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Project Summary

Technical Resource Document: Treatment Technologies for Metal/Cyanide-Containing Wastes, Volume III

Stephen A. K. Palmer, Marc A. Breton, Thomas J. Nunno, David M. Sullivan, and Norman F. Surprenant

The full document provides information that can be used by environmental regulatory agencies and others as a source of technical information for waste management options for hazardous liquid wastes containing heavy metals and/or cyanide compounds. These options include waste minimization, recycling, and treatment of waste streams. Emphasis has been placed on the collection and interpretation of performance data for proven technologies. These include: Metals: precipitation, coagulation/flocculation, chemical reduction, membrane separation technologies, activated carbon adsorption, ion exchange, electrolytic recovery, thermal recovery; Cyanides: alkaline chlorination, ozonation, biological treatment, thermal destruction.

These, and other potentially viable technologies, are described in terms of their actual performance in removing constituents of concern, their associated process residuals and emissions, and those restrictive waste characteristics that impact their ability to effectively treat the metal/cyanide wastes under consideration. Although emphasis is placed on performance data, cost and capacity data are also provided to assist the user of the document in assessing the applicability of technologies to specific waste streams.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research 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).

Background

Heavy metals and cyanides are widely used by all segments of American industry. Because of this, they are frequently detected in all media, including ground water. To combat the negative effects of environmental release that these and other hazardous materials may have on the environment, the 1984 amendments to the Resource Conservation and Recovery Act (RCRA) were promulgated. These amendments directed the U.S. Environmental Protection Agency (EPA) to ban certain wastes from land disposal to the extent required for the protection of human health and the environment. The ban for concentrated metal/cyanide wastes went into effect on July 8, 1987, 2-1/2 years following enactment of the amendments.

EPA has taken steps to meet this deadline by characterizing metal/cyanide waste generation, identifying waste management alternatives through case study development and literature surveys, and determining available capacity of disposal options. From these investigations, the Agency concluded that industry would be able to comply with the land disposal ban as scheduled. Although currently permitted treatment units are insufficient to accommodate the quantities of these metal/cyanide wastes currently land disposed, the Agency determined that sufficient capacity could be brought on-line by the statutory deadline.

The categories of wastes subject to the July 8, 1987 land disposal ban are identified in the May 28, 1986 Federal Register. They include any RCRA wastes with liquid fractions that contain heavy metals or total cyanides above the concentrations specified in Table 1. For the purposes of this regulation, the EPA has proposed use of the Paint Filter Test to determine liquid content and use of the Toxicity Characteristics Leaching Procedure (TCLP) to determine constituent concentrations. Any waste containing a carbon-nitrogen triple bond is considered to be a cyanide-containing waste. Metal/cyanide RCRA wastes containing concentrations below the threshold levels specified in Table 1 may be subject to land disposal restrictions at a later date; i.e., between 1988 and 1990.

Scope

The full Technical Resource Document provides information that can be used by environmental regulatory agencies and others as a source of technical information describing waste management options for wastes containing metals and/or cyanides. These options include waste minimization (i.e., source reduction, recycling/reuse) and use of various physical, chemical, thermal, and biological treatment processes. Emphasis has been placed on the collection and interpretation of performance data for proven technologies, however, the report also examines promising technologies which are still in the developmental stage.

The full document begins with a brief statement of purpose (Section 1.0) and a review of regulatory background (Section 2.0), which have been summarized above. This is followed by a review of the currently available data regarding metal/cyanide waste sources, characteristics (Section 3.0), quantities generated, existing management practices, and available unused treatment capacity (Section 4.0). This is followed by a summary of documented waste minimization practices (Section 5.0) and an evaluation of a wide range of treatment/recovery processes (Sections 6.0 through 15.0). In order of their presentation, the latter include:

- Metal Waste Treatment/Recovery Processes:
  - —Membrane Separation Technologies
  - —Liquid Extraction
  - —Adsorption Technologies
  - —Electrolytic Recovery
  - —Chemical Treatment
  - —Biological Treatment
  - —Thermal Destruction/Recovery

- Cyanide Waste Treatment/Destruction
  - —Physical Removal Processes
  - —Chemical Destruction Techniques
  - —Biological Treatment
  - —Thermal Destruction

These technologies are examined with emphasis placed on identifying process design and operating factors and waste characteristics that affect process performance and applicability. Cost data are also presented, as available, to assist the user in evaluating and selecting options The report concludes with an algorithm presenting considerations for the selection of treatment/recovery alternatives (Section 16.0). A brief synopsis of the contents of each technical section is provided below.

Metal/Cyanide Waste Sources and Characteristics (Section 3.0)

Available information describing important industrial uses, waste sources, and characteristics for metal/cyanides is summarized. An understanding of these topics is a prerequisite for evaluating the applicability of waste management alternatives, particularly source reduction and recycling options. Recognizing the wide variability of metal/cyanide waste characteristics and the lack of a comprehensive national data base describing these data, an industry by industry approach is taken to categorize waste sources. Industries that are high volume generators of RCRA metal/cyanide wastes are targeted. These include metal surface treatment and electroplating facilities, printed circuit board manufacturers, inorganic pigment manufacturers, petroleum refineries, wood preserving facilities, and others. These same industrial categories are used later to discuss industry specific waste minimization options.

Waste Quantity, Management Practices, and Treatment Capacity (Section 4.0)

The current status and limitations of the data base relative to existing RCRA waste generation, management practices, and available alternative treatment capacity are reviewed, noting that EPA is currently in the process of updating this data base. Much of the currently available data rely on recent interpretations of the EPA's 1981 RIA National Survey of large quantity generators and TSDFs and 1983 survey of small quantity generators. These data indicate that roughly 13 billion gallons of metal/cyanide RCRA waste is generated annually, the vast majority of which is wastewater streams from relatively few, very large generators.

Unfortunately, these data do not permit an assessment to be made regarding the characteristics of these wastes. Specifically, it cannot be determined what fraction of these wastes will be subject to the land disposal restrictions. A review

Table 1. *Concentration Limits for Defining Waste Management Alternatives (mg/L)*[a]

Constituent	*Maximum Allowable Concentration for Land Disposal in RCRA Facilities*	*Maximum Allowable Concentration for Exclusion from RCRA Management Provisions*[b]
Total Cyanide	*1,000*	*NA*
As	*500*	*5.0*
Cd	*100*	*1.0*
Cr^{6+}	*500*	*5.0*
Pb	*500*	*5.0*
Hg	*20*	*0.2*
Ni	*20*	*NA*
Se	*134*	*1.0*
Tl	*130*	*NA*
Ba	*No limit*	*100*
Ag	*No limit*	*5.0*

[a]*All concentrations refer to the liquid fraction of these wastes.*
[b]Federal Register. *40 CFR Subpart C §261.24. 45 FR 33119. May 19, 1980.*

f available waste characterization data suggests that, provided wastes are segregated prior to treatment, the quantity affected by the July 8, 1987 statutory provisions will be a modest fraction of the total waste generation figure stated above.

As part of its proposal to codify the land disposal restrictions for metal/cyanide wastes, the EPA estimated demand and supply of available alternative treatment capacity. Since the Agency lacked data on waste concentrations, it conservatively assumed that all liquid wastes currently land disposed require alternative capacity. Currently available capacity falls far short of this quantity. However, the EPA believes that by the statutory deadline, industry will be able to install treatment units (e.g., precipitation, chromium reduction, cyanide oxidation) which are capable of meeting the effluent concentrations specified by the land disposal restrictions. Other than presenting the EPA's analysis, no attempt was made in the full document to make national projections regarding the adoption of waste management alternatives. The extreme variability in physical, chemical, and flow characteristics between waste streams, and the lack of reliable data quantifying these variables, precludes making reliable projections.

Waste Minimization Practices (Section 5.0)

Waste minimization is discussed from the standpoint of two distinct areas of activity; recycle/reuse and source reduction; e.g., process modification and raw material substitution. These topics are described in general as they pertain to metal/cyanide wastes and then in terms of specific practices available to the industrial categories identified in Section 3.0. This section also provides information on Governmental and privately operated waste exchanges and a summary of documented waste minimization applications and their cost-effectiveness. It is noted that waste minimization activities are widely applied, particularly to metal-containing wastes, and will receive further impetus as a result of the land disposal ban.

Metal Waste Treatment/ Recovery Technologies (Section 6.0 Through 12.0)

Table 2 summarizes commonly used technologies for the treatment of metal-containing wastes, which were discussed in this document. These have

Table 2. *Summary of Treatment Technologies for Metal-Bearing Waste Streams*

Process	*Applicable Waste Streams*	*Stage of Development*	*Performance*	*Residuals Generated*
Physical Treatment Technologies				
Membrane Separation	*Aqueous waste streams containing 10-20 percent metals depending on the technology used.*	*Demonstrated technology for many process and waste streams.*	*Greater than 99 percent if properly utilized.*	*Generally none except for solids from ultrafiltration.*
Liquid-Liquid Extraction	*Aqueous, sludge, and solid wastes.*	*Limited use in hazardous waste field but widespread in mining and smelting industries.*	*Capable of yielding a solution which is 20-30 times more concentrated than feed.*	*Raffinate and regenerant stream may require post-treatment to remove residual extractant and metal, respectively.*
Carbon Adsorption	*Aqueous waste streams containing metal ions at low pH. Effective in treating chelated metals as well as metal cations.*	*Largely experimental with some field applications for treating hexavalent chromium and mercury containing waste streams.*	*Used as a primary treatment for removal of hexavalent chromium. With a Cr^{6+} influent concentration of 6 ppm, effluent concentration of Cr^{6+} remained below 0.05 ppm.*	*Spent carbon requires disposal or reactivation.*
Ion Exchange	*Effective for treating dilute aqueous waste streams as an end-of-pipe or polishing treatment.*	*Used in metal finishing and electroplating industries for recycling rinse solutions and concentrating waste metal solutions for efficient treatment.*	*Performance influenced by nature of functional group, ions available for exchange, and pH.*	*Regeneration solution requires treatment or disposal.*
DeVoe-Holbein	*Similar to ion exchange except capable of treating both dilute and concentrated solutions.*	*Newly developed process used in metal finishing industries, ore benefication, precious metals recovery, and chlor-alkali plants.*	*Performance reportedly shows high specificity. However more data are needed to assess utility.*	*Regenerant required but has good potential for recycling since typically high in metals content.*
Electrolytic Treatment	*Aqueous streams; high concentrations (greater than 1,000 ppm) are most efficiently removed.*	*Well developed and readily available from commercial vendors.*	*Performance varies greatly depending on the application and the particular electrolytic unit used; some units may remove over 90% of metals such as Cu, Pb, Zn, Av, Ag, and Cd.*	*Generally the metal is recovered in a usable form and no residual solids are generated.*

Table 2. Continued

<u>Chemical Treatment Methods</u>				
Precipitation	Aqueous streams; restrictions based on physical form, viscosity, and metal solubility.	Well developed, reliable process, suitable for automatic control.	Heavy metals; Cd, Cu, Pb, Hg, Ni, Ag, and Zn removed to 0.01 to 0.5 mg/L.	Effluent stream will requi[r]e secondary processing to remove and dispose of precipitated solids.
Coagulation/ Flocculation	Aqueous streams; for ppb concentrations two-stage process required, not readily applied to small, intermittent flows.	Well developed and readily available from commerical vendors.	Not considered a primary treatment but can achieve low residual levels.	Requires secondary processing and disposal.
Reduction	Primarily, aqueous chrome-bearing waste streams although sodium borohydride can treat most metals.	Well developed.	Chromium removal to 0.01 mg/L. Sodium borohydride able to remove Cu, Ni, Pb, Zn, Hg, Ag, Cd in the 0.01 to 1.0 mg/L range.	Effluent stream will requir[e] secondary processing to remove and dispose of reduced metal. Sodium borohydride introduces boron into the effluent stream.
Flotation	Aqueous streams containing 100 mg/L or less of metals. Restrictions based on physical form, oil and grease content.	Not fully developed, primarily at pilot plant stage of development.	Heavy metals Pb, Cu, Zn, Cr^{3+} removed to 0.03 to 0.4 mg/L.	Requires secondary treatment of metals-laden foamate.
<u>Biological Treatment Methods</u>				
	Aerobic and anaerobic technology suitable for dilute aqueous wastes; metal removal due to partitioning or precipitation.	Generally not used as primary treatment technology for metals.	May be used as final treatment for low concentrations of heavy metals (10 mg/L or less), may be used as pretreatment for resistant species.	Residual contamination likely, will usually require secondary treatment.
<u>Thermal Treatment Methods</u>				
Incineration	Organometalllics, metal wastes containing organics (e.g., solvent wastes containing metals).	Well developed reliable process. Numerous technologies available which can be opti-mixed according to waste characteristics. Process costs are high.	Can oxidize organic portion of metal-waste to virtual completion.	Air emissions, ash, scrubber effluents.
Pyrometallurgy (smelting, calcination)	Pyrometallurgy is applicable to most metal-bearing wastes. Effectiveness is directly proportional to metal content of waste.	Well developed and widely-available. Some commercial capacity available. Process costs are high (although typically lower than for incineration).	Can effect high-level (i.e., greater than 90 percent) recovery of metal or metal oxides from waste matrix.	Potential formation of toxic sludges.
Evaporation	Aqueous wastes with low non-volatile metals content, or wastes with high volatile metals content.	Well developed and widely-available.	Can effect high-level recovery of volatile metals or significant volume reduction of aqueous wastes.	Air emission sludges.
Crystallization	Primarily used for wastes from electroplating, pickling containing high levels of acids, water, or low molecular weight organics.	Well developed. Often used in conjunction with evaporation.	Can effect high level recovery.	Sludges.

been categorized in terms of treatment mechanism; i.e., physical, chemical, biological, and thermal processes. Physical and chemical processes apply to all waste types whereas biological methods are appropriate for dilute wastewaters containing metals (but not as a primary treatment method) and thermal techniques are applicable to organometallics. Each technology is discussed in terms of the following generalized areas: (1) process description; (2) theoretical considerations; (3) applicable waste types; (4) pretreatment and post-treatment requirements; (5) demonstrated performance in metal waste treatment; (6) cost of treatment; and (7) status and availability of the technology.

The limited scope of the full document did not permit a comprehensive evaluation of cradle-to-grave management of metal wastes. In particular, topics which are covered in limited detail include general waste pretreatment (e.g., sedimentation, filtration, flow equalization, trace organic removal) and post-treatment (e.g., sludge consolidation, pH adjustment, solidification) technologies. These topics have been considered in other EPA sponsored Technical Resource Documents produced as part of this and other series.

The following is a summary of metal treatment/recovery technologies considered in the full document.

Physical Treatment Technologies (Sections 6.0 Through 8.0)

Membrane Separation Technologies (Section 6.0)

Membrane technologies such as reverse osmosis (RO) and electrodialysis (ED) are used commercially to recover dissolved metals from aqueous wastes generated through electroplating or metal etching processes. The technologies are applicable to specific waste streams, provided pretreatment measures can be used to remove suspended and dissolved solids and ensure acceptable membrane lifetimes. Ultrafiltration (UF) is often used as a pretreatment for RO and ED. UF also is used to remove suspended solids following precipitation of metals from waste streams. RO and ED usually do not generate residuals providing the reject stream is recyclable.

Liquid-Liquid Extraction (Section 7.0)

Liquid-Liquid extraction involves the separation of a component from a waste solution by transfer to a second, immiscible solution, typically an inexpensive organic acid (e.g., kerosene). The process has gained widespread acceptance in the mining industry for metal recovery from aqueous discharges and in the smelting industry for metal recovery from sludges/solids in hydrometallurgical operations. However, due in part to the specificity of system design to particular applications, adoption of this processing technique for hazardous metal waste treatment has been limited. Performance capabilities are difficult to predict through generalized equations and, instead, require isotherm and kinetic data determined through laboratory scale studies. However, through support from equipment suppliers, successful systems have been designed for metal recovery from chlor-alkali plant discharges (Hg), pickling, plating, and etching baths, and metal finishing sludges including recovery of both heavy metals (Ni, Cr, Zn, Cu, Cd, and Ag) and cyanide.

Residuals generated from this process include the treated waste feed (raffinate), which may require post-treatment to remove residual extractant concentrations, and the regenerant, which will require treatment (e.g., electrolytic recovery) to recover the metals and permit reuse of the acid extractant.

Adsorption Technologies (Section 8.0)

Adsorption technologies for metals wastes include activated carbon, ion exchange, and DeVoe-Holbein treatment. Activated carbon adsorption involves separation of a substance from one phase, typically an aqueous solution, and the concentration of the substance at the surface of an activated carbon adsorbate. Activated carbon is generally used in granular form either in batch, column (both fixed-bed and countercurrent bed), or fluidized-bed operations, with fixed-bed being the most common.

Although promising results have been reported, activated carbon for inorganic compound removal from water is largely in the experimental stage. In addition, the number of commercial applications is small and data for full scale applications are limited.

Ion exchange is a versatile separation process used to remove metal contaminants from aqueous waste streams and to recycle or discharge the treated solution. Ion exchange techniques involve the use of an ion selective resin to remove ionic contaminants (metals) from solution. Three basic types of resins are employed; cation exchange resins, anion exchange resins, and metal selective chelating resins.

The major attraction of ion exchange is the broad range of resins manufactured to treat specific waste streams. The ion exchange resin will selectively remove only the toxic compound while allowing the nontoxic dissolved ionic solids to remain in solution. With proper resin selection, ion exchange can provide an effective pollution control method in a wide range of applications such as water purification and recycle end-of-pipe treatment, and chemical recovery.

DeVoe-Holbein is a technology similar to ion exchange using insoluble chelating compounds based on microbial siderophores which reportedly display a high degree of metal sequestering specificity. This technology has been successfully applied to recover concentrated metal/cyanide solutions such as plating and etching baths. However, due in part to the waste specific nature of its formulations and the fact that it has a single industrial supplier, estimates of cost and performance applicable to a range of industrial waste streams proved to be very difficult to obtain. Additional work is needed to demonstrate this technology.

Electrolytic Recovery (Section 9.0)

The primary use of electrolytic processes is for the removal of dissolved metals from rinsewaters generated by metal plating and etching processes. In this situation, an electrolytic cell is attached to the rinse bath following the plating or etching tank, and the rinse solution is circulated through the electrolytic cell. As the solution passes through the cell, dissolved metals ions are reduced and deposited on the cathode in elemental form. If cyanides are present, they may also be removed by oxidation at the anode forming carbon dioxide, ammonia and nitrogen.

There exist a number of different electrolytic cell designs. Some use very simple flat plate anode and cathode. Other, more complex designs, incorporate granular or porous cathodes. These designs increase the mass transfer of metal ions to the cathode by increasing the surface area of the cathode, and therefore have the ability to remove metals to a much lower concentration than flat plate electrodes. The use of one design over another depends upon the application. Noble metals such as gold and silver are not difficult to remove electrolytically, and therefore flat plate electrodes can be used. Metals such as copper, tin, lead, and cadmium are more difficult to remove and sometimes may require the use of the more complex electrolytic cell designs.

Chemical Treatment Technologies (Section 10.0)

Chemical treatmeht methods for metals wastes include precipitation, coagulation/flocculation, reduction, and flotation processes. Precipitation involves the alteration of the ionic equilibrium of a dissolved metallic compound to produce an insoluble precipitate. The process typically uses an alkaline reagent to cause the solubility of the metal ions to decrease, and thus precipitate out of solution. The chemicals most frequently used for precipitation of metals are hydroxides, sulfides, and carbonates. The overwhelming majority of present technology is based on hydroxide precipitation. However, in certain cases where heavy metals are complexed, or at concentrations below the level of minimum hydroxide solubility, sulfide precipitation is a viable alternative. Carbonate precipitation is also sometimes used in cases where it provides superior precipitation properties (cadmium) or lower effluent concentrations (nickel).

Precipitation is used most commonly to remove heavy metals from aqueous wastes. The precipitation process produces a sludge composed of metal hydroxides, metal carbonates or metal sulfides as well as the precipitating agent used. In some instances, precipitation can be used for organic-based liquids, although this application is very limited due to sedimentation problems in viscous media.

Coagulation/flocculation is aimed at removal of colloidal particles. A stable suspension of colloidal particles is characterized by a balance of repulsive forces and attractive forces. The coagulation process involves the destabilization of the suspension by neutralizing or decreasing the repulsive forces so that the particles will approach each other and agglomerate.

The coagulants/flocculants currently in commerical use are classified as inorganic, synthetic organic and naturally occurring polymers. The principal coagulants available are inorganics such as aluminum sulfate, lime, and iron salts. Synthetic organics such as anionic and cationic polyelectrolytes are typically added as coagulation/flocculation aids. Naturally occurring organics have seen limited use since the composition of natural products tends to fluctuate and they are susceptible to microbial degradation during storage.

The coagulation/flocculation process is usually performed after a precipitation step and the treated water is then permitted to settle. The precipitated sludge from the settling vessel is removed at 1 to 2 percent solids for further treatment while the overflow is typically polished by a multi-media filter and then discharged.

Chemical reduction as a waste treatment process is an established and well-developed technology. The reduction of hexavalent chromium's valence (oxidation) state to decrease toxicity and encourage precipitation is presently used as a treatment technology in numerous electroplating facilities. Major advantages of chemical reduction when used to reduce hexavalent chromium is operation at ambient conditions, automatic controls, high reliability, and modular process equipment.

The reduction reaction is one in which one or more electrons are transferred to the chemical being reduced (reductant) from the chemical initiating the transfer (the reducing agent). Hexavalent chromium can be reduced to trivalent chromium, which can then be removed by precipitation. The pH of the aqueous solution is reduced to about 2.0 with hydrochloric or sulfuric acid. The aqueous pH controls the reaction rate, which is extremely slow above pH 3. Then reducing agents such as sulfur dioxide and sodium metabisulfite are added. Lime or caustic soda is added to raise the pH and precipitate trivalent chromium. Precipitation is carried out at pH 8.5 to 9.5; in this range chromium hydroxide solubility is minimal.

An alternate reducing agent applicable to most heavy metals is sodium borohydride. Sodium borohydride has recently shown promise for reducing and removing soluble lead, including organo-lead salts.

Chemical flotation is a well established and developed technology for separating finely ground valuable minerals in the ore processing industry. However, recent research efforts have centered on applying this technology to the removal of low concentrations (100 mg/L or less) from industrial wastewaters. The advantages of chemical flotation include simplicity effectiveness, and moderate costs. In addition, low space requirements and a concentrated, easily handled sludge are major advantages over comparable metallic contaminant removal through chemical precipitation. While still primarily in the pilot plant stage of development, chemical flotation and most notably adsorbing colloid foam flotation, represents a feasible and economical method for removing heavy metals from wastewaters.

Biological Treatment (Section 11.0)

A large number of companies specialize in the design and construction of biological treatment systems. Aerobic systems are the most readily available, and their design and operation are complex, but manageable. The total number of biological treatment systems used for inorganic compound removal is unknown. However, the total number of facilities using some sort of aerobic biological treatment for biodegradable wastes is large, in excess of 2,000. The number of companies offering expertise in bioaugmentation and anaerobic treatment is relatively small, but this segment is expected to grow rapidly.

Biological treatment of metals using conventional equipment and acclimated strains is typically only capable of treating combined heavy metal influents of 10 mg/L. While improvements in reported values for biological treatment process tolerance limits for inorganic priority pollutants is encouraging, most processes are still in the developmental stage and have yet to be widely applied. In addition, the difficulty of disposing of a large, voluminous sludge-containing heavy metals limits available disposal options. Since the biological matrix surrounding the accumulated metallic species can readily degrade and release the entrapped metals into the environment, fixation, encapsulation, or other forms of secure disposal may be necessary.

Thermal Treatment/Recovery Technologies (Section 12.0)

Thermal treatment technologies such as incineration, calcination, smelting, evaporation/distillation, and crystallization have been used extensively to effect recovery of metals from certain metal-bearing hazardous wastes. Incineration processes are primarily used to handle organic wastes containing metals such as solvent rinses from metal treating or organometallic wastes such as tetraethyl lead. Pyrometallurgical processes (calcination and smelting) are primarily used to manage wastes from metal refining industries, e.g., specialty steelmaking. Evaporation/distillation and crystallization are often used to manage corrosive wastes from electroplating, pickling, or other metal finishing operations, or low-molecular weight organic wastes (e.g., solvents) containing metals.

All of the thermal treatment systems applicable to metal-bearing hazardous wastes employ well-developed technologies, with readily-available commercial capacity. However, the incineration of many metal wastes will require air pollution control devices to assure incineration emission compliance.

Cyanide Treatment/ Destruction Technologies (Sections 13.0 Through 15.0)

Table 3 summarizes information on technologies used for this treatment and destruction of cyanide-containing wastes which have been covered in this document. Concentrated cyanide solutions are sometimes recovered, generally by membrane and other separation technologies which are capable of segregating metal contaminants from the solution. Typically, however, cyanides are destroyed due to their low cost and relative ease of destruction. Processes for cyanide waste management are covered in the full document in similar fashion to metal wastes. A summary of these technologies is provided below.

Physical Separation Processes (Section 13.0)

Physical separation methods for cyanide bearing wastestreams include ion exchange and foam flotation. Ion exchange for the removal of cyanide has been limited to applications involving the treatment of low organic concentration waste streams. Anion exchange resins, in particular, are susceptible to severe fouling by insoluble oil and dissolved organic compounds. Therefore, the use of ion exchange is not practicable unless extensive pretreatment of the organics is practiced. Typically, ion exchange for cyanides removal has been applied as a polishing step to sorb any ferricyanide or other complexed cyanide residuals from oxidation processes such as alkaline chlorination. The environmental impact from this technology is that it concentrates cyanides in the regeneration step, creating a secondary stream that needs to be treated.

The advantages of this technology are that it has been demonstrated at both the bench-scale and pilot-scale. The equipment is compact, versatile, and is generally applicable to many different waste treatment situations. Limitations include the high cost of regenerative chemicals and the waste streams originating from the regeneration process are relatively high in pollutant concentration. In addition, if more than 25 mg/L of suspended solids and/or more than 20 mg/L of oil exists in the influent, filtration is required as pretreatment. Also, the stream to be treated should not contain any materials that cannot be removed by the backwash operation. Some organic compounds, particularly aromatics, will be irreversibly adsorbed by the resins, and this will result in decreased capacity.

Ion flotation/foam separation of cyanide bearing wastewaters has not yet been tested on a pilot-scale at an actual commercial facility. Most of the research that has been performed to date with flotation has focused on equipment development and process parameter definition. Although preliminary research has demonstrated the technical feasibility of the process, pilot-scale testing is needed to determine if sufficient cyanide recoveries can be achieved. Flotation could prove to be a cost-effective alternative to conventional treatment practices because of its minimal operating requirements.

Limited work has been done on the secondary treatment and disposal of the flotation concentrate. Since the concentrate contains precipitated ferri- and ferrocyanide which are not amenable to conventional oxidation technologies such as alkaline chlorination, alternate technologies such as wet air oxidation or UV/ozonation may be more appropriate. In addition, solidification and encapsulation of the residuals may be required prior to land disposal.

Chemical Destruction Processes (Section 14.0)

Chemical destruction methods for cyanide wastes include alkaline chlorination, ozonation, wet air oxidation, and sulfur-based treatment technologies. Alkaline chlorination systems have generally proven reliable if well maintained and equipped with well-designed Oxidation Reduction Process (ORP) control. The treatment technology cannot oxidize stable cyanide complexes such as ferrocyanides and has difficulty treating nickel cyanides. The most widespread application of cyanide oxidation through alkaline chlorination is in facilities using cyanides in electroplating operations.

A major environmental impact of this technology is the potential for evolution of toxic hydrogen cyanide gas at low pH levels. In cases where alkaline chlorination is used to treat dissolved complex cyanides and dissolved cyanides of heavy metals, sludges or metal hydroxides and carbonates are generated. These sludges can be recovered by filtration and treated by chemical fixation/solidification. This is particularly true in cases where the cyanide complex has not been destroyed and instead has been merely rendered insoluble and precipitated.

Ozonation appears best suited for treatment of very dilute waste streams, similar to those streams treated by the ozone based water disinfection processes now used in Europe. It does not appear to be cost competitive or technically viable for most industrial waste streams where organic concentration levels are 1 percent or higher. However, it may be viable for certain specific wastes with high levels of a contaminant of special concern and high reactivity.

Assuming adequate destruction of a contaminant by ozonation, the principal environmental impact would appear to be associated with ozone in the effluent vapor and liquid streams. However, thermal decomposition of ozone is effective and is used commercially to destroy ozone prior to discharge. Unreacted contaminants or partially oxidized residuals in the aqueous effluent may be a problem necessitating further treatment by other technologies. Presence of many such residuals will generally result in selecting a more suitable alternative technology.

The WAO process is available commercially, and reportedly well over 150 units are now operating in the field treating municipal and various industrial sludges. The process is used predominately as a pretreatment step to enhance biodegradability. Only a few units are now being used to treat industrial cyanide wastes. These include a unit in California and six other units currently operating in Japan and Europe.

The oxidation of specific contaminants in waste streams by the wet oxidation process is not highly predictable. Equip-

Table 3. *Summary of Treatment Technologies for Cyanide-Bearing Waste Streams*

Process	Applicable Waste Streams	Stage of Development	Performance	Residuals Generated
Physical Treatment Methods				
Ion Exchange	Aqueous wastes containing less than 25 mg/L suspended solids and 20 mg/L of oil and grease.	Primarily pilot plant stage with a few commercial plants.	Able to treat 48 mg/L of total cyanides to 0.5 mg/L.	Secondary processing and disposal required for spent regenerant and byproduct streams.
Foam Flotation	Aqueous wastes: restrictions based on oil and grease, chelator complexant, and competing ion concentrations.	Laboratory-scale.	Ninety-nine percent removal of amenable cyanide.	Cyanide laden concentrate will require secondary treatment and/or disposal.
Chemical Treatment Methods				
Alkaline Chlorination	Aqueous wastes: restrictions based on physical form, oil and grease content, suspended solids, viscosity, and iron content.	Well developed, reliable process, suitable for automatic control.	Can oxidize all free and most fixed cyanides to below 1 mg/L.	Possible process emissions and toxic sludges requiring secondary treatment
Ozonation	Aqueous wastes requires 1 percent or lower contaminant concentration.	Well developed and widely-available.	Able to oxidize free and fixed cyanides to low concentrations.	Unreacted ozone may be present in effluent vapor and liquid streams.
Wet Air Oxidation	Aqueous and sludge wastes containing up to 25,000 mg/L of cyanide.	Well developed and available at over 150 installations.	Ninety-nine percent destruction of total cyanide.	Post-treatment will be required of both liquid and vapor streams.
Sulfur-Based Oxidation	Aqueous wastes.	Not fully developed but has demonstrated potential.	Ninety-nine percent oxidation of simple cyanides.	Post-treatment will be required of both liquid and solid streams.
Biological Treatment Methods				
	Suitable for dilute aqueous waste streams.	Well developed for dilute streams, pilot plant stage for more concentrated wastes.	Able to completely oxidize cyanide concentrations of 10 mg/L if cyanides are amenable.	Residuals are generally non-toxic.
Thermal Treatment Methods				
Incineration	Organic cyanide-bearing wastes (e.g., acrylonitrile wastes), liquid wastes from cyanides production.	Well developed, and widely-available. Process costs are high.	Cyanide compounds have been destroyed to levels exceeding 99.99 percent.	Air emissions, scrubber effluents, ash.
Evaporation	Wastes containing low-molecular weight organics. Typically used for metal-finishing wastes.	Well developed and widely-available.	Capable of high level recovery of cyanides.	Air emissions, sludges.
Crystallization	Typically used for plating wastes.	Well developed and generally used in combination with evaporation system.	Capable of high level recovery of cyanides.	Sludges

ment manufacturers rely largely on the result of bench-scale results to tailor the design of full-scale WAO continuous units for specific wastes. Full-scale data confirm the results of WAO performance data obtained in bench- and pilot-scale studies.

Sulfur-based cyanide treatment technologies, while not fully developed, have demonstrated potential as a cyanide waste treatment process. Both reagents and equipment requirements are straightforward and simple. Application to industrial wastes is presently limited, but both polysulfide and sulfur dioxide based technologies have demonstrated high efficiencies in treating dilute and concentrated aqueous cyanide waste streams. Careful control of the treatment via multistaging of the reaction, careful control of pH, reagents, etc., are required.

The environmental impact of the processes discussed here relate to the unreacted contaminants and byproducts (thiocyanates) remaining in the waste stream. Additional treatment to prevent corrosion and meet thiocyaniate effluent guidelines usually will be required. Air emissions associated with the use of these technologies will be minimal, although some care must always be observed in pH adjustments to prevent hydrogen cyanide evolution.

Miscellaneous Cyanide Destruction Processes (Section 15.0)

The main miscellaneous cyanide destruction processes are biodegradation and thermal treatment. Biodegradation as a process for treating wastes containing cyanide is still in the developmental stage. Certain types of microorganisms have shown the ability to completely degrade low concentrations of simple cyanides. The major obstacle to implementation has been the inability of most conventional biosystems even when acclimated, to degrade fixed cyanides or simple cyanides in high concentrations. However, since the end products of complete biodegradation are nontoxic, continued research is advisable. In addition, many of the new bioaugmentation processes which can degrade fixed and/or concentrated cyanide wastes, may render biological treatment as a feasible alternative to conventional chemical or thermal destruction technologies.

Thermal treatment technologies which may be applied to cyanide-bearing hazardous wastes include incineration, evaporation, and crystrallization. The processing systems involved in each of these technologies are similar to those described for management of metal-bearing hazardous wastes. Test studies have indicated high potential levels of waste destruction (i.e., in excess of 99.99 percent) for the incineration of cyanide wastes. Incineration is most typically used to destroy cyanide wastes generated in organic chemical manufacturing, e.g., acrylonitrile production. Other cyanide waste candidates for incineration are waste organic cyanide compounds such as cyanogen.

Considerations for System Selection (Section 16.0)

The final section of the Technical Resource Document presents a comprehensive approach for the selection of a recovery/treatment process or processes for metal/cyanide hazardous waste management. The ultimate objective is to meet land disposal or discharge standards with the lowest possible cost, recognizing that waste minimization is a key aspect of cost benefit.

Process selection criteria are presented in the form of a generic algorithm, outlining pertinent considerations such as waste characteristics, cost, equipment availablility, and regulatory and institutional constraints. The importance of modeling and the need for experimental data are noted, and likely sources of such information are identified. Generalizations of the applicability of waste management alternatives are not emphasized, recognizing the limitations of this approach. Although each technology possesses certain definable ranges in cost and applicable waste types, as identified in the technology sections, suitability in a particular application is overwhelmingly dependent on site specific factors. In addition to wide variability in waste characteristics, these site specific factors include considerations such as potential for source reduction or waste reuse, availability of ancillary equipment and other onsite resources, and availability of offsite waste management services.

Stephen A. K. Palmer, Marc A. Breton, Thomas J. Nunno, David M. Sulllivan, and Norman F. Surprenant are with Alliance Technologies Corp., Bedford, MA 01730.

***L. H. Garcia** and **Robert C. Thurnau** are the EPA Project Officers (see below).*

The complete report, entitled "Technical Resource Document: Treatment Technologies for Metal/Cyanide-Containing Wastes, Volume III," (Order No. PB 88-143 896/AS; Cost: $56.95, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officers can be contacted at:

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U.S. Environmental Protection Agency
Cincinnati, OH 45268

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