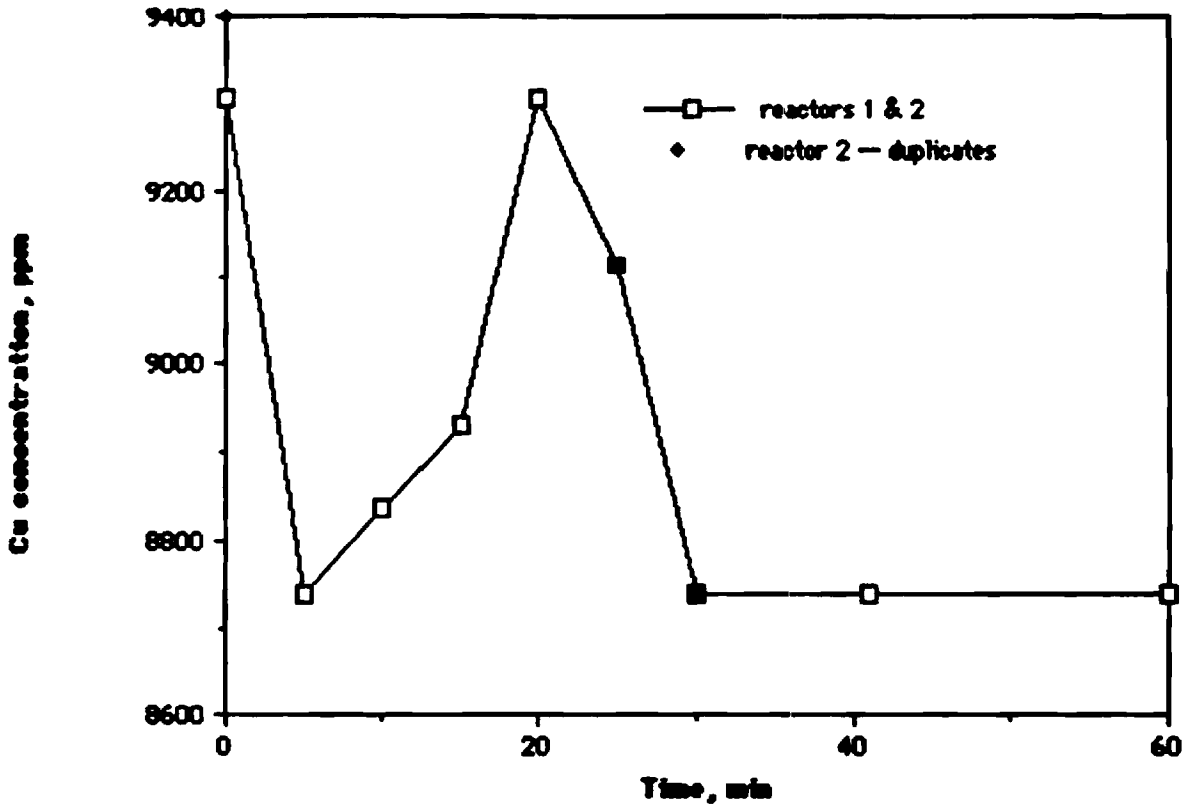

Figure 14a. Variation of Cu Concentration with Time
(2 g/L Mg shavings, RPM=175, DF=500X)

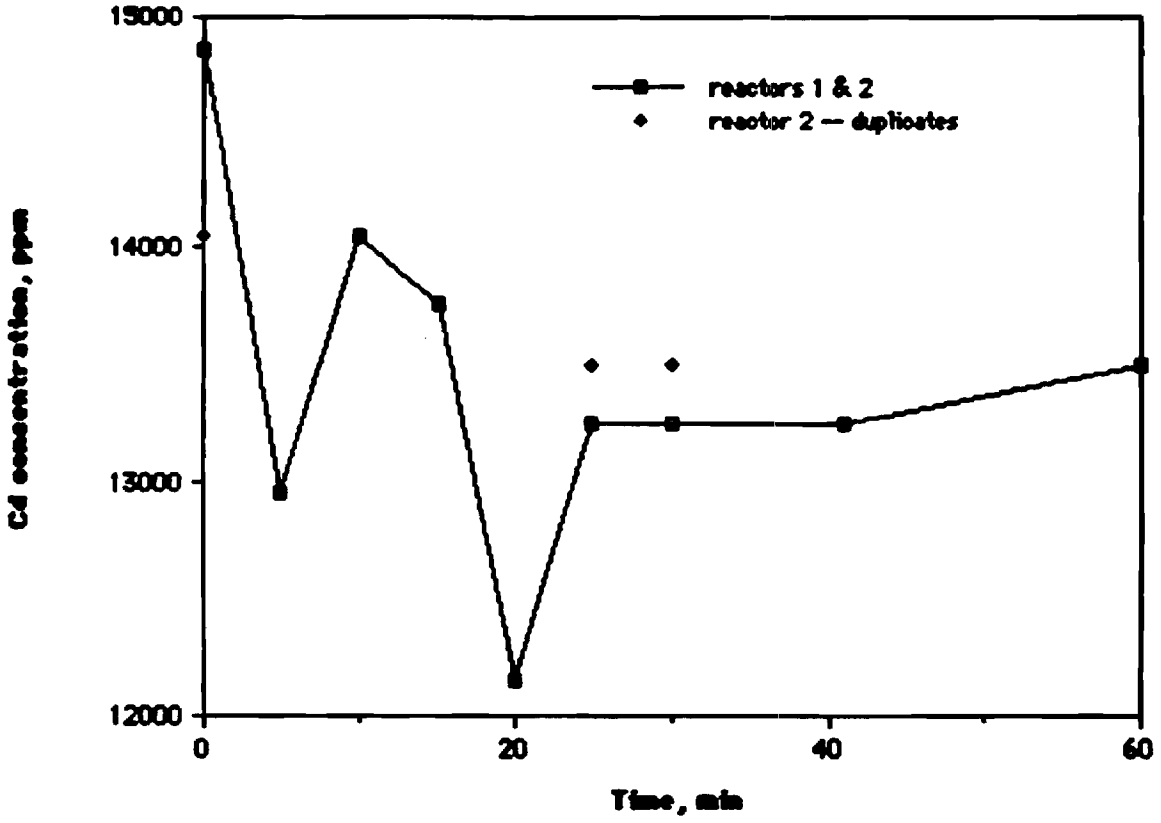

Figure 14b. Variation of Cd Concentration with Time
(2 g/L Mg shavings, RPM=175, DF=5000X)

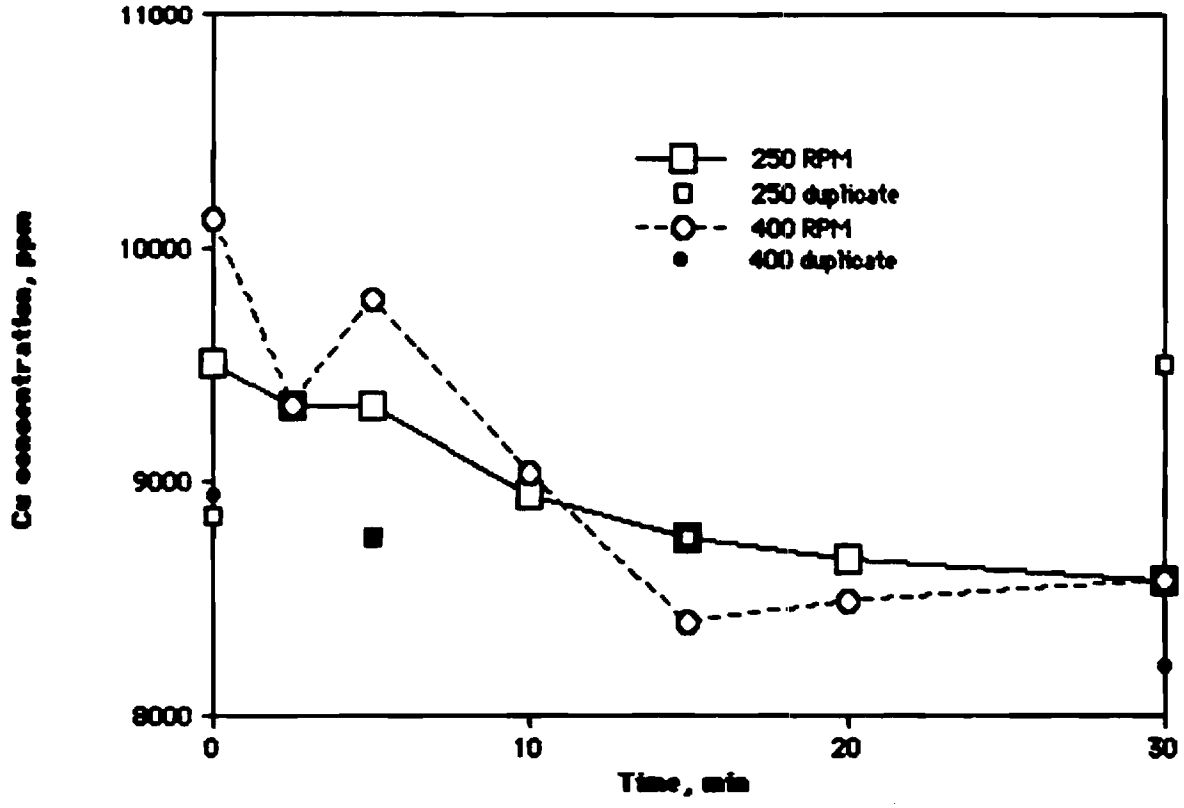

Figure 15a. Variation of Cu Concentration with Time
(2 g/L Mg shavings, RPM=250 & 400, DF=500X)

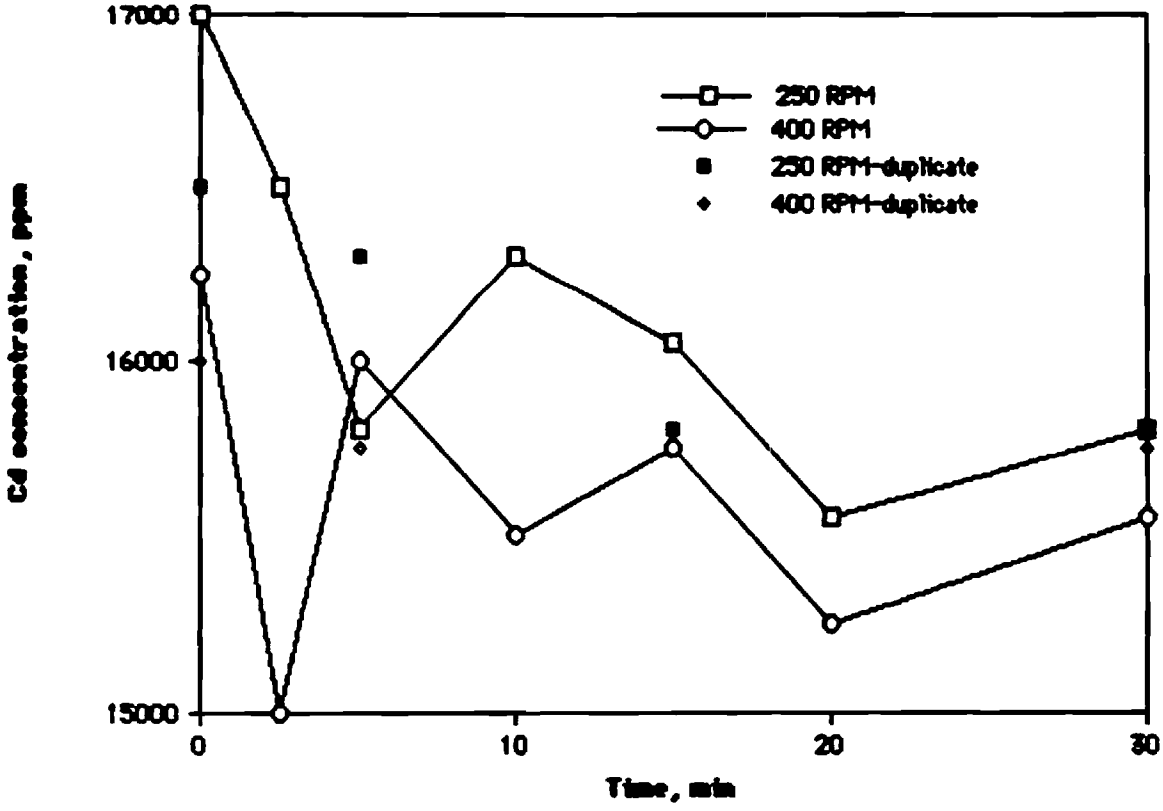

Figure 15b. Variation of Cd Concentration with Time

(2 g/L Mg shavings, RPM=250 & 400, DF=3000X)

concentration over time for each metal and for both mixing rates were similar.

The difference in the electrode potentials of Mg and Cu^{+} was larger than the difference between Mg and Cd^{2+}, and thus it was expected that Cu^{+} would be cemented to a larger extent, and indeed it was. The cementation reaction of $Cu^{2+}Cu^{+}$ on to Mg occurred very quickly, and the cementation of Cd^{2+} on Cu^{o} and Mg^{o} was happening just as quickly. A third metal, Pb^{2+}, was added to the solution in the reactor to determine if it would cement onto Mg before Cu^{+} and Cd^{2+} (Runs 5-1 through 5-4). The results obtained from these experiments could not be interpreted because the samples were filtered, and filtering altered true Pb^{2+} concentrations significantly. Although the difference in the electrode potentials of Mg and Pb^{2+} was even larger than the difference between Mg and Cu^{+}, no comparison could be made as far as quantities of metal ion cemented. This was the case because the concentration of Pb^{2+} was ten times less than that of the Cu^{2+}/Cu^{+} concentration and twenty times less than that of the Cd^{2+} concentration.

In Run 5-1, all three metals, Cu^{2+}/Cu^{+}, Cd^{2+}, and Pb^{2+} were present in the plating solution in the reactors. Figures 16a and 16b show the same trends in Cu^{+} and Cd^{2+} concentrations that the earlier experiments did. Figure 16c shows that the Pb^{2+} concentration was low at time 0, prior to the addition of the Mg shavings. The concentration of Pb^{2+} at time 0 was approximately 33% of the 100 ppm added, i.e. 35 ppm, a drop of 65 ppm from the

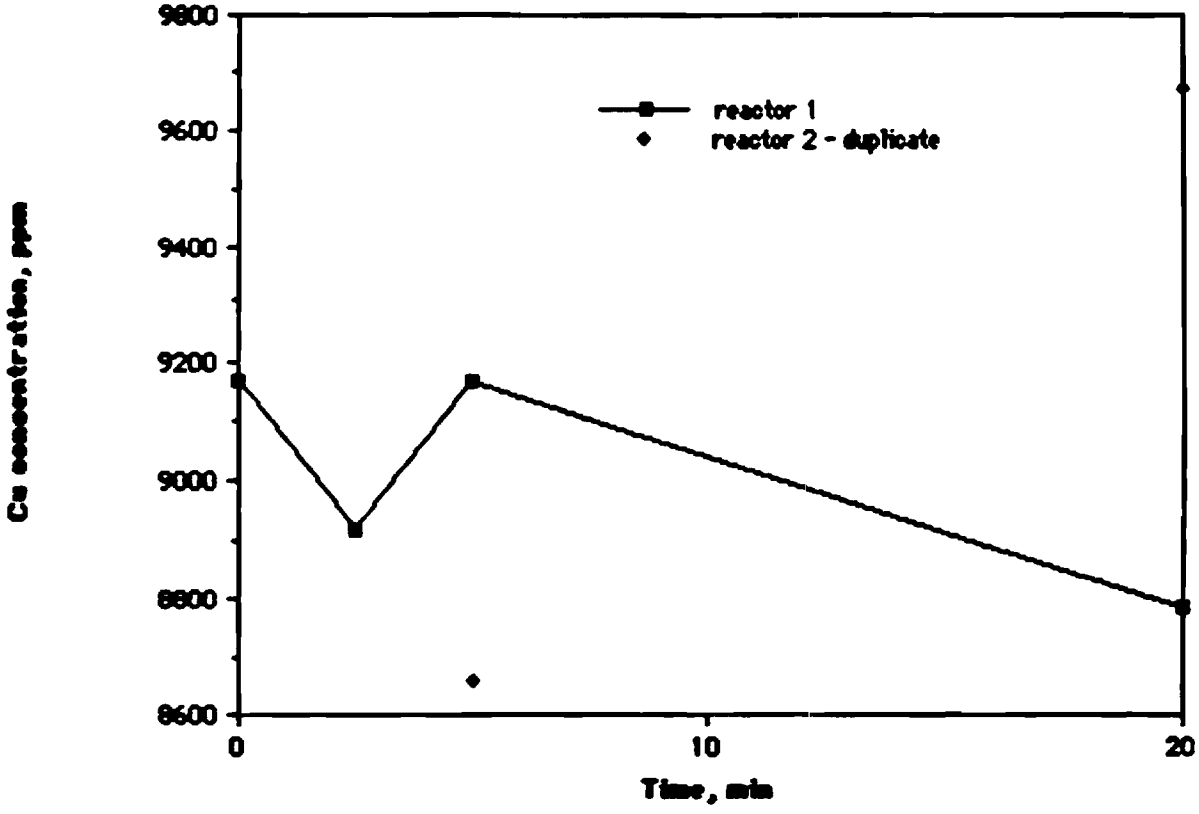

Figure 16a. Variation of Cu Concentration with Time
(2 g/L Mg shavings, RPM=300, DF=500X)

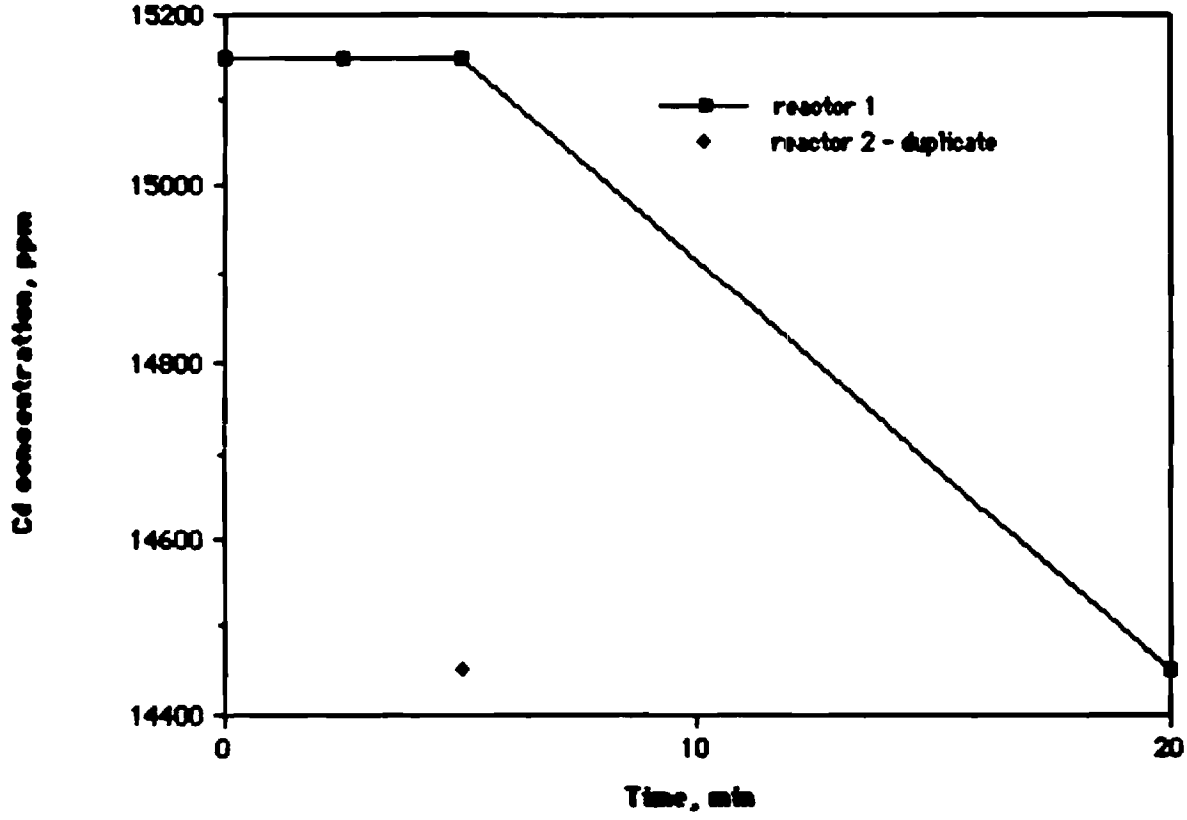

Figure 16b. Variation of Cd Concentration with Time
(2 g/L Mg shavings, RPM=300, DF=5000X)

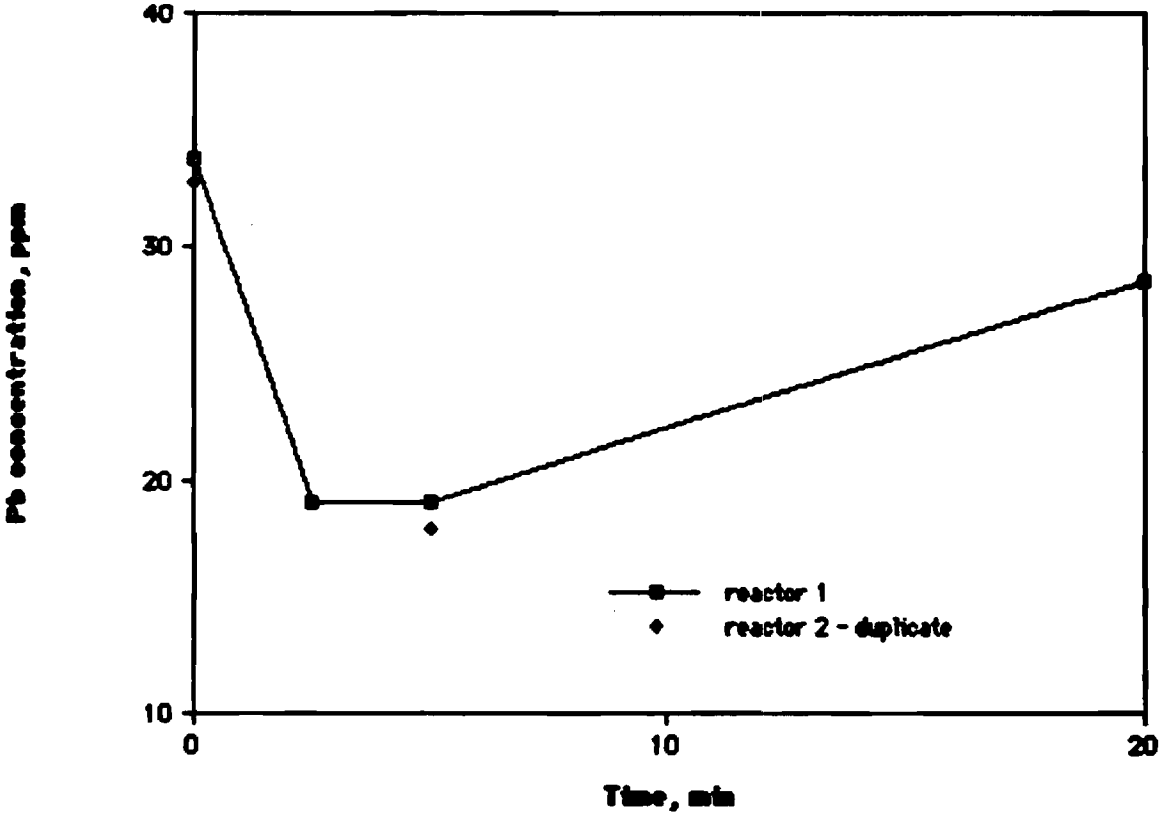

Figure 16c. Variation of Pb Concentration with Time
(2 g/L Mg shavings, RPM=300, DF=5X)

100 ppm that was added to the reactor. The QA/QC results showed an almost 100% recovery of the Pb^{2+} contaminant when added to deionized water. This decrease in Pb^{2+} concentration at time 0 was later found to be due to the filtering of the samples. Thus, all data collected for Pb^{2+} during this Run were not useful in showing the cementation process of Pb^{2+} onto Mg.

In Run 5-2, no Cu^{2+} contaminant solution was added to the plating solution. Thus the competition of active sites on the Mg shavings was reduced and the cementation rate of Pb^{2+} would be more noticeable. The Cd^{2+} concentration decreased in the same fashion it had in the previous experiments (Figure 17). Again, data collected on Pb^{2+} was not useful in evaluating the cementation process between Mg and Pb^{2+} because approximately 67% was retained on the Whatman #40 filter used to filter the samples.

In Run 5-3, no Cad-Sol solution, thus no Cd, was used in the plating solution, therefore the cementation rates of Pb^{2+} and Cu^{+} were more discernable. The Cu^{+} concentration decreased continuously from time 0 (Figure 18). This was different from the previously performed experiments. This continual decrease was probably due to the absence of Cd^{2+}. As mentioned earlier, the Cu^{2+} which was cemented by Mg went back into solution probably

because it was cementing Cd2+. Now, with no Cd^{2+} present in the plating solution, Cu^{2+}/Cu^{+} would not be expected to increase in concentration.

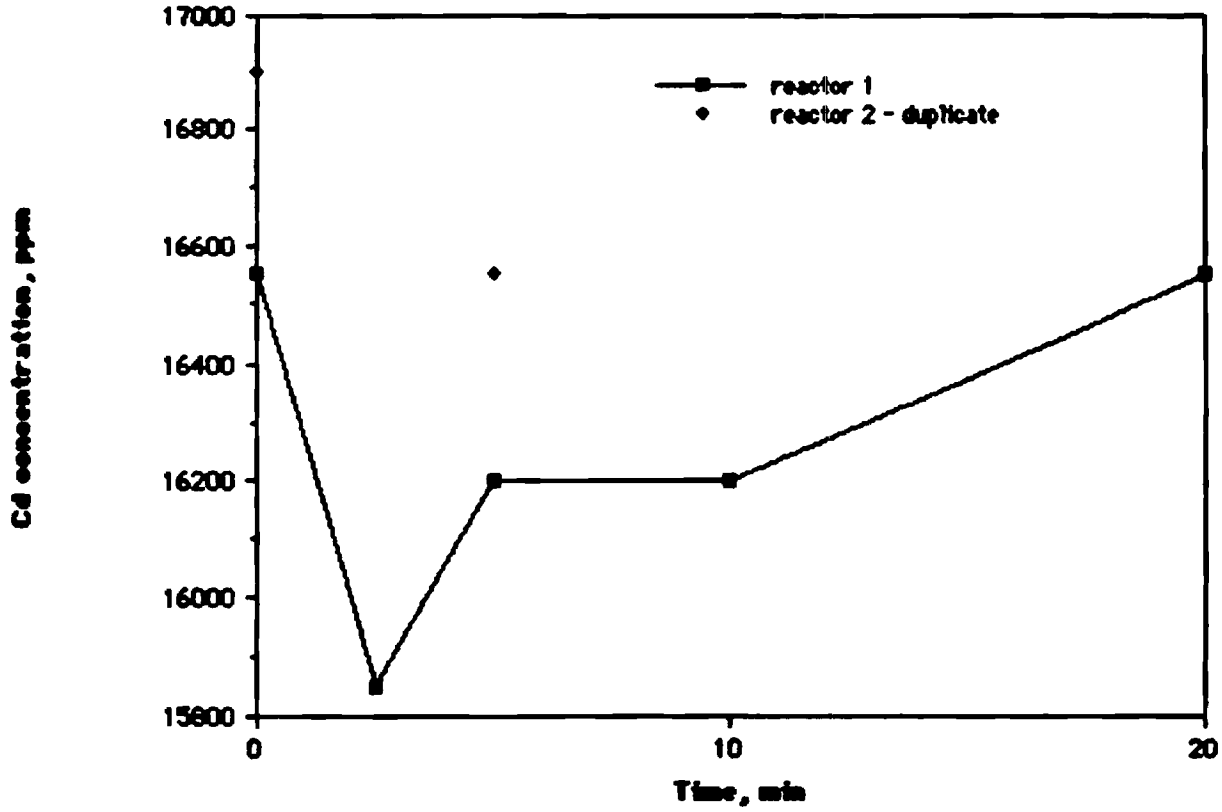

Figure 17. Variation of Cd Concentration with Time (2 g/L Mg shavings, RPM=300, DF=5000X, no Cu contaminant solution added)

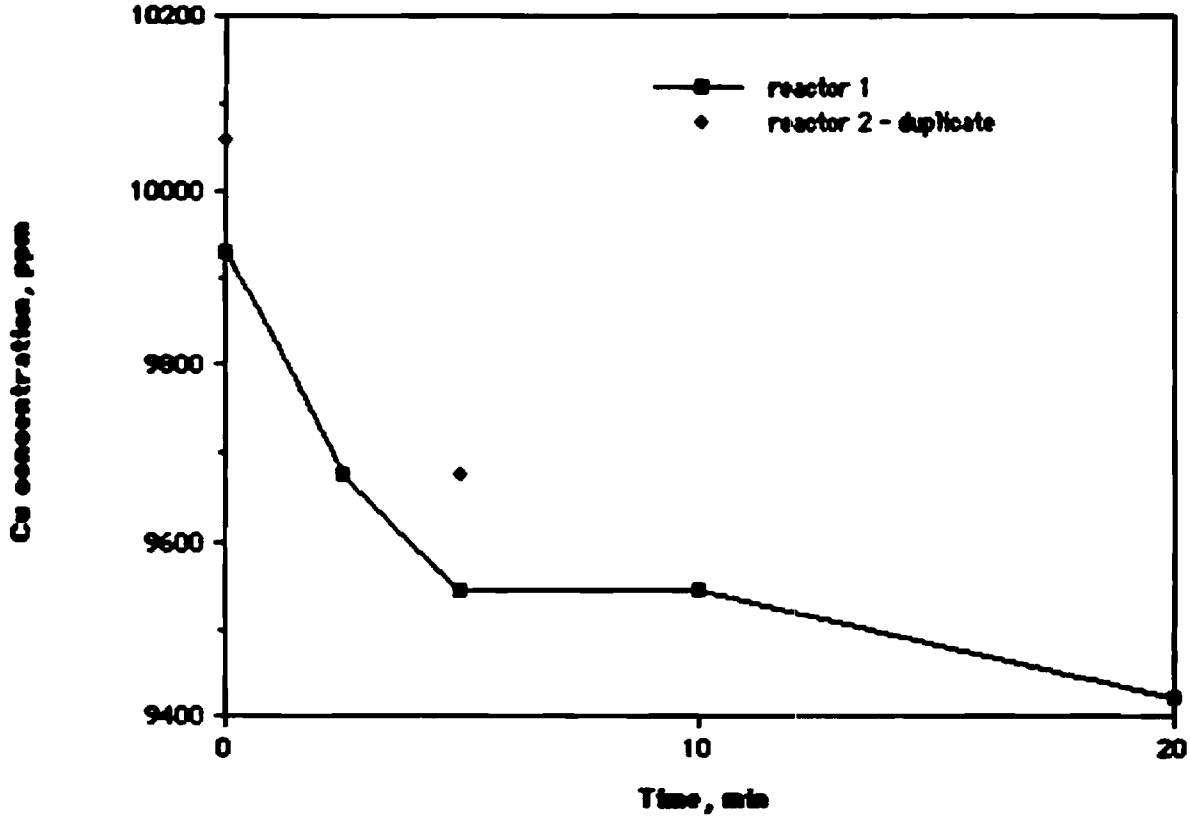

Figure 18. Variation of Cu Concentration with Time (2 g/L Mg shavings, RPM=300, DF=500X, no Cad-Sol solution added))

In Run 5-4, Cu wire was used as the sacrificial metal to cement Pb^{2+} and Cd^{2+}. The plating solution did include the Cad-Sol solution used in previous experiments. Figure 19a shows the Cu^{+} concentration increasing with time. This increase in Cu^{2+}/Cu^{+} was probably due to the cementation of Cd^{2+}. Figure 19b shows that the Cd^{2+} concentration followed the same pattern as it had in experiments using Mg shavings as the sacrificial metal. Because the electrode potential difference between Cu and Cd^{2+} was less than the difference between Mg and Cd^{2+}, it was expected that the Cu wire would cement smaller quantities of Cd^{2+}. However, Cu wire cemented identical quantities of Cd^{2+} and after the same time of mixing had elapsed as had the Mg shavings. This may have been due do a limiting reactant such as the surface area of the sacrificial metal.

As was mentioned earlier, the Pb^{2+} data obtained were not useful in evaluating rates of cementation. This was because the samples were filtered. The Pb^{2+} ions are very bulky, and were retained by the filter, thus not allowing the actual amount of Pb^{2+} in the sample to be analyzed. Run 6 was performed not only to confirm this fact, but also to view the effects of filtration on the Cu^{+} and Cd^{2+} concentrations. Figures 20a and 20b show that filtering did not have any significant effects on the Cu^{+} and Cd^{2+} concentrations. Figure 20c shows that filtering did have a significant effect on Pb^{2+} concentrations. The Pb^{2+} concentrations were reduced to approximately 30% of the actual values.

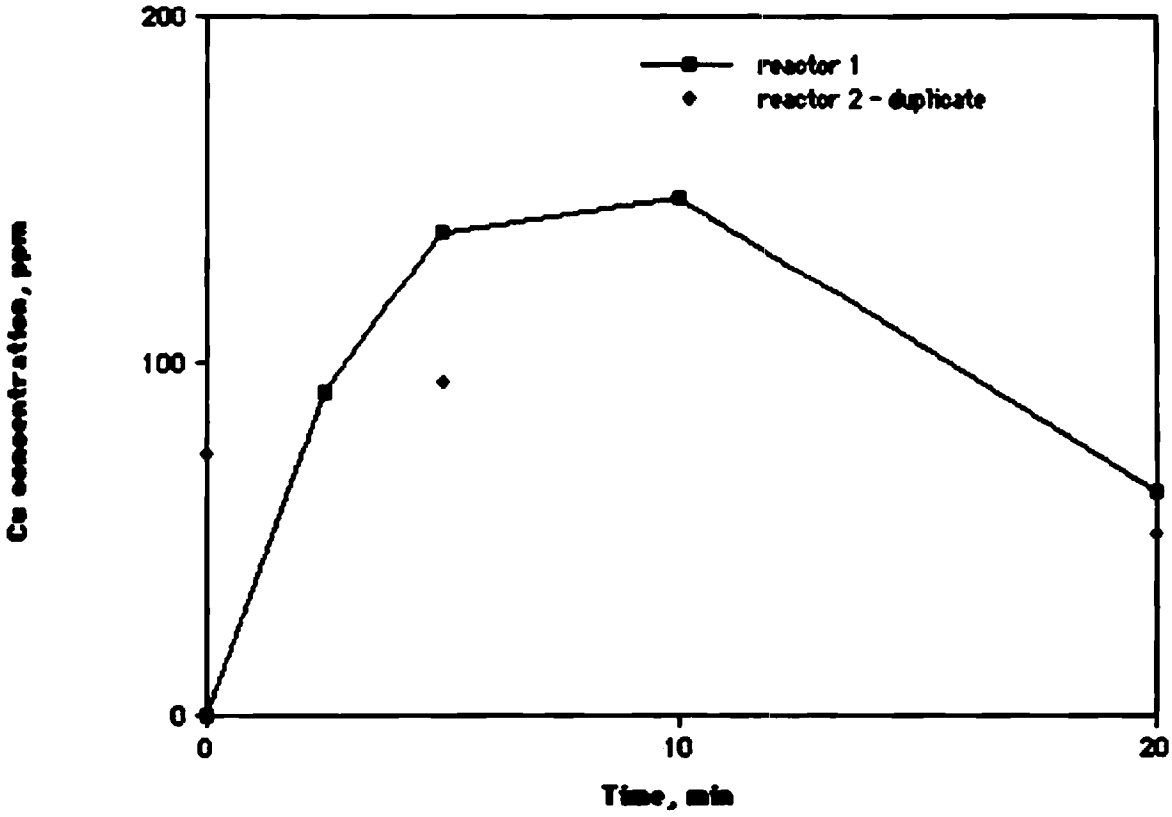

Figure 19a. Variation of Cu Concentration with Time
(6 g/L Cu wire, RPM=300, DF=300X, no Mg shavings added)

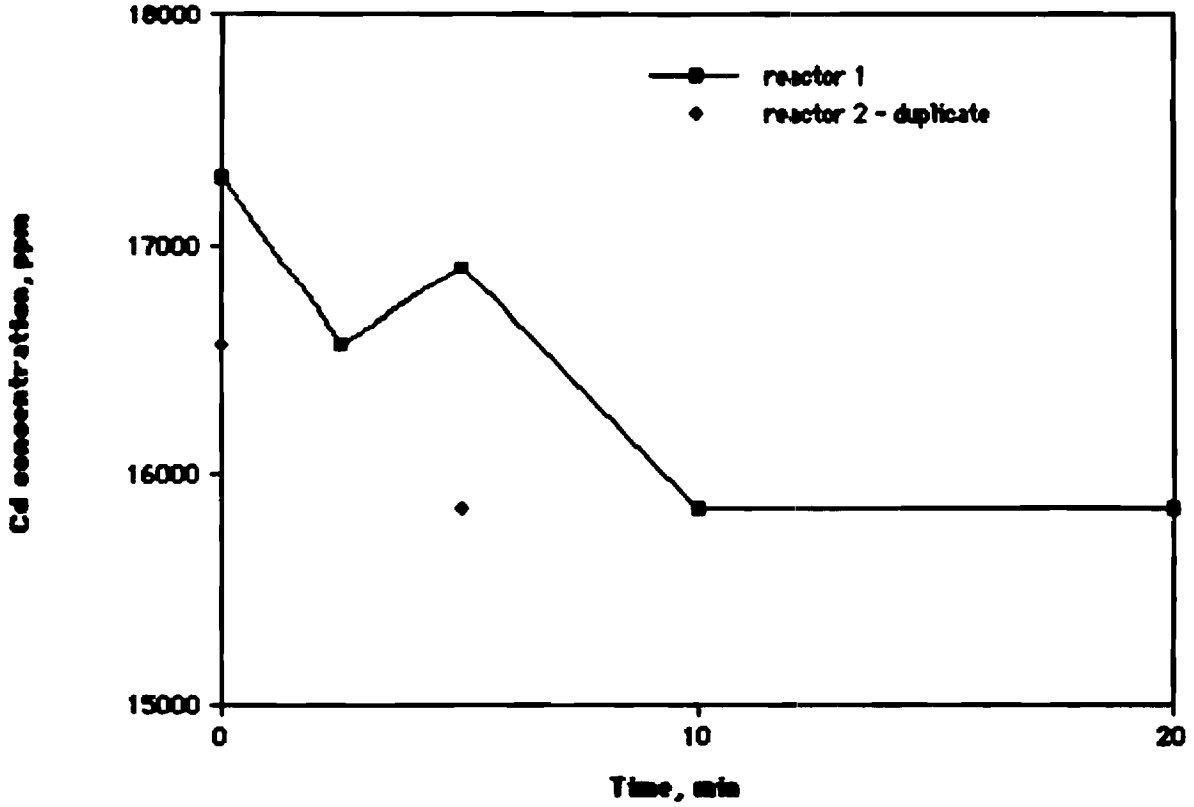

Figure 19b. Variation of Cd Concentration with Time
(6 g/L Cu wire, RPM=300, DF=5000X, no Mg shavings added)

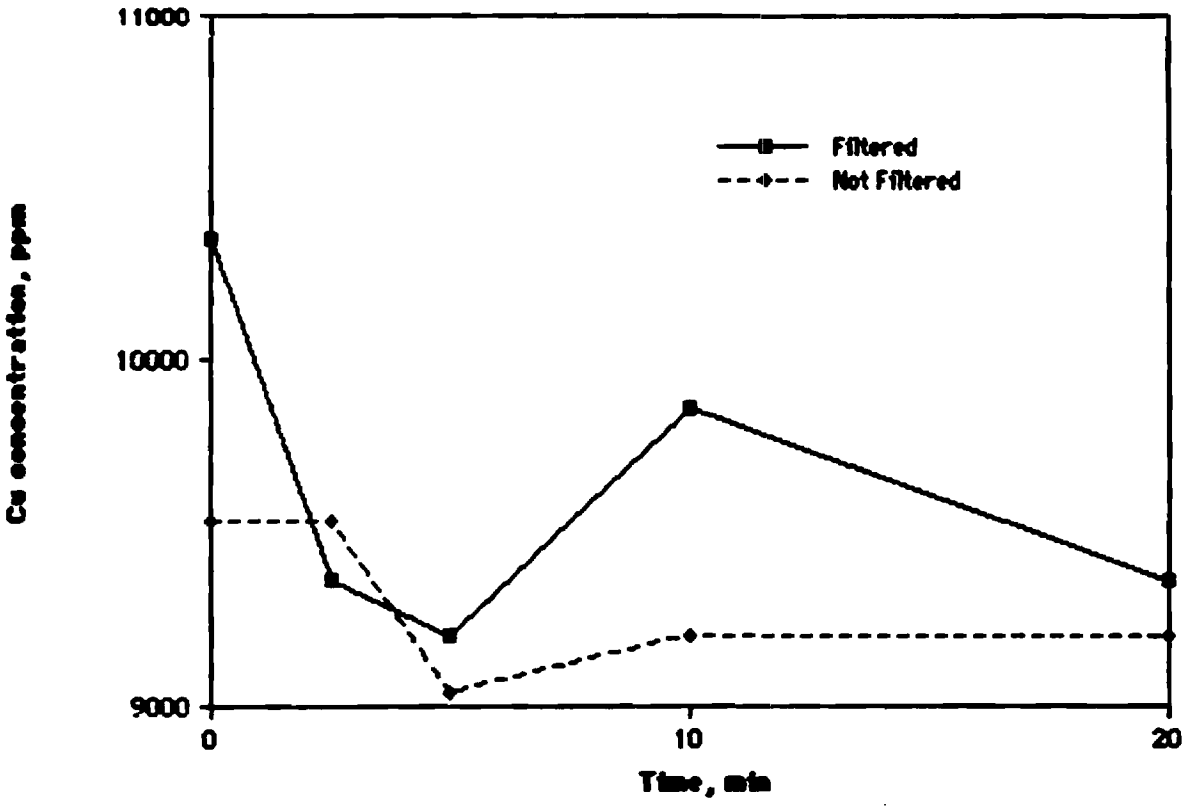

Figure 20a. Variation of Cu Concentration with Time
(2 g/L Mg shavings, RPM=300, DF=500X)

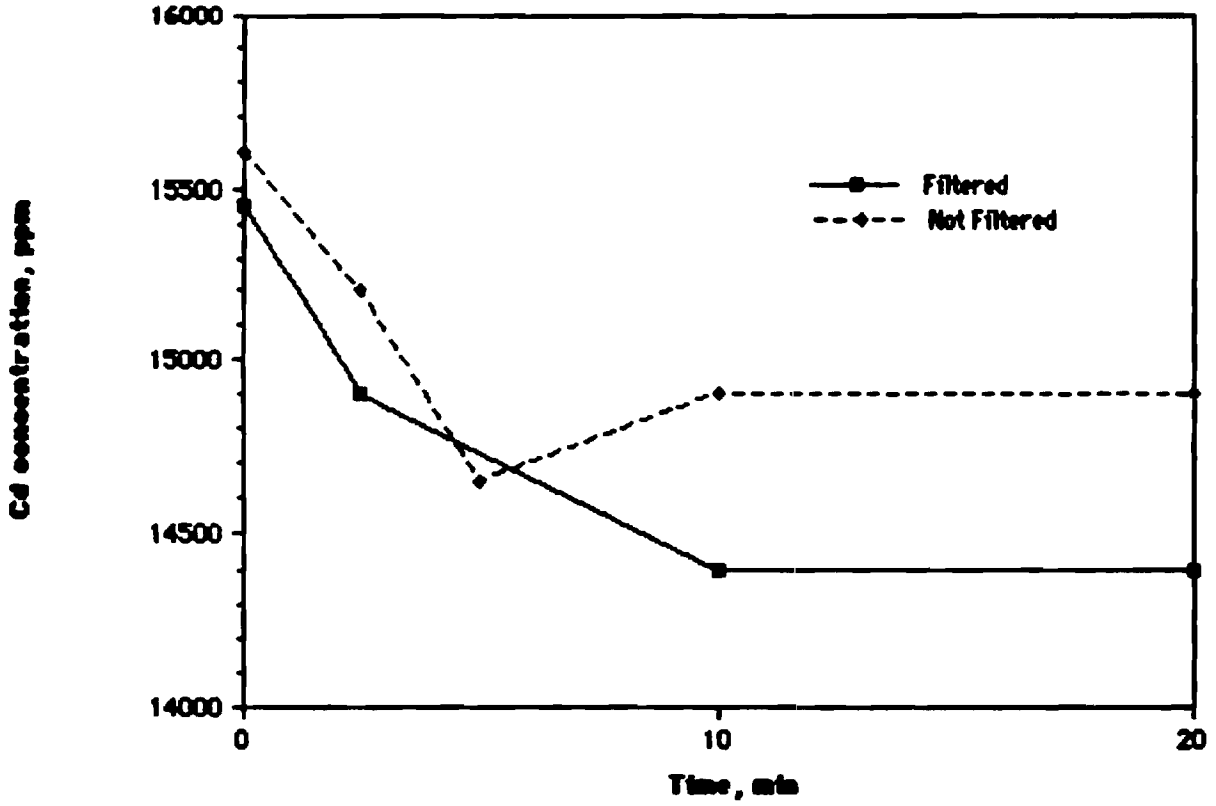

Figure 20b. Variation of Cd Concentration with Time
(2 g/L Mg shavings, RPM=300, DF=5000X)

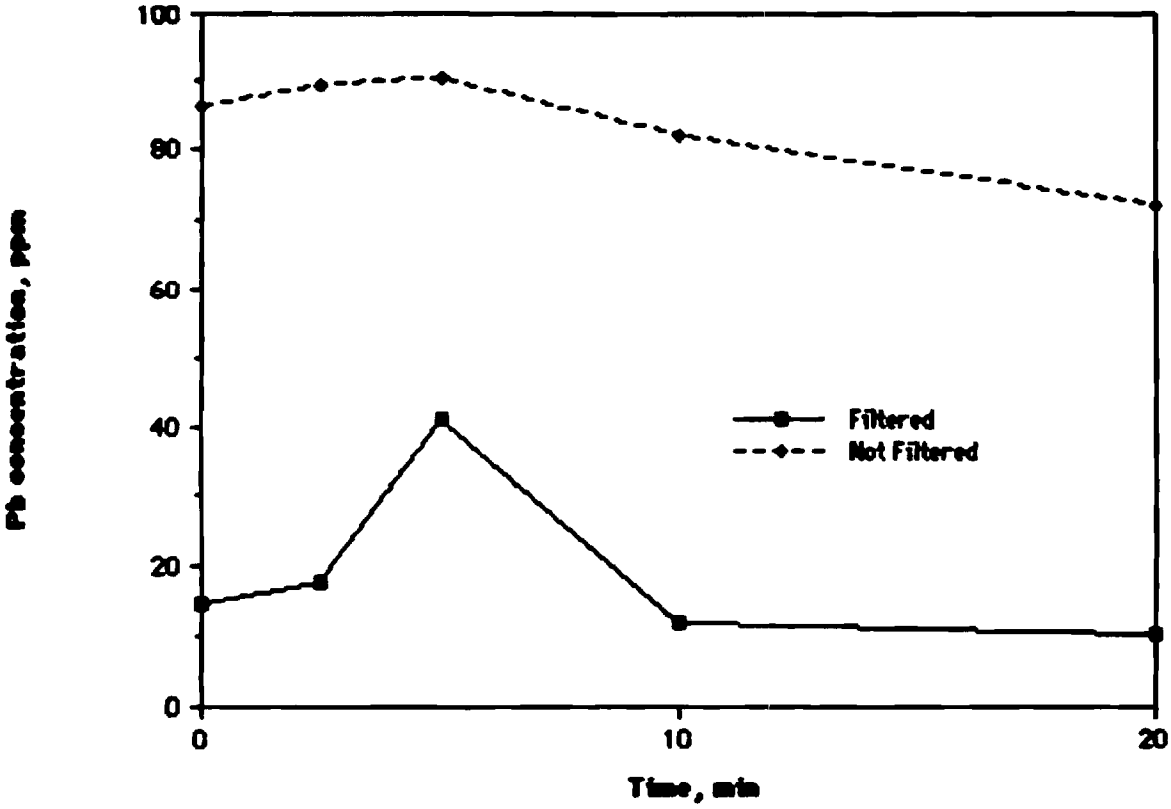

Figure 20c. Variation of Pb concentration with Time
(2 g/L Mg shavings, RPM=300, DF=5X)

When Pb^{2+} was added to the plating solution in Run 6, no decrease in Pb^{2+} concentration occurred in the unfiltered samples (Figure 20c). This was due to either the Pb2+ concentration was too low in comparison to the Cu^{+} and Cd^{+} concentrations and could not compete, or, the Pb^{2+} ion was too bulky and could not compete for active sites on the Mg shavings.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The use of magnesium or cadmium is not recommended for the cementation removal of copper impurities from cadmium-cyanide electroplating baths. The presence of cyanide in plating solutions lessens if not completely inhibits the ability of cadmium or magnesium to cement copper impurities. Also, the presence of other metal ions in the cadmium-cyanide plating bath can interfere with the ability of magnesium shavings to cement copper, because copper, once cemented, acts as a sacrificial metal for cadmium and goes back into solution.

Experiments were performed in the presence of various amounts of cyanide and in the complete absence of cyanide. The results of these investigations clearly demonstrated that cyanide interfered with the cementation process.

Magnesium cemented approximately 5% of the Cu^{+} i.e. 500 ppm, in approximately five minutes. However, the remaining magnesium and the cemented copper also cemented approximately 500 ppm Cd^{2+} ion. Thus, Mg would not be useful as a sacrificial metal to cement copper impurities from a cadmium-cyanide plating bath.

One experiment used copper wire to cement Cd^{2+}. This was done in order to confirm that cemented Cu^{2+} had the ability to cement Cd^{2+} as was determined in experiments using magnesium as the sacrificial metal.

On the basis of these results, further research is warranted to determine methods other than cementation for the removal of copper impurities from the cadmium cyanide bath or an eventual reuse and recycle of the electroplating bath. Some of these methods include electrowinning, electrolytic processes (low current dummying), or the use of chelating resins.

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