Copper Recovery and Cyanide Destruction with a Plating Barrel Cathode and a Packed-Bed Anode

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A batch electrochemical cell, consisting of a plating barrel cathode and a packed-bed anode, was used to recover copper from a waste acid copper sulfate solution and simultaneously to recover copper and destroy cyanide in a waste copper cyanide solution. The cyanide destruction experiments were carried out with and without the addition of NaCl. The concentrations of total cyanide, free cyanide and copper were measured as a function of electrolysis time at various solution temperatures, cell currents, barrel rotation speeds, barrel loadings, and barrel immersion levels. The total cyanide concentration was reduced from 580 ppm to less than 10 ppm. The average energy consumption was 80 to 340 kWh/kg of total cyanide destroyed, depending upon the operating conditions. A cost analysis indicates that the present electrolytic method is more cost effective than the conventional alkaline chlorination treatment for waste cyanide solutions. It also offers a cost advantage over a commercial carbon fiber electrolytic process because of a lower capital investment.

Metal cyanide compounds are extensively used in the electroplating and metal finishing industries. The process wastewater is toxic and disposal causes a loss of valuable materials. Cyanide wastes must be adequately treated before being discharged from the process plant.

The conventional method for cyanide treatment is chlorination.[1-3] By reacting with chlorine gas or sodium hypochlorite in alkaline solutions, cyanide is converted into CNO^-, CO_2, N_2, and NH_4^+. The cost of chlorination is high; it has the drawback that complex cyanides and strong cyanide solutions cannot be adequately treated. Incineration of cyanide waste and destruction of cyanide by thermal hydrolysis are alternate methods. The cost of incineration, including equipment, maintenance and operation, is also high. Although the cost of thermal hydrolysis is in the range of 10 to 35 percent of the cost of conventional chlorination treatment,[4-6] the method does not permit the recovery of heavy metal ions from waste plating solutions.

Electrochemical destruction of cyanide is a promising process. The method is capable of simultaneously recovering metal and destroying complex cyanides in waste plating solutions. Electrochemical oxidation of cyanide was first reported by Clevenger and Hall in 1913.[7] Since then, numerous reports have been published on this subject.[8-12] The electrochemical method can be accomplished by two different techniques: The first is based on electrodeposition of metal ions at the cathode and oxidation of cyanide to cyanate, carbon dioxide and nitrogen gases at the anode.[13-15] For a waste copper cyanide solution, the cathodic and anodic reactions may be described by the following equations:

Cathode reactions:

$$Cu(CN)_3^{2-} + e^- \rightarrow Cu + 3\ CN^- \quad (E^\circ = -1.09\ V) \quad (1)$$

$$Cu(CN)_2^- + e^- \rightarrow Cu + 2\ CN^- \quad (E^\circ = -0.43\ V) \quad (2)$$

$$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^- \quad (E^\circ = -0.83\ V) \quad (3)$$

Anode reactions:

$$CN^- + 2\ OH^- \rightarrow CNO^- + H_2O + 2\ e^- \quad (E^\circ = -0.97\ V) \quad (4)$$

$$CNO^- + 2\ OH^- \rightarrow CO_2 + \tfrac{1}{2}\ N_2 + H_2O + 3\ e^- \quad (E^\circ = -0.76\ V) \quad (5)$$

$$Cu(CN)_3^{2-} + 6\ OH^- \rightarrow Cu^+ + 3\ CNO^- + 3\ H_2O + 6\ e^- \quad (E^\circ = -0.69\ V) \quad (6)$$

$$4\ OH^- \rightarrow O_2 + 2\ H_2O + 4\ e^- \quad (E^\circ = 0.40\ V) \quad (7)$$

where E° is the standard reduction electrode potential vs. SHE at 25 °C.

The second technique is based on an in-situ liberation of chlorine by electrolysis of a cyanide waste to which sodium chloride has been added.[16-21] This technique is suitable for treating dilute electroplating rinsewater with a cyanide concentration less than 500 ppm. For a waste copper cyanide solution, the cathodic reactions are described by Reactions (1)–(3). The anodic reactions include Reactions (4)–(7) and the following additional reactions:

$$2\ Cl^- \rightarrow Cl_2 + 2\ e^- \quad (E^\circ = 1.36\ V) \quad (8)$$

$$Cl_2 + 2\ OH^- \rightarrow Cl^- + ClO^- + H_2O \quad (9)$$

$$2\ CN^- + 5\ ClO^- + 2\ OH^- \rightarrow 5\ Cl^- + N_2 + 2\ CO_3^{2-} + H_2O \quad (10)$$

For dilute plating waste and rinsewater, three-dimensional electrodes, such as a packed bed[22-25] and a fluidized bed,[25-27] are often used. This type of electrode has a large surface area and a high reaction rate per unit cell volume. A high mass transfer rate is needed to increase current efficiency for metal deposition reactions in dilute wastewater. For this aspect, a tumbling bed, such as a plating barrel, would be a good choice, where the relative movement of electrode particles with respect to the electrolyte improves mass transfer and current efficiency for metal deposition reactions. Several patents describe the use of tumbling bed electrodes to treat wastewater.[28-30] Oehr used a barrel plater as the anode for cyanide oxidation.[31] Tison described a bipolar tumbling bed electrochemical cell to recover copper from a dilute copper sulfate solution.[32,33] A comparison between the packed bed and tumbling bed electrodes for metal recovery was also discussed by Tison.[34] The tumbling bed has more uniform current and metal deposition distributions than those of the packed bed. The tumbling bed also offers a higher mass transfer rate than the packed bed because of the movement of particles. In a plating shop, an existing barrel plater may be used, and little investment is needed for in-house waste treatments.

This study examines the feasibility of using an electroplating barrel cathode and a packed-bed anode to recover metals and

Table 1
Test Solutions

Solution	Acid Copper Sulfate	Copper Cyanide (without NaCl)	Copper Cyanide (with NaCl)
Composition	0.1 M $CuSO_4$ 1 M H_2SO_4	0.0056 M CuCN 0.017 M NaCN 0.2 M NaOH pH 11–13	0.005 M CuCN 0.015 M NaCN 0.1 M NaOH 0.2–0.6 M NaCl pH 11–13
Volume (liter)	10	8–11	1.35
Copper Conc. (ppm)	6350	356	317
Total CN (ppm)		585	520
Free CN (ppm)		119	112
Temp., °C	20–27	25–65	25

destroy cyanide simultaneously in waste plating solutions. The effects of temperature, cell current, barrel rotation speed, barrel loading, and barrel immersion level were studied with waste copper sulfate and copper cyanide solutions.

Experimental Procedure

Test Solutions

Batch cell experiments were carried out to recover copper from an acid copper sulfate solution and simultaneously to recover copper and destroy cyanide in a copper cyanide solution, with and without the addition of NaCl. Table 1 lists the composition, volume and temperature of test solutions used in the experiments.

For the acid copper sulfate solution, 10 liters of an aqueous solution containing 0.1 M $CuSO_4$ and 1 M H_2SO_4 at 20 to 27 °C were used. The copper ion concentration in the solution was equivalent to 6350 ppm, as shown in Table 1.

For the copper cyanide solution without NaCl, 8 to 11 liters of an aqueous solution containing 0.0056 M CuCN, 0.017 M NaCN and 0.2 M NaOH were used. The solution composition corresponded to an initial concentration of 585 ppm of total cyanide, 119 ppm of free cyanide, and 356 ppm of copper. The tests were carried out in the temperature range of 25 to 65 °C.

For the copper cyanide solution with the addition of NaCl, 1.35 liters of an aqueous solution containing 0.005 M CuCN, 0.015 M NaCN, 0.1 M NaOH and 0.2 to 0.6 M NaCl at 25 °C were used. The initial concentrations of total cyanide, free cyanide and copper at the beginning of electrolysis were 520 ppm, 112 ppm, and 317 ppm, respectively.

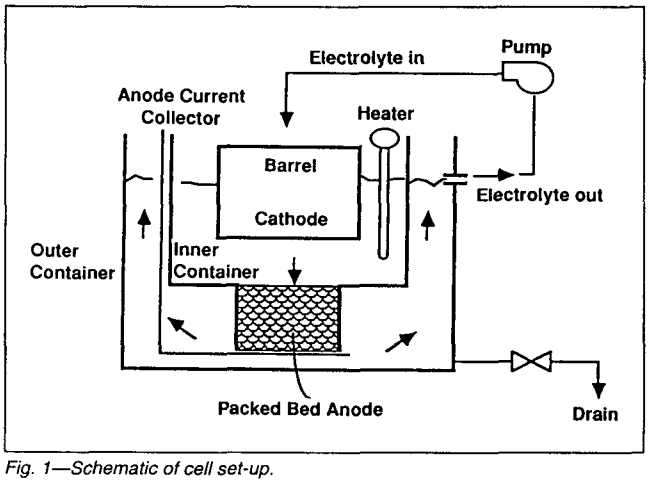

Fig. 1—Schematic of cell set-up.

Cell Set-up

The electrochemical cell used in the tests of acid copper sulfate solution and copper cyanide solution without NaCl is shown schematically in Fig. 1. The cell consisted of rectangular Plexiglas™ inner and outer containers. The total volume of the cell was approximately 12 liters. A variable speed plating barrel, 13 cm in diameter by 15 cm long,[a] loaded with copper shot was placed in the inner container as the cathode, to recover copper from the waste plating solutions. The diameter of the copper shot was 0.3 to 0.5 cm for the treatment of acid copper sulfate solutions, and 0.1 to 0.3 cm for copper cyanide solution. Two stainless steel balls 2.5 cm in diameter, coated with a thin layer of gold, were used as the dangler contacts in the plating barrel. A packed bed 13 x 13 x 10 cm (wlh), located on the bottom of the inner container, was used as the anode. For the acid copper sulfate solution, the anode bed was packed with lead shot 0.2 cm in diameter and a lead plate was used as the anode current collector. For the copper cyanide solution, the anode bed was packed with steel nails 0.2 cm in diameter by 3.8 cm in length and a stainless steel screen was used as the anode current collector. The test solution was recirculated between the outlet of the anode bed and the top of the plating barrel with a metering pump.[b] The solution flowed through mesh openings in the barrel walls to the interior of the plating barrel, where copper ions in the solution were cathodically deposited on copper shot, according to Reactions (1)–(2). The catholyte exited the screened barrel walls by gravity and flowed into the anode bed, where cyanide ion was oxidized to nontoxic chemical species, according to Reactions (4)–(6). The anolyte exited the packed bed by gravity and was recirculated by the metering pump through an overflow port on the outer container wall of the cell. The direction of solution flow is shown by the arrows in Fig. 1. The solution temperature in the cell was controlled by a quartz heater and a thermistor probe connected to an exterior temperature controller. Table 2 summarizes the experimental conditions of cell set-up.

For the copper cyanide solution with addition of NaCl, a small cell similar to that of Fig. 1 was used. The total volume of the small cell was approximately 6.5 liters. A miniature plating barrel 6.4 cm in diameter by 10 cm long,[c] loaded with copper shot, 0.1 to 0.3 cm in diameter, was used as the cathode. The dangler contact for the cathode bed was a copper cylinder 0.6 cm in diameter by 1.2 cm in length. The anodic packed bed below the plating barrel was 13 x 10 x 9 cm (wlh). It was packed with graphite pellets 0.3 cm in diameter by 0.5 cm in thickness. A piece of graphite felt, 1.25 cm thick, was used as the anode current collector. The experimental condition of cell set-up is shown in the third column of Table 2.

Test Procedures

For each run, a known amount of copper shot was placed in the plating barrel, which was then put into the cell filled with the test solution. The recirculation pump was turned on and the plating barrel began to rotate at a constant speed. After the solution temperature had been raised to the desired level by the temperature controller, a constant current from a DC power supply[d] was applied to the cell. The cell voltage and solution pH were monitored during the electrolysis. A small amount of

[a] Model 46A, Sterling Systems, Streamwood, IL.
[b] Masterflex L/S, Cole-Parmer Instrument Co., Chicago, IL.
[c] Snap-On Barrel, Singleton Co., Cleveland, OH.
[d] Model 6274B, Hewlett-Packard, Albany, NY.

Table 2
Cell Set-up

Solution		Acid Copper Sulfate	Copper Cyanide (without NaCl)	Copper Cyanide (with NaCl)
Cell Volume (L)		12	12	6.5
Cathode	Barrel size	13 x 15cm*	13 x 15cm*	6.4 x 10cm*
	Barrel speed	22 rpm	5, 10 rpm	9 rpm
	Dangler contact	2 stainless steel balls (2.54 cm dia.)	2 stainless steel balls (2.54 cm dia.)	1 copper cylinder (0.6 x 1.2 cm*)
	Materials	copper shot (dia. 0.3–0.5 cm)	copper shot (dia. 0.1–0.3 cm)	copper shot (dia. 0.1–0.3 cm)
	Barrel immersion (% barrel dia.)	75%	50–100%	50%
	Barrel loading (% barrel vol.)	25%	25–75%	50%
Anode	Size, cm	13 x 13 x 10#	13 x 13 x 10#	13 x 10 x 9#
	Materials	lead shot (0.2 cm dia.)	steel nails (0.2 x 3.8 cm*)	graphite pellets (0.3 x 0.5 cm*)
	Current collector	lead plate	stainless steel screen	graphite felt

* diameter x length
\# width x length x height

NaOH was periodically added to the cell to keep the solution pH above 11 during the treatment of copper cyanide solution. For the copper sulfate solution, a run was terminated when copper ion concentration was below 10 ppm. For the copper cyanide solutions, a run was terminated when the total cyanide concentration dropped below 10 ppm.

For the acid copper sulfate solution, 10 mL of sample solution were taken from the cell every one to two hours, and copper ion concentration was analyzed with a copper-ion-selective electrode and a double-junction Ag/AgCl reference electrode filled with 10-percent KNO_3 solution.

For the copper cyanide solution, 10 mL of sample solution were taken every one to two hours during the electrolysis. Free cyanide concentration was measured with a cyanide-ion-selective electrode and a double junction Ag/AgCl reference electrode. Afterwards, the sample was treated with 50 mL of 6 M H_2SO_4 in a distillation device. The gaseous HCN liberated was absorbed in a glass flask containing 100 mL of 1.25 M NaOH solution. The total cyanide absorbed in the NaOH solution was determined with the cyanide-ion-selective electrode. The sample left in the distillation flask was used to determine copper ion concentration with the copper-ion-selective electrode. For the copper cyanide solution containing NaCl, a small amount of $AgNO_3$ solution was added to precipitate Cl^- before the copper-ion-selective electrode was used to measure copper concentration.

Results and Discussion

Acid Copper Sulfate Solution

All the runs with acid copper sulfate solution were carried out in 10 liters of a solution containing 0.1 M $CuSO_4$ and 1 M H_2SO_4 at a barrel rotation speed of 22 rpm, a barrel immersion level of 75 percent of barrel diameter, and a solution recirculation rate of 3.1 mL/sec. The runs were made at room temperature; however, the solution temperature was raised by the cell current from 20 to 27 °C during the run. The experiments were carried out at cell currents of 6, 9, 12 and 15 A over a range of barrel loading of 25 to 75 percent of barrel volume.

Table 3 summarizes the results of copper recovery from the acid copper sulfate solution at various operating conditions. The average cathode current efficiency and energy consumption per kilogram of copper recovered were based on the reduction of cupric ion to copper and a copper concentration change in the solution from 6350 ppm to 10 ppm.

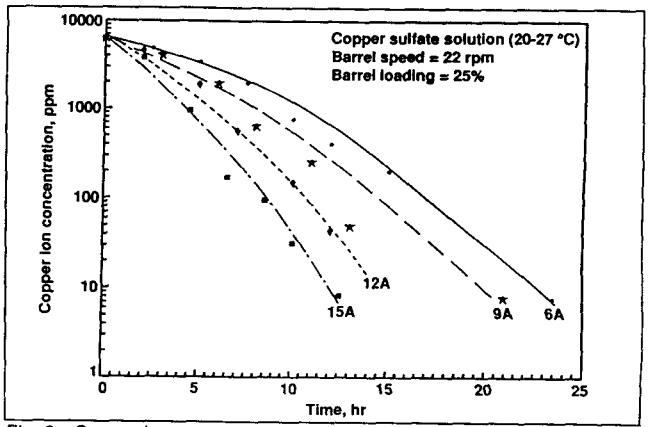

Fig. 2—Copper ion concentration vs. time for treatment of a waste copper sulfate solution.

Table 3
Results for the Recovery of Copper from an Acid Copper Sulfate Solution at 22–27 °C*

Test Variable	Cell Current (A)	Total Charge (C)	Barrel Load (%)*	Final Cu Ion Conc. (ppm)	Avg. Cu C.E. (%)	Avg. Energy (kWh/kg Cu)
Current	6	141	25	7.6	39.2	13.5
	9	170	25	7.9	32.4	25.8
	12	180	25	6.9	31.1	30.2
	15	187	25	8.2	29.5	33.5
Barrel Load (%)*	15	187	25	8.2	29.5	33.5
	15	172	50	8.9	33.4	29.6
	15	176	75	8.2	32.1	30.4

* Barrel rotation speed 22 rpm.
* % of barrel volume.

Figure 2 shows the changes in copper ion concentration with respect to electrolysis time at cell currents of 6, 9, 12 and 15 A. The data were obtained at a barrel loading of 25 percent of barrel volume. The rate of copper recovery increased with increasing cell current. Low cell current offered high current efficiency and low energy consumption. Table 3 shows that the average cathode current efficiency for copper deposition reaction decreased from 39 percent at a low cell current of 6 A, to 29 percent at a high cell current of 15 A. The average energy consumption per kilogram of copper deposited in the barrel increased from 13 kWh at 6 A to 30 kWh at 15 A. The instantaneous cathodic current efficiency and energy consumption per kilogram of copper recovered were calculated from the slope of the concentration vs. time curve by the following equations:

$$\text{C.E. (\%)} = \frac{26.8nV}{I}\left(\frac{dc}{dt}\right) \quad (11)$$

$$\text{Energy (kWh/kg Cu)} = \frac{E_{cell}I}{VM\left(\frac{dc}{dt}\right)} \quad (12)$$

where n is the number of electrons transferred in the electrode reaction, V is the solution volume in liters, I is the cell current (A), C is the concentration of copper ion in mol/L, t is the electrolysis time in hr, E_{cell} is the measured anode-to-cathode cell voltage (V), M is the molecular weight of copper in g/mol, and dc/dt is the slope of the concentration vs. time curve in mol/L/hr.

The instantaneous cathodic current efficiency and energy consumption at cell currents of 6 A and 15 A are plotted against copper ion concentration in Fig. 3. The runs with a 6-A cell current had higher current efficiency and lower energy consumption than those with cell current of 15 A. When the copper ion concentration dropped below 200 ppm, the current efficiency became less than 10 percent and energy consumption became greater than 100 kWh/kg Cu. At low copper ion concentrations, a large fraction of cell current was used for hydrogen ion reduction and a large amount of energy was needed to recover copper. The results indicate that the present electrochemical method is economical for the treatment of waste copper sulfate solution when copper ion concentration is above 200 ppm.

Figure 4 shows the instantaneous current efficiency and energy consumption for two barrel loadings of 25 and 75 percent of barrel volume at a cell current of 15 A. Barrel loading

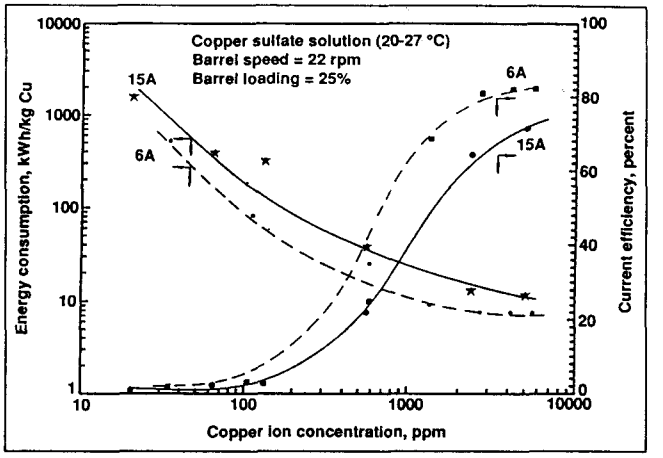

Fig. 3—Electric energy consumption and current efficiency vs. copper ion concentration for treatment of a waste copper sulfate solution.

of 75 percent produced higher current efficiency and lower energy consumption than 25 percent barrel loading. The improvement in current efficiency with high barrel loading was the result of increased cathode surface area available for copper deposition.

Copper Cyanide Solution without NaCl

The experiments for the treatment of copper cyanide solution were carried out with 8 to 11 liters of a solution containing 0.0056 M CuCN, 0.017 M NaCN and 0.2 M NaOH in the temperature range of 25 to 65 °C, at a recirculation rate of 0.8 mL/sec. To determine the effect of operating variables, four cell currents of 3, 6, 9 and 12 A, two barrel rotation speeds of 5 and 10 rpm, three barrel loadings of 25, 50 and 75 percent of barrel volume, and three barrel immersion levels of 50, 75 and 100 percent were used.

Table 4 summarizes the results for copper recovery and cyanide destruction for various operating conditions. The average cyanide current efficiency and energy consumption in the table were based on Reaction (4) and a change of total cyanide concentration from 580 ppm to 10 ppm.

Figure 5 shows the total cyanide, free cyanide and copper concentrations vs. electrolysis time for a run with a cell current of 6 A and a barrel speed of 10 rpm at 25 °C. The barrel loading was 50 percent of barrel volume and the barrel immersion level was 75 percent of barrel diameter. During the first four hr of electrolysis, there was a large drop in total cyanide concentration, while free cyanide concentration changed little. The small

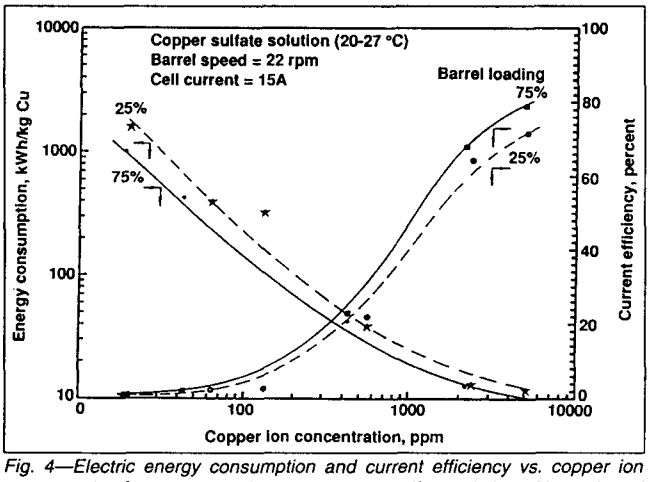

Fig. 4—Electric energy consumption and current efficiency vs. copper ion concentration for treatment of a waste copper sulfate solution with two barrel loadings.

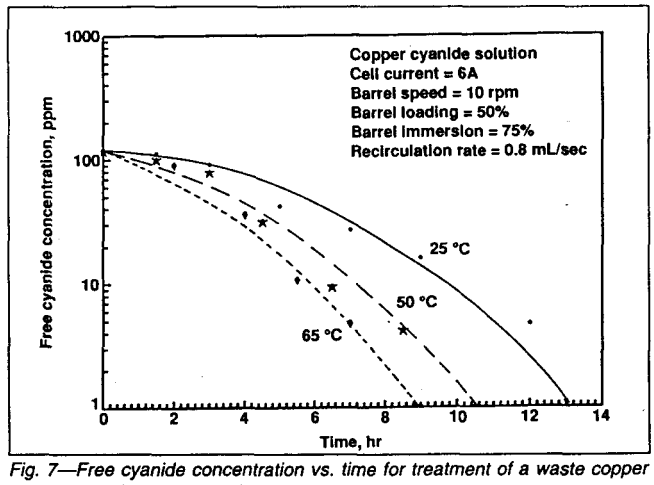

Fig. 7—Free cyanide concentration vs. time for treatment of a waste copper cyanide solution at three solution temperatures.

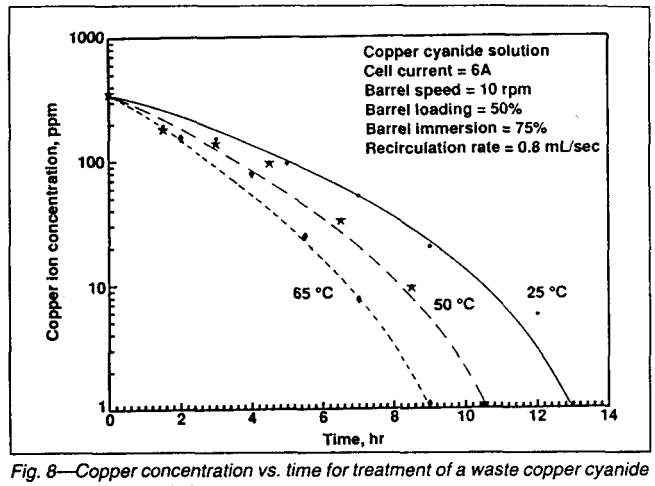

Fig. 8—Copper concentration vs. time for treatment of a waste copper cyanide solution at three solution temperatures.

and energy consumption values were calculated from the slope of the total cyanide vs. time curves, using equations (11) and (12), a value of n equal to 2, and molecular weight of CN-radical of 26 g/mol. The results indicate that as temperature increased, energy consumption was reduced and current efficiency for cyanide oxidation was improved. The improvement in cyanide current efficiency was especially large in the total cyanide concentration region of 100 to 400 ppm. At a cell temperature of 25 °C, the current efficiency for cyanide oxidation decreased sharply in the total cyanide concentration range of 100 to 200 ppm. At 65 °C, the regime of a sharp decrease in cyanide current efficiency changed to 70 to 100 ppm of total cyanide. When the total cyanide concentration became less than 70 ppm, the improvement in current efficiency by raising solution temperature was not obvious.

The results indicate that the present electrochemical method is economical for the treatment of copper cyanide solution when the total cyanide concentration is above 100 ppm, where the current efficiency for cyanide oxidation was greater than 18 percent and energy consumption was less than 200 kWh/kg of cyanide destroyed at a solution temperature of 65 °C.

2. *Effect of Cell Current.* The rates of cyanide destruction and copper recovery increased with increasing cell current; however, the current efficiency was lower and more energy was needed at higher cell current. Figure 10 shows the energy consumption and cyanide current efficiency vs. total cyanide concentration curves for two cell currents of 3 and 12 A at a solution temperature of 25 °C. The data were obtained at a barrel rotation speed of 10 rpm, barrel loading of 50 percent of barrel volume, and barrel immersion of 75 percent of barrel diameter.

At a cell current of 12 A, the cyanide current efficiency became less than 10 percent and energy consumption was greater than 400 kWh/kg CN when the total cyanide concentration dropped below 120 ppm. At a cell current of 3 A, the cyanide current efficiency was 18 percent and the energy consumption was 110 kWh/kg CN at a total cyanide concentration of 120 ppm. The results indicate that the present electrochemical method is more efficient at a low cell current of 3 A than at 12 A.

3. *Effect of Barrel Immersion, Speed and Loading.* The effects of barrel immersion level, rotation speed, and loading were small. According to the present experimental results shown in Table 4, the optimal barrel settings were: loading of 50 percent of barrel volume, immersion of 50 percent of diameter, and a rotation speed of 10 rpm.

Table 4 shows that the immersion level had no significant effect on the current efficiency for copper deposition and cyanide oxidation. A partially immersed barrel at 50 percent of diameter was slightly better than a fully immersed barrel in replenishing solution within the barrel bed.

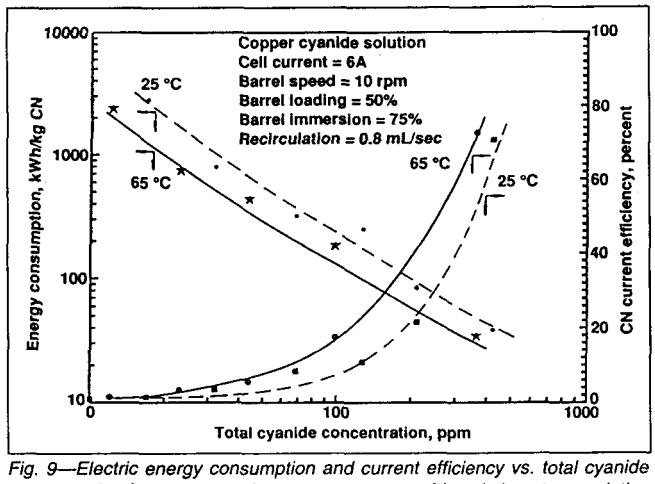

Fig. 9—Electric energy consumption and current efficiency vs. total cyanide concentration for treatment of a waste copper cyanide solution at two solution temperatures.

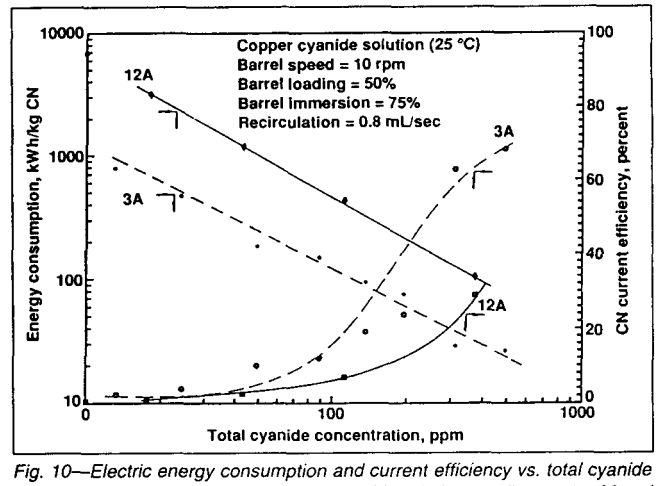

Fig. 10—Electric energy consumption and current efficiency vs. total cyanide concentration for treatment of a copper cyanide solution at cell currents of 3 and 12 A.

Table 5
Results of Copper Recovery and Cyanide Destruction in a Copper Cyanide Solution With the Addition of NaCl at 25 °C *

	Run 1	Run 2	Run 3	Run 4
NaCl Concentration (M)	0	0.2	0.4	0.6
Total Charge (C)	15	15	12	10.5
Final Total Cyanide Conc. (ppm)	7.6	2.9	2.3	2.0
Final Free Cyanide Conc. (ppm)	3.5	1.2	1.1	1.2
Final Copper Conc. (ppm)	5.4	1.1	1.1	1.4
Avg. Cyanide C.E. (%)	9.5	11.8	15.3	17.5
Energy Consumption (kWh/kg CN)	182	139	106	97

* Conditions:
Cell current, 3A
Barrel speed, 9 rpm
Barrel loading, 50%
Barrel immersion, 50%
Recirculation rate, 0.8 mL/sec

The effect of barrel rotation speed on cyanide oxidation is shown in Table 4. A speed of 10 rpm offered higher cyanide current efficiency and a lower energy consumption than at 5 rpm. This is because the mass transfer rate at 10 rpm was higher than at 5 rpm.

Table 4 shows that a barrel loading of 50 percent of volume offered higher cyanide current efficiency and lower energy consumption than at loadings of 25 percent and 75 percent of volume. The results agreed with the operating guideline discussed by Hignett, who pointed out that the optimal load level for a normal barrel plating operation should be around 60 percent of barrel volume.[35] The improvement from 25 to 50 percent loading resulted from increased cathode surface area available for copper deposition. When the rate of cathodic copper deposition increased, more free cyanide ions were released, and the anodic current efficiency was improved. There are two reasons for the better performance of a 50-percent loading over that of a 75-percent loading. The first reason is bed movement; particle motion with 50-percent loading was faster and offered a higher mass transfer rate than with a 75-percent loading. The second reason is current distribution. According to Geissman and Carlson, the current distribution in a plating barrel became less uniform with increasing barrel loading.[36] In a barrel with 75-percent loading, a large fraction of copper shot was relatively inaccessible to copper deposition reaction because of non-uniform current distribution.

Copper Cyanide Solution with Addition of NaCl

In the presence of Cl^- in a waste copper cyanide solution, ClO^- ions may be generated by anodic oxidation of chloride ions at a graphite anode, in agreement with Reactions (8) and (9). The ClO^- ions subsequently reacted with CN^- ions to produce non-toxic N_2 gas and CO_3^{2-} ions via Reaction (10). As a result, the destruction of cyanide in an electrochemical process may be accelerated by addition of NaCl to a waste plating solution. In the present study, several experiments were carried out with the addition of NaCl to 1.35 liters of a solution containing 0.005 M CuCN, 0.015 M NaCN and 0.1 M NaOH at 25 °C. The concentration of NaCl in the resulting solution, at the beginning of electrolysis, ranged from 0 to 0.6 M. The experiments were carried out in a small cell with a miniature plating barrel 6.4 cm in diameter by 10 cm long at a cell current of 3 A. A barrel rotation speed of 9 rpm, loading of 50 percent, immersion level of 50 percent and a solution recirculation rate of 0.8 mL/sec were used. Table 5 summarizes the experimental conditions and results.

Figures 11 and 12 show the total cyanide and copper concentration vs. electrolysis time curves, respectively, for four NaCl concentrations of 0, 0.2, 0.4 and 0.6 M. As expected, the rates of total cyanide destruction and copper recovery increased with increasing NaCl concentration. Figure 13 shows the instantaneous energy consumption and cyanide current efficiency vs. total cyanide concentration curves without NaCl and with 0.6 M NaCl. Without NaCl, the current efficiency was less than 10 percent when the total cyanide concentration dropped below 180 ppm. With the addition of NaCl to the test solution, ClO^- ions were produced at the anode during electrolysis. The subsequent reaction between the ClO^- ions and CN^- in bulk solution appeared to improve the current efficiency for cyanide oxidation in the overall electrolysis. For the run with 0.6 M NaCl, only when the total cyanide concentration dropped below 85 ppm, did the apparent current efficiency become less than 10 percent. The results indicate that the addition of NaCl improves the apparent current efficiency for cyanide oxidation and reduces the energy consumption per kilogram of cyanide destroyed.

Cost Analysis

A cost analysis was performed for an in-house cyanide treatment of a waste plating solution containing 580 ppm of total cyanide, using the present electrolytic process with the addition of 0.6 M NaCl. It was assumed that a spare plating barrel would be used as the cathode, and that the packed bed anode would be assembled by packing graphite pellets on the bottom of an electrolytic cell. The capital investment, consisting of a 700-liter cell tank, a recirculation pump, pipes, filters, rectifier, and installation was amortized over a 10-year period, using a straight line depreciation method and a zero interest rate. The electrolytic cell would be operated 20 hr/day and 300 days/yr, with a total of 490 kg of cyanide destroyed annually.

Based on the results of the present experimental studies, various operating costs were estimated. The estimated operating and capital investment costs were then pro-rated for one kilogram of cyanide destroyed by the waste treatment process. The results are listed in the third column of Table 6. For comparison, the operating and capital investment/kg of cyanide destroyed using the conventional chlorination method[3] and a carbon fiber electrolytic cell[21] are also listed on the first and second columns of Table 6. All costs in Table 6 were adjusted to 1992 U.S. dollars, using the cost information and price indexes listed in Refs. 37 and 38.

Capital investment for the chlorination and carbon fiber electrolytic methods was also amortized over a 10-year operating period, using the straight line depreciation method and zero interest rate. The cost of chlorination amounts to $71.81/kg of cyanide destroyed, because of the high operating costs for chemicals, labor, and disposal of solid sludges. The electrolytic treatment is more cost effective at $14.54/kg CN, using carbon fiber electrodes, and $12.52/kg CN, using a plating barrel cathode and packed bed anode. The operating cost of the present electrolytic process is slightly higher than that

Table 6
Cost Comparison of Conventional Chlorination and Electrochemical Treatment (ET) for Destroying 1.0 kg of Total Cyanide in Waste Plating Solutions (Based on 1992 dollars)

	Chlorination[3] a		ET Using Carbon Fiber[21] b		ET Using Plating Barrel c (present study)	
	Consumption (per kg CN) or Total Investment Cost	Cost ($/kg CN)	Consumption (per kg CN) or Total Investment Cost	Cost ($/kg CN)	Consumption (per kg CN) or Total Investment Cost	Cost ($/kg CN)
Operating Costs						
NaOH ($0.62/kg)[37]	8 kg	4.96	0.18 kg	0.11		
NaOCl ($0.12/L)[3] d	57 L	6.84				
Lime ($49.5/metric ton) [37]	0.008 metric ton	0.40				
NaCl ($0.11/kg) [37]			2.65 kg	0.29	5.0 kg	0.55
Electricity ($0.04/kWh)			20 kWh	0.80	100 kWh	4.00
Anode (replaced every 2 yrs.)				2.00		0.27 e
Labor & Maintenance ($10/hr)		42.00		4.00		4.00
Filter Cartridges (24/month)			0.14 piece	1.20	0.50 piece	1.20
Sludge Transportation [3] d ($0.19/metric ton-km)	0.84 metric ton-km	0.16				
Sludge Disposal ($253/ton) [3] d	0.036 metric ton	9.10				
Subtotal		63.46		8.40		10.02
Capital Costs						
Equalization Tank [3] d	$20,000	1.50 f				
Cyanide Oxidation Unit [3] d	$31,000	2.30 f				
Precipitation Reactor [3] d	$28,000	2.00 f				
Flocculator/Clarifier [3] d	$21,000	1.50 f				
Sludge Holding Tanks [3] d	$3,500	0.25 f				
Filter Press [3] d	$11,000	0.80 f				
Electrochemical Cell			$129,000 g	6.14 f	$12,100 h	2.50 f
Subtotal		8.35		6.14		2.50
Total		71.81		14.54		12.52

a. Initial total cyanide concentration: 50 ppm; Total cyanide destroyed per year: 1360 kg.
b. Initial total cyanide concentration: 1000-4500 ppm; Total cyanide destroyed per year: 2100 kg.
c. Initial total cyanide concentration: 580 ppm; Total cyanide destroyed per year: 490 kg.
d. Cost information taken from the indicated reference and adjusted with a cost index taken from Ref. [38].
e. 175 kg graphite at $0.35/kg [37] plus $200 for a graphite felt (1m x 1m) [37].
f. Capital cost was amortized over a 10-year period using a straight line depreciation method and zero interest.
g. Reactor: $102,000; rectifier and electrical connections: $4900; two filters: $3700; tanks: $17,000; installations: $1400.
h. 700-liter tank: $1100; pump and tubing: $1000; rectifier and electrical connections: $4900; two filters: $3700; installation: $1400.

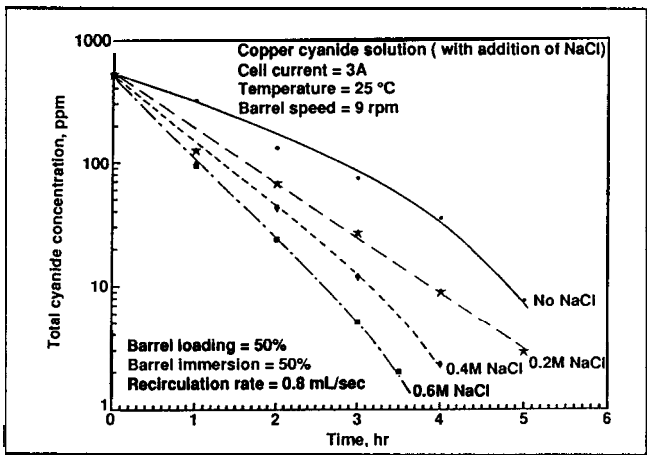

Fig. 11—Total cyanide concentrations vs. time for treatment of a copper cyanide solution with four NaCl concentrations.

of the carbon fiber electrolytic method. This is a result of a low initial cyanide concentration of 580 ppm and a high electrical requirement of 100 kWh/kg CN used in the cost estimate of the present electrolytic process.

In the carbon fiber electrolytic method,[21] a waste cadmium cyanide solution containing 1,000 to 4,500 ppm of total cyanide and an electric energy consumption of 20 kWh/kg CN destroyed were used in the analysis. The present electrolytic method has a lower capital investment cost, which results in a net saving of $2.00/kg of cyanide destroyed over the carbon fiber electrolytic method. The cost figures in Table 6 do not include any credits resulting from metal recovery at the cathode. The present electrolytic treatment method would become more cost-effective if a more concentrated waste cyanide solution were used for the treatment.

Findings

For an acid copper sulfate solution, copper ion concentration was reduced from 6350 ppm to less than 10 ppm with an average cathode current efficiency of 29 to 40 percent and an energy consumption of 13 to 33 kWh/kg of copper recovered.

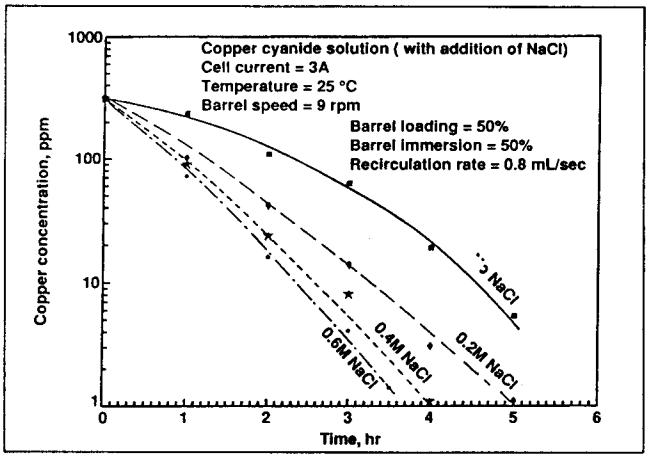

Fig. 12—Copper concentration vs. time for treatment of a copper cyanide solution with four NaCl concentrations.

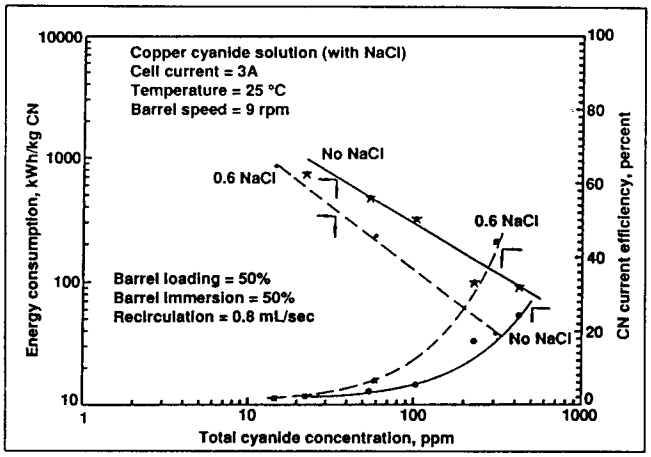

Fig. 13—Electric energy consumption and current efficiency for cyanide oxidation vs. total cyanide concentration for treatment of a copper cyanide solution without NaCl and with 0.6 M NaCl.

For a copper cyanide solution, the total cyanide concentration was reduced from 580 ppm to below 10 ppm, free cyanide from 120 ppm to 1 ppm, and copper from 356 ppm to 1 ppm, with an average cyanide current efficiency of 9 to 23 percent and an average energy consumption of 80 to 340 kWh/kg of cyanide destroyed, depending upon the operating conditions. The cathode and anode current efficiencies increased and energy consumption decreased with: (1) increasing solution temperature; (2) decreasing cell current; (3) increasing NaCl concentrations.

The optimal barrel settings were found to be: Rotation speed of 10 rpm; loading of 50 percent of barrel volume; and an immersion level of 50 percent of barrel diameter.

A cost analysis indicates that the present electrolytic method is more cost effective than the conventional chlorination method, and has a small cost advantage over a commercial carbon fiber electrolytic process, because of a lower capital investment.

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References

1. Ohio River Valley Sanitation Commission, "Methods for Treating Metal-Finishing Wastes," Cincinnati, OH (1953).
2. M.R. Watson, "Pollution Control in Metal Finishing," pp. 147–178, Noyes Data Corp., Park Ridge, NJ (1973).
3. S.A.K. Palmer, M.A. Breton, T.J. Nunno and D.M. Sullivan, "Metal Cyanide Containing Wastes Treatment Technologies," pp. 602–624, Noyes Data Corp., Park Ridge, NJ (1988).
4. A.P. Cadotte, R.G.W. Laughlin, H.L. Robey and D. Cobb, *Plat. and Surf. Fin.*, **68**, 63 (Nov., 1981).
5. H.L. Robey, *Plat. and Surf. Fin.*, **70**, 79 (Jun., 1983).
6. T.C. Tan and W.K. Teo, *Plat. and Surf. Fin.*, **74**, 70 (Apr., 1987).
7. G.H. Clevenger and M.L. Hall, *J. Electrochem. Soc.*, **24**, 271 (1913).
8. J.T. Byrne, W.S Turnley and A.K. Williams, *J. Electrochem. Soc.*, **105**, 607 (1958).
9. M.R. Hillis and C. Lopez-Cacicedo, *Ger. Offen.* 2600084 (1978).
10. T.C. Tan, W.K. Teo and D.-T. Chin, *Chem. Eng. Commun.*, **38**, 125 (1985).
11. R.B. Valencia, Jr., MS Thesis, Dept. of Chem. Engineering, Univ. of Waterloo, Waterloo, Ontario, Canada, 1969.
12. E.V. Mitrofanov and V.N. Flerov, *Electrokhimiya,* **8**, 1165 (1972).
13. M.C. Dart, J.D. Gentles and D.G. Renton, *J. Appl. Chem.*, **13**, 55 (1963).
14. H. Tamura, T. Arikado, H. Yoneyama and Y. Matsuda, *Electrochim. Acta,* **19**, 273 (1974).
15. E. Kubankova, *Koroze Ochv Mater,* **18**, 93 (1974).
16. J.P. Wiaux, T.T. Nguygen and S.A. Titalyse, *Metal Fin.*, **31**, 49 (Nov., 1990).
17. M. Fujikawa, *Mizu Shori Gijutsu,* **12**(9), 39 (1971).
18. A.M. Ueda, *Japan Kokai Tokkyo Koho,* **80**, 111; 892 (1980).
19. J. Drogen and L. Pasek, *Electroplat. and Metal Fin.*, **18**, 310 (1965).
20. R. Nagendran, N.V. Pathasarthy and K.S.G. Doss, *Plat. and Surf. Fin.*, **54**, 179 (Nov., 1967).
21. D.T. Vachon, W. Bissett, B.A. Calver and G.C. Dickson, *Plat. and Surf. Fin.*, **73**, 68 (Apr., 1986).
22. D.-T. Chin and B. Eckert, *Plat. and Surf. Fin.*, **63**, 38 (Oct., 1976).
23. A.K.P. Chu, M. Fleischmann and G.J. Hills, *J. Appl. Electrochem.*, **4**, 323 (1974).
24. S.P. Ho, Y.Y. Wang and C.C. Wan, *Water Res.*, **24**, 1317 (1990).
25. G. Kreysa, *Electrochim. Acta,* **23**, 1351 (1978).
26. B.D. Barker and B.A. Plunkett, *Trans. IMF,* **54**, 104 (1976).
27. A.G. Tyson, *Plat. and Surf. Fin.*, **71**, 44 (Dec., 1984).
28. D. Schab, H.-J. Lange and K. Hein, DD-Pat. 114624 (1975).
29. A. Kirchhof, K. Hein and D. Schab, DD-Pat. 231585 (1986).
30. R. Kammel and H.W. Liber, U.S. patent 4,123,340 (1978).
31. K.H. Oehr, Paper 579 presented at the Electrochemical Society Meeting, Seattle, WA, May 21–26, 1978.
32. R.P. Tison, *J. Electrochem. Soc.*, **128**, 317 (1981).
33. R.P. Tison and B.J. Howie, *Plat. and Surf. Fin.*, **71**, 54 (Sept., 1984).
34. R.P. Tison, *Environ. Prog.*, **2**, 70 (1983).
35. J.B. Hignett, *Metal Finishing Guidebook and Directory Issue,* Vol. 78, Metals and Plastics Publications, Hackensack, NJ, 1980; p. 84.

36. W.C. Geissman and R.A. Carlson, *Proc. AES Annual Tech. Conf.*, p. 153 (1952).
37. "Chemical Marketing Report," pp. 27–31, August 31, 1992.
38. *Chemical & Engineering News*, **70** (26), 48 (1992).
39. "AESAR 1992–1993 Catalog," AESAR/Johnson Matthey, Ward Hill, MA (1992).


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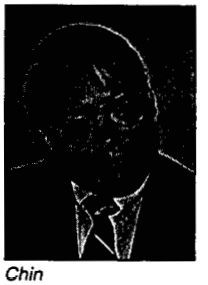
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