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Development and Application of the Waste-Plus-Waste Process for Recovering Metals From Electroplating and Other Wastes

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 7877

Development and Application of the Waste-Plus-Waste Process for Recovering Metals From Electroplating and Other Wastes

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DEVELOPMENT AND APPLICATION OF THE WASTE-PLUS-WASTE PROCESS FOR RECOVERING METALS FROM ELECTROPLATING AND OTHER WASTES

by

Andrew A. Cochran [1] and Lawrence C. George [2]

ABSTRACT

Laboratory-scale research was conducted by the Bureau of Mines to develop a new process for treating electroplating and other wastes. Various acid and alkaline cyanide wastes were combined under controlled conditions to neutralize the wastes and to almost completely precipitate the metals and cyanides. The metals were subsequently recovered for recycling; the cyanides can also be easily recycled. The process was successfully used to treat the major types of electroplating and etching wastes, containing Cd, Cr, Cu, Ni, and Zn, and to treat both concentrated and dilute wastes. The economic aspects of treating concentrated electroplating, etching, and anodizing wastes are especially attractive because of the low cost of mixing two wastes, the high value of the recovered metals, and the simplicity of the recovery procedures. The filtrates from the waste-plus-waste step were relatively harmless compared with the original wastes and met Public Health Service standards for free cyanide content. Free cyanide ions were not detected in most of the filtrates; the limit of detection was 0.03 ppm. Only small amounts of HCN were produced during the neutralization; the HCN was collected and neutralized.

INTRODUCTION

As part of its research aimed at effecting pollution abatement, the Bureau of Mines has been engaged in studies to develop technically feasible, low-cost processes for recovering metals and other valuable materials from a wide variety of electroplating and other industrial wastes. The lack of technology for treating plating wastes to recover metal and cyanide values has encouraged the disposal of spent solutions to sewers and streams. These solutions contain large tonnages of scarce, costly metals; in many cases the metal content of the solutions is greater than that of the ores now being processed. The solutions also contribute to stream and ground-water pollution; another desirable consequence of recovering these metals is the reduction of this water pollution. Most of the waste treatment processes developed in the past have faults in that either they produce new wastes, do not recover the metals and other values for recycling, or are so costly that voluntary adoption by

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industry is unlikely. The research described herein outlines an innovative process for treating wastes that does not appear to have these shortcomings.

The consumption and estimated loss of nickel by the electroplating industry in the United States in the recent past is given in table 1. The data are from Bureau of Mines Mineral Yearbooks (2, 4-7, 15, 22).[3] The nickel losses shown in table 1 are due to the discarding of spent or poisoned plating baths, dragout losses from rinse solutions, and other wastes. The decrease in nickel consumption in 1952 was due to the stockpiling of nickel brought about by the Korean war. The consumption and loss of nickel has generally increased since 1952.

TABLE 1. - Consumption and assumed loss of nickel by the electroplating industry

Nickel consumed or lost	Yearly totals, thousand short tons						
	1948	1952	1956	1960	1964	1968	1970
Anodes..........	14	7	16	16	19	22	21
Soluble Ni......	7	.3	1	1	2	4	3
Total......	21	7	17	17	21	26	24
Loss[1]..........	4	1	3	3	4	5	5

[1] Losses are based on the assumption that Ni plating is 80 pct efficient.

The large quantity of industrial wastes discharged into streams in the Missouri River Basin has been documented in two Bureau of Mines publications (8, 23); no doubt the volume of such wastes has increased in subsequent years. The removal of chromium from electroplating wastes has been described (3, 16, 18-19). The treatment of cyanide (CN) wastes to reduce their toxicity has received extensive coverage in the literature (1, 3, 9, 14, 16, 20). One patent describes the recovery of copper from CN waste as cuprous cyanide (24); however, not many processes have been developed to recover the metals and CN in these wastes for reuse. Furthermore, conventional methods of destroying CN often require equipment that is too expensive for small electroplating shops and offers little economic incentive even to large plating shops. The Bureau of Mines published three reports describing the waste-plus-waste (WPW) process for treating electroplating and other wastes (11-13), which is an inexpensive procedure involving the addition of an acid waste to an alkaline CN waste to neutralize the wastes and precipitate most of the metals and CN from both wastes. The process has been patented (10). The metals and CN can be recovered for reuse in subsequent processing. The studies herein were carried out to determine the applicability of the WPW process to a wide variety of solutions.

COMPOSITION OF SOME CONCENTRATED WASTES

When small articles are electroplated they are often supported on racks upon which metal is also deposited. The metal built up on the racks is

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[3] Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

removed periodically by rack-stripping solutions. These solutions are often rich in metal values; the compositions of some are given in table 2. The HNO_3 wastes are concentrated nitric acid rack-stripping solutions that were used hot until they were no longer effective. Upon cooling, a large quantity of precipitate (in one instance, largely nickel nitrate plus some copper and iron nitrates) appeared. Partial analyses of the cold solutions are given in table 2. The Cr wastes are chromic acid solutions; they were used to anodize aluminum or to etch printed circuit boards. The CN wastes are alkaline rack-stripping solutions that contain sodium cyanide and sodium m-nitrobenzenesulfonate. The letters A, B, and C refer to different industrial firms, and the final numbers are batch numbers. Blank spaces in table 2 and the following tables mean that no analysis was made. The high concentrations of valuable metals given in table 2 make these waste products very interesting from economic, as well as ecological, points of view.

TABLE 2. - Compositions of some concentrated wastes, g/l

Waste	Free CN	Ag	Co	Cr	Cu	Fe	Na	Ni
HNO_3-A1			1.3		49	2.1		190
HNO_3-A2		<0.001	6.7		65	3.1		97
Cr-B1				51	52		1.3	.01
Cr-B2				30	56	.06		.003
Cr-B3				28	57	.06		.003
Cr-C			.004	43	.06	.05	.07	.015
CN-A1	90				19	15		5.1
CN-A2	52				19	.72	98	5.5
CN-B1	62	2.2			8.6	<.01	83	4.6
CN-B2	113	.9			7.7	.06	75	.01
CN-B3	94	5.5			5.9	<.01	105	1.4
CN-B4	26	28.9			1.4	.20	17	.01

The estimated annual metal losses in spent rack-stripping solutions and chromic acid etching solutions from only two electroplating companies are given in table 3. These three types of waste represent large losses of valuable metals. As there are approximately 20,000 electroplating plants in the United States (9), it is evident that the significant quantities of metals being discarded represent potential profits for future recovery processes.

TABLE 3. - Annual loss of metals from two industrial electroplating companies

Waste	Metal loss, short tons[1]					
	Ag	Co	Cr	Cu	Fe	Ni
HNO_3-A...............		0.08		2.9	0.1	6.2
CN-A..................				3.4	1.9	1.2
CN-B..................	0.37			.2	<.1	<.1
Cr-B..................			0.6	.9	<.1	<.1
Total..........	.37	.08	.6	7.4	2.0	7.4

[1] Tonnages are based on the mean analyses of from 3 to 10 samples.

EXPERIMENTAL PROCEDURES AND RESULTS

Preliminary test work was carried out on samples of the HNO_3 waste. Hydrated lime ($Ca(OH)_2$) was added to adjust the pH of the solution to 2.3 to 2.7, which caused $Fe(OH)_3$ to precipitate. In some tests, after filtration, copper and nickel were selectively precipitated by further addition of lime; at pH 5.5, a $Cu(OH)_2$ precipitate containing 26.6 pct copper and 0.01 pct nickel was obtained. No iron was detected. Adjustment of the pH to 9.5 caused $Ni(OH)_2$ to precipitate.

In other tests, the copper was almost completely recovered by controlled potential electrolysis at 0.1 to 0.3 volt. The copper was very pure; spectrographic analysis revealed only a trace of silicon. The remaining nickel solution was evaporated to dryness, leaving a residue containing (in pct) 21.8 Ni, 0.05 Fe, and 0.01 Cu.

Waste-Plus-Waste Treatment Method

Although the preceding procedures are technically feasible, methods of reducing the cost of such treatment were sought. For example, the addition of the acid wastes to the strongly alkaline CN wastes, under carefully controlled conditions, was considered as an inexpensive first step to neutralize both wastes and precipitate the metals and cyanides. This procedure would be more dangerous if the order of addition were reversed (if CN waste were added to acid waste), or if too much acid were added to a waste with a high CN content, or if the acid were added too rapidly, because in these instances larger amounts of highly poisonous hydrogen cyanide (HCN) gas would be produced by the chemical reactions and evolved. The possible evolution of HCN is undoubtedly one of the reasons why the WPW procedure was not developed in industry for treating CN wastes; the combination of acid and CN is forbidden in most industries.

Wastes containing HNO_3 or Cr were added slowly from a burette with stirring to various CN wastes in a fume hood until the pH value of the mixture was approximately neutral. In most instances this caused almost complete precipitation of all the metals and free CN as metal cyanides and hydroxides. In many tests helium gas was passed over the liquid surface and through a gas bubbler containing 0.1 molar NaOH solution to collect any HCN produced during the neutralization. After the wastes were combined, the mixed metal cyanide precipitate (plus metal hydroxides in some tests) was filtered off. Both the filtrate and the NaOH solution were then analyzed for free CN ion content by means of a calibrated electrode that is sensitive to this ion.

In a typical test, the filtrate contained less than 0.03 ppm free CN ions, which was the limit of detection. The allowable limit for free CN ions in drinking water is 0.2 ppm (21). Chemical, X-ray diffraction, and differential thermal analyses revealed that the precipitate contained CuCN, $Ni(CN)_2 \cdot 4H_2O$, and $Cu_2Fe(CN)_6 \cdot 7H_2O$. The mixed CN precipitate contained (in pct) 24.0 Ni, 23.6 Cu, and 0.9 Fe.

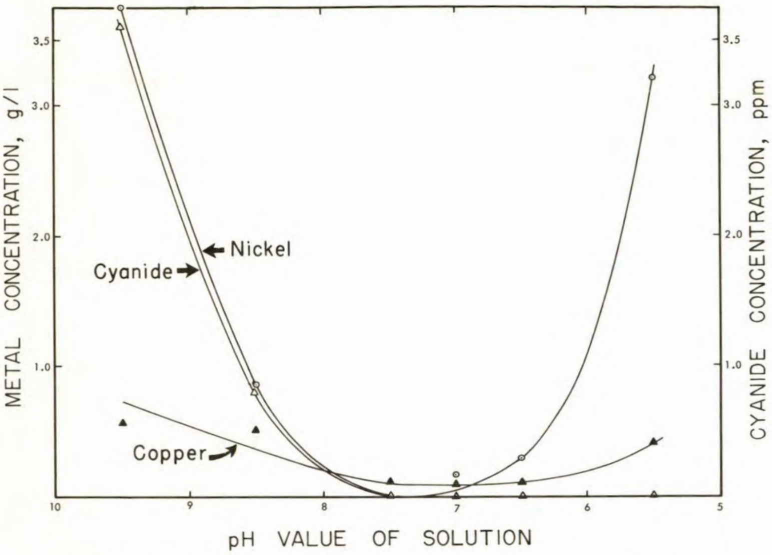

FIGURE 1. - Analyses of filtrates from addition of HNO_3-A1 waste to CN-A1 waste.

Six tests were made in which an HNO_3 waste was added to a CN waste until six different final pH values, ranging from 5.5 to 9.5, were attained. The precipitates were filtered off and the filtrates were analyzed. The results are shown in figure 1. As acid was added and the pH of the mixture decreased to around 7, the concentrations of the metals and free CN decreased to very low values. Further additions of acid introduced metal ions that were not precipitated and excess acid. The iron content of the filtrates was 0.02 g/l or less at all pH values investigated and is not shown. Figure 1 shows that a pH of about 7.5 was the optimum value for the maximum precipitation of Cu, free CN, and Ni from these two wastes.

The results of similar tests on other combinations of wastes are shown in figures 2-7; the optimum pH values for figures 2, 3, 4, 5, 6, and 7 were 7, between 7 and 7.5, between 7 and 7.5, 6, 6, and between 5.5 and 6, respectively. Alternatively, a step procedure could be used to maximize metal recovery. For example, figure 3 shows that acidifying the CN wastes to a pH of 8 will maximize precipitation of the nickel. Following separation of the nickel, further acidification to a pH of 6.5 would maximize copper and silver recovery. The iron content of the filtrates from these tests was negligible. Free CN concentrations were below the detection limit of 0.03 ppm throughout the pH ranges in figures 3-4 and are not shown. Figures 5-7 show the results of adding a Cr waste to three CN wastes. Chromium was not precipitated as completely as the other metals and free CN at the optimum pH value. The concentration of chromium in the WPW filtrates at the optimum pH ranged from 1.0 to 4.3 pct of the original concentration in the Cr waste. The chromium in the WPW filtrates at pH 6 to pH 8 must be water-soluble, hexavalent chromium because trivalent chromium is insoluble in this range. The decrease in the concentration of hexavalent chromium in this pH range may possibly be due to the oxidation of cyanides by the chromium, with the concomitant reduction of chromium to the trivalent form, which would precipitate. Chromium could be precipitated as completely as the other metals if it were reduced to the trivalent form either before or during the WPW procedure.

Further Studies of WPW Filtrates

Additional results of the WPW treatment are given in table 4. For each combination of wastes, the filtrates were analyzed at either four or five

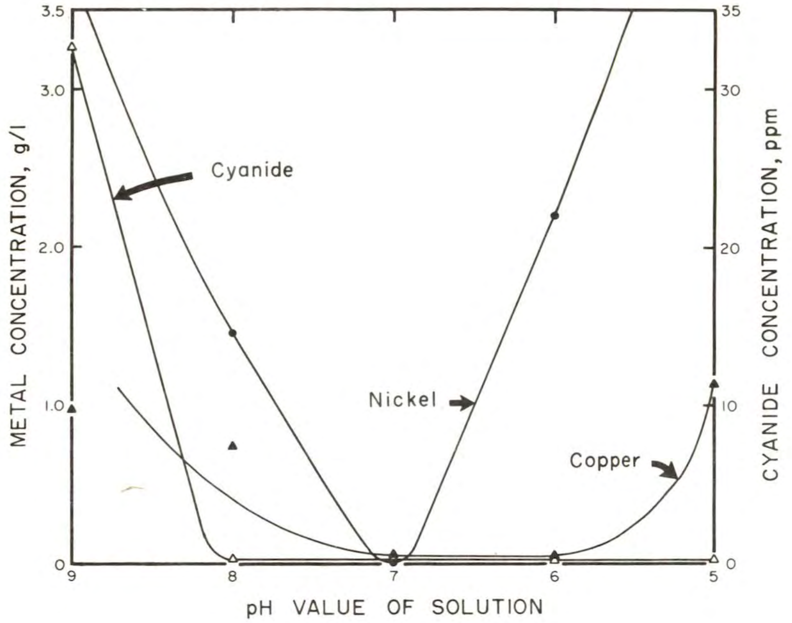

FIGURE 2. - Analyses of filtrates from addition of HNO_3-A1 waste to CN-A2 waste.

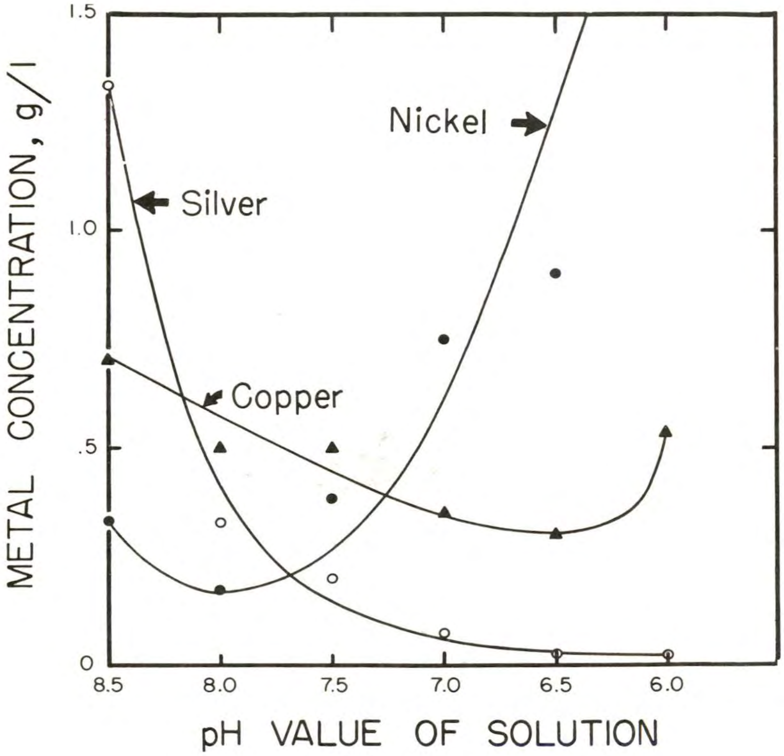

FIGURE 3. - Analyses of filtrates from addition of HNO_3-A1 waste to CN-B3 waste.

final pH values from pH 5 to pH 9; table 4 contains only the results obtained at the optimum pH value for each combination. Near the point of neutrality the combined wastes usually formed a thick slurry. With the exception of tests 1, 2, and 4, the CN waste was diluted with an equal volume of water before the acid waste was added. By decreasing the viscosity of the slurries, the dilution increased the mixing rate and reaction rate of these concentrated wastes. Free CN ions could not be detected in most of the filtrates. Even in test 3, the free CN content of the filtrate was only about one millionth of that in the original waste. The detection limit for free CN was originally 0.08 ppm; refinements in the procedure later lowered the limit to 0.03 ppm. The total CN (free CN plus complexed CN) was determined by a modified Serfass (17) method that is given in the appendix; the method involves converting all the CN to HCN, which is collected and measured. The Serfass method does not determine which of the complexed cyanides are present. The acceptable limit for iron-cyanide complexes in waste water is 6 ppm (9); the limit for total complexed CN has not been established.

TABLE 4. - Waste-plus-waste treatment of some concentrated wastes

Test	CN waste + acid waste	Final pH	Analysis of filtrates, g/l[1]								ml HCN evolved per liter CN waste
			Free CN, ppm	Total CN, ppm	Ag	Co	Cr	Cu	Fe	Ni	
1	A2+Cr-B2	5	[2]<0.08				0.09	0.20		<0.001	
2	A2+Cr-B3	6	[2]<.08				.11	.25		<.001	
3	A2+HNO_3-A1	7	.05					.05	<0.001	.009	1.4
4	B3+HNO_3-A1	7-8	[2]<.03	9	0.07			.19	<.011	.19	[2]<.06
5	B4+HNO_3-A1	7-8	[2]<.03	3	.07			.01	<.005	.04	1.0
6	B1+HNO_3-A1	7-8	[2]<.03	2	.01			.17	<.010	.015	.43
7	B2+HNO_3-A1	7-8	[2]<.03	4	.01			.22	<.010	.14	.23
8	B3+HNO_3-A2	7	[2]<.03	4	.17	0.05		.92	<.013	.35	4.2
9	B1+HNO_3-A2	7	[2]<.03	9	.03	.03		.39	<.011	.23	2.0
10	B4+HNO_3-A2	7	[2]<.03		.45			.06	<.01	.06	2.7
11	B2+HNO_3-A2	5	[2]<.03		.004	.027		.16	.018	.18	31
12	B3+Cr-B3	6	[2]<.03		.24		1.4	.41	<.01	<.01	6.7
13	B1+Cr-B2	6	[2]<.03		.11		1.5	.32	<.01	<.01	12

[1] CN analysis is ppm.
[2] Not detected.

Table 4 also indicates that small but widely varying amounts of HCN (in milliliters HCN at 25° C and atmospheric pressure) were produced when the various wastes were combined. The largest amount (test 11) corresponds to only 0.4 cubic feet of HCN per 100 gallons of CN waste, which could easily and safely be neutralized in a commercial plant by bubbling it through a NaOH solution. The amount of HCN produced probably depends on the rate of addition of the acid waste, the intensity of stirring, and the compositions of the

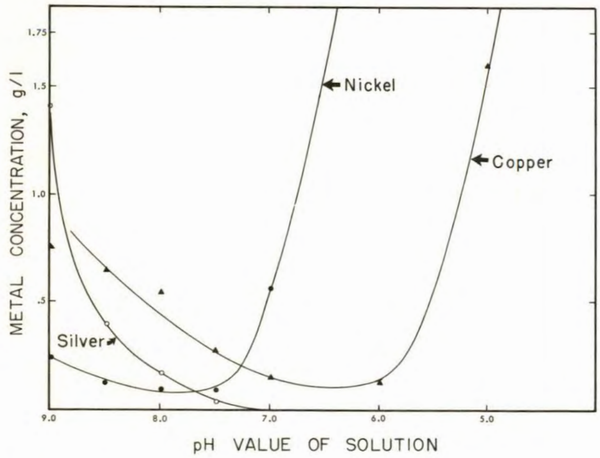

FIGURE 4. - Analyses of filtrates from addition of HNO_3-A1 waste to CN-B1 waste.

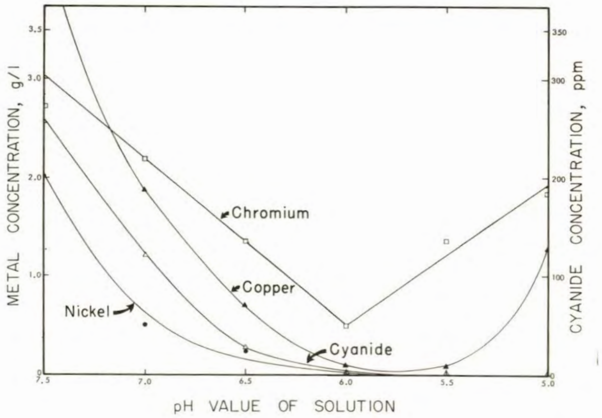

FIGURE 5. - Analyses of filtrates from addition of Cr-B1 waste to CN-A1 waste.

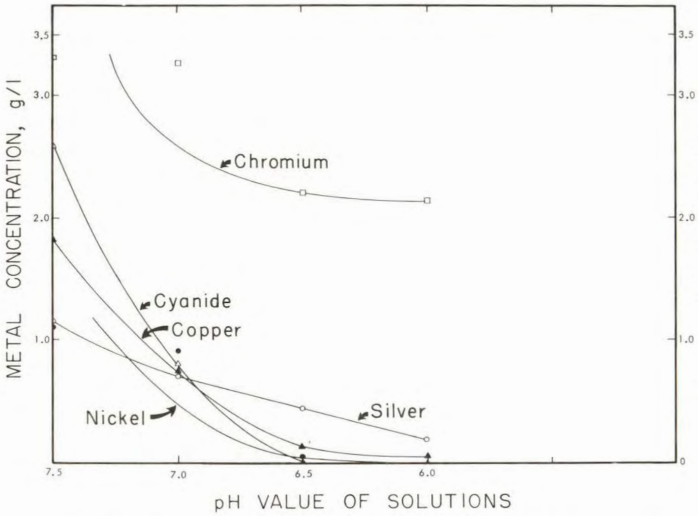

FIGURE 6. - Analyses of filtrates from addition of Cr-B1 waste to CN-B1 waste.

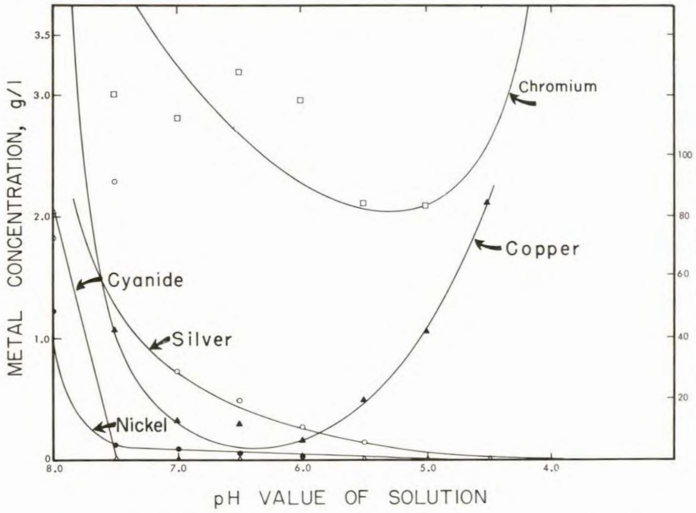

FIGURE 7. - Analyses of filtrates from addition of Cr-B1 waste to CN-B3 waste.

wastes being treated. With a deficiency of metal ions in both wastes, a larger evolution of HCN would be expected. With inadequate stirring, more HCN would be evolved by localized pockets of acid. The allowable limits in drinking water of some of the metals listed in table 4 are, in ppm: Ag 0.05, Cr^{6+} 0.05, Cr^{3+} 1, Cu 1, Fe 0.3, and Ni 2 (21). Although the filtrates do not meet drinking water standards, comparison of tables 2 and 4 shows the enormous reduction in concentrations of dissolved metals and CN after the WPW step. The chromium in the WPW filtrates is probably water-soluble, hexavalent chromium.

Some of the WPW slurries were easy to filter, others were less so. For the latter slurries, centrifugation or sedimentation are alternative methods of separation.

Further analyses of WPW filtrates, at or near the optimum final pH values, are given in table 5. The major impurity is either sodium nitrate or sodium sulfate, depending on the type of acid waste used. Free CN was not detected in any of these filtrates. Sodium m-nitrobenzenesulfonate (from the CN wastes) and its decomposition products probably account for the carbon content of these filtrates. Although these filtrates do not meet all water quality standards, a large percentage of the original toxicity was removed by the WPW treatment. Dilution or further treatment would be required to meet all the Public Health Service standards for drinking water; allowable limits for sulfate and nitrate ions are 250 ppm and 45 ppm, respectively (21).

TABLE 5. - Partial analysis of filtrates from waste-plus-waste treatment of some concentrated wastes, g/l[1]

Test	CN waste + acid waste	Final pH	Free CN, ppm	Total CN, ppm	Total C	Na	NO_3	Total S
1	A1+Cr-B2	6	[2]<0.08		3.5	19.9	4.1	18.7
2	A1+Cr-B3	6	[2]<.08		4.2	16.4	5.9	25.7
3	A1+HNO_3-A1	7	[2]<.08		4.0	14.5	48.2	.5
4	A1+HNO_3-A2	7	[2]<.08		5.4	13.1	41.0	.5
5	A2+HNO_3-A1	6.5	[2]<.03		4.6	12.4	16.3	.3
6	B3+HNO_3-A1	8	[2]<.03	23	8.8	22.6	20.3	.6
7	B4+HNO_3-A1	8	[2]<.03	62	3.7	10.1	13.6	.3
8	B1+HNO_3-A1	8	[2]<.03	16	6.8	18.4	12.7	.7
9	B2+HNO_3-A1	8	[2]<.03	10	7.2	19.4	22.3	1.4
10	B3+HNO_3-A2	7	[2]<.03	4	11.7	28.7	29.7	.8

[1] CN analysis is ppm.
[2] Not detected.

To determine the extent of applicability of the WPW procedure, tests were made on dilute rinse wastes in which a mixed acid (MA) waste was added to a CN waste. The results are given in table 6. The final number in the nomenclature is a batch number. In some tests a small amount of a more concentrated acid waste was added to the MA waste before the neutralization step to assist the precipitation of CN. In the first six tests in table 6 no such addition was made. The CN contents of the filtrates from the 1-hour tests (tests 4-6) were not as low as desired. In a 3-hour test (test 3, 1 hour addition followed by 2 hours mixing) the free CN was reduced to an undetectable level. Additions of small amounts of HNO_3 or Cr wastes resulted in very satisfactory removal of CN in tests of shorter duration (tests 8-12). The addition of ferrous iron (as $FeSO_4 \cdot 7H_2O$) removed the free CN effectively but not the complexed CN (tests 14-15). Only very small amounts of HCN were evolved.

Cadmium and Zinc Electroplating Wastes

Wastes containing Cd, Cr, Cu, Ni, and Zn constitute the most serious pollution problems in the electroplating industry. Treatment of wastes containing Cr, Cu, and Ni has already been described. The results of applying the WPW treatment to both concentrated and dilute wastes containing cadmium (Cd) and zinc (Zn) are given in tables 7 and 9. In the tests summarized in table 7, the acid wastes used were nitric acid (HNO_3) rack-stripping solutions and a chromium etching solution from company F (Cr-F). The first three lines in table 7 give the compositions of the Cd, Zn, and Cr-F wastes. Most of the WPW filtrates met the Public Health Service standards for free CN. The best results of the treatment of the Cd waste were obtained at a final pH value of 8, partly because most of the cadmium was precipitated as the hydroxide (cadmium cyanide is soluble in water). The cadmium concentration in the filtrate was less than 1 pct of that in the original waste. At pH 7, more cadmium stayed in solution and more nickel (from the HNO_3 waste) appeared in the filtrate. The zinc waste was most effectively treated by adding the HNO_3 waste to a final pH value of 8. Only very small amounts of HCN were evolved in these tests. The limits for cadmium and zinc in drinking water are 0.01 ppm and 5 ppm, respectively (21).

TABLE 6. - Waste-plus-waste treatment of some dilute wastes

Test	Company D wastes	Addition to acid waste	Total addition and mixing time, hr	pH	Analysis of wastes and WPW filtrates, ppm												ml HCN evolved per liter CN waste
					Free CN	Total CN	Ca	Co	Cr	Cu	Fe	Mg	Na	Ni	Pb	Zn	
	CN-1			9.2	0.14	47	38		<1	20	<2	24	260	11	<1	<1	
	CN-2			9.4	59	344	<1		<1	150	5	20	590	<1		28	
	MA-1			3.2	[1]<.03	4.1	84	<1	45	4	<2	25	110	<1		5	
	MA-2			2.9			72		<1	<1	<1	30	110			10	
1	CN-1 + MA-1	None	3	7	.05	14			12	2	<2			7		<1	[1]<0.31
2	CN-1 + MA-1	None	3	6	.09	7.8			30	<2	<2			5		3	1.0
3	CN-1 + MA-1	None	3	5	[1]<.03	5.9			22	<2	<2			2		3	3.9
4	CN-1 + MA-1	None	1	7	.07	11											1.0
5	CN-1 + MA-1	None	1	6	.11	5.1											.63
6	CN-1 + MA-1	None	1	5	.05	3.3											1.3
7	CN-1 + MA-1	5% HNO_3-A2	1	7	.03	15											[1]<.31
8	CN-1 + MA-1	5% HNO_3-A2	1	6	[1]<.03	7.8											[1]<.31
9	CN-1 + MA-1	5% HNO_3-A2	1	5	[1]<.03	6.9											.35
10	CN-1 + MA-1	5% Cr-C	1	5	.07	9.2											.68
11	CN-1 + MA-1	5% Cr-C	2	5	[1]<.03	10											1.4
12	CN-2 + MA-2	10% Cr-C	1-1/2	6	[1]<.03	1.2											12
13	CN-2 + MA-2	10% Cr-C	5	5	[1]<.03	1.5											7.6
14	CN-2 + MA-2	8.2g/l Fe^{++}	3/4	6	[1]<.03	185											4.6
15	CN-2 + MA-2	8.2g/l Fe^{++}	3/4	5	[1]<.03	88											13

[1] Not detected.

TABLE 7. - Waste-plus-waste treatment of concentrated cadmium and zinc cyanide wastes

Company E CN waste	Acid waste	pH	Analysis of wastes and WPW filtrates, g/l[1]									ml HCN evolved per liter CN waste
			Free CN, ppm	Total CN, ppm	Cd	Cr	Cu	Fe	Na	Ni	Zn	
Cd		13.9	12,000	44,900	7.3		0.11	2.9	44.2			
Zn		13.6	1,390	6,100			.001	.69	38.0		9.4	
	Cr-F	<.1				19.1	25.5	.04			34.0	
Cd	HNO_3-A1	9	.14	2,000	<.013		.70	.026		1.55	<.013	0.17
		8.5	.10	406	<.011		.74	.023		.26	.011	.27
		8	.05	94	.06		.43	<.01		.14	.13	.28
		7	[2]<.03	150	.64		.41	<.01		4.0	.18	.14
Zn	HNO_3-A2	8	[2]<.03	5.5			.12	.012		.58	.13	.25
		7	[2]<.03	8.9			.30	.014		3.7	1.4	.22
		6	[2]<.03	1.3			.32			4.1	1.4	.62
Zn	Cr-F	8	.20	201		1.97	1.62	.011		.08	.36	.39
		7	.29	178		1.43	1.23	.013		.09	.57	.23
		6	[2]<.03	8.9		.57	.84	<.01		.03	.87	3.2
		5	[2]<.03	3.6		.52	.56	<.01		<.01	3.2	21.8

[1] CN analysis is ppm.
[2] Not detected.

Partial compositions of some dilute electroplating wastes (rinses) containing cadmium cyanide (CN-Cd) and zinc (CN-Zn, HCl-Zn) are given in table 8. The results of WPW tests on these solutions are given in table 9 (the residues left after the evaporation of the WPW filtrates were too small to analyze). The solutions were stirred 1 hour after neutralization and before filtration. The first three lines in the table are the wastes; the next two lines are combinations thereof. The CN contents of the filtrates were not as low as desired. To correct this, either 10 pct of a chromium anodizing waste (Cr) or 5 pct of a nitric acid rack-stripping waste (HNO_3) was added to the acid waste before the neutralization step (balance of table). The data indicate the following: Results were best when 5 pct HNO_3 was used, not as good when 10 pct of the Cr waste was used, and worst when neither of these wastes were used. Results were better for the CN-Zn rinse than for the CN-Cd rinse, possibly because the CN-Cd rinse is so much more concentrated. The results of tests 6-8 were entirely satisfactory. The filtrate from test 4 meets the stringent standards for free CN but not for total CN. In tests on the CN-Cd rinse, it appears that there were insufficient metal ions to precipitate all the cyanides; consequently more HCN was evolved.

TABLE 8. - Partial analysis of dilute cadmium and zinc wastes

Company G waste	Analysis, g/l						
	Cd	Co	Cr	Cu	Fe	Na	Zn
CN-Cd	0.29	<0.001	<0.001	0.008	0.04	4.35	0.03
CN-Zn	<.001		<.001		.007	.30	.04
HCl-Zn	<.001	<.001	<.001	<.001	.10	.02	.32

TABLE 9. - Waste-plus-waste treatment of dilute cadmium and zinc wastes

Test	Company G wastes	Addition to acid waste	pH	CN content of wastes and WPW filtrates, ppm		ml HCN evolved per liter CN waste
				Free	Total	
	CN-Cd		11.9	1,350	1,470	
	CN-Zn		11.3	39	61	
	HCl-Zn		2.5			
1	CN-Cd+HCl-Zn	None	5	14	280	82
2	CN-Zn+HCl-Zn	None	5	2.1	11	8.7
3	CN-Cd+HCl-Zn	10% Cr-C	5	6.6	167	155
4	CN-Cd+HCl-Zn	5% HNO_3-A2	5	.04	229	28
5	CN-Zn+HCl-Zn	10% Cr-C	5	.04	12	7.5
6	CN-Zn+HCl-Zn	5% HNO_3-A2	7	[1]<.03	6.8	.05
7	CN-Zn+HCl-Zn	5% HNO_3-A2	6	[1]<.03	5.2	.04
8	CN-Zn+HCl-Zn	5% HNO_3-A2	5	[1]<.03	6.3	.07

[1] Not detected.

According to an official of the U.S. Environmental Protection Agency, the WPW process will probably find widespread use in industry as an inexpensive first step to remove essentially all of the cyanides and most of the metals from electroplating and other wastes, followed by conventional water purification treatment to remove the remaining pollutants.

Recovery of Metals and Alloys From Cyanide Precipitate

In some tests, the mixed metal cyanide precipitate was heated in air at 250° C, which converted the metals to oxides and destroyed the CN. The oxides were identified by X-ray diffraction as NiO, CuO, and FeO. When heated in air the mixed cyanides ignited and oxidized spontaneously, possibly due to the presence of organic compounds and occluded nitrates. The mixed metal oxides were digested at 100° C for 2 hours in 10 pct H_2SO_4 solution, which converted about 95 pct of the oxides to sulfates. The acid solution was filtered and evaporated nearly to dryness. This product was dissolved in water and the pH was adjusted to about 2.5 by adding $Ca(OH)_2$, which caused the precipitation of $Fe(OH)_3$ and $CaSO_4$. After filtration, copper was recovered from the filtrate by controlled potential electrolysis at 0.1 to 0.3 volt. The copper deposits contained approximately 0.01 pct nickel; no iron was detected. For analytical purposes, the remaining $NiSO_4$ solution was evaporated to dryness; the residue contained, in pct, 32.9 Ni, 0.02 Cu, and 0.01 Fe. According to an industrial electroplater, this nickel solution could be recycled directly to plating baths.

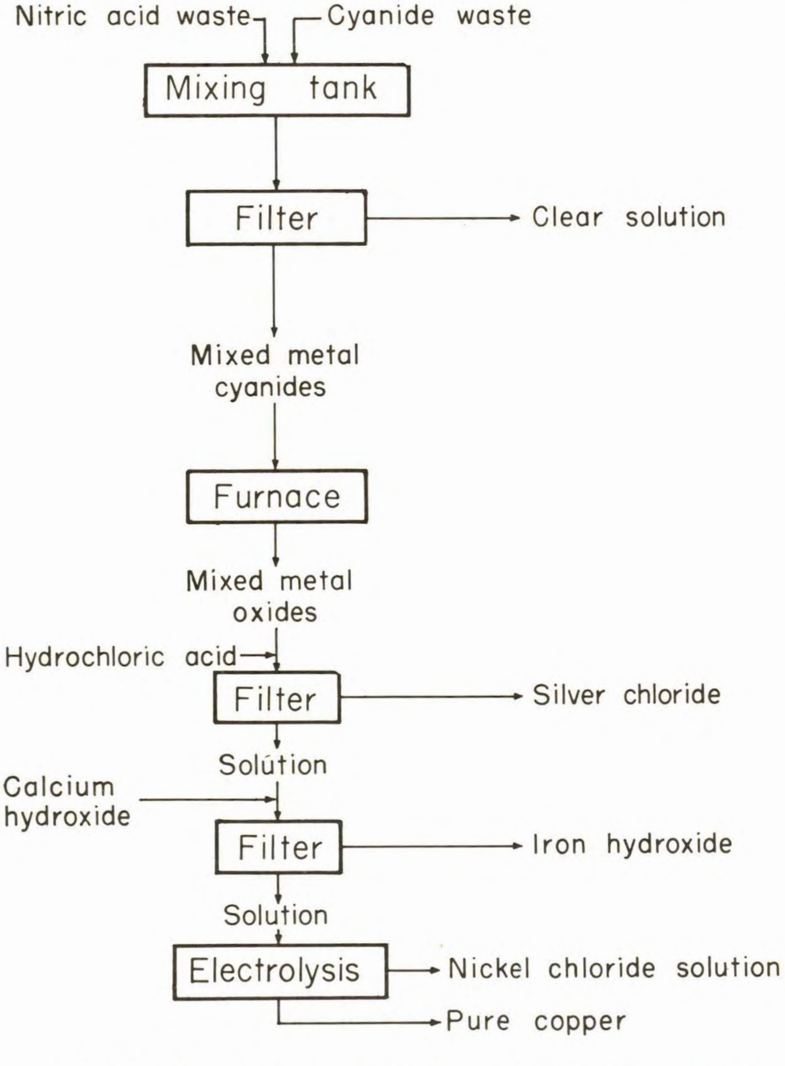

FIGURE 8. - One variation of metal recovery process.

A pollution-free alternative to the furnacing of the mixed metal cyanide precipitate would be to treat the precipitate with acid in a closed vessel to convert all the cyanides to HCN gas, and use a carrier gas to bubble the HCN through a NaOH solution to produce NaCN for recycling back to electroplating baths.

In other tests the mixed metal oxides were pelletized (1/4- to 1/2-inch diameter) with an aqueous starch solution binder. In 2-hour tests, one batch was reacted at 600° C with CO, another batch at 700° C with hydrogen, and a third batch at 900° C with hydrogen. All of the pellets were reduced and contained, in pct, 63 Ni, 33 Cu, and 0.9 Fe. The mechanical strength of the reduced pellets increased with increasing temperature. Another alloy produced by this method contained about 60 pct copper and 40 pct nickel. These mixed metal pellets probably could be used in the production of Monel or similar alloys.

A number of variations in the recovery procedure was employed; the variation shown in figure 8 was used when silver was present. Nickel carbonate could be used in place of $Ca(OH)_2$ in this procedure. The dried AgCl product was heated for 2 hours at 1,000° C with an equal weight of a salt mixture consisting of 75 pct NaCl and 25 pct Na_2CO_3. After cooling, the salts were washed away with water, leaving a button of metallic silver that contained, in pct, 99.1 Ag, 0.03 Cu, and less than 0.001 each of Ni and Fe.

CONCLUSIONS

The waste-plus-waste process is a promising and apparently inexpensive method of treating the major types of electroplating and etching wastes, containing Cd, Cr, Cu, Ni, and Zn, to neutralize the wastes and to recover practically all the metals and cyanides for recycling. If desired, the WPW process could be followed by conventional water purification treatment to remove the remaining contaminants. The process worked well on both concentrated and dilute wastes. The economic incentive for treating concentrated electroplating, etching, and anodizing wastes is especially great because of the low cost of mixing two wastes, the large quantities of valuable metals present, and the simplicity of the procedures for recovering the metals or alloys.

The WPW step requires no reagents, destroys most of the toxicity of the wastes, concentrates the metals in both wastes by precipitating them as cyanides and hydroxides, generates only very small amounts of HCN, and produces filtrates that meet the stringent Public Health Service standards for free cyanide ion content. Free cyanide was not detected in most of the filtrates. The process was also successfully used to recover silver from wastes. The filtrates from the waste combination step were relatively innocuous; even if they were discarded by industrial firms, most of the original pollution from this source would be eliminated. However, the filtrates would require dilution or further treatment to meet all the water quality standards. Chromium must be reduced to the trivalent form before it is recovered by the WPW process. In some combinations of wastes there were insufficient metal ions to precipitate all the cyanides; this situation was corrected by first adding a small amount of a more concentrated acid waste to the acid waste under study, before the neutralization step.

Because small amounts of HCN are produced by the WPW process, equipment for collecting and neutralizing this gas would be necessary in industrial installations. A ventilated mixing tank with instruments for monitoring the pH value and the cyanide concentration of the mixed wastes would be required. The air-HCN mixture from the mixing tank would be bubbled through a NaOH solution to produce a salable NaCN byproduct. Small electroplating plants could accumulate the mixed metal cyanides and hydroxides until enough is on hand to justify processing for recovery of metals and cyanides.

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APPENDIX.--MODIFIED SERFASS ANALYSIS FOR TOTAL CYANIDE CONTENT

The apparatus is shown in figure A-1. The procedure is as follows:

1. Place 100 ml of 1$\underline{M}$ NaOH solution in the scrubber trap.

2. Pour 100 ml of distilled or demineralized water into the round bottom flask.

3. Add 50 ml of 0.125$\underline{M}$ $HgCl_2$ and 25 ml of 2.5$\underline{M}$ $MgCl_2$ solution through the funneled ebulator tube.

4. Start suction through the scrubber side arm such that the ebulator bubbles every 2 or 3 seconds.

5. Add 10 ml of sample through the funneled ebulator tube.

6. After 2 minutes add 25 ml of concentrated orthophosphoric acid through the funneled ebulator tube.

7. Heat the sample rapidly with a heating mantle while regulating the internal pressure to produce bubbles every 2 or 3 seconds.

8. When reflux is obtained, allow the solution to reflux for at least 2-1/2 hours.

9. Remove the sample from the scrubber and dilute with nine times its volume of distilled or demineralized water.

10. Prepare standard cyanide solutions (10^{-2} to $10^{-5}$$\underline{M}$ CN) by diluting 0.1$\underline{M}$ NaCN stock solution with 0.1$\underline{M}$ NaOH stock solution. The stock solutions $\underline{\text{must}}$ be prepared not more than 7 days prior to making the standard cyanide ion solutions, which must be prepared fresh daily.

11. Standardize the cyanide specific ion electrodes using the standard solutions.

12. Analyse the unknown solution for CN using the standardized electrodes.

13. If the result is more than 1,000 ppm CN, dilute the original sample as needed and rerun the procedure.

To estimate the reliability of this analytical method for total CN, known weights of pure cyanide compounds were analyzed at different concentrations. The results, given in table A-1, show that the analytical error was lower at high CN concentrations than at low concentrations. The average error was 5.1 pct for concentrations of 50 to 520 ppm and 19 pct for concentrations of 2.5 to 25 ppm.

TABLE A-1. - Error in total CN analysis by modified Serfass method

CN concentration, ppm	Analytical error, pct		
	$K_3Fe(CN)_6$	$K_4Fe(CN)_6 \cdot 3H_2O$	2NaCN+CuCN
520	-10.0		-2.5
250	-13.0	-2.4	-10.4
100	-.4	-1.3	+4.9
50	-5.6	+1.2	+4.8
25	+4.8	+17.6	-36.3
5	-15.5	-20.0	-20.0
2.5	+8.9		+29.6

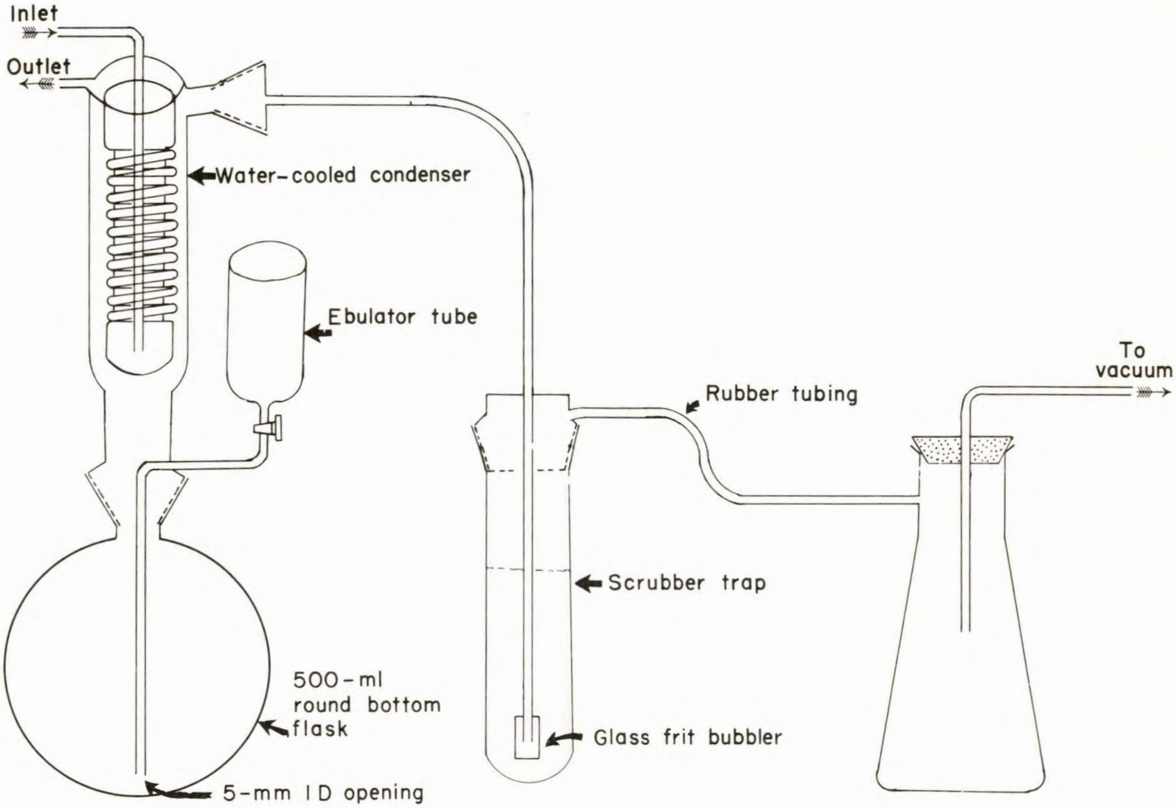

FIGURE A-1. - Apparatus for total cyanide analysis.

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