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# Selective Electrowinning of Silver and Gold From Cyanide Process Solutions

By F. H. Nehl, J. E. Murphy, G. B. Atkinson, and L. A. Walters

UNITED STATES DEPARTMENT OF THE INTERIOR



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**Report of Investigations 9464**

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### UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A•h	ampere hour	mm	millimeter
°C	degree Celsius	ms	millisecond
μg/mL	microgram per milliliter	pct	percent
min	minute	V	volt
mL	milliliter		

# SELECTIVE ELECTROWINNING OF SILVER AND GOLD FROM CYANIDE PROCESS SOLUTIONS

By F. H. Nehl,<sup>1</sup> J. E. Murphy,<sup>2</sup> G. B. Atkinson,<sup>3</sup> and L. A. Walters<sup>2</sup>

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## ABSTRACT

The U.S. Bureau of Mines investigated the selective electrowinning of Ag and Au from cyanide solutions contaminated with Cu with the goal of decreasing the amount of Cu codeposited. Decreasing Cu codeposited will reduce refinery costs. Direct current was applied to the cell in pulsed and square wave voltages at 0.070 A·h per 150 mL of solution. Times tested for each cycle ranged from 1 to 10,000 ms. Graphite, lead, and stainless steel were evaluated as electrode materials. Square wave electrowinning at 70° C gave the best separation of Ag and Au from Cu. Applying 2.5 V during the duty cycle, 0.0 V the rest of the period, a duty cycle of 10 to 30 pct, and a period of 100 to 1,000 ms gave the following results: Ag concentrations decreased from 34 to 0.1 µg/mL, Au concentrations decreased from 54 to 0.2 µg/mL, and Cu concentrations remained almost constant at 560 µg/mL.

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## INTRODUCTION

One stage of the cyanide leach process to extract sub-micrometer Au particles from disseminated Au ores frequently uses electrolysis. Metals are electrowon from a solution containing Ag, Au, and Cu as cyanide complexes. The electrolyte commonly has Ag and Au concentrations in the 10- to 50- $\mu\text{g}/\text{mL}$  range, while Cu concentration, depending on the ore, may be as high as 500  $\mu\text{g}/\text{mL}$ .

The electrolysis process produces a metallic product containing Ag, Au, and Cu that is fire refined to doré metal. This product is normally shipped to a precious metals refinery for final purification and production of Ag and Au bullion.<sup>4</sup> It would be advantageous if the electrowinning process could be made more selective for removing only the Ag and Au and leaving the Cu behind in the cyanide solution. This would produce a metal product

that contained little Cu. Such a product would be cheaper to refine since refinery charges increase with increasing Cu content in the metal. A procedure investigated at the U.S. Bureau of Mines used a commercial electrowinning cell feed solution contaminated with Cu and produced an electrowon product essentially free from contained Cu. The procedure is relatively simple and could be immediately applicable to primary Ag and Au producers that process Cu-containing electrowinning cell feed, but no data on the cost of this change are available. This would be a complex function dependent on the gold producer. The cost would depend on the amount of Cu in the bullion, the penalty assessed by the refiner, the available equipment, and the technical ability of the people running the plant.

## EXPERIMENTAL

The current was supplied and controlled by a Princeton Applied Research (PAR) 371<sup>5</sup> potentiostat-galvanostat regulated by an EG&G-PARC 175 universal programmer. Current and elapsed time were monitored using a Fluke 220B data logger. Total current was recorded by a Curtis 1002 integrator. Voltage waveforms were displayed on a Leader LBO-515 dual trace oscilloscope.

All room temperature experiments used a 250-mL Pyrex glassware beaker as the cell vessel. The solution was stirred with a magnetic stir bar and external stirring plate. For each of the experiments performed at room temperature, 150 mL of electrolyte was used.

Two different electrode assemblies were used in the room temperature experiments. The simpler was a lead sheet cathode, 1 mm thick and 25 mm wide, and a single graphite anode, 4 mm thick and 38 mm wide. These were immersed 40 mm into the electrolyte. A wooden holder maintained the electrode spacing at 20 mm. The second assembly retained the lead cathode, but used twin graphite anodes, one on each side of the cathode. These anodes were 4 by 25 mm, immersed 40 mm, and spaced 20 mm from the central lead cathode with a wooden electrode holder. Experiments with the single electrode assembly used a cyanide heap leach solution containing 17  $\mu\text{g}/\text{mL}$  Ag, 6.1  $\mu\text{g}/\text{mL}$  Au, and 120  $\mu\text{g}/\text{mL}$  Cu as electrolyte.

The twin anode electrode assembly was used for the electrolysis of "cell feed" obtained from an operating gold mine. This solution was a carbon strip solution that is typical of the actual feed to a commercial Ag and Au electrowinning cell and contained more Au and Cu than the solution used with the single electrode assembly. Over the course of the experiments, three separate samples of this electrolyte were obtained, each containing different levels of Ag, Au, and Cu. Concentrations ranged from 3.4 to 34  $\mu\text{g}/\text{mL}$  Ag, 21 to 54  $\mu\text{g}/\text{mL}$  Au, and 340 to 560  $\mu\text{g}/\text{mL}$  Cu. A typical solution analysis (table 1) shows the concentration of several different elements present in the solution.

Table 1.—Typical cell feed composition, micrograms per milliliter

Al . . . . .	31	Mo . . . . .	< 1
As . . . . .	< 10	Na . . . . .	129
Ba . . . . .	< .2	Nb . . . . .	1.6
Be . . . . .	.03	Ni . . . . .	120
Bi . . . . .	< 8	P . . . . .	< 30
Ca . . . . .	< 8	Pb . . . . .	< 4
Cd . . . . .	.32	Sb . . . . .	< 8
Co . . . . .	1.1	Si . . . . .	160
Cr . . . . .	2.5	Sn . . . . .	1.9
Cu . . . . .	340	Sr . . . . .	.07
Fe . . . . .	200	Ti . . . . .	< .7
K . . . . .	40	V . . . . .	1.3
La . . . . .	2.4	W . . . . .	< 8
Li . . . . .	< .7	Y . . . . .	.27
Mg . . . . .	6.5	Zn . . . . .	11
Mn . . . . .	.08	Zr . . . . .	< 3

<sup>1</sup>Grams per liter.

<sup>4</sup>McQuiston, F. W., Jr., and R. S. Shoemaker. Gold and Silver Cyanidation Plant Practice. Soc. Min. Eng. AIME (N.Y.), v. 2, 1981, pp. 47-52.

<sup>5</sup>Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

Voltages used in the experiments were either pulsed or square wave. In pulsed electrowinning tests, a voltage was applied to the cell for only a specific portion of some period. When the pulse was not being applied to the cell, the cell had no outside applied potential. Specific conditions for pulsed voltages might be a 2.0-V pulse with a 10-pct duty cycle and a 10-ms period. This would signify a 2.0-V pulsed voltage applied to the electrowinning cell for 1 ms of every 10-ms period. Similarly, a 20-pct duty cycle with a 100-ms period would signify a 20-ms pulse every 100-ms period. Periods used for the pulse work described here ranged from 1 to 10,000 ms. Periods were varied to determine if the selectivity of the electrowinning was dependent on the period length. Applied voltages were 2.0 and 2.5 V.

Square wave electrowinning applied a definite voltage to the cell at all times. One voltage of interest was applied to the cell for a specific portion of some period. When that voltage stopped, a second voltage was applied for the remainder of the period. Square wave electrolysis is described using a pair of voltages, a duty cycle, and a period. The duty cycle refers to the percentage of the period the largest voltage is applied to the cell. A square wave experiment listed as 2.0 to 1.0 V, 20-pct duty cycle, 10-ms period described an electrowinning test with a 2.0-V potential applied for 2 ms of a 10-ms period. A 1.0-V potential was applied for the remaining 8 ms of the 10-ms period. The total ampere hours passed through the cell was monitored and held the same for each series of experiments. A total of 0.070 A·h per 150 mL of electrolyte was applied in each experiment.

Some commercial Au electrowinning cells are operated at 70° C, the temperature sustained in the cells because of the inherent inefficiency of the electrolysis process.<sup>6</sup> Electrowinning tests using both pulsed and square wave voltages were run at 70° C in a stirred glass cell to examine the effect of elevated temperature on electrowinning performance.

Experiments performed at 70° C used a jacketed 150-mL beaker as the cell vessel. Heated water from a Lauda K2 circulating water bath flowed through the cell jacket. Evaporation was held to a minimum with a layer of 6.4 mm hollow polypropylene balls floating on 90 mL of electrolyte. Stirring was via a magnetic stir bar and an external stir plate. The electrode configuration was the same as the twin anode electrode assembly. Electrolyte for the 70° C experiments was cell feed obtained from an operating mine. The first sample contained 94 µg/mL Ag, 21 µg/mL Au, and 540 µg/mL Cu, and the second sample contained 34 µg/mL Ag, 54 µg/mL Au, and 560 µg/mL Cu. Both pulsed and square wave voltages were tested in the high-temperature experiments. Current passed through the cell in each experiment was 0.042 A·h per 90 mL of electrolyte, which is equivalent to 0.070 A·h per 150 mL of electrolyte used in room temperature tests.

Experiments investigating the effect of electrode composition used a twin anode cell. The twin anodes caused a more uniform cathode deposit than a single anode. Anode material was either 4-mm-thick by 25-mm-wide graphite or 2-mm-thick by 25-mm-wide stainless steel perforated with 2.3-mm-diam holes. Both were immersed 40 mm in the electrolyte solution. Cathode materials tested were lead sheet, lead wool, and steel wool. The lead sheet was 1 mm thick by 25 mm wide, cut from lead flashing 2 mm thick, and rolled to a 1-mm thickness. The lead wool and steel wool were contained in a flat basket made of perforated polypropylene with inside dimensions of 28 mm wide, 48 mm tall, and 5 mm deep. A stainless steel post inserted in the center served as current carrier. The electrolyte for the electrode materials experiments contained 34 µg/mL Ag, 54 µg/mL Au, and 560 µg/mL Cu. All experiments for evaluating electrode materials were conducted at 70° C using the jacketed and blanketed cell.

## RESULTS

Results from pulsed electrowinning tests on a solution relatively low in concentration of precious metals are summarized in table 2. The initial electrolyte contained 17 µg/mL Ag, 6.1 µg/mL Au, and 120 µg/mL Cu. A 2.0-V pulsed current was applied to the cell. Results show

that for equal ampere hours passed through the electrowinning cell at differing periods, the Cu content of the electrolyte remained relatively constant. The lowest concentration of precious metals in solution was generally obtained when the period was 1,000 ms or less and the duty cycle was less than 60 pct. Decreasing concentration of metals in solution translates into deposition of the metals onto the cathode for subsequent recovery.

<sup>6</sup>Filmer, A. O. The Electrowinning of Gold From Carbon-In-Pulp Eluates. Paper in Carbon-In-Pulp Technology for the Extraction of Gold. Australia Inst. Min. Metall., 1982, pp. 49-66.

**Table 2.—Electrolyte analyses after 2.0-V pulsed electrowinning at room temperature, micrograms per milliliter**

Duty cycle, pct	1 ms			10 ms			100 ms			1,000 ms			10,000 ms		
	Ag	Au	Cu	Ag	Au	Cu	Ag	Au	Cu	Ag	Au	Cu	Ag	Au	Cu
10	<0.05	<0.1	100	NA	NA	NA	<0.05	<0.1	120	3.5	2.5	119	10.0	5.1	127
20	.07	.1	91	<0.05	<0.1	122	<.05	<.1	106	1.3	.5	119	6.8	2.7	123
30	.4	.1	99	<.05	<.1	93	1.7	.6	97	.8	.3	117	4.9	2.1	128
40	.8	.3	96	.7	.3	104	1.9	.7	97	.4	<.1	115	4.1	1.7	121
50	1.6	.6	98	.8	.3	97	3.2	1.1	100	.3	<.1	117	3.6	1.1	121
60	1.0	.3	96	1.2	.4	104	2.7	1.0	100	.4	.1	112	2.6	1.3	120
70	1.7	.6	99	1.2	.4	100	2.3	.8	100	.8	.3	110	2.0	.6	119
80	.8	.3	96	1.6	.5	100	4.4	1.5	102	3.4	1.2	105	.8	.3	116
90	3.5	1.2	100	2.5	.9	102	2.2	.8	100	2.9	1.0	105	1.7	.6	111
100	4.5	1.5	101	3.9	1.5	108	3.1	1.1	97	1.8	.6	112	1.5	.5	93

NA Not available.

NOTE.—Initial solution analyses, in micrograms per milliliter: 17 Ag, 6.1 Au, 120 Cu.

Fresh cathodes were used for each experiment. The surface of each cathode was analyzed by X-ray fluorescence after the experiment. The results were qualitative and confirmed the solution analyses. For example, a 2.0-V pulse experiment was run using a 40-pct duty cycle and a 10-ms period. During the experiment, the Ag concentration decreased from 3.4 to 1.5  $\mu\text{g/mL}$ , the Au concentration decreased from 25.9 to 13.6  $\mu\text{g/mL}$ , and the Cu concentration stayed at 320  $\mu\text{g/mL}$ . Fluorescence data showed 20 times more weight of Ag and Au than Cu in the metal coating the cathode. A duplicate experiment was run at a 100-pct duty cycle. In this experiment, the Ag concentration dropped from 3.4 to 3.2  $\mu\text{g/mL}$ , the Au concentration dropped from 25.9 to 21.5  $\mu\text{g/mL}$ , and the Cu concentration dropped from 320 to 310  $\mu\text{g/mL}$ . Fluorescence data showed only 1.5 times more weight of Ag and Au than Cu in the metal coating the cathode.

Further experiments investigated pulsed electrowinning of Ag and Au from solutions used as feed in commercial electrowinning cells. Cell feed contained 3.4  $\mu\text{g/mL}$  Ag, 25.9  $\mu\text{g/mL}$  Au, and 340  $\mu\text{g/mL}$  Cu. The electrowinning cell was operated at 2.0 and 2.5 V with a 10-ms period. Results listed in table 3 show that final concentrations of Ag in the electrolyte were lowest at a duty cycle of 10 pct. Gold concentrations were lowest at a 40-pct duty cycle for a 2.0-V pulsed electrowinning test and at a 60-pct duty cycle for a 2.5-V pulsed electrowinning test. Although the concentrations of Ag and Au did not reach the low levels shown in table 2 for a 10-ms period and 2 V, their concentrations did decrease without a significant decrease in Cu concentration.

**Table 3.—Electrolyte analyses after pulsed electrowinning for 10-ms period at room temperature, micrograms per milliliter**

Duty cycle, pct	2.0 V			2.5 V		
	Ag	Au	Cu	Ag	Au	Cu
10	0.2	22.8	320	1.0	23.0	340
20	.8	22.0	320	1.6	20.2	350
30	1.1	20.2	320	2.1	20.7	330
40	1.5	13.6	320	2.7	18.8	340
50	2.4	13.8	320	3.0	20.2	340
60	2.8	15.5	310	2.9	16.4	340
70	3.0	19.1	310	3.1	21.0	340
80	3.0	19.4	310	3.0	22.0	340
90	3.0	21.3	310	3.1	21.8	340
100	3.2	21.5	310	3.3	23.6	310

NOTE.—Starting electrolyte analyses, in micrograms per milliliter: 3.4 Ag, 25.9 Au, 340 Cu.

Pulsed electrowinning successfully deposited Ag and Au on the cathode while leaving Cu in solution. Square wave electrolysis tests were performed on another sample of electrowinning cell feed. The cell feed contained 94  $\mu\text{g/mL}$  Ag, 20.9  $\mu\text{g/mL}$  Au, and 540  $\mu\text{g/mL}$  Cu. A 2.0- to 1.0-V square wave was applied to the cell for a 10-ms period (table 4). The square wave was at least as successful as the 2.0 or 2.5 V pulse in electrowinning Ag and was clearly superior to pulsed electrowinning in removing Au from solution. The square wave electrowinning cell produced an electrolyte that contained less than 1  $\mu\text{g/mL}$  Ag and 1  $\mu\text{g/mL}$  Au at the 10 and 20 pct duty cycles compared with the best results of 0.2  $\mu\text{g/mL}$  Ag and 16.4  $\mu\text{g/mL}$  Au from the pulsed electrowinning cell.

**Table 4.—Electrolyte analyses after square wave electrowinning for 10-ms period at room temperature, micrograms per milliliter**

Duty cycle, pct	2.0- to 1.0-V square wave		
	Ag	Au	Cu
10 .....	0.1	0.4	570
20 .....	.8	.5	570
30 .....	1.7	.8	520
40 .....	3.0	1.0	550
50 .....	3.0	1.0	550
60 .....	43.0	9.5	540
70 .....	55.0	11.7	540
80 .....	67.0	14.5	540
90 .....	82.0	17.8	560
100 .....	83.0	18.0	540

NOTE.—Starting electrolyte analyses, in micrograms per milliliter: 94 Ag, 20.9 Au, 540 Cu.

Table 5 shows a summary of results from tests run at 70° C for both a 2.0-V pulsed voltage and a 2.0- to 1.0-V square wave voltage. Results similar to those from room temperature experiments were obtained. The pulsed electrolysis selectively electrowon both Ag and Au from the electrolyte. This produced a solution that contained less Ag and Au and more Cu than that produced by normal electrolysis, i.e., 100 pct in table 5. Square wave electrolysis at 70° C exhibited the same advantages over pulsed electrolysis as were exhibited at room temperature. More precious metals were removed from the solution and less Cu was removed with square wave electrolysis than with pulsed electrolysis. These effects, for both pulsed and square wave electrolysis, are most pronounced in the lower duty cycles, especially the 10 and 20 pct for the square wave experiments.

**Table 5.—Electrolyte analyses after pulsed and square wave electrowinning for 10-ms period at 70° C, micrograms per milliliter**

Duty cycle, pct	2.0-V pulse			2.0- to 1.0-V square wave		
	Ag	Au	Cu	Ag	Au	Cu
10 ...	27	9.2	718	5	0.6	493
20 ...	56	12.1	544	7	.5	482
30 ...	60	9.2	689	42	6.1	387
40 ...	60	7.5	485	20	3.1	391
50 ...	71	10.5	378	61	6.2	336
60 ...	58	7.7	273	52	5.6	275
70 ...	69	11.3	364	49	7.6	348
80 ...	78	14.1	425	50	8.0	337
90 ...	72	13.8	407	50	9.4	360
100 ..	59	10.8	387	59	10.8	387

NOTE.—Starting electrolyte analyses, in micrograms per milliliter: 94 Ag, 20.9 Au, 540 Cu.

Results from normal electrolysis are shown at the 100-pct duty cycle in table 5. At these conditions, 37 pct of the Ag, 48 pct of the Au, and 28 pct of the Cu were electrowon. Pulsed electrolysis at a 10-pct duty cycle electrowon 71 pct of the Ag, 56 pct of the Au, and no Cu. Square wave electrolysis at a 10-pct duty cycle electrowon 95 pct of the Ag, 97 pct of the Au, and 9 pct of the Cu. Pulsed and square wave electrolysis can recover more Ag and Au with less Cu contamination for the same kilowatt hour input than current commercial practice.

All previous experiments used a lead sheet cathode and graphite anode(s). High surface area cathodes and stainless steel anodes are in common use commercially.<sup>7</sup>

Experiments investigating the performance of different electrode materials were carried out using a stirred glass cell held at a temperature of 70° C. The current was applied as a 2.0- to 1.0-V square wave with a 10-ms period and a 30-pct duty cycle. Cathodes tested were lead sheet and steel wool packed in a perforated plastic box. Anodes tested were perforated stainless steel and graphite. Results from the experiments are summarized in table 6. A total current of 0.042 A·h passed through the cell in each experiment. Since the applied voltage was the same in each case, the time for the total current to pass through was a measure of the cell resistance. The higher the cell resistance, the longer it took for current to pass through. The results show that a cell with a steel wool cathode had lower resistance than a cell with a lead sheet cathode with either graphite or stainless steel anodes.

Further experiments were conducted to compare the performance of lead wool and steel wool cathodes. An electrowinning cell was operated at a 2.5- to 1.0-V square wave, a 10-ms period, and 70° C. Solution analyses are shown in table 7. Little difference in electrowinning performance was found between the two cathode materials.

Square wave electrowinning experiments, using stainless steel anodes and steel wool cathodes, were conducted to determine the effect of the length of the period on metal concentrations. Table 8 is a summary of electrolyte analyses after square wave electrowinning experiments using a 2.5- to 0.0-V potential and periods ranging from 10 to 10,000 ms at 70° C. The initial electrolyte contained 34 µg/mL Ag, 54 µg/mL Au, and 560 µg/mL Cu. The data in table 8 show that a 2.5- to 0.0-V square wave efficiently electrowon Ag and Au with periods ranging from 10 to 10,000 ms. At 10 ms, the Au was electrowon most efficiently at 40- to 60-pct duty cycle, while at 10,000 ms, Au was electrowon most efficiently at 10- and 20-pct duty cycle.

<sup>7</sup>McKetta, J. J., ex. ed. Encyclopedia of Chemical Processing and Design. Marcel Dekker, Inc., v. 24, 1986, p. 398.

**Table 6.—Effect of electrode material on cell resistance and selectivity**

Electrode material		Elapsed time, <sup>1</sup> min	Analysis, $\mu\text{g/mL}$		
Cathode	Anode		Ag	Au	Cu
Lead sheet . . . .	Graphite . . . . .	40	2.6	2.0	474
Steel wool . . . .	. .do. . . . .	20	.3	.4	456
Lead sheet . . . .	Stainless steel . . .	260	.1	.4	382
Steel wool . . . .	. .do. . . . .	80	.1	.2	504

<sup>1</sup>Time for 0.042 A·h to pass through the cell.

NOTE.—Starting electrolyte analyses, in micrograms per milliliter: 34 Ag, 54 Au, 560 Cu. Operating conditions: 2.0- to 1.0-V square wave, 30-pct duty cycle, 10-ms period, 70° C.

**Table 7.—Electrolyte analyses after 2.5- to 1.0-V square wave electrowinning with lead wool or steel wool cathodes for 10-ms period and 70° C, micrograms per milliliter**

Duty cycle, pct	Ag		Au		Cu	
	Lead	Steel	Lead	Steel	Lead	Steel
10 . . . . .	0.2	0.1	0.5	0.3	576	546
20 . . . . .	.1	.1	.1	.1	574	521
30 . . . . .	.1	.1	.1	.1	511	503
40 . . . . .	.1	.1	.1	.1	355	386
50 . . . . .	2.5	.4	.5	.5	314	364
60 . . . . .	3.2	.4	1.2	.5	244	383
70 . . . . .	5.7	2.5	2.9	4.3	282	401
80 . . . . .	2.7	3.0	3.1	5.1	308	374
90 . . . . .	4.3	5.6	5.6	9.5	325	392
100 . . . . .	6.1	7.2	7.6	12.4	340	424

NOTE.—Starting electrolyte analyses, in micrograms per milliliter: 34 Ag, 54 Au, 560 Cu.

**Table 8.—Electrolyte analyses after square wave electrowinning at 2.5- to 0.0-V potential and 70° C, micrograms per milliliter**

Duty cycle, pct	10 ms			100 ms			1,000 ms			10,000 ms		
	Ag	Au	Cu	Ag	Au	Cu	Ag	Au	Cu	Ag	Au	Cu
10 . . .	25.1	35.9	402	0.1	1.1	568	0.1	0.1	526	0.1	<0.1	503
20 . . .	1.1	42.8	518	.1	<.1	707	.1	.2	519	.1	<.1	519
30 . . .	.2	3.8	556	.1	<.1	583	.1	.2	501	.2	.6	504
40 . . .	.1	<.1	627	.1	<.1	556	.1	.2	428	.6	1.4	491
50 . . .	.2	<.1	672	.3	.4	501	.3	.5	437	2.2	3.8	504
60 . . .	.1	.1	529	.7	.9	480	1.1	1.9	401	1.8	3.0	424
70 . . .	.2	.2	471	.7	1.1	467	1.0	2.0	411	2.8	5.4	457
80 . . .	1.2	1.9	428	1.9	3.2	439	3.4	5.2	401	2.8	4.4	406
90 . . .	3.9	5.8	419	3.3	5.3	434	3.1	5.0	406	4.0	6.8	468
100 . .	7.2	12.4	424	4.0	6.6	541	3.4	5.5	401	2.1	3.4	369

NOTE.—Starting electrolyte analysis, in micrograms per milliliter, 34 Ag, 54 Au, 560 Cu, stainless steel anode, steel wool cathode.

Results in tables 7 and 8 can be compared for the 10-ms period to determine the differences between the 2.5- to 1.0-V square wave and the 2.5- to 0.0-V square wave. Changing the square wave from 2.5-1.0 to 2.5-0.0 V shifted the duty cycle percentage that produced electrolytes low in precious metals concentration to a higher percentage. The 2.5- to 1.0-V square wave produced electrolytes low in

Ag at duty cycles of 10 to 40 pct while the 2.5- to 0.0-V square wave duplicated this at duty cycles of 30 to 70 pct. The 2.5- to 1.0-V square wave produced electrolytes low in Au at duty cycles from 20 to 40 pct while the 2.5- to 0.0-V square wave duplicated this at duty cycles of 40 to 70 pct.

## DISCUSSION OF RESULTS AND CONCLUSIONS

The reaction mechanism depositing Ag and Au but not Cu was not determined in this work. It is speculated that the deposition of Ag and Au but not Cu may be due to the relative rates of redissolution of Ag, Au, and Cu. All the metals were probably electrowon while the pulsed voltage was present or the high-voltage portion of the square wave was on. When the pulsed voltage was stopped or the low-voltage portion of the square wave was present, the Cu was redissolved faster by the cyanide solution than the Ag or Au. This decreased the concentrations of Ag and Au in the electrolyte without decreasing Cu concentrations, which resulted in producing an electroplate high in Ag and Au and low in Cu. Kinetic studies on the dissolution of Ag, Au, and Cu in cyanide systems could verify this mechanism.

Both pulsed and square wave electrolysis of solutions containing precious metals selectively decreased the Ag and Au concentrations while leaving the Cu concentrations relatively unchanged. Pulsed electrowinning at 2.0 V with periods ranging from 1 to 10,000 ms was successful in lowering the Ag and Au concentrations of the solution below 1  $\mu\text{g}/\text{mL}$  in the most favorable circumstances. Pulsed electrowinning at 2.5 V was also effective in removing Ag and Au from solution, but apparently offered no advantage over a 2.0-V pulse. Both room temperature and 70° C

pulsed electrowinning decreased concentrations of precious metals, but not to the low concentrations obtained from square wave electrowinning.

Square wave electrowinning was shown to be effective for selective electrowinning both Ag and Au from solutions containing Cu. This electrowinning technique was tested at room temperature and 70° C. Adjustments to the magnitude and duration of the square wave were used to tailor the technique to the desired goal. Square waves of 2.0 to 1.0, 2.5 to 1.0, and 2.5 to 0.0 V, with periods ranging from 1 to 10,000 ms resulted in electroplating Ag and Au from solutions containing Cu.

Anodes tested were graphite or perforated stainless steel, and cathodes tested were lead sheet, lead wool, and steel wool. All materials were found to be satisfactory. Graphite anodes are more conductive, but are fragile compared with stainless steel. Lead sheet is an inexpensive material, but is heavy and has a relatively low surface area. Lead and steel wool have high surface areas.

Production of bullion containing less Cu could have an immediate impact on Au producers. Precious metals refineries increase refining charges with increasing Cu content of metal submitted to them. Lower Cu content in the metal produced by the electroplating cells means decreased refinery fees for the gold producer.