Segmented Porous Electrode Flow Reactors For the Electrochemical Treatment of Commingled Metal Plating Wastes

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The objective was to develop a segmented, porous flow-through electrode reactor for selective separation and recovery of metals from dilute aqueous mixtures. Copper, nickel, zinc, silver and cadmium in low-concentration binary and ternary mixtures were selectively removed with a reticulated vitreous carbon (RVC) reactor by potentiostatic electrodeposition and deposits recovered by electrodissolution. Metal electrodeposition rates were not significantly dependent on flow rate and RVC porosity, but were dependent on pH. The multi-stage RVC reactor was successful in the selective removal and recovery of metals from ternary mixtures of Ag/Cu/Zn and Cu/Cd/Zn. Although not directly addressed in this research project, the removal and recovery of metals in recirculating, on-line rinses following a plating process is a possible application of controlled potentiostatic electrodeposition.

Removal and recovery of metals from aqueous waste streams is becoming an increasingly important issue because of growing economic and environmental concerns. Waste streams from plating and circuit board processing contain significant amounts of metals that must be removed before the stream can be discharged. Various methods based on chemical precipitation, evaporation, reverse osmosis, electrodialysis and ion exchange have been developed for waste stream treatment.[1]

The method examined in this study was electrodeposition of metals; sufficiently large differences in reduction potentials may selectively remove metals from commingled mixtures. The metal with the highest reduction potential is removed first, leaving the other metals in solution. The other metals are then removed individually in turn by subsequent successive decrease in reduction potentials. If each metal is electrodeposited on separate potentiostatically controlled cathodes, recovery and reuse could be greatly simplified.

Reticulated vitreous carbon (RVC) was used as cathode. This material has a honeycomb, open-pore type structure, giving it a high surface-area-to-volume ratio. It is inexpensive and readily available commercially and can be obtained in various grades of porosity, ranging from 10 ppi (pores per inch) to 100 ppi with corresponding surface areas of 4.9 to 66 cm^2/cm^3, respectively. The void volume of RVC is greater than 97 percent, with the result that fluids flowing through it experience very low pressure drops.

The objective of this study was to develop a multistage, segmented porous flow-through reactor, which would selectively separate metals from dilute commingled mixtures of metal ions. Metals would be removed selectively by potentiostatic electrodeposition in separate stages of porous electrodes and then recovered by electrodissolution. Solutions containing copper, nickel, zinc, silver and cadmium were examined, as well as the effects of pH and potential on the rate of electrodeposition and electrodissolution, to determine conditions for the most efficient metal removal and recovery. Different supporting electrolytes were tested for facile removal and recovery. Various complexing agents were studied to determine their efficacy for the selective removal of nickel and zinc from binary mixtures.

Table 1
Characteristics of Reticulated Vitreous Carbon (RVC) as Electrode Material*

RVC porosity pores/lin inch (ppi)	Specific Surf. Area (cm^2/cm^3)	Total Surf. Area (cm^2)	Pressure Drop (cm H_2O)
60	36.1	181.5	1.27
30	17.7	89.1	0.51

*ERG Products, Oakland, CA.

Background

Fixed flow-through porous electrodes are known to be effective for the removal of metal ions from solutions by electrodeposition. Dilute solutions containing various metals, ranging from copper, silver, lead, mercury and antimony, have been studied. RVC electrodes have been previously investigated for metal ion removal.[2-5]

Bennion and Newman reported that porous carbon chips are effective for removal and recovery of copper from sulfate solutions (pH 2.5).[6] Their cell consisted of two beds of porous carbon with more than 90 percent of the solution flowing through the cathode bed and the rest through the anode bed.

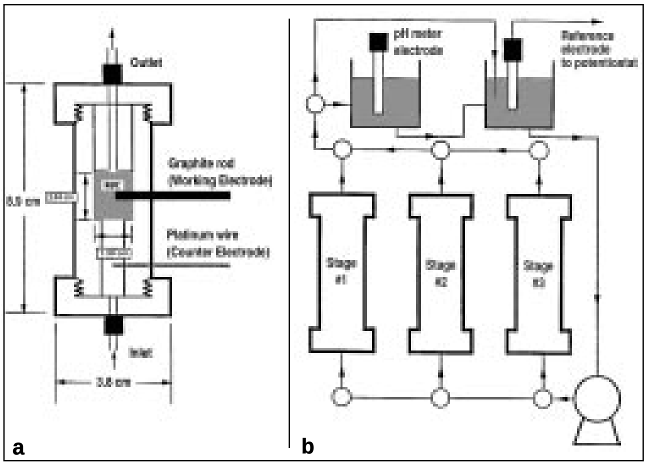

Fig. 1—(a) Single-stage RVC reactor; (b) Three-stage segmented RVC reactor.

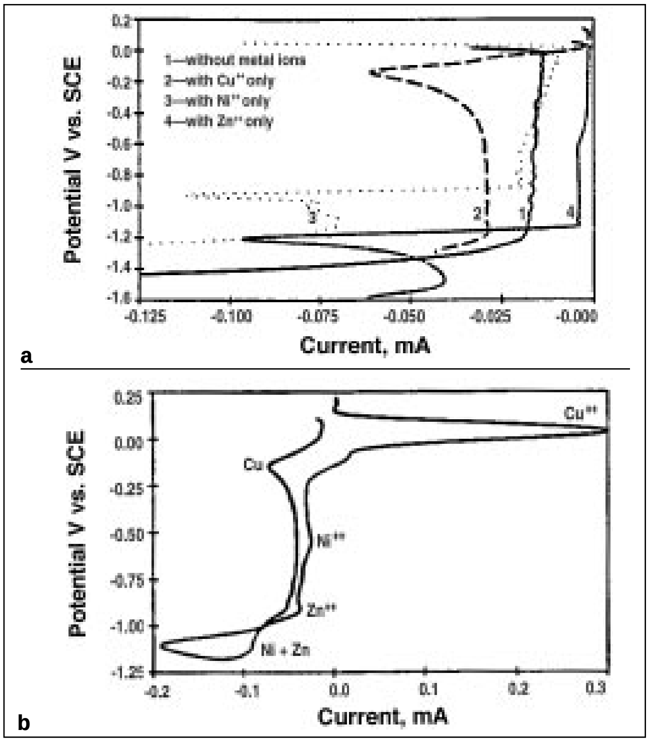

Fig. 2—(a) Potential sweep (10 mV/sec) of Cu, Ni and Zn electrodeposition on glassy carbon disk from single-component solutions (500 ppm); (b) Cyclic voltammogram (glassy carbon disk, 10 mV/sec) of a ternary Cu/Ni/Zn mixture. Initial concentration of each metal ion, 500 ppm.

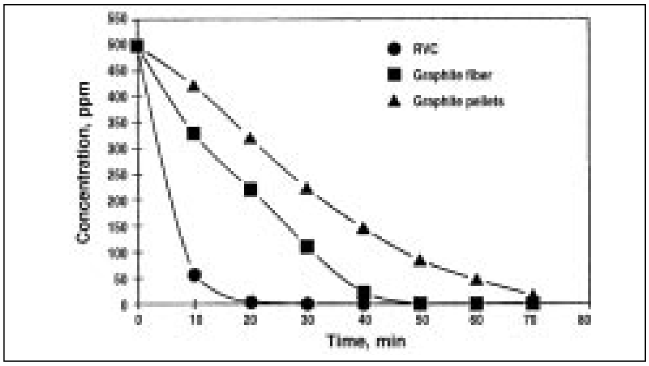

Fig. 3—Removal of Cu in flow reactors containing different carbon packing materials: [Cu^{+2}], 500 ppm; pH 5.6; 54.8 mL/min; -0.3 V vs. SCE.

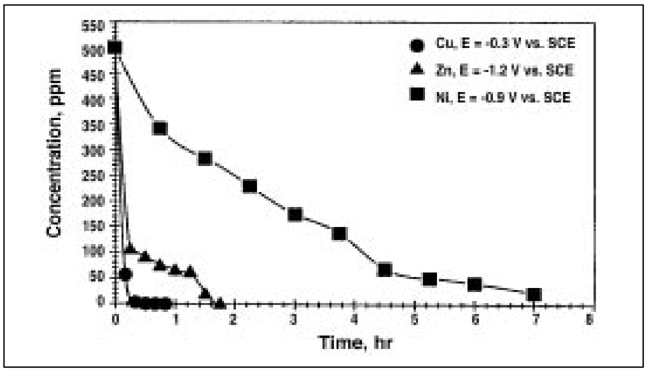

Fig. 4—Removal of Cu, Ni and Zn from single-component solutions: $[M^{+2}]_{initial}$, 500 ppm; 54.8 mL/min.

After deposition of copper in the cathode compartment, the reactor was inverted and the polarity reversed. Ninety-seven liters of solution were processed in approximately 131 hr, and the concentration of copper was reduced from 667 ppm to less than 1 ppm.

Wenger and Bennion also examined the removal of copper from sulfate solutions.[7] The previous cell[6] was modified by using a membrane to separate the anode and cathode beds. The copper concentration was reduced from 800 ppm to less than 1 ppm at the cathode, and simultaneously increased from 0.4 M to 0.7 M at the anode.

Ghosh used two graphite-packed beds with a membrane separator to remove copper from sulfate solutions.[8] The anode bed oxidized ferrous ions from a dilute ferrous chloride solution, while the cathode bed reduced copper ions from the sodium sulfate solution. Ninety-nine percent of the copper was removed from the feed stream containing 700 ppm of copper.

Chu *et al.*,[9] using a granular graphite-packed bed, extracted copper from acidic sulfate solutions containing 0.1 mM (6.4 ppm) Cu^{+2} and achieved removal efficiency as high as 80 percent in a single-pass operation. During multiple-pass operation, the efficiency for copper removal was as high as 98 percent.

Kuhn and Houghton[10] reported galvanostatic removal of antimony from a sulfuric acid solution (1 M), from 100 ppm down to 5 ppm, using a bed of lead shot pellets. Higher currents and flow rates resulted in higher removal efficiencies. Improved metal removal was obtained with thicker beds, while varying the bead size had only a modest effect.

Van Zee and Newman[11] galvanostatically removed silver from solutions containing silver nitrate, sodium thiosulfate, sodium bisulfate, and sodium bromide with a porous flow-through electrode constructed of carbon particles similar to the one made earlier.[6] After electrodeposition, the beds were inverted and the polarity reversed to remove the silver deposit. Silver concentrations were reduced from 1000 ppm to less than 1 ppm.

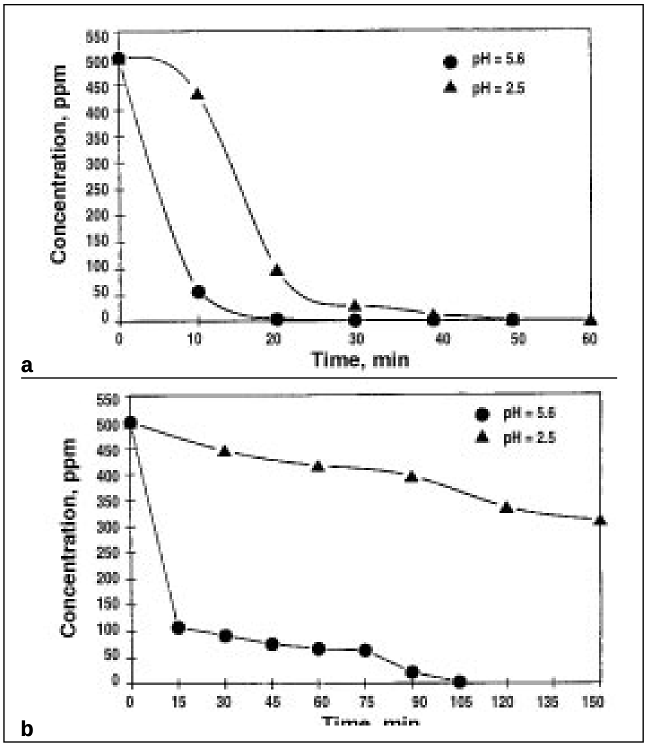

Fig. 5—(a) Effect of pH on removal of Cu from a ternary solution (Cu/Ni/Zn): $[M^{+2}]_{initial}$, 500 ppm; 54.8 mL/min; -0.3 V vs. SCE; (b) Effect of pH on removal of Zn from a single-component solution: $[Zn^{+2}]_{initial}$, 500 ppm; 54.8 mL/min; -1.2 V vs. SCE.

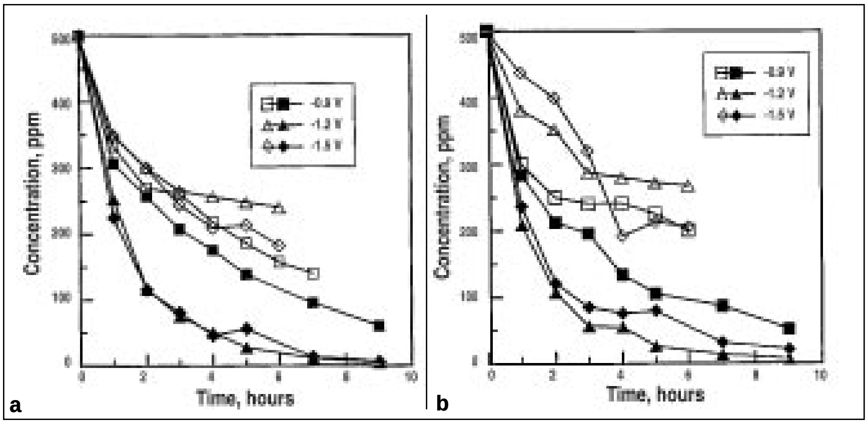

Fig. 6—(a) Removal of Ni from a Ni/Zn mixture with pH maintained at 6 (closed points) and pH not controlled (open points): 54.8 mL/min; (b) Removal of Zn from a Ni/Zn mixture with pH maintained at 6 (closed points) and pH not controlled (open points): 54.8 mL/min.

Alkire and Gracon[12] used a porous flow-through electrode consisting of a stack of platinum screen disks and deposited copper from a solution of 2 mM (122 ppm) $CuSO_4$ in 1.5 M H_2SO_4. Current distribution was determined by analyzing the amount of copper deposited on each disk. At low flow rates, the current was nonuniform over the face of the electrode, indicating that most of the copper deposited upstream. At higher flow rates, current was uniform and the mass transfer coefficient was independent of position of the electrode.

Matlosz and Newman[2] used an RVC cylindrical electrode (12.7 cm long, 5.08 cm dia.) to remove mercury from contaminated brine. The mercury was reduced from 55 ppm to 0.018 ppm at the lowest flow rate of 10 mL/min.

Wang and Dewald[3] used an RVC electrode (100 ppi, 1.3 cm long, 0.55 cm diam) to remove dilute metal ions (~μM) from single metal solutions of copper, lead, silver and a binary mixture of copper and lead. Copper removal efficiency was 90 percent. Copper and lead co-deposited with complete removal of copper and 95-percent removal of lead. Scanning electron micrographs of copper and silver deposits show that the metal deposits were not continuous and areas of the RVC were left bare. No appreciable clogging was indicated.

Pletcher *et al.*[4] used RVC electrodes to remove copper from acidic sulfate solutions. The concentration was reduced from 10 ppm to less than 0.5 ppm and from 2.5 ppm to less than 0.1 ppm. Various porosity grades of RVC (10 to 100 ppi) were tested, with the most rapid deposition obtained with the highest porosity RVC. Oxygen decreased the current efficiency, but chloride ions had no effect on metal removal. In a single-pass reactor using a 40-cm-long RVC electrode, copper concentrations decreased from 10 ppm to 0.1 ppm, with an efficiency of 90 percent.[5]

Zhou *et al.*[13] studied the effects of feed rates and pulsed current on single-pass removal of copper from acidic sulfate solutions through a packed-bed of irregular graphite particles. Pulsed current enhanced the mass transfer rate; however, no improvement over direct current was noted at the higher feed rate (2.5 L/min). A high duty cycle was better at high frequencies, whereas a low duty cycle was better at low frequencies.

Schwartz *et al.*[14] used a 2-stage RVC flow reactor to reduce silver in concentrated nitric acid solutions (4 M) from 0.5 M to less than 1 ppm. Cobalt in acidic sulfate solutions was reduced from 100 ppm to 2 ppm in a single-stage reactor.

Experimental Procedure

Figure 1a shows the experimental single-stage RVC reactor; the RVC (60 ppi unless otherwise noted) was cut from sheets into cylinders with dimensions of 1.59 cm diam. and 2.54 cm length. Specific surface areas vary with the porosity grade, ranging from about 4.9 cm^2/cm^3 for 10 ppi to 66 cm^2/cm^3 for 100 ppi. Most experiments were run with 60 ppi RVC, with occasional use of 30 ppi. Table 1 lists some characteristics of the two RVC sizes.

The cylindrical cell was constructed from polymethyl methacrylate (3.8 cm diam and 8.9 cm high). The RVC rested in the center of the hollow cylindrical cell and was held in place by a plastic plug above it. A 0.32 cm graphite rod, inserted through a plastic Swagelock™ cap in the side, provided electrical contact for the RVC. The counter electrode was a thin platinum wire, either tightly coiled (0.5 mm thick) or straight (1 mm thick). The platinum wire was set in a plastic screwcap and positioned inside the cell through an opening below the RVC. The flow was upward, with the counter electrode positioned upstream of the RVC. The ends were threaded caps with O-rings to provide seals. Tapered joints with Tygon™ tubing at the ends of each cap connected the cell to the solution reservoirs. Flow was usually maintained at 54.8 mL/min by a variable speed pump.

The reference electrode was a saturated calomel electrode (SCE) placed in the solution reservoir. A potentiostat was used to control the potential and

Table 2
Effect of Complexing Agents on Removal From Ni/Zn Binary Solutions

Complexer	Solubility Constant log K$^{Ref. 16}$		Concentration ppm (16.1 mM)	% Removal	
	Ni	Zn		Ni	Zn
edetateNa_2	18.50	16.40	5413	54	69
citrateNa_3	5.35	4.86	4150	45	80
tartrateKNa	2.60	2.66	3380	63	80
pyrophosphateNa_4	7.01	8.70	4279	67	78

Initial concentrations: 8.8 mM Ni + 7.6 mM Zn = 16.1 mM total (500 ppm each). Applied potential: -1.2 V vs. SCE; pH 6; time, `~8 hrs; flow rate, 54.8 mL/min.

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[a] Model 250A, Orion Instruments, Inc., Menlo Park, CA.

[b] Model 303, Perkin Elmer Corp., Norwalk, CT.

measure the current. A separate reservoir with a flow by-pass held the probe of a pH/temperature monitor.[a] If the pH was difficult to monitor because of flow effects, the by-pass was engaged. The pH was controlled by periodic additions of 1 M sulfuric acid or 1 M sodium hydroxide, as needed.

The schematic for the three-stage RVC (60 ppi) reactor system is shown in Fig. 1b. Individual flow-through reactors were used for each stage. Tygon tubing was used to connect the reactor system and the reservoirs. Teflon™ T-valve stopcocks were used to control the flow of solution to each stage.

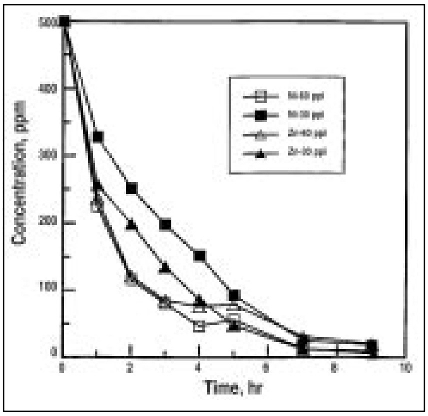

Fig. 7—Removal of Ni and Zn from a Ni/Zn mixture with different RVC porosity: 54.8 mL/min; pH 6; -1.5 V vs. SCE.

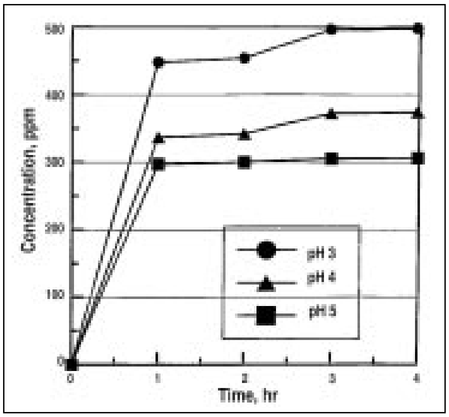

Fig. 8—Effect of pH on anodic stripping of Cu: 54.8 mL/min, +0.3 V vs. SCE.

The solutions were prepared with the sulfate salts of the metals except for silver (silver nitrate). The supporting electrolyte was 0.5 M sodium sulfate and initial metal ion concentrations ranged from 400 to 500 ppm. Solutions were used the same day they were prepared. When complexing agents were added, the solution was allowed to stand for approximately one hour before the start of an experiment. The total volume of solution in a single cell experiment was 100 mL. For the 3-stage system, the total volume was 150 mL.

Current efficiency is defined as the ratio of the charge consumed by metal deposition to the total charge passed. The charge consumed by electrodeposition was calculated by measuring the mass of the metal deposit. The total charge passed was calculated by monitoring the current over time with a laboratory microcomputer.

Samples were taken from the reservoir at regular time intervals and analyzed with an atomic absorption spectrophotometer.[b] After the experiments, the cell was disassembled and washed thoroughly with distilled water. The RVC electrode was used again after soaking in 10-percent (v/v) nitric acid to remove any metal deposits. RVC electrodes could be reused several times. The amount of residual metal deposits in the RVC or on the platinum counter electrode was determined by soaking the electrodes in a known volume of 10-percent (v/v) nitric acid, then analyzing the solution for metal content by atomic absorption spectrophotometry.

Results and Discussion

Polarization Behavior

Polarization experiments were carried out with a stationary electrochemical system, using a glassy carbon disk as the cathode. The anode consisted of a coiled platinum wire, and a saturated calomel electrode (SCE) served as the reference. Dilute solutions containing copper, nickel and zinc at approximately 500 ppm were examined. A linear potential sweep (10 mV/sec) was applied to the glassy carbon electrode from the rest potential to -1.5 V vs. SCE in single component solutions (Fig. 2a). Copper started to deposit at -0.2 V vs. SCE; nickel deposited at -0.9 V and zinc at -1.2 V. A cyclic voltammogram (10 mV/sec) was carried out on a ternary mixture containing all three metals (Fig. 2b). A current peak at -0.2 V indicated copper deposition. The peak at +0.2 V represents copper dissolution. Although nickel and zinc co-deposited at -1.1 V, electrodissolution of these two metals occurred at the respective potentials of -0.5 V and -0.85 V.

Reactor Performance With Different Packing Materials

The effectiveness of different packing materials on the potentiostatic removal of single-component copper, nickel and zinc solutions (500 ppm) was investigated. Applied potentials for electrodeposition of copper, nickel and zinc were set at -0.3 V, -0.9 V, and -1.2 V vs. SCE, respectively. For removal of copper (Fig. 3), RVC (60 ppi) performed better than either graphite fiber or graphite pellets; pellets were the least effective. With RVC, only 20 min were required for almost complete removal of copper. For graphite fiber, however, 60 min were necessary for equivalent removal of copper from the solution; even longer times were required with graphite pellets.

For nickel removal, carbon fiber was better than RVC in the first four hr of electrodeposition (data not shown). After four hr, however, RVC packing was more effective; for example, at the end of five hr, the RVC packing had removed 90 percent of the nickel, while removal with carbon fiber was 81 percent. For removal of

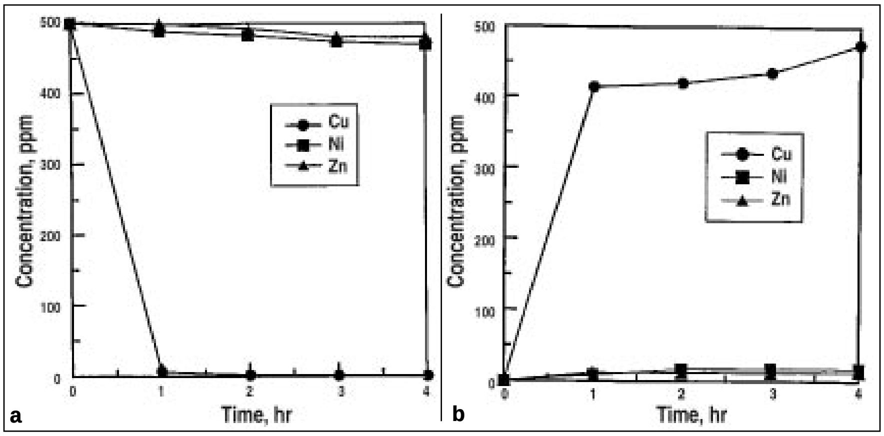

Fig. 9—(a) Removal of Cu from a ternary solution (Cu/Ni/Zn): 54.8 mL/min; (b) Recovery of Cu from deposit of Fig. 9a: 54.8 mL/min.

zinc, RVC packing performed better than graphite felt (data not shown).

Graphite pellets (4 mm diam.) have the smallest specific surface area (5.41 cm^2/cm^3) and a correspondingly lower removal efficiency. Although fiber (300 cm^2/cm^3) and felt (350 cm^2/cm^3) have higher specific surface areas, RVC (36.1 cm^2/cm^3), with a lower specific surface area, performed better. This indicates that other factors are involved in determining flow reactor performance. More uniform deposits throughout the reactor bed were obtained with the RVC. Inasmuch as RVC has fairly uniform pore distribution, more uniform electrolyte flow was obtained by minimizing undesirable hydrodynamic effects, such as channeling. For heterogeneous electrochemical reactions, the factors affecting the performance of flow-through porous carbon electrodes include the effective surface area, mass transfer rate, flow distribution, current distribution, ohmic resistance and pressure drop. In order to obtain high reaction rates, optimization of these competing factors is necessary.

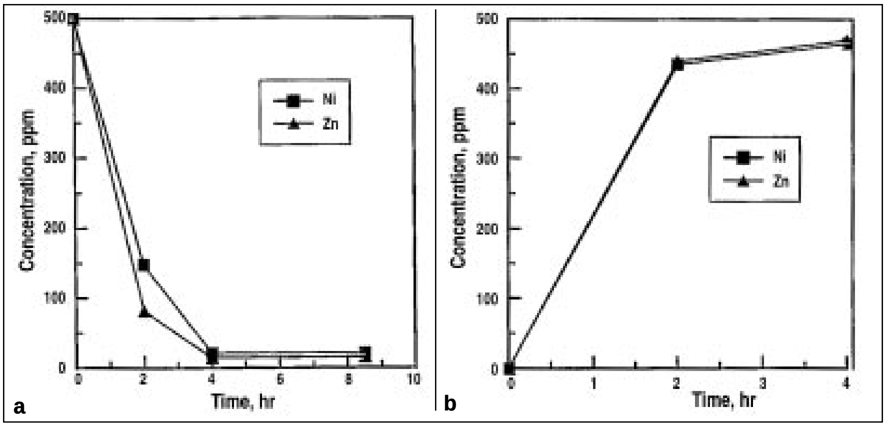

Fig. 10—(a) Removal of Ni and Zn from a Ni/Zn solution: 54.8 mL/min; (b) Recovery of Ni and Zn from deposit of Fig. 10a: 54.8 mL/min.

Removal of Cu, Ni and Zn From Binary and Ternary Mixtures

Metal ions from single-component solutions of copper, nickel and zinc were removed, using the experimental flow-through electrode reactor. A constant potential (-0.3 V, -0.9 V and -1.2 V vs. SCE for Cu, Ni and Zn, respectively) was applied to the RVC bed (60 ppi) while solution was passed through the reactor at a flow rate of 54.8 mL/min. The initial concentration of the metal ions was approximately 500 ppm, and the pH was maintained between 5 and 6.

For electrodeposition of copper, the concentration dropped to levels below 1 ppm after 30 min, resulting in a current efficiency (CE) of 99 percent, as shown in Fig. 4. Zinc required almost two hr to lower the concentration to less than 1 ppm. The current efficiency was about 20 percent. This low CE was a result of the high rate of hydrogen evolution. Nickel exhibited the lowest rate of electrodeposition. Seven hr were required to reduce the concentration below 20 ppm. The current efficiency was below 20 percent; substantial evolution of hydrogen was observed.

Studies of removal of Cu, Ni and Zn from binary and ternary mixtures in single flow-through RVC (60 ppi) reactors have been reported.[15] A binary mixture of Cu/Ni was passed through the reactor (-0.3V vs. SCE) at 54.8 mL/min. Copper was completely removed in less than 30 min with accompanying nine percent loss of nickel. An identical experiment was carried out with a Cu/Zn mixture. Copper was completely removed from the solution in less than 30 min with no loss of zinc.

Removal of copper from a ternary mixture of Cu/Ni/Zn was then studied at a potential of -0.3 V and a flow rate of 54.8 mL/min. Copper was completely removed in 30 min without significant loss of nickel or zinc.

Selective removal of nickel from a Ni/Zn binary mixture was also examined at an applied potential of -0.9 V vs. SCE. Substantial amounts of zinc co-deposited with nickel, although the reduction potential for zinc was determined to be 0.3V more negative than -0.9 V. The rate of nickel co-deposition was considerably less than from the single-component solution. After 6 hr, 40 percent of the nickel remained in the binary solution; in the single-component solution, approximately eight percent remained after 6 hr at -0.9 V (Fig. 4). The rate of zinc deposition was approximately the same as that of nickel. After 6 hr, 31 percent of the zinc remained in solution; in the single-component solution, zinc was completely removed in two hr at -1.2 V (Fig. 4).

Co-deposition of nickel and zinc precluded selective removal of these metals from solution. The effects of pH and potential on electrodeposition from binary mixtures of nickel and zinc were studied in an attempt to prevent or minimize co-deposition.

Removal of the individual metals from ternary solutions of Cu, Ni and Zn was easier at higher initial solution pH, compared to lower pH; for example, see Fig. 5a. Removal of Cu or Ni from single-component solutions was not dependent on pH, however. On the other hand, higher initial pH resulted in substantial increase in the rate of removal of Zn from the single-component solution (Fig. 5b).

In reactor performance studies, potentiostatic removal of metal ions was conducted in the recycle mode. Experiments showed that potentiostatic removal of Cu at two different flow rates (54.8 and 105.3 mL/min) was essentially the same. Therefore, the flow rate of 54.8 mL/min was used in all subsequent experiments.

Table 3
Ni/Zn Recovery vs. EDTA Concentration

$EDTANa_2$ Concentration		**% Recovery**		**R mols EDTA / mols metals**
ppm	**mM**	**Ni**	**Zn**	
0	0	99	99	0
1000	3.0	79	88	0.19
2000	6.0	27	68	0.37
5413	16.1	54	69	1.00

Initial metal concentrations: 8.5 mM Ni + 7.6 mM Zn (500 ppm each).
Applied potential: -1.2 V vs. SCE; pH 6.0; time, 8 hr; flow rate, 54.8 mL/min.

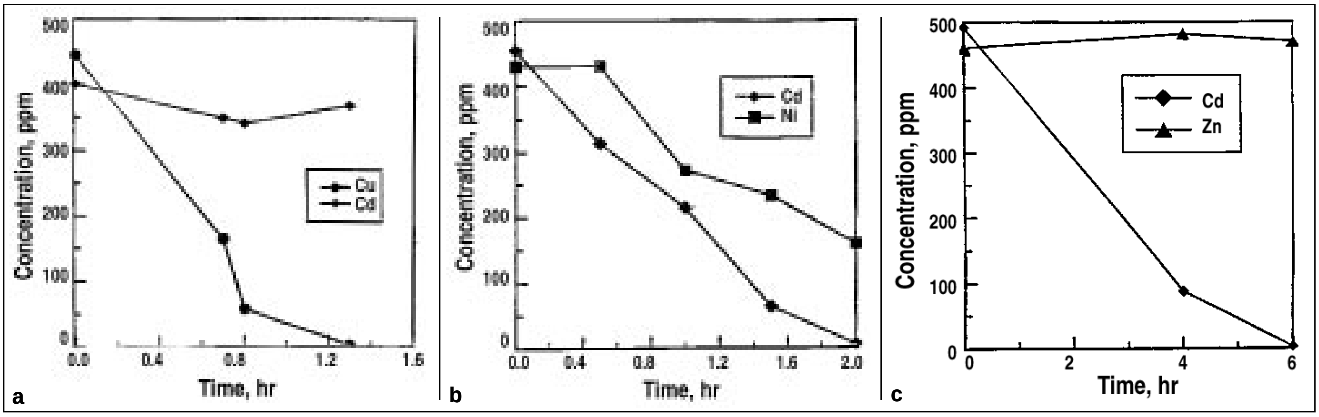

Fig. 11—(a) Removal of Cu and Cd from a Cu/Cd mixture: 54.8 mL/min; pH 3; -0.2 V vs. SCE; (b) Removal of Cd and Ni from a Cd/Ni mixture: 54.8 mL/min; pH 6; -0.6 V vs. SCE; (c) Removal of Cd and Zn from a Cd/Zn mixture: 54.8 mL/min; pH 3; -0.6 V vs. SCE.

The effect of maintaining the pH at 6 during metal deposition was then examined with a binary mixture of Ni/Zn over a range of potentials: -0.9 V, -1.2 V and -1.5 V (Figs. 6a and 6b). These figures also compare Ni and Zn deposition when the pH was not kept constant. Nickel and zinc co-deposited at approximately equal rates. At lower potentials, the rates of deposition were significantly higher when the pH was constant at 6.0 than when pH was not controlled.

Removal of nickel and zinc from a binary mixture, using 30 ppi RVC electrodes was compared with a porosity of 60 ppi (Fig. 7). The applied potential was set at -1.5 V, and pH was controlled at 6.0 ±0.5. Nickel and zinc co-deposited at rates that were essentially the same for the two grades of RVC. In subsequent experiments, a 60-ppi RVC was used because of its greater surface area.

The effect of pH on anodic stripping of copper deposits from the RVC was also examined (Fig. 8). After deposition, fresh 0.5 M sodium sulfate was passed through the cell at 54.8 mL/min. A potential of +0.3V was applied to the electrode with the pH maintained at 3, 4 and 5. Decreasing the pH improved recovery of the copper deposit. At pH 3, 99 percent recovery was achieved after four hr, compared to 61 percent recovery of copper at pH 5.

Recovery of Cu deposited from a ternary solution of Cu/Ni/Zn was studied at pH 6.0 with a flow rate of 54.8 mL/min. Copper was first removed from the solution at -0.3 V (Fig. 9a) and reduced below one ppm after four hr with some loss of zinc and nickel; six percent Ni and four percent Zn were removed, along with Cu, after four hr. A fresh solution of 0.5 M sodium sulfate (pH 3.0) replaced the spent solution. A potential of +0.3V was then applied; Cu along with the small amounts of Ni and Zn were stripped from the RVC (Fig. 9b). After four hr, 95 percent of Cu had been recovered. In single component solutions Cu was completely removed in one hr (Fig. 4); in the ternary solution, approximately six ppm of copper remained after one hr.

Recovery of nickel after co-deposition from a Ni/Zn mixture was examined. The binary solution of nickel and zinc was maintained at pH 6.0 with a flow rate of 54.8 mL/min. At -1.2 V, 94 percent Ni and 97 percent Zn were removed after approximately nine hr (Fig. 10a). A fresh sodium sulfate solution of pH 3 was added. At -0.8 V, Ni and Zn non-selectively dissolved from the RVC after 4 hr (Fig. 10b). Ninety-four percent Ni and 93 percent Zn were stripped from the RVC; selective recovery of nickel and zinc was not achieved.

Metals that co-deposit as alloys, especially those exhibiting "anomalous" co-deposition (*e.g.*, Ni-Zn), present difficulties in selective potentiostatic recovery from commingled waste streams (Figs. 10a, b). The addition of complexing ligands was investigated as a possible approach to increase selective removal. Selective complexation, or an increased difference in the reduction potentials, might result in improved separation. Ethylenedinitrilotetraacetate (EDTA), citrate, tartrate, and pyrophosphate ligands were investigated. Table 2 shows their stability constants for nickel and zinc[16] and their effects on the removal of nickel and zinc from mixed solutions. Although addition of complexing agents decreased the percent removal of both nickel and zinc, some degree of selectivity was obtained: citrate > EDTA > tartrate > pyrophosphate.

Because EDTA shows the greatest difference in the stability constants, it was investigated further with varying molar ratios with respect to total metal concentrations (R). The results are shown in Table 3.

Low-concentration EDTA (R = 0.19) slightly inhibited removal of both metals with some separation. Increasing the concentration (R = 0.37) further lowered the removal rate; however, the nickel removal rate was greatly reduced compared to zinc, resulting in enhanced separation. Further increase of EDTA to equimolar concentrations resulted in increased removal of nickel. EDTA additions inhibited the potentiostatic removal of both nickel and zinc from mixed solutions. An apparent preferential complexing of nickel may account, however, for a larger reduction potential at some optimum ratio < 1. Varying the ratios of complexing agents to total metal concentrations may exhibit similar improved separation.

Other approaches to improve the individual recovery of codeposited metals removed potentiostatically from mixed waste solutions may require multi-stage processes involving separate electrolytes for electrodissolution or combinations of chemical and electrochemical processes.

Cadmium Binary Mixtures

Because codeposition of nickel and zinc precluded use of the ternary Cu/Ni/Zn mixture to test the concept of the segmented RVC reactor system, other possible ternary metal mixtures were investigated. A series of runs with a single flow-through reactor was carried out with binary mixtures containing cadmium. Cadmium was found to deposit at -0.6 V vs. SCE. The Cu/Cd mixture was tested at an applied potential of -0.2 V (Fig. 11a); the pH was maintained at 3 with a flow rate of 54.8 mL/min. Complete removal of Cu was accomplished after approximately 1.5 hr with 12 percent Cd codeposited.

A Cd/Ni mixture (pH 6) was studied at -0.6 V (Fig. 11b); co-deposition of Ni and Cd occurred. After two hr, 99 percent Cd had been removed, along with 63 percent Ni.

A Cd/Zn mixture (pH 3) was studied at -0.6 V (Fig. 11c). Better separation resulted with this binary mixture because more than 99 percent removal of the cadmium was achieved after six hr with no significant loss of zinc. These experiments showed that Cd, Cu and Zn could be used as components in a ternary mixture to test the concept of the segmented, multi-stage system.

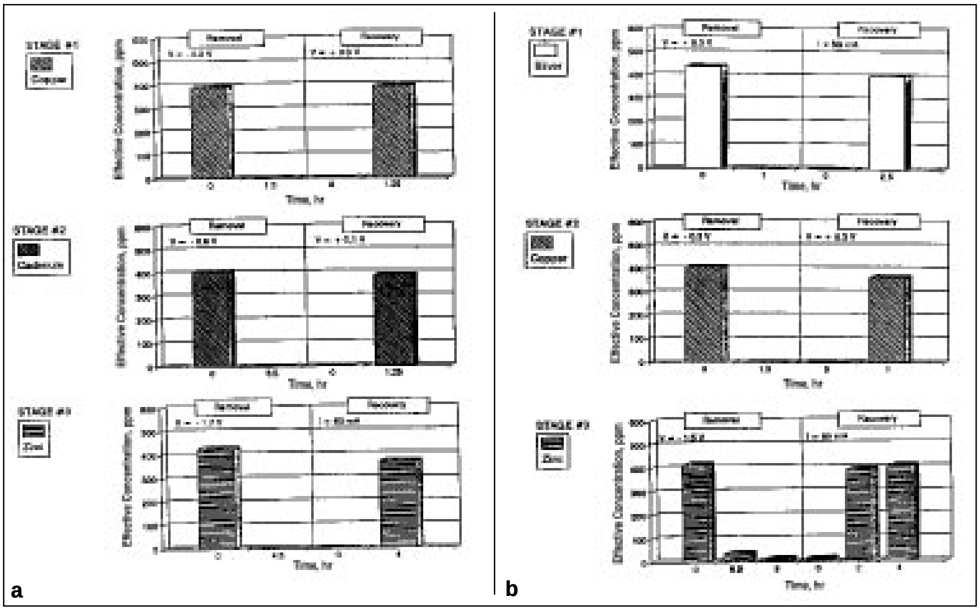

Fig. 12—(a) Removal and recovery of Cu, Cd and Zn from a ternary Cu/Cd/Zn mixture in a three-stage segmented RVC reactor: 54.8 mL/min; (b) Removal and recovery of Ag, Cu and Zn from a ternary Ag/Cu/Zn mixture in a three-stage segmented RVC reactor: 54.8 mL/min.

Silver Mixtures

Silver was another metal examined as a possible component of a ternary mixture. Silver was found to deposit at +0.2 V vs. SCE; the pH could not be readily controlled (the initial pH of 5 rapidly dropped to a steady value of about 3). Silver proved extremely easy to remove selectively from mixtures with other metals. Binary mixtures of Ag with Cu and Zn were studied, using a single flow-through reactor at +0.2 V and a flow rate of 54.8 mL/min. Silver was completely removed from each binary mixture in less than one hour without significant loss of the other metal; the detailed experimental data have been reported elsewhere.[14]

Complete Ag recovery could not be accomplished with a sodium sulfate supporting electrolyte; however, complete recovery of Ag can be achieved, using sodium nitrate (0.5 M) as the supporting electrolyte (pH 1). It should be noted that the solubility of silver nitrate is more than two orders of magnitude greater than silver sulfate. These results show Ag to be a promising component in a ternary mixture to test the segmented reactor system.

Three-stage Segmented Systems

Experiments indicated that ternary mixtures containing Ag, Cu, Cd or Zn could be separated, after which the metals could be recovered. The ternary mixtures chosen were Cu/Cd/Zn and Ag/Cu/Zn. The mixture of Cu/Cd/Zn was first studied with the three-stage segmented system (Fig. 12a). The ternary solution at an initial pH of 5 (not controlled) was passed through Stage #1 at -0.2 V vs. SCE with a flow rate of 54.8 mL/min. After 1.5 hr, complete removal of Cu was achieved without significant loss of Zn, though nine percent of the Cd codeposited. The final pH was 3.

The solution, which was maintained at pH 6, was next passed through Stage #2 set at -0.6 V vs. SCE. Complete removal of Cd was accomplished after 3.5 hr with 6 percent Zn codepositing with the Cd.

The Cu-free and Cd-free solution maintained at pH 6 was then passed through Stage #3 (-1.7 V vs. SCE) to remove the remaining zinc. After 4.5 hr, the zinc was completely removed from solution.

The rate of zinc removal at -1.7 V was nearly double that at -1.5 V. Because no other ions are present during the last stage of metal ion removal, the reactor could be operated under galvanostatic control to further increase the rate of Zn deposition.

The metal deposits in each stage were recovered next. Sodium sulfate solution maintained at pH 3 was passed through Stage #1 at a flow rate of 54.8 mL/min. After 1.25 hr, complete removal of the Cu deposit was achieved. The solution (maintained at pH 3) was then passed through Stage #2 (+0.1 V). After 1.25 hr, complete recovery of Cd from the RVC was obtained. The Zn deposit was then recovered from Stage #3 at 60 mA with the pH maintained at 3. After four hr, 89 percent of the zinc was recovered with 11 percent retained by the RVC.

The Ag/Cu/Zn mixture was studied next with the segmented reactor system (Fig. 12b). The solution (initial pH of 5.1) was passed through Stage #1 (+0.3V vs. SCE) at a flow rate of 54.8 mL/min. After one hr, the pH dropped to 3.2. Complete removal of the silver was achieved after one hr without significant loss of either copper or zinc. The silver-free solution was then passed through Stage #2 (-0.3V); the initial pH was 3.2 and was not controlled. After 1.5 hr, complete removal of copper was accomplished without significant loss of zinc and a final pH of 2.8. Once the silver and copper ions had been selectively removed, the solution was passed through Stage #3(-1.5 V). After nine hr, 97 percent of the zinc had been removed from the solution.

The sodium sulfate solution, with the pH maintained at 3, was then passed through Stage #3 again. After four hr at 60 mA, two percent of the zinc was retained by the RVC, with 98 percent of the zinc recovered. Fresh 0.5 M sodium sulfate solution (maintained at pH 3) was then passed through Stage #2 (+0.3 V). After one hr, complete removal of the copper deposit was obtained. A solution of 0.5 M sodium nitrate (pH

1) was then passed through Stage #1. After 2.5 hr at 50 mA, eight percent Ag was retained by the RVC, and 92 percent Ag was recovered.

Summary

1. Multi-stage, segmented flow-through reactor systems are effective in potentiostatic separation and recovery of heavy metals from dilute, commingled waste streams.
2. Porous, flow-through carbon electrodes are effective media for electrochemical deposition and recovery of heavy metals from dilute waste streams: RVC > carbon fiber > carbon pellets.
3. Cyclic voltammograms are useful in determining the feasibility of electrochemical separation from mixed solutions.
4. Generally, metals that exhibit "anomalous" alloy codeposition (*e.g.* Ni-Zn) are removable but not separable by potentiostatic electrodeposition from mixed solutions. Multi-stage processes involving different electrolytes or combination of chemical and electrochemical treatments may be required for selective recovery. Additions of appropriate complexing ligands may facilitate enhancement for more complete separation in the recovery of codeposited metals from mixed waste streams.
5. Optimization and control of solution pH is required for efficient removal and recovery of the individual metals.
6. Although not directly addressed in this research project, the potentiostatic removal and recovery of metallic ions in recirculating on-line rinses following individual plating processes is a possible, implied application. Controlled potentiostatic recovery should permit deposition of the major element in these rinses without codeposition of low concentrations of metallic impurities that may be present in the plating solution, eliminating or minimizing these impurities in the recovered deposit. The selection of suitable cathode substrates in the potentiostatic depositing reactor may permit the use of the deposit as anodes in the plating solution. Alternatively, electrodissolution of the deposit in a suitable electrolyte should permit reuse as additions to the plating solution.

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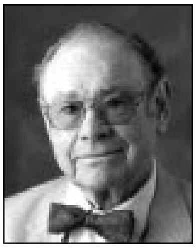

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