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RECOVERY OF NONFERROUS METALS FROM METAL FINISHING INDUSTRY WASTES

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ABSTRACT

Flexible schemes have been devised for recovery of nonferrous metals (copper, chromium, nickel and zinc) from metal finishing industry waste acids and hydroxide sludges. Evaluations conducted with bench scale experimentation established technical feasibility for adaptations of solvent extraction, precipitation and ion exchange separation processes. It was demonstrated with industrial waste samples that by tailoring several separation stages appropriate for specific waste compositions for complex mixtures of widely varying character that efficient separations can be achieved for copper, chromium, nickel or zinc from contaminant metals such as aluminum, chromium or iron.

INTRODUCTION

A principal objective of the present work has been to develop technically feasible separation regimes for some of the more complex industrial wastes containing non-ferrous metals, notably copper and nickel where the presence of metals of lesser economic value such as aluminum, chromium and iron are contaminating components that discourage recycling.

The separation processes selected have consisted primarily of solvent extraction, precipitation and ion exchange. Technical feasibility has been evaluated in bench scale experimentation using simulated waste mixtures and several industrial wastes, notably electrochemical machining sludges, spent catalysts, plating wastes, brass industry water treatment sludge and waste mineral acids.

The suggested separation regimes described here are considered to be applicable in large part to the difficult sludges created by past practices in cleaning up water effluents, many of which are now abandoned. There are many accumulations of waste solids on industrial sites created in past years but now made obsolete by more enlightened practice in minimizing toxic wastes. These accumulations may very well be potential superfund sites. It is evident that there are a number of incentives favoring recovery of nonferrous metals from industrial wastes such as the oxide/hydroxide solids. These incentives include waste volume minimization, detoxification, resource conservation and reduction in exposure of the generator or subsequent property owner to liability for creation of hazardous waste.

METAL RECOVERY FROM COMPLEX WASTES

Adaptations of hydrometallurgical separation processes are considered to by preferable to pyrometallurgical separation processes for a number of reasons (1).

1) lower capital costs
2) lower operating costs
3) potentially high metal recovery
4) potential for reduced labor costs through automatic control
5) reduced water and air pollution problems
6) greater suitablity for low grade and complex metal systems
7) provide advantages in by-product recovery and recycling

The adaptations of hydrometallurgical separation processes from conventional application to metal extraction from ores to waste systems requires some reorientation to deal with the significant differences in the character of these two kinds of systems. Metal finishing waste solids differ drastically in such parameters as

1) smaller total volumes of solids originating from a given source
2) higher concentrations for metals to be recovered

3) drastic differences in physical and chemical character of solid systems
4) more numerous geographic origins for wastes
5) greater variations in physical and chemical composition

A recent review has been conducted of the hydrometallurgical separation processes applicable to nonferrous metal wastes and a summary generated for the reduction to practice based on a systematic review of the chemical literature over the past ten years (2).

Separation processes applicable to metals in aqueous acid or alkaline solution consist of adsorption, cementation, electrowinning, ion exchange, membrane processes, precipitation and solvent extraction. Separation processes applicable to solid metal wastes consist of biological separations, flotation, magnetic separations, pyrometallurgy and solvent partition. Solubilization of the solid waste systems available for conversion to systems amenable to soluble metal separations can be achieved by a variety of procedures such as reaction with acids, alkalies, chlorination, sulfidization/sulfation, alloying, volatilization and certain biological reductions. Acid solubilization is the most applicable treatment process for metal oxide/hydroxide waste sludges.

Extensive work has been conducted by Twidwell, Dahnke, et al. (3,4) from bench scale to pilot plant for separation of complex metal wastes using separation processes such as sulfuric acid solubilization, iron separation by jarosite precipitation, copper separation by solvent extraction, cadmium and zinc separation by solvent extraction, chromium separation by precipitation as lead chromate and nickel by crystallization as a nickel sulfate.

In addition to these experimental evaluations there are at least two commercial plants notably Recontck and Encycle currently in operation for treating hazardous metal wastes in which nonferrous metal recovery is conducted (5,6) using a variety of hydrometallurgical separation processes.

The separation processes selected for the present work consist of solvent extraction, selective precipitation and ion exchange based on the state of development of these separation processes and the potential for application to actual industrial waste solids with favorable economics. Originality is not claimed for the individual separation processes but rather the object is to provide an insight how appropriate combinations of modified separation processes can achieve promising separations for actual industrial wastes. In addition to these separation processes, oxidation with hydrogen peroxide is used to destroy organic components present and in an alkaline environment to convert trivalent chromium to the hexavalent form to enhance separation by solubilization.

EXPERIMENTAL PROCEDURES

Solvent Extraction Separations

Solvent extraction can be conducted in stages with progressively increasing pH by addition of sodium hydroxide to optimize the separation of the metals of interest in complex acid solutions of metals (7). The extractions were conducted with three sequential 5 minute shake tests in a 250 ml deparatory funnel with 50 to 100 ml of the waste solutions and 50 ml of the extractant solution. Extraction agent concentrations ranged from 5 to 20 wt % and solvents consisted of naphtha, toluene, and xylene. Extraction agents consisted principally of commercial agents such as di-2-ethylhexyl phosphoric acid (Albright and Wilson DI2EHPA 95%), 2-hydroxy 5 nonyl bensophenone oxime (Henkel HSLIX 64N) various oximes (Henkel LIX 63, LIX622), dinonyl naphthalene sulfonic acid (King Industries SYNEX DN-052) and bis (2,4,4 trimethyl pentyl) phosphoric acid (American Cyanamid CYANEX 272) with extraction agents present in weight ratios of 5.0 to 25 the amounts of metal present in the aqueous phase.

The transfer efficiency of metal from the aqueous to the solvent phase was determined from analysis of the equilibrium metal concentrations in the aqueous phase following the shake tests. Metal analyses were based on atomic absorption analyses by a commercial analytical laboratory (Phoenix Environmental Laboratories, Manchester, CT).

Evaluations of metal recovery from the solvent phases were conducted by a two-stage extraction of the metal loaded solvent phases with 20 wt % H_2SO_4 with analysis of the metal recovered into the acid phases to establish metal recovery and solvent phase regeneration efficiency. Details on selection of extraction agents and experimental evaluations have been published (7).

Metal Separation by Precipitation

The evaluations of metal separation from acid solutions of mixed metals were conducted in limited pH range with precipitating agents (NaOH, Na_3PO_4, Sodium Oxalate) added in excess of no more than 20-25 wt % of the amount of the particular metal to be precipitated.

Hydroxide Precipitation. Iron hydroxide precipitations were conducted with NaOH at a maximum pH of 4.5 and in some cases with addition of 200 to 1000 PPM of selected anionic surfactants (acetic acid or ethylene diaminetetraacetic acid) prior to each pH adjustment with NaOH (8).

Phosphate Precipitation. Solid sludges containing trivalent metal cations, iron, chromium and/or aluminum, along with divalent metal cations, copper, nickel and/or zinc and solubilized in aqueous sulfuric acid were subjected to staged phosphate precipitation. Sodium phosphate in an amount 10 percent in excess of the stoichiometric amount for the iron present was mixed at room temperature with the solution adjusted for a pH range of 1 to 2 with sodium hydroxide. The iron phosphate precipitate was separated by filtration. Then sodium phosphate in an amount 10 percent in excess of the stoichiometric amount for the chromium present was mixed at room temperature with the solution adjusted to a pH range of 2.5 to 3.5 with sodium hydroxide. The chromium phosphate precipitate was separated by filtration.

Oxalate Precipitation. The oxalate precipitations of nickel were conducted with addition of sodium oxalate in a pH range of 4 to 5 in an amount 1.5 times the stoichiometric requirement for the nickel present (9).

Ion Exchange

The ion exchange separations of nickel were conducted with a chelate type resin (Amberlite XRC-718) following removal of iron, copper, aluminum, zinc and trivalent chromium.

Oxidation of Waste Solutions

Aeration of solutions with additions of 3 wt % hydrogen peroxide in a glass column with air dispersion was conducted at temperatures from 25 to 75 °C for destruction of organics, cyanide and organic complexing agents and for conversion of chromium (III) to the hexavalent state (VI). Aeration oxidation tests were conducted with 50-100 cm^3 of solution aerated with 100-200 cm^3/min. air flow at one atmosphere in a cylindrical glass column (5 cm x 45 cm) equipped with a fine dispersion frit for periods from 2 to 8 hours in a pH range of 2 to 6. The extent of oxidation destruction of the organic components was established by determination of the total organic carbon (TOC).

Alkaline/Oxidation Leach

Selected sludges containing high chromium were subjected to an alkaline leach with sodium carbonate in aqueous hydrogen peroxide. Sodium carbonate in an amount stoichiometric with the chromium present and with enough excess to provide a pH of at least 10 in 3 wt % hydrogen peroxide solution was mixed with the sludge, the mixture heated to a least 250 °C, the water was evaporated and the dried residue leached with fresh sodium carbonate and 3 wt % hydrogen peroxide solution to solubilize the trivalent chromium oxidized to hexavalent chromium as sodium chromate.

Separation Procedures for Nickel Wastes

Waste Systems. The nickel wastes consisted of electrochemical machining (ECM) filter cake, a nickel hydroxide sludge, a waste mineral acid, a spent nickel hydrogenation catalyst and a spent electroless nickel plating solution. The compositions are shown in Table 1.

TABLE 1

WASTE COMPOSITIONS

WASTE	COMPOSITION – WT % Fe	Cr	Cu	Ni	Zn	OTHER METALS (PPM)
ELECTROCHEMICAL MACHINING (ECM) FILTER CAKE	1.7	1.5	—	4.4	—	—
NICKEL HYDROXIDE SLUDGE	0.020	0.0076	0.78	5.7	0.0028	Sn 1100 Al 360 Ba 6 Pb 300
WASTE MINERAL ACID	0.71	0.0023	1.6	3.0	1.4	Cd 280 Mn 100 Pb 79 Sn 750
SPENT NICKEL CATALYST	—	—	—	25.0	—	—
SPENT ELECTROLESS NICKEL	0.0027	0.00013	0.0017	0.288	0.0020	Pb 8.7

Separation Regime. A seven stage separation regime was used to make the desired metal recovery and make the effluent suitable to meet EPA emission standards (Fig. 1.)

In Stage 1 the solid wastes, the ECM filter cake, the nickel hydroxide sludge and the nickel catalyst were solubilized in 20 wt % H_2SO_4.

In Stage 2 the acid solutions of the wastes were adjusted with NaOH of $Na_2CO_3$to bring the pH into a range of 2-6.

In Stage 3 nonselective solvent extraction was conducted to remove contaminant metals such as iron, copper or zinc. Binary mixtures of diethylhexyl phosphoric acid (DI2EHPA) and LIX agents (LIX 64 or LIX 622) consisting of 20 wt % in naphtha solvent were used at pH 3 to remove copper and iron. Solvent extractions in naphtha solvent were used at a pH range of 5 to 6 with binary mixtures of DI2EHPA plus LIX 64 (LIX 63) as 20 wt % in naphtha solvent if zinc as well as copper and iron were present.

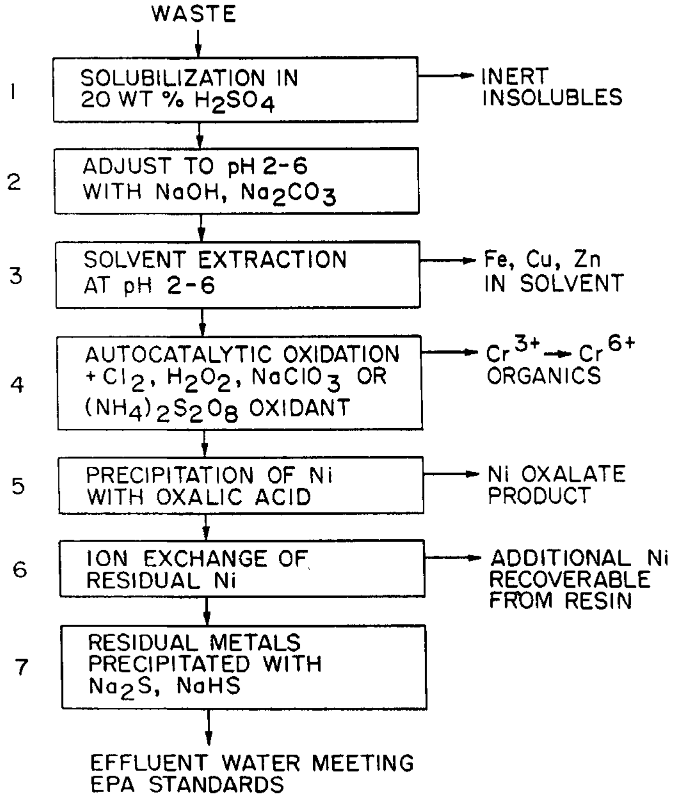

Figure 1 **SEPARATION STAGES**

In Stage 4 additions of 3 wt % H_2O_2 were used to oxidize the Cr^{3+} to Cr^{6+} and destroy organics present.

In Stage 5 oxalic acid was added in about 25% excess of stoichiometric of the amount required to form the insoluble precipitate of the oxalate with the nickel present in solution.

In Stage 6 the treated solutions from stage 5 were passed through a bed of chelate-type cation exchange resin (Amberlite XRC718).

In Stage 7 the residual metals were precipitated with NaHS addition and filtered to remove these metals as the sulfides.

TABLE 2

SUMMARY OF SEPARATION RESULTS

WASTE	WASTE NICKEL CONTENT (WT %)	SEPARATION STAGES	NICKEL WT % RECOVERED BY OXALATE PRECIPITATION	NICKEL WT % RECOVERED BY ION EXCHANGE	RESIDUAL NICKEL (PPM)
E C M	4.4	1, 2, 3, 5, 6	99.0	0.88	3.5
NICKEL HYDROXIDE	5.7	1, 2, 3, 5, 6	96.9	3.0	6.0
MINERAL ACID	3.0	2, 3, 5, 6	96.9	3.1	10.0
NICKEL CATALYST	25.0	1, 2, 5, 6	99.9	0.07	18.0
ELECTROLESS NICKEL	0.29	4, 6	92.5	2.2	217.0

RESULTS AND DISCUSSION

The results of separation schemes for several industrial wastes: five nickel wastes, two plating wastes and a brass industry water treatment sludge, from bench scale evaluations are described here.

Summary of Nickel Separations Results

The results of the nickel separations for the five wastes using the separation regime in Fig. 1 are summarized in Table 2. By using all six separations stages with the ECM filter cake and the nickel hydroxide sludge nickel recoveries of 99.0 and 96.9 wt % respectively as the oxalate were obtained. Additional recoveries of 0.88 and 3.0 wt % of the nickel were recovered using the sixth ion exchange separation stage. By using separation stages 2 through 6 but omitting the oxidation stage 4, nickel recoveries better than 99.9 wt % were obtained. By using four stages, 1, 2, 5 and 6, and omitting the solvent extraction (stage 3) and oxidation (stage 4) nickel recoveries better than 99.9 wt % were obtained. The electroless nickel waste separation was the least successful. Using oxidation and ion exchange stages (4 and 6) only a nickel recovery of 94.7 wt % nickel and a relatively high residual nickel concen-

TABLE 3

CHROMIUM AND IRON SEPARATION BY PHOSPHATE PRECIPITATION

SOLID WASTE	METAL	* INITIAL METAL PPM	FINAL METAL CONC. IN SOLUTION - PPM		
			IRON PHOSPHATE PRECIPITATION	COPPER SOLVENT EXTRACTION LIX 64N	CHROMIUM PHOSPHATE PRECIPITATION
			pH3		
Chromium-Nickel plating waste	Fe	1200.	7.3 (0.989)		
	Cu	330.	2.4 (0.988)		
	Cr	22000.	170. (0.986)		
	Ni	730.	17. (0.959)		
	Zn	40.	1.0 (0.955)		
			pH2	pH2	pH4
Brass* Industry Sludge	Fe	9200	1100 (0.89)		
	Cu	7400	2300 (0.73)	330 (0.97)	
	Cr	1100	360 (0.71)		52 (0.96)
	Ni	190	67 (0.69)		47 (0.80)
	Zn	3300	1100 (0.71)		510 (0.87)

* Solubilized in 20 wt% H_2SO_4

Note: values in parantheses are total weight fractions of metal removed at given separation stage.

tration, 217 PPM was obtained. The nickel residuals obtained for these systems using the sulfidation precipitation can reasonably be expected to meet EPA emission standards. A more extended discussion of these separations has been published (10).

Plating Wastes

Two plating wastes were examined to develop metal recovery options. One waste was a mixed metal hydroxide, generated in cleaning up waste waters from spent plating solutions. This waste consisted principally of chromium (22 wt %) with minor amounts of nickel (0.7 wt %), copper (0.3 wt %) and iron (1.2 wt %). A second waste consisted of a spent electroless nickel plating solution which contained appreciable residual nickel (2790 PPM) and one or more organic complexing additives, (such as acetic, aminoacetic, hydroxyacetic, citric, lactic, malic, succinic or ethy-

TABLE 4

CHROMIUM SEPARATION BY ALKALINE/OXIDATION LEACH

SOLID WASTE	METAL	INITIAL METAL CONC. WT. FRACTION	METAL WT. FRACTION SOLUBILIZED IN Na_2CO_3/H_2O_2 LEACH
Chromium - Nickel Plating	Cr	0.22	0.92
	Cu	0.003	0.02
	Ni	0.007	0.02
Brass Water Treatment Sludge	Cr	0.09	0.90
	Cu	0.09	0.11
	Zn	0.05	0.22

lene diaminetetraacetic (EDTA) acids); a reducing agent, sodium hypophosphite, and possibly a stabilizer typical of electroless plating solutions.

In the case of the first plating waste (Table 3) recovery of both chromium and nickel was desired. One separation alternative examined consisted of phosphate precipitation of the acid solubilized mixed hydroxide with the objective of precipitating the trivalent iron and chromium leaving the nickel in solution for subsequent concentration and recovery. Twidwell and Dahnke (4) have reported considerable success for separations of chromium (III) and iron (III) from divalent cations such as copper, nickel and zinc in an acid pH regime. Efforts to achieve separation of chromium (III) and iron (III) by addition of sodium phosphate within the pH range of 1 to 3 were successful but at the expense of unacceptable losses of copper, nickel and zinc by coprecipitation with the chromium and iron phosphates (Table 3). Using a two stage phosphate precipitation and employing a copper solvent extraction prior to or after the initial iron phosphate precipitation provided no additional advantage for the metal separations desired.

TABLE 5

METAL CONTAMINANT REMOVAL BY SOLVENT EXTRACTION - ELECTROLESS NICKEL
(Single stage extraction at pH 5 with LIX 63 + Di2EHPA)

Metal (Initial PPM)	% Metal Extracted	PPM Residual Metal
Fe (27)	3.0	26.2
Cu (17)	74.0	4.5
Ni (2790)	17.0	2320.0
Zn (20)	95.0	1.1
Cr (1.3)	76.0	0.31
Pb (8.7)	67.0	2.9

A sceond separation approach for the first plating waste that proved more successful consisted of an alkaline (NaOH) oxidation (H_2OH_2) leach of the mixed metal hydroxides as received. Using the leaching process, which has been described above, the bulk of the chromium could be recovered as a solution of sodium chromate, suitable for concentration and recovery, leaving a concentrated residue of the iron and nickel (Table 4) suitable for recovery as a nickel or stainless steel recycle feed stock.

The second waste consisting of a spent electroless nickel was evaluated for nickel recovery or possible rehabilitation by contaminent removal. A promising treatment consisted of mild air oxidation to destroy the organic complexing agents followed by nickel recovery as the oxalate. A modification of the separation scheme devised for nickel wastes was used. This simplified separation regime appropriate for an electroless plating solution, consisted of destruction of the bulk of the organics by aeration oxidation at 25-75 ° C followed by separation of the nickel with a promising high recovery of 99.7 percent as the insoluble oxalate, with a purity providing potential marketability.

An alternative to the treatment (Table 5) for the spent electroless nickel plating solutions which consisted of oxidation destruction of the organic components and nickel separation as insoluble oxalate is rehabilitation by non-selective solvent extraction (11) removal of the contaminant metals iron, copper, zinc, chromium (III) and lead using a binary mixture of LIX 63 and DI2EHPA (20 wt %) in naphtha solvent at pH5. High removals of all these contaminant metals except iron were obtained in a single stage extraction. Some nickel (17%) is lost in the process but the refined electroless nickel can be replenished with fresh nickel salts and the chemical additives, providing the organics have not undergone degradation.

Brass Industry Water Treatment Sludge

The most formidable waste examined, a brass industry water treatment sludge, consisted of a complex mixture of hydroxides of iron, chromium (III), copper, nickel and zinc with a low concentration of organics of indeterminate composition. The composition of this hydroxide mixture after solubilization in 20 wt % H_2SO_4 is shown in Table 3.

One separation alternative evaluated was the phosphate precipitation described above that was also applied to the chromium-nickel plating sludge (Table 3). Efforts to enhance the separation by solvent extraction with LIX agents prior or after the iron phosphate precipitation in a two stage separation regime did not improve the separations. It is evident that for this waste iron and chromium removed by phosphate precipitation occurs at a high level but with an unacceptable coprecipitation of the copper and zinc that are also potentially attractive recovery candidates.

The most successful separation alternative for this acid solubilized brass industry waste was the alkaline/oxidation leach to separate the chromium as sodium chromate (Table 4). Metals such as copper and zinc which are insoluble in the sodium carbonate-hydrogen peroxide leach solution can be solubilized in 20 wt % H_2SO_4 and subjected to staged solvent extraction for recovery if present in amounts providing attractive economics using a separation scheme such as shown in Fig. 1.

CONCLUSIONS

The incentives for metal separation and waste detoxification consist of 1) creation of metal credits to offset treatment cost, 2) waste minimization and resource conservation, and 3) avoiding exposure to liability for generation of hazardous waste.

The results presented here for several diverse waste systems have demonstrated on a bench scale that by adapting established conventional separation technology that feasible recovery schemes can be devised to recover nonferrous metals, notably copper and nickel from complex industrial waste sludges. The accumulations of industrial water treatment sludges that are the inheritance from now obsolete practices and that are potential candidates for superfund status are the wastes most appropriate for consideration of these adaptations of hydrometallurgical processes for detoxification if not metal recovery.

Acknowledgement is made to Lewis Publishing Co for permission to use copyrighted material from Ref. 10 for Figure 1 and Tables 1 and 2.

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