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Project Summary

Recovery of Metals from Sludges and Wastewaters

This report presents information on the state-of-the-art of metals recovery technologies to assist in identifying waste-management options for metal-bearing sludges and wastewaters that may be regulated under the Resource Conservation and Recovery Act (RCRA). Only a few of the technologies addressed in this report (e.g., electrowinning, high-temperature metals recovery [HTMR]) are directly applicable to the recovery of metals from wastes; other technologies treat the wastes to a physical form that may be amenable to eventual metals recovery.

Wastewaters can be treated effectively by several methods. Precipitation processes have been widely used to remove arsenic, cadmium, chromium (+3), copper, iron, manganese, nickel, lead, and zinc from metal-bearing wastewaters. For economic reasons, electrowinning is a commercial technology that has normally been restricted to the treatment of wastewaters containing noble metals such as gold and silver.

After appropriate pretreatment, sludges can be effectively treated by HTMR processes. These processes allow for the direct recovery of metals from sludges. The economic feasibility depends on the amount of sludges treated and the amount of metals contained in the sludges. Membrane separation processes such as microfiltration (MF) and ultrafiltration (UF) can be used in combination with chemical treatment for the physical separation of metal sludges. Leaching may be used to extract cadmium, chromium, copper, lead, nickel, and zinc directly from sludges by using various process trains.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Section 3004 of the Resource Conservation and Recovery Act (RCRA), as amended by the Hazardous and Solid Waste Amendments of 1984, prohibits placing untreated RCRA-regulated hazardous wastes in or on the land. Waste management options are needed to help recyclers comply with these regulations. In the full report, summarized here, we address the following processes that are amenable for recovery of metals from hazardous wastes: chemical precipitation, electrolytic recovery, HTMR, membrane separation, leaching, ion exchange and evaporation. For each of these technologies, the following parameters are summarized: (1) design specifications of applicable processes, (2) waste characteristics affecting performance, (3) pretreatment/posttreatment requirements, (4) available performance data, and (5) availability of the technology and feasibility for treating various hazardous waste categories.

Waste Chacterization

This report covers nine major metal-waste-producing industries:

(1) metal coatings; (2) smelting and refining of nonferrous metals; (3) paint, ink, and associated products; (4) petroleum refining; (5) iron and steel manufacturing; (6) photographic industry; (7) leather tanning; (8) wood preserving; and (9) battery manufacturing. Waste streams from each of these industries have unique characteristics; however, the wastes also contain common metals, such as aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), silver (Ag), and zinc (Zn).

Table 1 presents the number of metal-waste generators (as of 1983) by Standard Industrial Classification (SIC) code for the major industry categories discussed in the report.

Table 2 indicates the amount and number of generators of metal-bearing wastes by D (wastes which are hazardous because they exhibit a particular hazardous characteristic), F (wastes from non-specific sources), and K (wastes from specific sources) EPA hazardous waste codes. Until very recently, only about half of the industries that generate metal-bearing wastes recovered the metals from wastewaters and sludges.

Table 3 presents brief descriptions of the hazardous wastes generated from the major industry categories included in the report.

Table 1. *Number of Major Metal-Waste Generators, by SIC Code, in 1983*

SIC Code No.	SIC Description	No. of Facilities
3471	Plating and surface finishing	4,287
2851	Paints and allied products	2,145
3479	Metal coating and allied products	2,902
3714	Motor vehicle parts and accessories	4,151
2819	Industrial inorganic chemicals	2,183
3341	Metals, nonferrous, secondary	876
3400	Fabricated metal products	55,380
9711	National security	393
3721	Motors and generators	966
3900	Miscellaneous manufacturing industries	32,867
3356	Metal, nonferrous, rolling, drawing	384
2893	Printing ink	609
3312	Blast furnaces, steel mills	1,229
3321	Foundries, gray iron	1,229
4911	Electric services	2,614
2869	Industrial organic chemicals	1,160
2821	Plastics material	1,529
3662	Radio and TV communication equipment	4,656
3679	Electronic components	5,392
3711	Motor vehicle bodies	1,040
3545	Machine tool accessories	3,432

Table 2. *Nationwide Metal-Waste-Generation Data by Waste Group*

	Waste Volume, 10^6 gal/yr	Percent of Total Metals	Number of Generators
D Wastes	3685	46.9	3860
F Wastes	3920	49.9	2091
K Wastes	219	2.8	402

Metals Recovery Technologies

Chemical Precipitation

Precipitation of metal-laden wastewaters involves adding chemicals to alter the physical state of the dissolved or suspended metals and to facilitate their removal through sedimentation. These precipitates may then be processed further for metals recovery. Chemicals used to effect precipitation include: caustic soda, lime, ferrous and sodium sulfide, soda ash, sodium borohydride, and sodium phosphate. Some wastewater constituents, e.g., hexavalent chromium, cannot be effectively precipitated without first chemically reducing the metal to a more favorable form for precipitation. Reducing agents typically used by industry include sulfur dioxide, sodium bisulfite, sodium metabisulfite, and ferrous sulfate. Coagulation chemicals may be needed to enhance settling times of the precipitated metal particles. Examples of coagulants currently used by industry include lime, alum, and synthetic polyelectrolytes.

Chemical precipitation is commonly used to treat metal-bearing wastewaters from electroplating, pigment manufacture, the photographic industry, leather tanning, wood preserving, the electronics industry, battery manufacture, and nonferrous metal production. Approximately 75% of all electroplating facilities use precipitation in the treatment of their wastewaters. The process is several decades old, and chemical feed reagents are being improved to yield better metal removals from the aqueous phase.

Specific waste characteristics that affect the performance of chemical precipitation systems include (1) the concentration and type of metals, (2) the concentration of total dissolved solids, (3) the concentration of complexing agents, and (4) the concentration of oil and grease.

Pretreatment of wastewaters before metals precipitation can involve segregation, removal of large solids, flow equalization, cyanide destruction (if applicable), chrome reduction, oil separation, neutralization, and/or waste treatment of the individual process streams.

Sand filtration is a common post-precipitation/sedimentation effluent treatment technique. If concentrations in the effluent do not meet discharge standards, additional metal treatment technologies (e.g., ion exchange, reverse osmosis) may be needed.

Electrolytic Recovery

Electrolytic processes are used extensively to recover metals from industrial wastewaters. The electrolytic cell is the basic device used in electrolytic recovery operations. The cell consists of an anode and a cathode immersed in an electrolyte. When current is applied, dissolved metals in the electrolyte are reduced and deposited on the cathode. Because the metal(s) removed from solution can be reused, the technology, termed "electrowinning," is con-

Table 3. Metal-Bearing Hazardous Wastes From Major Industry Categories

EPA Hazardous Waste No.	Hazardous Waste Description	Listed Constituent(s)
F006	Wastewater treatment sludges from electroplating operations except the following: (1) sulfuric acid anodizing of aluminum; (2) tin plating on carbon steel; (3) zinc plating (segregated basis) on carbon steel; (4) aluminum or zinc-aluminum plating on carbon steel; (5) cleaning/stripping associated with tin, zinc, and aluminum plating on carbon steel; and (6) chemical etching and milling of aluminum.	Cadmium, hexavalent chromium, nickel, cyanide (complexed)
F007	Spent cyanide plating bath solutions from electroplating operations.	Cyanide/salts
F008	Plating sludges from the bottom of plating baths from electroplating operations where cyanides are used in the process.	Cyanide/salts
F009	Spent stripping and cleaning bath solutions from electroplating operations where cyanides are used in the process.	Cyanide/salts
F019	Wastewater treatment sludges from the chemical conversion coating of aluminum.	Cadmium, hexavalent chromium, cyanide (complexed)
K002	Wastewater treatment sludge from the production of chrome yellow and orange pigments.	Hexavalent chromium, lead
K003	Wastewater treatment sludge from the production of molybdate orange pigments.	Hexavalent chromium, lead
K004	Wastewater treatment sludge from the production of zinc yellow pigments.	Hexavalent chromium
K005	Wastewater treatment sludge from the production of chrome green pigments.	Hexavalent chromium, lead
K006	Wastewater treatment sludge from the production of chrome oxide green pigments (anhydrous and hydrated).	Hexavalent chromium
K007	Wastewater treatment sludge from the production of iron blue pigments.	Cyanide (complex), hexavalent chromium
K008	Oven residue from the production of chrome oxide green pigments.	Hexavalent chromium
K048	Dissolved air flotation (DAF) float from the petroleum refining industry.	Hexavalent chromium, lead
K049	Slop oil emulsion solids from the petroleum refining industry.	Hexavalent chromium, lead
K050	Heat exchanger bundle-cleaning sludge from the petroleum refining industry.	Hexavalent chromium
K051	API separator sludge from the petroleum refining industry.	Hexavalent chromium, lead
K052	Tank bottoms (leaded) from the petroleum refining industry.	Lead
K060	Ammonia still lime sludge from coking operations.	Arsenic
K061	Emission control dust/sludge from the primary production of steel in electric furnaces.	Hexavalent chromium, lead, cadmium
K062	Spent pickle liquor generated by steel-finishing operations of facilities within the iron and steel industry.	Hexavalent chromium, lead
K064	Acid plant blowdown slurry/sludge resulting from the thickening of blowdown slurry from primary copper production.	Lead, cadmium

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sidered a recovery process. If a membrane is used between the cathode and the anode for the selective transport of some ions, the process is called electrodialysis. Electrowinning is most effective for recovery of noble metals such as gold and silver. These metals have high electrode potentials and are easily reduced and deposited on the cathode. Metals such as cadmium, copper, chromium, lead, tin, and zinc can be removed, but a greater amount of current is required. Electrowinning is very effective for plating solutions used in printed circuit boards; these contain chelated metals that are difficult to remove by other means.

Electrowinning of metals is a particularly attractive process because it completely eliminates the generation of a metal-bearing sludge. Its applicability, however, is limited to waste streams containing metals in solution such as cadmium, copper, chromium, gold, lead, silver, tin, or zinc. For dilute solutions, electrowinning can be difficult because of the low mass-transfer rates; however, mass transfer rates can be enhanced both by agitating the solution and by increasing the effective surface area of the cathode.

The principal area of application of electrodialysis is the recovery of metals from electroplating bath rinse waters.

In many cases, the wastewater must be filtered before it is fed through the electrolytic reactor. Adjustment of pH is a necessary pretreatment measure because the waste pH affects metal speciation.

Metal recoveries of up to 98% from plating rinse waters have been demonstrated with the use of high-surface area (HSA) electrodes.

Several vendors are currently manufacturing electrodialysis systems for treatment of wastes from gold, chromium, silver, and zinc cyanide plating operations and from nickel plating operations. Other successful electrodialysis applications include recovery of metals from tin and trivalent chromium baths and the recovery of chromic acid and sulfuric acid from spent brass etchants. Electrowinning and electrodialysis systems have both been used extensively in industrial applications.

High-Temperature Metals Recovery (HTMR)

Several types of HTMR processes are currently available or under development for the recovery of metals from sludges generated either directly by industrial processes or from the treatment of industrial wastewaters. These HTMR processes may involve plasma-based or high-temperature fluid-wall reactor systems (which use elec-

(continued on p.4)

Table 3. (Continued)

EPA Hazardous Waste No.	Hazardous Waste Description	Listed Constituent(s)
K065	Surface impoundment solids contained in and dredged from surface impoundments at primary lead smelting facilities.	Lead, cadmium
K066	Sludge from treatment of process wastewater and/or acid plant blowdown from primary zinc production.	Lead, cadmium
K069	Emission control dust/sludge from secondary lead smelting.	Hexavalent chromium, lead, cadmium
K086	Solvent washes and sludges, caustic washes, and sludges from cleaning tubs and equipment used in the formulation of ink from pigments, driers, soaps, and stabilizers containing chromium and lead.	Lead, hexavalent chromium
K090	Emission control dust or sludge from ferro chromium silicon production.	Chromium
K100	Waste leaching solution from acid leaching of emission control dust/sludge from secondary lead smelting.	Hexavalent chromium, lead, cadmium
D004	Characteristic waste based on concentrations.	Arsenic
D006	Characteristic waste based on concentrations.	Cadmium
D007	Characteristic waste based on concentrations.	Chromium
D008	Characteristic waste based on concentrations.	Lead
D009	Characteristic waste based on concentrations.	Mercury
D011	Characteristic waste based on concentrations.	Silver

tricity as the energy source) or coal/natural- gas-based technologies.

HTMR processes are applicable only for the processing of sludges, not for wastewaters. One significant advantage of the HTMR processes is that other toxic constituents in the wastes, such as complexed cyanides/organics, would also be destroyed at the high temperatures (>1100°C) prevailing in the furnaces.

Important waste characteristics affecting the performance of HTMR processes include: (1) concentrations of undesirable volatile metals, (2) boiling points of the metal constituents, and (3) thermal conductivity of the waste. Pretreatment requirements for HTMR processes vary with the type of process. This may include operations such as drying of feed sludges or pelletizing with special additives. The crude metallic oxides produced in certain HTMR processes must be further treated for separation and recovery of metals. Gases from the high temperature furnaces must be treated before atmospheric release.

The INMETCO Plant in Ellwood City, PA (which utilizes a rotary hearth/electric furnace) and the Horsehead Waelz Kiln in Palmerton, PA, have processed hazardous wastes (sludges) under an Interim Permit status. The INMETCO Plant has processed the following waste codes: F006, K061, K062, D006, D007, and D008. The Horsehead Waelz kiln has processed F006, F019, K061, D006, and D008.

Horsehead has two operating Waelz plants in the United States—one at Palmerton, PA, and one at Calumet City, IL. The Palmerton plant has three Waelz kilns with a total capacity of 270,000 tons/yr; the Calumet plant has one kiln with a capacity of 80,000 tons/yr. The INMETCO plant is capable of treating 50,000 tons of wastes per year. Both of the Horsehead Waelz plants as well as the INMETCO plant are operated primarily to treat steelmaking electric arc furnace dust (K061); however, as previously mentioned, they are capable of treating other sludges. A third Horsehead Waelz plant with a capacity of 60,000 tons/yr is planned for Rockwood, TN.

Membrane Separation

The commercially available membrane processes for removal of metals from industrial wastewaters are microfiltration, ultrafiltration, reverse osmosis, and electrodialysis. Microfiltration (MF) and ultrafiltration (UF) are used in combination with chemical treatment for the physical separation of metal sludges. Reverse osmosis (RO) and electrodialysis (ED) are used to recover plating compounds from rinse water and to enable reuse of rinse waters.

MF and UF membranes cannot be applied directly to recover metals present as dissolved solids in wastewaters. UF, however, can be used as a pretreatment method for RO units to avoid fouling of the RO membranes.

When applied to heavy metal wastes with appropriate pretreatment chemistry, the metal content of the effluent can be extremely low. Each application requires treatability studies to integrate the chemical pretreatment and the MF/UF membrane system.

If oil and grease are present, additional pretreatment of the waste stream will be required. Well-run precipitation/UF and MF systems can achieve metal removals greater than 99%. Over 150 full-scale industrial systems, ranging in size up to 400 gal/min, have been installed in the electroplating, printed circuit board manufacturing, battery manufacturing, and photographic processing industries.

RO systems consist of several modules connected in series, or parallel, or a combination of both. The application of RO to the treatment of metal-containing wastes is limited by the pH range in which the membrane can operate. Cellulose acetate membranes cannot be used on waste streams where the pH is much above 7. The amide or polysulfone membranes, however, have a pH range of 1 to 12. Collodial matter, low-solubility salts, and dissolved organics can seriously inhibit the effectiveness of RO. Pretreatment steps such as pH adjustment, carbon adsorption, chemical precipitation, or filtration are therefore recommended to ensure extended service life of RO systems. Systems are being used commercially to recover brass, hexavalent chromium, copper, nickel, and zinc from metal-finishing solutions.

Leaching

Leaching is a process in which a solid material is contacted with a liquid solvent for selectively dissolving some components of the solid into the liquid phase. Leaching can sometimes be used to extract various metals from sludges. The goals of this process are: (1) to dissolve the metals in a liquid phase to produce a solution that can be reused directly in a process or from which the metal can be recovered by other techniques, such as electrowinning; and (2) to produce a secondary sludge that is nonhazardous or from which additional metals can be reclaimed by other processes. Several leaching agents can potentially be used, including sulfuric acid, ferric sulfate, ammonia or ammonium carbonate, hydrochloric acid, sulfur dioxide, ferric chloride, nitric acid, or a caustic solution. Selection of a suitable solvent and unit process depends on the chemical state and physical environment of the metals.

Sludges that contain only one metal often can be sent directly to a refiner for reclamation; however, in some operations (e.g., electroplating), all metals are precipitated from solution in the same wastewater treatment plant, usually as hydroxides. A process train with numerous unit operations, therefore, is necessary to separate each metal. Complete recovery of the metals typically includes electrowinning of the leachate.

At the Recontek waste recycling facility in Newman, IL, zinc-bearing solutions are leached with alkaline solutions, whereas non-zinc sludges are treated with acidic solutions. Zinc-bearing sludges are digested at approximately 80°C with sodium hydroxide for a sufficient period of time, cooled, and filtered. The filtrate is processed in a zinc cementation tank to precipitate metals more electronegative than zinc (e.g., lead, cadmium) and then pumped to a zinc electrowinning system. The non-zinc sludge waste from the digester (primarily copper and nickel) is digested with sulfuric acid and filtered to produce a residue containing precious metals (e.g., gold, silver). The filtrate is then sent to the copper electrowinning system for production of copper cathodes.

Ion Exchange

Ion exchange is a treatment technology applicable to (1) metals in wastewaters where the metals are present as soluble ionic species (e.g., Cr^{+3} and CrO_4^{-2}); (2) nonmetallic anions such as halides, sulfates, nitrates, and cyanides; and (3) water-soluble, ionic organic compounds including (a) acids such as carboxylics, sulfonics, and some phenols, at a pH sufficiently alkaline to yield ionic species, (b) amines, when the solution acidity is sufficiently acid to form the corresponding acid salt, and (c) quaternary amines and aklylsulfates.

Ion exchange is a reversible chemical reaction in which an ion from solution is substituted for a similarly charged ion attached to an immobile solid particle. The use of this process is practical only on wastewaters and sludge leachates. In conventional ion exchange, metal ions from dilute wastewater solutions are exchanged for ions electrostatically held on the surface of the exchange medium. Ion exchange systems have proven to be effective in the removal of barium, cadmium, chromium (VI), copper, lead, mercury, nickel, selenium, silver, uranium, and zinc.

Evaporation

Evaporation is a simplified recovery system for the separation of substances based on volatility differences. Although the technology is established, recent advancements have made mechanical evaporation a more viable cost-efficient method for metals recovery. The four basic types of evaporators used in the electroplating industry today are rising-film, flash, submerged-tube, and atmospheric.

Conclusions

Only a few of the technologies addressed in this report (e.g., electrowinning, HTMR) are directly applicable to recovering metals from wastes; other technologies treat the wastes to a physical form that may be amenable to eventual metals recovery.

Commercial waste recycling facilities render services that are important if metals are to be recovered as opposed to being treated and disposed. Technologies used at the metals recovery facilities include chemical precipitation, leaching, electrowinning, and evaporation.

Current information on metals recovery technologies show that combinations of technologies may often be required to recover metals from wastewaters and sludges. Additional studies are needed to determine the specific combinations of methods that will most effectively recover metals from different types of wastes.

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The complete report, entitled "Recovery of Metals from Sludges and Wastewaters," (Order No. PB91-220384/AS; Cost: $23.00, subject to change) will be available only from:
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