FINAL
BEST DEMONSTRATED AVAILABLE TECHNOLOGY (BDAT) BACKGROUND DOCUMENT ADDENDUM FOR

CYANIDE WASTES

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1. INTRODUCTION AND SUMMARY

This document provides the Agency's rationale and technical support for selecting the constituents to be regulated in F019 nonwastewaters and wastewaters and for developing proposed best demonstrated available technology (BDAT) treatment standards for those regulated constituents. This document is an addendum to the Best Demonstrated Available Technology (BDAT) Background Document for Cyanide Wastes (F006-F012), dated June 1989. In the Second Third Final Rule (54 FR 26611), the Agency promulgated a treatment standard for total cyanide in F006 through F009 nonwastewaters as 590 mg/kg. While the Agency stated that F019 wastes were different from F006-F009 wastes because the F019 wastes contained high concentrations of iron-cyanide complexes, review of the waste characterization data for F006 wastes indicates that many F006 wastes also contain high concentrations of iron-cyanide complexes that are somewhat similar. Based on this information, the Agency is promulgating treatment standards for F019 based on a transfer from F006 wastes.

According to 40 CFR 261.31, waste code F019 is generated from the chemical conversion coating process and is listed as "wastewater treatment sludges from chemical conversion coating of aluminum." The waste as generated is typically, by BDAT definition, a nonwastewater since it usually contains greater than 1 percent total suspended solids (TSS). (For the purpose of determining the applicability of the treatment standards, wastewaters are defined as wastes containing less than 1 percent (weight basis) total suspended solids and less than 1 percent (weight basis) total organic carbon (TOC). Wastes not meeting this definition are nonwastewaters.)

The Agency has determined that BDAT for both F019 nonwastewaters and wastewaters is alkaline chlorination for cyanide followed by chemical reduction, precipitation, filtration, and stabilization for metals (chromium) based on transfer of data from similar wastes.

Table 1-1 summarizes the proposed treatment standards for F019 nonwastewaters and wastewaters.

In Section 2 of this document, generation and characterization of waste code F019 will be discussed. This waste is generated as a wastewater treatment sludge from treatment of chromate conversion coating solutions that contain hexavalent chromium and may also contain dissolved ferricyanide compounds. In Section 3, applicable and demonstrated technologies for cyanide and metals will be discussed. Applicable technologies for cyanide were specified on the basis of treatment of waste conversion coating solutions before generation of the wastewater treatment sludge, as well as on the basis of applicability to treatment of cyanide in the sludge. Section 4 presents the data available to EPA on treatment of complexed cyanide wastes. Section 5 identifies the Best Demonstrated Available Technology (BDAT). Sections 6 and 7 present selection of the regulated constituents and the calculation of BDAT treatment standards, respectively.

Table 1-1 BDAT Treatment Standards for F019

Constituent	Maximum for any single grab sample — Nonwastewater: Total concentration (mg/kg)	Maximum for any single grab sample — Nonwastewater: TCLP leachate concentration (mg/l)	Maximum for any single grab sample — Wastewater: Total concentration (mg/l)
Cyanide (amenable)	30	NA	0.86
Cyanide (total)	590	NA	1.20
Chromium (total)	NA	5.2	0.32

NA = Not applicable.

2. INDUSTRIES AFFECTED AND WASTE CHARACTERIZATION

The following waste from chemical conversion coating operations in the metal finishing industry, defined in 40 CFR 261.31, is subject to the land disposal restriction prohibitions of RCRA according to the schedule shown in 40 CFR 268.10-11:

F019: Wastewater treatment sludge from the chemical conversion coating of aluminum.

Section 2.1 describes the industries affected by the land disposal restrictions for F019 and presents a description of the chemical conversion coating process. Section 2.2 summarizes the available waste characterization data for this waste code. The listed wastes F006-F012, generated from electroplating (common metals electroplating, anodizing, chemical etching and milling, and metal cleaning and stripping) and metal heat treating operations, were addressed in the Best Demonstrated Available Technology (BDAT) Background Document for Cyanide Wastes (USEPA 1989c).

2.1 Industries Affected and Process Description

The listed waste F019 is generated from chemical conversion coating of aluminum. Facilities using chemical conversion coating operations are considered by EPA to be part of the metal finishing industry. In the preamble to the Effluent Limitations Guidelines for the Metal Finishing Industry (48 FR 32482, July 15, 1983), the Agency identified 13,500 facilities in the metal finishing industry, which may use any of 46 electroplating and metal finishing unit operations (including electroplating, heat treating, and chemical conversion coating).

Users of chemical conversion coating operations generally fall under Standard Industrial Classification (SIC) code series 3000, which comprises fabricated metal products except machinery and transportation equipment; machinery except electrical; electrical and electronic machinery, equipment, and supplies; transportation equipment; measuring, analyzing, and controlling instruments; and miscellaneous manufacturing industries. Chemical conversion coating operations are found throughout the country.

Chemical conversion coating operations include the following metal finishing processes: chromating, phosphating, metal coloring, and passivating. In chemical conversion coating operations, a portion of the base metal is converted to a protective film formed by the coating solution.

In chromating, aqueous solutions containing hexavalent chromium and other active organic or inorganic compounds are used to apply a hard surface coating that is corrosion resistant. Chromate coatings are usually applied only to aluminum surfaces, but can also be applied to galvanized surfaces. Phosphating and coloring involve formation of surface metallic phosphates, oxides, or other compounds that impart a color to the metal while also forming a protective coating. Phosphate conversion coatings are primarily used on steel and galvanized surfaces, but can be applied to aluminum. Oxide coatings (coloring) are applied primarily to galvanized surfaces. Passivating is the formation of a protective film on metals, particularly stainless steel and copper, by immersion in acid, cyanide, or aqueous organic chemical solutions.

Chromating is the most common chemical conversion coating process used to apply a coating to aluminum parts. Chromate coatings are applied from acid solution containing a source of hexavalent chromium (e.g., sodium chromate or chromic acid) and a strong oxidant (e.g., hydrofluoric acid or nitric acid). Chromate films are formed by the reaction of hexavalent chromium with the metal surface. Certain anions, referred to as "activators," are necessary for the formation of chromate coatings. Cyanide is used as an activator, usually in the form of ferricyanide $(Fe(CN)_6)^{-3}$ ion. Other anions commonly used as activators include acetates, formates, sulfates, chlorides, fluorides, nitrates, phosphates, and sulfamate ions (USEPA 1982).

Following application of chemical conversion coatings, the parts are usually rinsed in a bath or with a water spray. Wastewaters could be generated from chemical conversion coating operations as rinsewaters or as spent solutions. These wastes contain hexavalent chromium and may contain cyanide. Wastewater treatment sludges generated from treatment of these wastes are the listed waste F019.

2.2 Waste Characterization

This section presents the waste characterization data available to the Agency for F019 waste. The major constituents of this waste and their approximate concentrations are summarized in Table 2-1. Table 2-2 presents the concentrations for BDAT list constituents and other parameters identified as constituents of F019 wastes. Waste characterization data for electroplating waste are provided in Table 2-3. F012 waste compositional data submitted in the National Survey of Hazardous Waste Generators are provided in Table 2-4. Generally, F019 wastes contain no organic BDAT constituents. Chromium concentrations can be as high as 10 percent, zinc concentrations several percentage points, and cyanide up to 4,000 ppm. Other BDAT metals present include antimony, arsenic, barium, beryllium, cadmium, copper, lead, mercury, nickel, selenium, thallium, and vanadium.

2.3 Treatability Groups

Since all F019 wastewaters and nonwastewaters are produced from the chemical conversion coating of aluminum, the Agency has decided that presentation of the treatment standards on a waste code basis (according to the wastewater and nonwastewater forms of the waste) provides a sufficient distinction of the treatability groups.

Table 2-1 Approximate Major Constituent Analysis of F019 Waste, as Generated

Constituent	Concentration (percent)
BDAT list metals:	
Chromium (total)	<0.1 - 9
Zinc	<0.1 - 3
Other BDAT list metals	<0.1
Cyanide (total)	<0.1 - 0.4
Other solids (e.g., filter aid)	2 - 35
Water	65 - 98
Total	100

Table 2-2 F019 Waste Composition Data

Constituent/parameter (units)	Concentration (source)																
	(1)	(2)	(2)	(3)	(4)	(4)	(4)	(4)	(4)	(4)	(4)	(4)	(4)	(4)	(4)	(4)	(4)
BDAT Inorganics Other Than Metals (mg/kg)																	
Cyanide (total)	2,470	7.76	3.93	-	<0.22	-	<4	<4	-	<0.001	<0.001	0.24	0.12	<0.10	3,824	1.35	<0.08
Cyanide (amenable)	I	7.76	ND	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BDAT Metals (mg/kg)																	
Arsenic	9.05	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Barium	21.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Beryllium	0.09	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cadmium	7.24	0.212	0.288	-	<2	-	-	-	-	-	-	-	-	28	-	<0.01	-
Chromium (hexavalent)	3.76	-	-	-	-	-	<0.04	<0.2	-	-	-	-	-	25	-	<0.23	-
Chromium (total)	10,700	6,540	150	289	8,400	23,000	34,800	9,490	16,500	14,000	14	14,430	8,330	49,000	3,352	3,700	90,000
Copper	1.19	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Lead	-	-	-	<17	<60	-	-	-	-	-	-	-	-	8.4	-	41	-
Mercury	0.19	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Nickel	1.65	3.25	3.08		<4	-	-	-	-	-	-	-	-	39	-	47	-
Vanadium	6.69	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Zinc	31,400	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Other Parameters																	
Total solids (percent)	20.2	-	-	-	-	20-35	-	-	20	32	2	30	20	28	2	-	-

- = Not analyzed.
ND = Concentration reported as "zero."
I = Not determined because of analytical interference.

References:

(1) Zimpro 1989.
(2) MRI 1987.
(3) AES 1981.
(4) Versar 1986. Compilation of data from EPA delisting petitions.

Table 2-3 Summary of Waste Composition Data for F006-F012 Wastes

Constituent/parameter	Concentration (percent) F006	F007	F008	F009
Cyanide (as NaCN)	<0.1-0.5	5-10	2-10	5-20
BDAT List Metals				
Cadmium	0-2	0-2	0-2	0-2
Chromium	0-30	<0.1	<0.1	<0.1
Copper	0-3	0-1	0-2	0-2
Lead	0-3	<0.1	<0.1	<0.1
Nickel	0-17	0-2	0-2	0-2
Zinc	0-9	0-2	0-2	<0.1
TOTAL BDAT METALS	<0.1-30	~2	~2	~2
BDAT Organics	<0.1	<0.1	<0.1	<0.1
Iron				
Other Non-BDAT Inorganics (primarily sodium carbonate and/or calcium hydroxide)	20-40	20-40	35-40	20
Water	30-80	55-70	55	60-73
Oil and grease	0-4	<0.1	<0.1	<0.1

Constituent/parameter	Concentration (percent) F010	F011	F012	P-codes
Cyanide (as NaCN)	1-4	3-20	<0.1-12	1-50
BDAT List Metals				
Cadmium	-	<0.1	<0.1	-
Chromium	-	<0.1	<0.1	-
Copper	-	<0.1	<0.1	0-50
Lead	-	<0.1	<0.1	-
Nickel	-	<0.1	<0.1	0-50
Zinc	-	<0.1	<0.1	0-50
TOTAL BDAT METALS	<1	0.2	0.1	0-50
BDAT Organics	<0.1	<0.1	<0.1	-
Iron				<0.1
Other Non-BDAT Inorganics (primarily sodium carbonate and/or calcium hydroxide)	1-99	20-80	28-40	-
Water	0	0-77	60	-
Oil and grease	1-99	<0.1	<0.1	-

- = Not available

Table 2-4 F012 Waste Composition Data

Constituent/parameter (units)	Concentration (source) (1)	(2)	(2)	(3)	(4)
<u>BDAT Inorganics Other Than Metals</u> (mg/kg)					
Cyanide (total)	21	26,800	8,400	1,500	60,000-65,000
Fluoride	6.5	-	-	-	-
<u>BDAT Metals</u> (mg/kg)					
Barium	98	-	-	-	-
Cadmium	5.31	-	-	-	<100
Chromium (hexavalent)	-	-	-	-	350
Chromium (total)	11	-	-	-	-
Copper	307	-	-	-	-
Lead	28	-	-	-	500-600
Nickel	758	-	-	-	400-500
Silver	0.73	-	-	-	-
Vanadium	6.7	-	-	-	-
Zinc	54	-	-	-	-
<u>BDAT Volatile Organics</u> (μg/kg)					
Acetone	250	-	-	-	-
Chloroform	110	-	-	-	-
Methylene chloride	11	-	-	-	-
Toluene	28	-	-	-	-
<u>BDAT Semivolatile Organics</u> (μg/kg)					
Bis(2-ethylhexyl) phthalate	1,600	-	-	-	-
<u>PCBs</u> (μg/kg)					
Aroclor 1254	35	-	-	-	-
<u>Non-BDAT Metals</u> (mg/kg)					
Iron	2,880	-	-	-	-
Sodium	1,276	-	-	-	-
<u>Non-BDAT Inorganics Other Than Metals</u> (mg/kg)					
Chloride	992	-	-	-	-
Sulfate	6,900	-	-	-	-

Table 2-4 (continued)

Constituent/parameter (units)	Concentration (source) (1)	(2)	(2)	(3)	(4)
<u>Other Parameters</u>					
Total solids (%)	60.5	-	-	-	-
Total organic carbon (mg/kg)	540	-	-	-	-
Oil and grease (mg/kg)	432	-	-	-	-
pH	-	-	-	10.5-11.0	-

- = Not analyzed.

References:
(1) USEPA 1988d.
(2) USEPA 1980.
(3) Environ 1985.
(4) CyanoKEM 1987.

3. APPLICABLE/DEMONSTRATED TREATMENT TECHNOLOGIES

Section 2 presented waste characterization information showing the main constituents were BDAT list metals and cyanide. The applicable and demonstrated treatment technologies for cyanide wastes were discussed in detail in the original cyanide wastes background document. Alkaline chlorination treatment for the other metal finishing cyanide wastes (F006-F012) was found to be demonstrated for F019, based on the treatment data available to EPA.

Technologies for treatment of BDAT list metals in F019 are also discussed in the original background document. The applicable and demonstrated technologies that EPA has identified for metals treatment in F019 wastes are chemical reduction, chemical precipitation, filtration, and stabilization.

3.1 Applicable Treatment Technologies for Cyanide

The technologies applicable to treatment of cyanide in F019 wastes are those technologies that treat cyanide in the complexed form. The Agency has identified alkaline chlorination, wet air oxidation, and ultraviolet-light-enhanced ozonation (UV/ozonation) as applicable for treatment of complexed cyanide in F019 wastes.

Alkaline chlorination is a process that oxidizes ions or compounds to render them nonhazardous or to make them more amenable to subsequent removal or destruction processes. The basic principal of alkaline chlorination is that inorganic cyanides and some dissolved organic compounds can be chemically oxidized to yield carbon dioxide, water, salts, and simple organic acids. Species are oxidized by the addition of a chemical oxidizing agent that is itself reduced.

Aqueous cyanide wastes are typically treated in a batch alkaline chlorination process. Caustic is used to keep the pH alkaline, usually between 8.5 and 10.0. Cyanide destruction can be carried essentially to completion within 2-24 hours, depending upon the extent of interfering conditions.

Wet air oxidation is a high-temperature, high-pressure oxidation process in which the oxidizing agent is dissolved oxygen. At elevated temperatures, oxygen is an effective oxidizing agent for wastes containing organics or oxidizable inorganics such as cyanide. Typical operating temperatures for the treatment process range from 175 to 325°C (approximately 350 to 620°F). The pressure is maintained at a level high enough to prevent excessive evaporation of the liquid phase at the selected operating temperature (typically between 300 and 3,000 psi). At these elevated temperatures and pressures, the solubility of oxygen in water is dramatically increased, thus providing a strong driving force for the oxidation reactions.

UV/ozonation is a chemical oxidation process in which the oxidizing agent is dissolved ozone (supplied as an O_3/O_2 mixture). Ozone is a much stronger oxidizing agent than oxygen. Because it is very unstable, however, it must be generated just prior to being fed to the oxidation reactor. Ozone addition is controlled similarly to the addition of chlorine in alkaline chlorination. Ultraviolet (UV) light enhances the rate of the ozone oxidation reaction. Ultraviolet light is supplied by immersion of UV lamps in the solution. Wet air oxidation and chemical oxidation (by ozone and other oxidizing agents) are described in the Treatment Technology Background Document (USEPA 1989b).

Incineration is not considered applicable for treatment of cyanide in F019 wastes because these wastes are normally generated as inorganic wastewater treatment sludges. EPA would, however, consider incineration as applicable to treatment of F019 wastes containing significant concentrations of oil and grease or other organic constituents.

EPA believes, as was detailed in the background document for cyanide wastes, that the treatment technologies applicable for treatment of cyanides (especially complexed cyanides) in wastewater treatment sludges such as F019 are also applicable for treatment of the wastewaters from which these sludges are generated. In fact, the Agency believes that the most effective treatment for cyanide in F019 wastes and other wastewater treatment sludges containing cyanide is to treat the wastewaters for cyanide by one of the applicable technologies before generation of the wastewater treatment sludge because the applicable cyanide treatment technologies discussed above are designed to treat aqueous waste streams. (Refer to the development of nonwastewater cyanide treatment standards for F006-F012 as detailed in the BDAT background document for cyanide wastes (USEPA 1989c).)

3.2 Demonstrated Treatment Technologies for Cyanide

EPA has identified alkaline chlorination, wet air oxidation, and UV/ozonation as demonstrated treatment technologies for cyanide in F019 wastes. Alkaline chlorination is in commercial use at several facilities for treatment of electroplating sludges (F006-F009 wastes) containing organics and cyanides. Ozonation and wet air oxidation are currently used for treatment of wastes containing organic constituents, and EPA believes these could be applied commercially to cyanide wastes.

4. PERFORMANCE DATA BASE

This section presents the data available to EPA on treatment of complexed cyanide wastes in wastes similar to F019. Wastes similar to F019 are wastes that contain cyanide primarily in the complexed form.

4.1 Cyanide Treatment Data

The BDAT background document for cyanide wastes (USEPA 1989c) presented the data available to the Agency at the time on the treatment of cyanide wastes. Since promulgation of the Second Third land disposal restrictions, EPA has reviewed data for alkaline chlorination, wet air oxidation, and UV/ozonation of various electroplating wastes for treatment of F019 waste and treatment of a similar waste containing complexed iron cyanides.

Table 4-1 presents data from alkaline chlorination of various electroplating wastes consisting of F006, F007, F008, F009, F011, F012, D002, D003, P029, P030, and P106 wastes. A variety of cyanide-containing wastes were treated by this alkaline chlorination process. Fourteen different sample sets are presented. In addition, the Agency's development of categorical wastewater discharge standards for the Metal Finishing industry set standards at 0.86 mg/l for amenable cyanide and 1.2 mg/l for total cyanide. Data supporting the Metal Finishing cyanide standards are found in Development Document for Effluent Limitations Guidelines and Standards for the Metal Finishing Point Source Category (EPA 440/1-83/091, June 1983, pp. VII-126 to VII-153). These data are presented in Appendix A.

Table 4-2 presents the results of a bench-scale batch wet air oxidation treatment test of F019 waste. The waste tested was an F019 filter cake generated at an aluminum conversion coating facility. The waste was slurried with water before wet air oxidation treatment. The treated wastewater and treated nonwastewater are the residuals generated following subsequent chemical precipitation and filtration treatment. The test runs are presented.

Table 4-3 presents the results of bench-scale testing of UV/ozonation treatment of an F009 waste in which the cyanide content was complexed cyanide. This waste was collected at an electroplating facility after destruction of amenable cyanide by alkaline chlorination treatment. EPA feels that this waste is similar to wastewaters from chemical conversion coating of aluminum because the cyanide content of both wastes is primarily in the complexed form. Also, this waste was generated from a similar process in the metal finishing industry and did not contain significant concentrations of other oxidizable compounds. UV/ozonation treatment was applied to eight test runs.

The data in Table 4-3 give the untreated and treated total waste composition for total cyanide before and after UV/ozonation treatment. The residuals from UV/ozonation treatment were not treated for metals removal; therefore, no data are presented for BDAT list metals and no data are available to indicate how much of the cyanide remaining after UV/ozonation would be found in either wastewater or nonwastewater residuals.

4.2 BDAT List Metals Treatment Data

4.2.1 Wastewaters

No performance data are available for treatment of F019 wastewaters for metals. EPA would expect F019 wastewaters to be similar in waste characteristics to K062 wastewaters in terms of the type and concentration of metals present. The K062 wastewaters tested by the

Agency had chromium concentrations of up to 7000 mg/l (see Table 4-4). F019 wastewaters would be expected to contain lower concentrations of chromium because they are typically generated by filtering F019 nonwastewaters. The F019 nonwastewaters should have very little dissolved chromium since the chromium conversion rinses are generally treated for chromium prior to generating F019 nonwastewaters. Both wastes are generated from metal finishing processes in which no organics would be expected to be present. Data for treatment of K062 by chemical reduction followed by chemical precipitation and filtration are presented in Table 4-4.

4.2.2 Nonwastewaters

No performance data are available for treatment of metals in F019 nonwastewaters. (Wet air oxidation and UV/ozonation do not treat the metals in the wastes.) However, data are available for stabilization of metals in F006 (wastewater treatment sludges from electroplating operations). Both F019 and F006 are wastewater treatment sludges generated from metal finishing operations and are expected to have similar chemical compositions. Treatment data from F006 waste show chromium present at up to 43,000 mg/kg, which is a level comparable to that expected to be found in F019 nonwastewaters (see Tables 2-1 and 2-2). Neither waste is expected to contain concentrations of organic compounds that would affect stabilization treatment. Therefore, the Agency believes that the F006 treatment data sets represent a level of treatment performance that can be achieved for metals in F019 nonwastewaters using stabilization. The performance data for stabilization of F006 appear in Table 4-5.

Table 4-1 Alkaline Chlorination Data Submitted by Plant C During the Public Comment Period

Sample Set No. 1[a] - for Treatment of F007, F008, D003, and P106

	Concentration		
Constituent/parameter	Untreated waste (mg/l)	Treated wastewater (mg/l)	Treated nonwastewater (mg/l)
BDAT Inorganics Other Than Metals			
Cyanide (total)	71,759	0.95	357
BDAT List Metals			
Copper	4,193	-	-
Nickel	136	-	-
Cadmium	2,995	-	-
Chromium	323	-	-
Lead	184	-	-
Zinc	2,319	-	-
Non-BDAT List Metals			
Iron	2,936	-	-
Other Parameters			
pH	11.2	-	-
TOC	<2%	-	-

- = Not analyzed.

[a]Batch consisted of a mixture of liquids and drummed solids including waste codes F007, F008, D003, and P106.

Reference: CyanoKEM 1989.

Table 4-1 (continued)

Sample Set No. 2[a] - for Treatment of F009, F012

Constituent/parameter	Concentration Untreated waste (mg/l)	Treated wastewater (mg/l)	Treated nonwastewater (mg/l)
BDAT Inorganics Other Than Metals			
Cyanide (total)	12,000	0.95	153
BDAT List Metals			
Copper	1,339	-	-
Nickel	4,088	-	-
Cadmium	300	-	-
Chromium	592	-	-
Lead	327	-	-
Zinc	750	-	-
Non-BDAT List Metals			
Iron	6,200	-	-
Other Parameters			
pH	11.0	-	-
TOC	<2%	-	-

- = Not analyzed.

[a]Batch consisted of a mixture of liquids and drummed solids including waste codes F009 and F012.

Reference: CyanoKEM 1989.

Table 4-1 (continued)

Sample Set No. 3[a] - for Treatment of F009, D002, D003, and P030

Constituent/parameter	Concentration: Untreated waste (mg/l)	Concentration: Treated wastewater (mg/l)	Concentration: Treated nonwastewater (mg/l)
BDAT Inorganics Other Than Metals			
Cyanide (total)	17,206	<0.014	351
BDAT List Metals			
Copper	8,400	-	-
Nickel	1,290	-	-
Cadmium	7,610	-	-
Chromium	239	-	-
Lead	129	-	-
Zinc	5,150	-	-
Non-BDAT List Metals			
Iron	5,520	-	-
Other Parameters			
pH	11.2	-	-
TOC	<2%	-	-

- = Not analyzed.

[a]Batch consisted of a mixture of liquids and drummed solids including waste codes F009, D002, D003, and P030.

Reference: CyanoKEM 1989.

Table 4-1 (continued)

Sample Set No. 4[a] - for Treatment of F007, F009, and D002

Constituent/parameter	Concentration		
	Untreated waste (mg/l)	Treated wastewater (mg/l)	Treated nonwastewater (mg/l)
BDAT Inorganics Other Than Metals			
Cyanide (total)	25,936	<0.014	374
BDAT List Metals			
Copper	3,266	-	-
Nickel	7,172	-	-
Cadmium	1,482	-	-
Chromium	707	-	-
Lead	173	-	-
Zinc	2,389	-	-
Non-BDAT List Metals			
Iron	11,917	-	-
Other Parameters			
pH	11.5	-	-
TOC	<2%	-	-

- = Not analyzed.

[a]Batch consisted of a mixture of liquids and drummed solids including waste codes F007, F009, and D002.

Reference: CyanoKEM 1989.

Table 4-1 (continued)

Sample Set No. 5[a] - for Treatment of F007, F008, D003, and P029

Constituent/parameter	Concentration: Untreated waste (mg/l)	Treated wastewater (mg/l)	Treated nonwastewater (mg/l)
BDAT Inorganics Other Than Metals			
Cyanide (total)	16,914	<0.014	235
BDAT List Metals			
Copper	5,343	-	-
Nickel	151	-	-
Cadmium	3,412	-	-
Chromium	408	-	-
Lead	99	-	-
Zinc	3,483	-	-
Non-BDAT List Metals			
Iron	3,670	-	-
Other Parameters			
pH	11.0	-	-
TOC	<2%	-	-

- = Not analyzed.

[a]Batch consisted of a mixture of liquids and drummed solids including waste codes F007, F008, D003, and P029.

Reference: CyanoKEM 1989.

Table 4-1 (continued)

Sample Set No. 6[a] - for Treatment of F011, F012, D002, and P106

	Concentration		
Constituent/parameter	Untreated waste (mg/l)	Treated wastewater (mg/l)	Treated nonwastewater (mg/l)
BDAT Inorganics Other Than Metals			
Cyanide (total)	59,421	0.028	245
BDAT List Metals			
Copper	922	-	-
Nickel	259	-	-
Cadmium	3,223	-	-
Chromium	180	-	-
Lead	142	-	-
Zinc	5,143	-	-
Non-BDAT List Metals			
Iron	3,810	-	-
Other Parameters			
pH	11.3	-	-
TOC	<2%	-	-

- = Not analyzed.

[a]Batch consisted of a mixture of liquids and drummed solids including waste codes F011, F012, D002, and P106.

Reference: CyanoKEM 1989.

Table 4-1 (continued)

Sample Set No. 7[a] - for Treatment of F007 and F009

Constituent/parameter	Concentration: Untreated waste (mg/l)	Treated wastewater (mg/l)	Treated nonwastewater (mg/l)
BDAT Inorganics Other Than Metals			
Cyanide (total)	31,994	0.028	169
BDAT List Metals			
Copper	15,739	-	-
Nickel	1,897	-	-
Cadmium	944	-	-
Chromium	100	-	-
Lead	124	-	-
Zinc	3,187	-	-
Non-BDAT List Metals			
Iron	403	-	-
Other Parameters			
pH	11.2	-	-
TOC	<2%	-	-

- = Not analyzed.

[a]Batch consisted of a mixture of liquids and drummed solids including waste codes F007 and F009.

Reference: CyanoKEM 1989.

Table 4-1 (continued)

Sample Set No. 8 - for Treatment of F007

Constituent/parameter	Concentration Untreated waste (mg/l)	Treated wastewater (mg/l)	Treated nonwastewater (mg/l)
BDAT Inorganics Other Than Metals			
Cyanide (total)	41,900	<0.014	189
BDAT List Metals			
Copper	19,510	-	-
Nickel	2,683	-	-
Cadmium	1,350	-	-
Chromium	100	-	-
Lead	138	-	-
Zinc	4,708	-	-
Non-BDAT List Metals			
Iron	498	-	-
Other Parameters			
pH	11.5	-	-
TOC	<2%	-	-

- = Not analyzed.

Reference: CyanoKEM 1989.

Table 4-1 (continued)

Sample Set No. 9[a] - for Treatment of F006, F009, F011, D002, and D003

Constituent/parameter	Concentration: Untreated waste (mg/l)	Concentration: Treated wastewater (mg/l)	Concentration: Treated nonwastewater (mg/l)
BDAT Inorganics Other Than Metals			
Cyanide (total)	18,882	<0.014	106.3
BDAT List Metals			
Copper	11,654	-	-
Nickel	1,925	-	-
Cadmium	792	-	-
Chromium	3,658	-	-
Lead	289	-	-
Zinc	5,357	-	-
Non-BDAT List Metals			
Iron	6,713	-	-
Other Parameters			
pH	10.3	-	-
TOC	<2%	-	-

- = Not analyzed.

[a]Batch consisted of a mixture of liquids and drummed solids including waste codes F006, F009, F011, D002, and D003.

Reference: CyanoKEM 1989.

Table 4-1 (continued)

Sample Set No. 10[a] - for Treatment of F006 and F012

Constituent/parameter	Concentration: Untreated waste (mg/l)	Treated wastewater (mg/l)	Treated nonwastewater (mg/l)
BDAT Inorganics Other Than Metals			
Cyanide (total)	1,270	0.17	143
BDAT List Metals			
Copper	2,319	-	-
Nickel	6,739	-	-
Cadmium	1,903	-	-
Chromium	14,079	-	-
Lead	662	-	-
Zinc	19,163	-	-
Non-BDAT List Metals			
Iron	7,786	-	-
Other Parameters			
pH	10.0	-	-
TOC	<2%	-	-

- = Not analyzed.

[a]Batch consisted of a mixture of liquids and drummed solids including waste codes F006 and F012.

Reference: CyanoKEM 1989.

Table 4-1 (continued)

Sample Set No. 11[a] - for Treatment of F007, F009, D002, P029, and P030

Constituent/parameter	Concentration: Untreated waste (mg/l)	Treated wastewater (mg/l)	Treated nonwastewater (mg/l)
BDAT Inorganics Other Than Metals			
Cyanide (total)	22,820	1.16	114.1
BDAT List Metals			
Copper	7,910	-	-
Nickel	450	-	-
Cadmium	3,109	-	-
Chromium	<100	-	-
Lead	124	-	-
Zinc	4,695	-	-
Non-BDAT List Metals			
Iron	832	-	-
Other Parameters			
pH	11.2	-	-
TOC	<2%	-	-

- = Not analyzed.

[a]Batch consisted of a mixture of liquids and drummed solids including waste codes F007, F009, D002, P029, and P030.

Reference: CyanoKEM 1989.

Table 4-1 (continued)

Sample Set No. 12[a] - for Treatment of F007, F009, F012, and D003

Constituent/parameter	Concentration: Untreated waste (mg/l)	Treated wastewater (mg/l)	Treated nonwastewater (mg/l)
BDAT Inorganics Other Than Metals			
Cyanide (total)	12,085	<0.014	252.4
BDAT List Metals			
Copper	8,165	-	-
Nickel	138	-	-
Cadmium	128	-	-
Chromium	<116	-	-
Lead	105	-	-
Zinc	325	-	-
Non-BDAT List Metals			
Iron	248	-	-
Other Parameters			
pH	10.7	-	-
TOC	<2%	-	-

- = Not analyzed.

[a]Batch consisted of a mixture of liquids and drummed solids including waste codes F007, F009, F012, and D003.

Reference: CyanoKEM 1989.

Table 4-1 (continued)

Sample Set No. 13 - for Treatment of D002

Constituent/parameter	Concentration: Untreated waste (mg/l)	Concentration: Treated wastewater (mg/l)	Concentration: Treated nonwastewater (mg/l)
BDAT Inorganics Other Than Metals			
Cyanide (total)	10,902	0.07	203.1
BDAT List Metals			
Copper	355	-	-
Nickel	160	-	-
Cadmium	7,050	-	-
Chromium	120	-	-
Lead	125	-	-
Zinc	9,940	-	-
Non-BDAT List Metals			
Iron	1,530	-	-
Other Parameters			
pH	11.8	-	-
TOC	<2%	-	-

- = Not analyzed.

Reference: CyanoKEM 1989.

Table 4-1 (continued)

Sample Set No. 14[a] - for Treatment of F009, F011, D002, and D003

Constituent/parameter	Concentration Untreated waste (mg/l)	Treated wastewater (mg/l)	Treated nonwastewater (mg/l)
BDAT Inorganics Other Than Metals			
Cyanide (total)	16,010	0.07	94.4
BDAT List Metals			
Copper	6,272	-	-
Nickel	223	-	-
Cadmium	4,063	-	-
Chromium	133	-	-
Lead	124	-	-
Zinc	6,012	-	-
Non-BDAT List Metals			
Iron	3,511	-	-
Other Parameters			
pH	11.5	-	-
TOC	<2%	-	-

- = Not analyzed.

[a]Batch consisted of a mixture of liquids and drummed solids including waste codes F009, F011, D002, and D003.

Reference: CyanoKEM 1989.

Table 4-2 Wet Air Oxidation Data for Treatment of F019

Sample Set #1

Constituent/parameter	Untreated waste (mg/l)	Treated wastewater (mg/l)	Treated filter cake (mg/kg)
	Concentration		
BDAT Inorganics Other Than Metals			
Cyanide (amenable)	241	5.0	22.9
Cyanide (total)	293	5.07	22.9
Fluoride	38.9	24.7	0.17
Sulfide	<1.0	<1.0	-
BDAT List Metals			
Antimony	<0.005	<0.005	465
Arsenic	0.08	0.13	114
Barium	2.7	0.21	138
Beryllium	0.007	<0.001	0.32
Cadmium	2.1	0.013	102
Chromium (total)	1,230	1.9	72,800
Copper	0.36	0.053	48.7
Lead	14.7	0.003	816
Mercury	0.00035	0.0011	<0.02
Nickel	0.88	0.007	46
Selenium	0.05	0.25	<20
Thallium	<0.14	0.0095	<5
Vanadium	0.31	0.006	<0.5
Zinc	4,900	4.6	261,000
Non-BDAT List Metals			
Iron	190	0.13	12,000
Other Parameters (units)			
COD (mg/l)	10,500	1,750	-
pH (-)	8.54	7.95	-

Design and Operating Parameters

Parameter (units)	Design value	Operating value
Oxidation Temperature (°C)	NA	200
Time at Temperature (min)	60	60

- = Not analyzed.
NA = Not applicable.
Reference: Zimpro 1988.

Table 4-2 (continued)

Sample Set #2

	Concentration		
Constituent/parameter	Untreated waste (mg/l)	Treated wastewater (mg/l)	Treated filter cake (mg/kg)
BDAT Inorganics Other Than Metals			
Cyanide (amenable)	241	<0.02	142
Cyanide (total)	293	0.058	142
Fluoride	38.9	30.9	0.15
Sulfide	<1.0	<1.0	-
BDAT List Metals			
Antimony	<0.005	<0.005	460
Arsenic	0.08	0.22	135
Barium	2.7	0.35	145
Beryllium	0.007	<0.001	0.29
Cadmium	2.1	0.007	99
Chromium (total)	1,230	1.9	68,600
Copper	0.36	0.046	34
Lead	14.7	0.008	586
Mercury	0.00035	0.001	<0.02
Nickel	0.88	0.011	43
Selenium	0.05	<0.005	<20
Thallium	<0.14	0.005	<5
Vanadium	0.31	<0.005	<0.5
Zinc	4,900	4.6	257,000
Non-BDAT List Metals			
Iron	190	0.08	11,000
Other Parameters (units)			
COD (mg/l)	10,500	3,040	-
pH (-)	8.54	7.90	-

Design and Operating Parameters

Parameter (units)	Design value	Operating value
Oxidation Temperature (°C)	NA	240
Time at Temperature (min)	60	60

- = Not analyzed.
NA = Not applicable.
Reference: Zimpro 1988.

Table 4-2 (continued)

Sample Set #3

Constituent/parameter	Concentration: Untreated waste (mg/l)	Treated wastewater (mg/l)	Treated filter cake (mg/kg)
BDAT Inorganics Other Than Metals			
Cyanide (amenable)	241	<0.02	18
Cyanide (total)	293	0.133	18
Fluoride	38.9	38.9	0.23
Sulfide	<1.0	<1.0	-
BDAT List Metals			
Antimony	<0.005	<0.005	469
Arsenic	0.08	<0.005	109
Barium	2.7	0.77	166
Beryllium	0.007	<0.01	0.32
Cadmium	2.1	<0.04	105
Chromium (total)	1,230	24	74,100
Copper	0.36	0.12	66
Lead	14.7	0.916	584
Mercury	0.00035	0.0008	<0.02
Nickel	0.88	0.21	48
Selenium	0.05	<0.005	<20
Thallium	<0.14	0.005	<5.0
Vanadium	0.31	<0.05	<0.5
Zinc	4,900	15.2	279,000
Non-BDAT List Metals			
Iron	190	0.08	15,200
Other Parameters (units)			
COD (mg/l)	10,500	2,120	-
pH (-)	8.54	7.8	-

Design and Operating Parameters

Parameter (units)	Design value	Operating value
Oxidation Temperature (°C)	NA	280
Time at Temperature (min)	60	60

- = Not analyzed.
NA = Not applicable.
Reference: Zimpro 1988.

Table 4-3 Performance Data for UV/Ozonation Treatment of Complexed Cyanide F009 Waste

Constituent	Concentration Untreated waste (mg/l)	Concentration Treated waste (mg/l)
Sample Set No. 1		
Cyanide (total)	61	53
Sample Set No. 2		
Cyanide (total)	61	53
Sample Set No. 3		
Cyanide (total)	61	36
Sample Set No. 4		
Cyanide (total)	61	49
Sample Set No. 5		
Cyanide (total)	61	37
Sample Set No. 6		
Cyanide (total)	61	63
Sample Set No. 7		
Cyanide (total)	61	25
Sample Set No. 8		
Cyanide (total)	1,355	1,170

Table 4-3 (continued)

Design and operating parameters:

Parameter	Design value[a]	Operating value SS#1	SS#2	SS#3	SS#4	SS#5	SS#6	SS#7	SS#8
UV output (watts)	5.0	1.9	3.5	5.0	5.0	5.0	5.0	0	5.0
Temperature (°C)	60-68	40-65	63-66	62-66	22-27	66	66	62-68	66
Ozone concentration (wt %)	>3.0	3.5	3.0	3.0	3.0-3.1	3.0	0	3.0	2.5-4.0
Gas flow rate (l/min)	0.5	0.5	0.5	0.5	0.5	0.2-0.5	0	0.5	0.25-0.5
Time (hr)	1	1	1	1	1.1	1.1	1	1	1
pH	8 or 10-12	10.5-11.8	10.6	10.4	10.8-11.3	8.0	8.0	8.0	8.0

[a]Design values were varied for each sample set to determine the effect of these variables on the treated waste cyanide concentration.

Reference: IITRI 1989.

Table 4-4 Chemical Precipitation Treatment Performance Data
for K062 - EPA-Collected Data

Sample Set #1

Constituent	Untreated K062 waste (mg/l) Sample no. 801	Untreated K062 waste (mg/l) Sample no. 802	Untreated waste composite[a] (mg/l) Sample no. 805	Treated waste (wastewater) (mg/l) Sample no. 806
Arsenic	3	<1	<1	<0.1
Cadmium	<5	<5	13	<0.5
Chromium (hexavalent)	I	I	893	0.011
Chromium (total)	1800	7000	2581	0.12
Copper	865	306	138	0.21
Lead	<10	<10	64	<0.01
Nickel	3200	2600	471	0.33
Zinc	<2	<2	116	0.125

Design and Operating Parameters

	Design value	Operating value
pH	8-10	9

I = Color interference.

[a]The untreated waste composite is a mixture of the untreated K062 waste streams shown on this table, along with other non-K062 waste streams.

Reference: USEPA 1988b.

Table 4-4 (continued)

Sample Set #2

Constituent	Untreated K062 waste (mg/l) Sample no. 801	Untreated K062 waste (mg/l) Sample no. 802	Untreated waste composite[a] (mg/l) Sample no. 813	Treated waste (wastewater) (mg/l) Sample no. 814
Arsenic	3	<1	<1	<0.1
Cadmium	<5	<5	10	<0.5
Chromium (hexavalent)	I	I	807	0.12
Chromium (total)	1800	7000	2279	0.19
Copper	865	306	133	0.15
Lead	<10	<10	54	<0.01
Nickel	3200	2600	470	0.33
Zinc	<2	<2	4	0.115

Design and Operating Parameters

	Design value	Operating value
pH	8-10	9

I = Color interference.

[a]The untreated waste composite is a mixture of the untreated K062 waste streams shown on this table, along with other non-K062 waste streams.

Reference: USEPA 1988b.

Table 4-4 (continued)

Sample Set #3

Constituent	Untreated K062 waste (mg/l) Sample no. 817	Untreated K062 waste (mg/l) Sample no. 802	Untreated waste composite[a] (mg/l) Sample no. 821	Treated waste (wastewater) (mg/l) Sample no. 822
Arsenic	3	<1	<1	<0.1
Cadmium	<5	<5	5	<0.5
Chromium (hexavalent)	I	I	775	I
Chromium (total)	1700	7000	1990	0.20
Copper	425	306	133	0.21
Lead	<10	<10	<10	<0.01
Nickel	100310	2600	16330	0.33
Zinc	7	<2	3.9	0.140

Design and Operating Parameters

	Design value	Operating value
pH	8-10	10

I = Color interference.

[a]The untreated waste composite is a mixture of the untreated K062 waste streams shown on this table, along with other non-K062 waste streams.

Reference: USEPA 1988b.

Table 4-4 (continued)

Sample Set #4

Constituent	Untreated K062 waste (mg/l) Sample no. 827	Untreated K062 waste (mg/l) Sample no. 802	Untreated K062 waste (mg/l) Sample no. 817	Untreated waste composite[a] (mg/l) Sample no. 829	Treated waste (wastewater) (mg/l) Sample no. 830
Arsenic	2	<1	3	<1	<1
Cadmium	<5	<5	5	<5	<0.5
Chromium (hexavalent)	I	I	I	0.6	0.042
Chromium (total)	142	7000	1700	556	0.10
Copper	42	306	425	88	0.07
Lead	<10	<10	<10	<10	<0.01
Nickel	650	2600	41000	6610	0.33
Zinc	3	<2	7	84	1.62

Design and Operating Parameters

	Design value	Operating value
pH	8-10	9

I = Color interference.

[a]The untreated waste composite is a mixture of the untreated K062 waste streams shown on this table, along with other non-K062 waste streams.

Reference: USEPA 1988b.

Table 4-4 (continued)

Sample Set #5

Constituent	Untreated K062 waste (mg/l) Sample no. 801	Untreated K062 waste (mg/l) Sample no. 802	Untreated K062 waste (mg/l) Sample no. 817	Untreated waste composite[a] (mg/l) Sample no. 837	Treated waste (wastewater) (mg/l) Sample no. 838
Arsenic	3	<1	3	<1	<0.1
Cadmium	<5	<5	5	<5	<0.5
Chromium (hexavalent)	I	I	I	917	0.058
Chromium (total)	1800	7000	1700	2236	0.11
Copper	865	306	425	91	0.14
Lead	<10	<10	<10	18	0.01
Nickel	3200	2600	41000	1414	0.31
Zinc	<2	<2	7	71	0.125

Design and Operating Parameters

	Design value	Operating value
pH	8-10	8

I = Color interference.

[a]The untreated waste composite is a mixture of the untreated K062 waste streams shown on this table, along with other non-K062 waste streams.

Reference: USEPA 1988b.

Table 4-4 (continued)

Sample Set #6

Constituent	Untreated K062 waste (mg/l) Sample no. 801	Untreated K062 waste (mg/l) Sample no. 802	Untreated waste composite[a] (mg/l) Sample no. 845	Treated waste (wastewater) (mg/l) Sample no. 846
Arsenic	3	<1	<1	<0.1
Cadmium	<5	<5	<5	<0.5
Chromium (hexavalent)	I	I	734	I
Chromium (total)	1800	7000	2548	0.10
Copper	865	306	149	0.12
Lead	<10	<10	<10	<0.01
Nickel	3200	2600	588	0.33
Zinc	<2	<2	4	0.095

Design and Operating Parameters

	Design value	Operating value
pH	8-10	8

I = Color interference.

[a]The untreated waste composite is a mixture of the untreated K062 waste streams shown on this table, along with other non-K062 waste streams.

Reference: USEPA 1988b.

Table 4-4 (continued)

Sample Set #7

Constituent	Untreated K062 waste (mg/l) Sample no. 801	Untreated K062 waste (mg/l) Sample no. 802	Untreated waste composite[a] (mg/l) Sample no. 853	Treated waste (wastewater) (mg/l) Sample no. 854
Arsenic	3	<1	<1	<0.1
Cadmium	<5	<5	10	<0.5
Chromium (hexavalent)	I	I	769	0.12
Chromium (total)	1800	7000	2314	0.12
Copper	865	306	72	0.16
Lead	<10	<10	108	<0.01
Nickel	3200	2600	426	0.40
Zinc	<2	<2	171	0.115

Design and Operating Parameters

	Design value	Operating value
pH	8-10	9

I = Color interference.

[a]The untreated waste composite is a mixture of the untreated K062 waste streams shown on this table, along with other non-K062 waste streams.

Reference: USEPA 1988b.

Table 4-4 (continued)

Sample Set #8

Constituent	Untreated K062 waste (mg/l) Sample no. 859	Untreated K062 waste (mg/l) Sample no. 801	Untreated waste composite[a] (mg/l) Sample no. 861	Treated waste (wastewater) (mg/l) Sample no. 862
Arsenic	<1	3	<1	<0.1
Cadmium	<5	<5	<5	<0.5
Chromium (hexavalent)	0.220	I	0.13	<0.01
Chromium (total)	15	1800	831	0.15
Copper	151	865	217	0.16
Lead	<10	<10	212	<0.01
Nickel	90	3200	669	0.36
Zinc	7	9	151	0.13

Design and Operating Parameters

	Design value	Operating value
pH	8-10	9

I = Color interference.

[a]The untreated waste composite is a mixture of the untreated K062 waste streams shown on this table, along with other non-K062 waste streams.

Reference: USEPA 1988b.

Table 4-4 (continued)

Sample Set #9

Constituent	Untreated K062 waste (mg/l) Sample no. 867	Untreated K062 waste (mg/l) Sample no. 801	Untreated K062 waste (mg/l) Sample no. 802	Untreated waste composite[a] (mg/l) Sample no. 869	Treated waste (wastewater) (mg/l) Sample no. 870
Arsenic	<0.1	3	<1	<1	<0.1
Cadmium	<0.5	<5	<5	<5	<0.5
Chromium (hexavalent)	0.079	I	I	0.07	0.041
Chromium (total)	6	1800	7000	939	0.10
Copper	5	865	306	225	0.08
Lead	<1	<10	<10	<10	<0.01
Nickel	4	3200	2600	940	0.33
Zinc	0.4	<2	<2	5	0.06

Design and Operating Parameters

	Design value	Operating value
pH	8-10	10

I = Color interference.

[a]The untreated waste composite is a mixture of the untreated K062 waste streams shown on this table, along with other non-K062 waste streams.

Reference: USEPA 1988b.

Table 4-4 (continued)

Sample Set #10

Constituent	Untreated K062 waste (mg/l) Sample no. 801	Untreated waste composite[a] (mg/l) Sample no. 885	Treated waste (wastewater) (mg/l) Sample no. 862
Arsenic	<3	<1	<0.10
Cadmium	<5	<5	<0.5
Chromium (hexavalent)	I	0.08	0.106
Chromium (total)	1800	395	0.12
Copper	865	191	0.14
Lead	<10	<10	<0.01
Nickel	3200	712	0.33
Zinc	<2	5	0.070

Design and Operating Parameters

	Design value	Operating value
pH	8-10	9

I = Color interference.

[a]The untreated waste composite is a mixture of the untreated K062 waste streams shown on this table, along with other non-K062 waste streams.

Reference: USEPA 1988b.

Table 4-4 (continued)

Sample Set #11

Constituent	Untreated K062 waste (mg/l) Sample no. 801	Untreated K062 waste (mg/l) Sample no. 859	Untreated waste composite[a] (mg/l) Sample no. 893	Treated waste (wastewater) (mg/l) Sample no. 894
Arsenic	3	<1	<1	<0.10
Cadmium	<5	<5	23	<5
Chromium (hexavalent)	I	0.220	0.30	<0.01
Chromium (total)	1800	15	617	0.18
Copper	865	151	137	0.24
Lead	<10	<10	136	<0.01
Nickel	3200	90	382	0.39
Zinc	<2	7	135	0.100

Design and Operating Parameters

	Design value	Operating value
pH	8-10	9

I = Color interference.

[a]The untreated waste composite is a mixture of the untreated K062 waste streams shown on this table, along with other non-K062 waste streams.

Reference: USEPA 1988b.

Table 4-5 Treatment Performance Data for Stabilization of F006 Waste

Source	Oil and grease (mg/kg)	TOC (mg/kg)	Mix ratio[a]	Metal concentrations (ppm)										
				Arsenic	Barium	Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Selenium	Silver	Zinc
Unknown														
Unstabilized														
As received	1,520	14,600		-	36.4	1.3	1270	40.2	35.5	-	435	-	2.3	1560
TCLP				<0.01	0.08	0.01	0.34	0.15	0.26	<0.001	0.71	<0.01	0.01	0.16
Stabilized														
TCLP			0.2	<0.01	0.12	0.01	0.51	0.20	0.30	<0.001	0.04	0.06	0.03	0.03
Auto parts manufacturing														
Unstabilized														
As received	60	1,500		-	21.6	31.3	755	7030	409	-	989	-	6.62	4020
TCLP				<0.01	0.32	2.21	0.76	368	10.7	<0.001	22.7	<0.01	0.14	219
Stabilized														
TCLP			0.2	<0.01	0.50	0.50	0.40	5.4	0.40	<0.001	1.5	0.06	0.03	36.9
TCLP			0.5	<0.01	0.42	0.01	0.39	0.25	0.36	<0.001	0.03	0.11	0.05	0.01
Aircraft overhauling facility														
Unstabilized														
As received	37,000	137,000		-	85.5	67.3	716	693	25.7	-	259	-	39	631
TCLP				0.01	1.41	1.13	0.43	1.33	0.26	<0.001	1.1	<0.01	0.02	5.41
Stabilized														
TCLP			0.2	<0.01	0.33	0.06	0.08	1.64	0.03	<0.001	0.23	0.07	0.20	0.05
TCLP			0.5	<0.01	0.31	0.02	0.20	1.84	0.41	<0.001	0.15	0.11	0.05	0.03
Aerospace manufacturing (mixture of F006 & F007)														
Unstabilized														
As received	3,870	8,280		-	0.74	1.69	12.9	18.5	11.4	-	234	-	6.26	8.86
TCLP				<0.01	0.83	0.66	7.58	4.12	6.86	0.003	158	<0.01	1.64	2.28
Stabilized														
TCLP			1.0	<0.01	0.52	<0.01	0.40	0.23	0.20	<0.001	4.35	0.17	0.09	0.05
TCLP			1.5	<0.01	1.18	0.01	0.34	0.19	0.36	<0.001	2.47	0.20	0.15	0.03

Table 4-5 (Continued)

Source	Oil and grease (mg/kg)	TOC (mg/kg)	Mix ratio[a]	Metal concentrations (ppm) Arsenic	Barium	Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Selenium	Silver	Zinc
Zinc plating														
Unstabilized														
As receiuved	1,150	21,200		-	17.2	1.30	110	1,510	88.5	-	37	-	9.05	90,200
TCLP				-	0.84	0.22	0.18	4.6	0.45	<0.001	0.52	-	0.16	2,030
Stabilized														
TCLP			0.2	<0.01	0.20	0.01	0.23	0.30	0.30	<0.001	0.10	0.08	0.03	32
TCLP			0.5	<0.01	0.23	0.01	0.30	0.27	0.34	<0.001	0.02	0.14	0.04	0.04
Unknown														
Unstabilized														
As received	20,300	28,600		-	14.3	720	12,200	160	52	-	701	-	5.28	35,900
TCLP				<0.01	0.38	23.6	25.3	1.14	0.45	<0.001	9.78	<0.01	0.08	867
Stabilized														
TCLP			0.2	<0.01	0.31	3.23	0.25	0.20	0.24	<0.001	0.53	0.04	0.04	3.4
TCLP			0.5	<0.01	0.19	0.01	0.38	0.29	0.36	<0.001	0.04	0.09	0.06	0.03
Small engine manufacturing														
Unstabilized														
As received	2,770	6,550		-	24.5	7.28	3,100	1,220	113	-	19,400	-	4.08	27,800
TCLP				<0.01	0.07	0.3	38.7	31.7	3.37	0.003	730	<0.01	0.12	1,200
Stabilized														
TCLP			0.2	<0.01	0.30	0.02	0.21	0.21	0.30	<0.001	16.5	0.05	0.03	36.3
TCLP			0.5	<0.01	0.33	0.01	0.76	0.20	0.36	<0.001	0.05	0.11	0.05	0.04
Circuit board manufacturing[b]														
Unstabilized														
As received	130	550		-	12.6	5.39	42,900	10,600	156	-	13,000	-	12.5	120
TCLP				<0.01	0.04	0.06	360	8.69	1.0	<0.001	152	<0.01	0.05	0.62
Stabilized														
TCLP			0.2	<0.01	0.04	0.01	3.0	0.40	0.30	<0.001	0.40	0.04	0.03	0.02
TCLP			0.5	<0.01	0.14	0.01	1.21	0.42	0.38	<0.001	0.10	0.07	0.05	0.01

Table 4-5 (Continued)

Source	Oil and grease (mg/kg)	TOC (mg/kg)	Mix ratio[a]	Metal concentrations (ppm) Arsenic	Barium	Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Selenium	Silver	Zinc
Unknown														
Unstabilized														
As received	30	10,700		-	15.3	5.81	47.9	17,600	169	-	23,700	-	8.11	15,700
TCLP				<0.01	0.53	0.18	0.04	483	4.22	<0.001	644	<0.01	0.31	650
Stabilized														
TCLP			0.2	<0.01	0.32	0.01	0.10	0.50	0.31	<0.001	15.7	0.07	0.03	4.54
TCLP			0.5	<0.01	0.27	0.01	0.2	0.32	0.37	<0.001	0.04	0.07	0.05	0.02
Unknown														
Unstabilized														
As received	1,430	5,960		-	19.2	5.04	644	28,400	24,500	-	5,730	-	19.1	322
TCLP				0.88	0.28	0.01	0.01	16.9	50.2	<0.001	16.1	<0.45	<0.01	1.29
Stabilized														
TCLP			0.2	<0.02	0.19	<0.01	0.03	3.18	2.39	<0.001	1.09	<0.01	<0.01	0.07
TCLP			0.5	<0.02	0.08	<0.01	0.21	0.46	0.27	<0.001	0.02	<0.01	<0.01	<0.01

[a] $\text{Mix ratio} = \frac{\text{weight of reagent}}{\text{weight of waste}}$

[b] Circuit board manufacturing waste is not in its entirety defined as F006; however, an integral part of the manufacturing operation is electroplating. Treatment residuals generated from treatment of these electroplating wastes are F006.

Reference: CWM 1987.

5. IDENTIFICATION OF THE BEST DEMONSTRATED AVAILABLE TECHNOLOGY (BDAT)

This section presents the rationale for the determination of best demonstrated available technology (BDAT) for treatment of F019 wastes. For both cyanide and metals treatment, the Agency examined all of the available data for the demonstrated technologies to determine whether one of the technologies performed significantly better than the others. Next, the "best" performing treatment technology was evaluated to determine whether the resulting treatment is available. To be "available," a technology (1) must provide substantial treatment and (2) must be commercially available to the affected industry. If the best demonstrated technology is "available," then this technology represents BDAT.

5.1 BDAT for Treatment of Cyanide

Section 4 presents data for treatment of various electroplating wastes by alkaline chlorination followed by filtration (Table 4-1). These data show significant reduction in the concentrations of amenable and total cyanide.

The Agency believes that this process is likely to incorporate repetitive treatment for the concentrated cyanide wastes, i.e., greater than 30,000 ppm of total cyanides. This belief is based on information received from a commercial treatment facility (CyanoKEM 1989). The fact that repetitive treatment is necessary does not call into question the achievability of the cyanide standard by one-step alkaline chlorination processes. It only reflects that the wastes may be heavily concentrated with cyanide and complexing metals. Normal chemical conversion wastes contain much lower concentrations of these cyanides. Also, the Agency notes that if F019 wastewater treatment sludges at chemical conversion facilities do not meet the cyanide treatment standards, these wastes can be held in a holding tank and resolubilized and treated again by the plant's alkaline chlorination system. Most important, all existing data (public comments to this rulemaking and the Agency's review of the Generator Survey data, which corroborates the information in the public comments) show that the final cyanide treatment standard is being achieved by over 90 percent of the industry by performance of existing treatment systems.

Section 4 also presents data for treatment of F019 by wet air oxidation followed by filtration (Table 4-2). These data show significant reduction in the concentrations of amenable and total cyanide in both the wastewater filtrate and the nonwastewater filter cake generated. However, different analytical methods were used to analyze for amenable cyanide: Method 9012 in Test Methods for Evaluating Solid Waste, SW-846 and Method 412F in "Standard Methods for Examination of Water and Wastewater," 16th Edition. In addition, dilution values of the samples cannot be explained with available data.

Table 4-3 presents data on UV/ozonation treatment of an F009 waste that was generated following alkaline chlorination treatment and thus had a high concentration of complexed cyanide. However, the UV/ozonation treatment data were not directly comparable to the wet air oxidation data because the "treated waste" data do not reflect settling and/or filtration to separate solids and generate wastewater and nonwastewater residuals. Therefore, these data were not considered "best" in further development of the BDAT treatment standards for F019 wastes.

EPA has no other data for treatment of cyanide in F019 wastes or similar wastes; therefore, the Agency has determined that alkaline chlorination represents "best" treatment for cyanide in F019 wastes. Alkaline chlorination is "available" because it is a commercially available technology, used throughout industry, and it provides substantial treatment. Therefore, alkaline chlorination represents BDAT for cyanide in F019 waste (both nonwastewaters and wastewaters). A summary of the accuracy adjustment of treatment data for total cyanide in electroplating wastes is presented in Table 5-1 (at the end of this section).

5.2 BDAT for Treatment of Metals

Treatment of F019 wastes for cyanide destruction by alkaline chlorination generates both wastewater and nonwastewater residuals that are likely to require further treatment for BDAT list metals.

5.2.1 Wastewaters

No treatment data are available for treatment of metals in F019 wastewaters. EPA does, however, have treatment data for wastes (K062) believed to be similar to F019 wastewaters in terms of the type and concentration of BDAT list metals present and in terms of waste characteristics affecting treatment performance (as discussed in Section 4.2.1). These treatment data are based on chemical reduction followed by chemical precipitation and filtration. The Agency determined that the treatment performance data for K062 represented a well-designed, well-operated treatment system (see Table 5-2).

The treatment data for chemical reduction followed by chemical precipitation and filtration have been determined to represent "best" treatment, based on evaluation of all data available to the Agency for treatment of wastewaters containing high concentrations of chromium at the time of promulgation of the First Third land disposal restrictions (USEPA 1988b). Since that time, EPA has found no data on treatment of chromium-containing wastewaters by the BDAT technology for K062 or by any other technology. This technology is "available" because it provides substantial treatment of BDAT list metals and the individual processes are each commercially available. Therefore, chemical reduction of hexavalent chromium followed by chemical precipitation and filtration represents BDAT for BDAT list metals in F019 wastewaters.

5.2.2 Nonwastewaters

No treatment data are available to the Agency for treatment of metals in F019 nonwastewaters. EPA does, however, have stabilization data for metal-containing nonwastewater treatment sludges (F006) believed to be similar to F019 nonwastewaters generated as a residual following cyanide treatment (as discussed in Section 4.2.2). The Agency determined that the treatment performance data for F006 stabilization represent a well-designed and well-operated treatment system (USEPA 1988a).

The stabilization data for F006 show TCLP chromium concentration is reduced from up to 360 mg/l in the untreated waste down to less than 1.5 mg/l in the stabilized waste (see Table 5-3).

The Agency has no reason to believe that the use of other processes could improve the level of performance achieved by stabilization. Therefore, stabilization is "best." This treatment system is "available" because the components of the treatment system are commercially available and provide substantial treatment. Therefore, stabilization represents BDAT for BDAT list metals in F019 wastewater treatment sludges and also in the nonwastewater residuals from treatment of F019 by wet air oxidation followed by chemical reduction, chemical precipitation, and filtration. The accuracy-corrected performance data used to develop metals treatment standards for F019 are presented in Tables 5-2 and 5-3.

Table 5-1 Summary of Accuracy Adjustment of Treatment Data for Total Cyanide in Electroplating Wastes

	Untreated waste concentration (mg/l)	Measured treated waste concentration (mg/l)	Percent recovery for matrix spike test	Accuracy-correction factor	Accuracy-adjusted concentration (mg/l)
<u>Alkaline Chlorination</u>					
Sample Set No. 1	71,759	0.95	94	1.06	1.01
Sample Set No. 2	12,000	0.95	94	1.06	1.01
Sample Set No. 3	17,206	<0.014	94	1.06	<0.015
Sample Set No. 4	25,936	<0.014	94	1.06	<0.015
Sample Set No. 5	16,914	<0.014	94	1.06	<0.015
Sample Set No. 6	59,421	0.028	94	1.06	0.030
Sample Set No. 7	31,994	0.028	94	1.06	0.030
Sample Set No. 8	41,900	<0.014	94	1.06	<0.015
Sample Set No. 9	18,882	<0.014	94	1.06	<0.015
Sample Set No. 10	1,270	0.17	94	1.06	0.18
Sample Set No. 12	12,085	<0.014	94	1.06	<0.015
Sample Set No. 13	10,902	0.070	94	1.06	0.074
Sample Set No. 14	16,010	0.070	94	1.06	0.074

Table 5-2 Accuracy-Corrected Performance Data for Chromium in K062 Wastewaters

	Untreated waste composite[a] (mg/l)	Treated waste (mg/l)	Percent recovery[b]	Correction factor	Corrected value (mg/l)
Sample Set No. 1	2581	0.12	68	1.47	0.1764
Sample Set No. 2	2279	0.12			0.1764
Sample Set No. 3	1990	0.20			0.294
Sample Set No. 4	556	0.10			0.147
Sample Set No. 5	2236	0.11			0.162
Sample Set No. 6	2548	0.10			0.147
Sample Set No. 7	2314	0.12			0.1764
Sample Set No. 8	831	0.15			0.2205
Sample Set No. 9	939	0.10			0.147
Sample Set No. 10	395	0.12			0.1764
Sample Set No. 11	617	0.18			0.2646

[a]The untreated waste composite is a mixture of the untreated K062 waste streams shown on this table, along with other non-K062 waste streams.

[b]The percent recovery has been taken from Table 7-14 of the Onsite Engineering Report from Horsehead Resource Development Company (USEPA 1987).

Reference: USEPA 1988b.

Table 5-3 Accuracy-Corrected Performance Data for Chromium in F006 Nonwastewaters Treatment by Stabilization

Source	Mix ratio[a]	Untreated waste concentration as received (mg/l)	Untreated waste concentration (TCLP) (mg/l)	Accuracy-adjusted treated waste concentration (TCLP) (mg/l)
Auto part manufacturing	0.5	755	0.76	0.45
Aircraft overhauling	0.2	716	0.43	0.09
Unknown	0.5	12,200	25.3	0.44
Small engine manufacturing	0.5	3,100	38.7	0.89
Circuit board manufacturing	0.5	42,900	360	1.41

[a]mix ratio = $\frac{\text{weight of reagent}}{\text{weight of waste}}$

Source: USEPA 1988a.

6. SELECTION OF REGULATED CONSTITUENTS

As discussed in EPA's Methodology for Developing BDAT Treatment Standards (USEPA 1989a), the Agency has developed a list of BDAT hazardous constituents from which the constituents to be regulated are selected. EPA may revise this list as additional data and information become available. The list is divided into the following categories: volatile organics, semivolatile organics, metals, inorganics other than metals, organochlorine pesticides, phenoxyacetic acid herbicides, organophosphorus insecticides, PCBs, and dioxins and furans.

This section describes the process used to select the constituents to be regulated. The process involves developing a list of potential regulated constituents and then eliminating those constituents that would not be treated by the chosen BDAT or that would be controlled by regulation of other constituents in the waste.

6.1 Identification of BDAT List Constituents in F019

As discussed in Sections 2 and 4, the Agency has characterization data and performance data for the treatment of F019. These data have been used to determine which BDAT list constituents may be present in the waste and thus which ones are potential candidates for regulation. These constituents are amenable and total cyanides, fluoride, sulfide, antimony, arsenic, barium, beryllium, cadmium, total chromium, copper, lead, mercury, nickel, selenium, thallium, vanadium, and zinc.

6.2 Constituents Selected for Regulation

Based on the characterization and performance data for F019 presented in Sections 2 and 4, the Agency is proposing to regulate total cyanide, amenable cyanide, and total chromium. EPA is not regulating copper and zinc for the wastes in this subcategory because these constituents are not listed in Appendix VIII of 40 CFR Part 261 as elemental constituents but rather as specific compounds (i.e., copper cyanide, zinc phosphide, and zinc cyanide). In any case, treatment of the other BDAT list metals by chemical precipitation and/or stabilization will also reduce leachate concentrations of both of these metals in wastewater and nonwastewater treatment residuals. Based on EPA's knowledge of the chemical conversion coating process, the Agency would not expect any other BDAT list constituents to be commonly found in these wastes at treatable concentrations. The only other BDAT list constituents expected to be present in F019 would be other BDAT list metals. These constituents are expected to be found, if at all, at much lower concentrations than chromium. Nickel and zinc were detected at greater than 1,000 ppm in two of the F019 wastes for which characterization data were given. These metals, when detected in F019 waste, are expected to be treated by a well-designed and well-operated BDAT treatment system for both nonwastewaters and wastewaters.

7. CALCULATION OF BDAT TREATMENT STANDARDS

This section presents the calculation of the BDAT treatment standards for the regulated constituents determined in Section 6. As discussed in the Methodology for Developing BDAT Treatment Standards (USEPA 1989a), the following steps were taken to derive the BDAT treatment standards for F019.

The Agency evaluated the compositional similarities between F019 wastewaters and nonwastewaters and F006-F009 wastewaters. The similarities included composition, concentration, and treatability. Based on these similarities, the Agency is promulgating treatment standards for amenable and total cyanide in F019 wastewaters and nonwastewaters based on the performance of alkaline chlorination treatment of electroplating wastes. For wastewaters the extensive data used in the development of Metal Finishing categorical wastewater discharge standards was used as the basis for BDAT. Because of analytical difficulties in analyzing for amenable cyanides in F019 nonwastewaters, the amenable cyanide treatment standards for nonwastewaters are based on 5 percent of the total cyanide standard. Based on the data available to the Agency, it was determined that the precision of the SW-846, Method 9010, for amenable cyanide is 5 percent of the total cyanide concentration. The basis for this estimate is discussed in "Standard Methods for the Examination of Water and Wastewater" in which the precision for the analytical method is estimated to be 5 percent. Since the "Standard Methods for the Examination of Water and Wastewater" procedure is essentially identical to the precision of SW-846, Method 9010, EPA believes that the 5 percent value is transferrable to the analysis performed using SW-846, Method 9010. The data used in the development of treatment standards for these wastes represent the performance of well-designed, well-operated treatment systems.

For BDAT list metal constituents, the treatment standards for nonwastewaters are based on transfer of performance data from stabilization of F006 wastewater treatment sludges and the treatment standards for wastewaters are based on transfer of performance data from treatment of K062 wastes by chemical reduction followed by chemical precipitation and filtration. It was previously determined in the associated background documents (USEPA 1988a, USEPA 1988b) that the data used in development of treatment standards for these wastes represented the performance of well-designed, well-operated treatment systems.

As described in the methodology, analytical accuracy-corrected constituent concentrations were calculated for all regulated BDAT list constituents. An arithmetic average of concentration levels for each constituent and a variability factor for each constituent were then determined. The variability factor represents the variability inherent in the treatment process and the sampling and analytical methods. Variability factors are calculated based on the treatment data for each of the regulated constituents. The general methodology for calculating variability factors is presented in Appendix A of the methodology document.

The BDAT treatment standard for each constituent to be regulated in this rulemaking was determined by multiplying the average accuracy-corrected total composition by the appropriate variability factor, with the exception of cyanide in wastewaters where the standards were transferred from Metal Finishing categorical wastewater discharge standards. These data are presented in Appendix A. The calculations of the treatment standards for F019 wastewaters and nonwastewaters and chromium are presented in Tables 7-1, 7-2, and 7-3, respectively. The treatment standards are shown in Table 7-4.

Table 7-1 Calculation of Wastewater Treatment Standards for Total and Amenable Cyanide

Regulated constituent	Mean effluent concentration (mg/l)	Variability factor	Treatment standard (mg/l))
Cyanide (total)	0.18	6.68	1.20
Cyanide (amenable)	0.06	14.31	0.86

Standards transferred from Metal Finishing:

	CN,T	CN,A
Mean effluent concentration (mg/l)	0.18	0.06
Variability factors	6.68	14.31
Treatment standard (mg/l)	1.20	0.86

Table 7-2 Calculation of Nonwastewater Treatment Standards for Total Cyanide for F006, F007, F008, and F009 Wastes Based on Generation of F006 Waste by a Well-Operated Treatment Process Consisting of Alkaline Chlorination, Chemical Precipitation, Filtration, and Sludge Dewatering

Regulated constituent (units)	Accuracy-adjusted treated waste concentration[a]	Mean treated waste concentration	Variability factor (VF)	Treatment standard (total composition)
Nonwastewater (mg/kg):				
Cyanide (total)	390.11	242.9	2.4	590
	166.56			
	383.68			
	408.0			
	256.5			
	267.43			
	185.01			
	206.78			
	116.02			
	156.11			
	124.54			
	275.58			
	221.83			
Cyanide (amenable)	b			30

[a]To calculate the treatment standard for amenable cyanides, the Agency has taken into account the precision of the analytical methods for cyanide analysis based on performance of alkaline chlorination.

[b]Because of analytical difficulties in analyzing for amenable cyanides in F019 wastewaters and nonwastewaters, the amenable cyanide treatment standards are based on 5 percent of the total cyanide standard. Based on the data available to the Agency, it was determined that the precision of the SW-846, Method 9010 for amenable cyanide is 5 percent of the total cyanide concentration. The basis for this estimate is discussed in "Standard Methods for the Examination of Water and Wastewater" in which the precision for the analytical method is estimated to be 5 percent. Since the "Standard Methods for the Examination of Water and Wastewater" procedure is essentially identical to the precision of SW-846, Method 9010, EPA believes that the 5 percent value is transferrable to the analysis performed using SW-846, Method 9010.

Table 7-3 Calculation of BDAT List Metals Treatment Standards for F019

	Arithmetic average of corrected treatment values (mg/kg)	Variability factor	Treatment standard (mg/kg)
Wastewater			
Chromium (total)	0.19	1.69	0.32
Nonwastewater			
Chromium (total)	0.66	7.94	5.2

3219g

Table 7-4 BDAT Treatment Standards for F019

Constituent	Maximum for any single grab sample: Nonwastewater — Total concentration (mg/kg)	Nonwastewater — TCLP leachate concentration (mg/l)	Wastewater — Total concentration (mg/l)
Cyanide (amenable)	30	NA	.086
Cyanide (total)	590	NA	1.20
Chromium (total)	NA	5.2	0.32

NA - Not applicable.

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APPENDIX A

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TREATMENT OF CYANIDE WASTES - SINGLE OPTION

INTRODUCTION

This subsection describes the technique recommended for cyanide treatment, discusses the mean cyanide concentrations found, identifies the recommended daily maximum and monthly maximum average concentrations for cyanide and presents alternative treatments for the destruction of cyanide.

The following paragraphs describe the chlorine oxidation technique recommended for the treatment of cyanide bearing wastes.

RECOMMENDED TREATMENT TECHNIQUE

Oxidation By Chlorination

Cyanides are introduced as metal salts for plating and conversion coating or are active components in plating and cleaning baths. Cyanide is generally destroyed by oxidation.

Chlorine is used primarily as an oxidizing agent in industrial waste treatment to destroy cyanide. Chlorine can be used in the elemental or hypochlorite form. This classic procedure can be illustrated by the following two step chemical reaction:

1. $Cl_2 + NaCN + 2NaOH = NaCNO + 2NaCl + H_2O$

2. $3Cl_2 + 6NaOH + 2NaCNO = 2NaHCO_3 + N_2 + 6NaCl + 2H_2O$

The reaction presented as equation(2) for the oxidation of cyanate is the final step in the oxidation of cyanide. A complete system for the alkaline chlorination of cyanide is shown in Figure 7-25.

The cyanide waste flow is treated by the alkaline chlorination process for oxidation of cyanides to carbon dioxide and nitrogen. The equipment often consists of an equalization tank followed by two reaction tanks, although the reaction can be carried out in a single tank. Each tank has an electronic recorder-controller to maintain required conditions with respect to pH and oxidation-reduction potential (ORP). In the first reaction tank, conditions are adjusted to oxidize cyanides to cyanates. To effect the reaction, chlorine is metered to the reaction tank as required to maintain the ORP in the range of 350 to 400 millivolts, and 50% aqueous caustic soda is added to maintain a pH range of 9.5 to 10. In the second reaction tank, conditions are maintained to oxidize cyanate to carbon dioxide and nitrogen. The desirable ORP and pH for this reaction are 600 millivolts and a pH of 8.0. Each of the reaction tanks is equipped with a propeller agitator designed to provide approximately one turnover per minute. Treatment by the batch process is accomplished by using two tanks, one

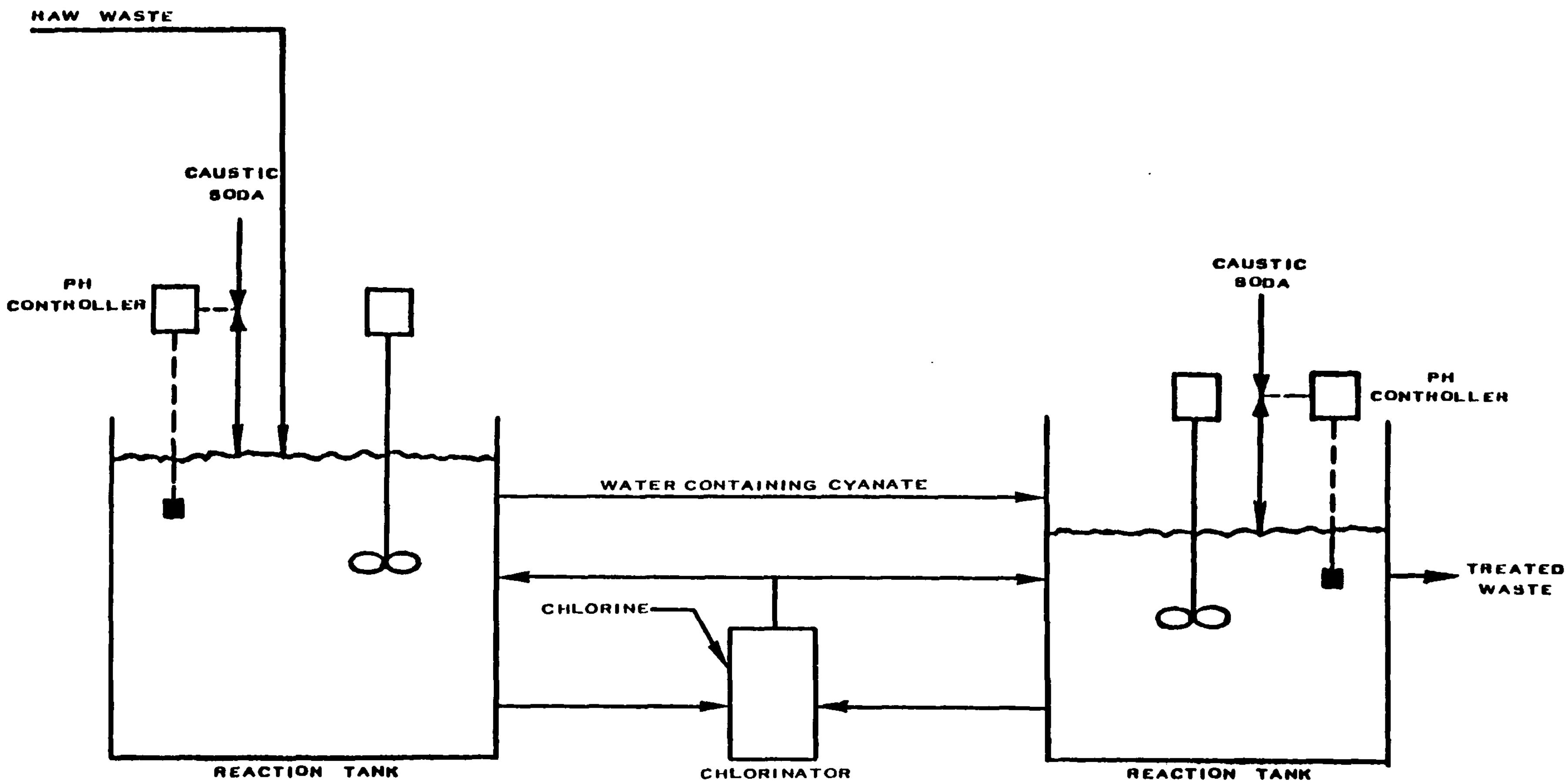

FIGURE 7-25

TREATMENT OF CYANIDE WASTE BY ALKALINE CHLORINATION

for collection of waste over a specified time period, and one tank for the treatment of an accumulated batch. If dumps of concentrated wastes are frequent, another tank may be required to equalize the flow to the treatment tank. When the holding tank is full, the liquid is transferred to the reaction tank for treatment. After treatment, the supernatant is discharged and the sludges are collected for removal and ultimate disposal.

Application

The oxidation of cyanide waste by chlorine is a classic process and is found in most plants using cyanide. This process is capable of achieving efficiencies of 99 percent or greater and effluent levels that are nondetectable. Chlorine has also been used to oxidize phenols, but use of chlorine dioxide for this purpose is much preferred because formation of toxic chlorophenols is avoided.

Some advantages of chlorine oxidation for handling process effluents are operation at ambient temperature, suitability for automatic control, and low cost. Some disadvantages of chlorine oxidation for treatment of process effluents are that toxic, volatile intermediate reaction products must be controlled by careful pH adjustment, chemical interference is possible in the treatment of mixed wastes, and a potentially hazardous situation exists when chlorine gas is stored and handled.

Performance

Performance for cyanide oxidation was determined by evaluating the amenable cyanide effluent data from visited plants. Amenable cyanide was evaluated because treatment for cyanide is almost exclusively performed by alkaline chlorination. This form of treatment focuses upon oxidizing the cyanide which is amenable to chlorination.

Amenable cyanide data from visited plants are listed in Table 7-52. The table has the following four columns:

1. ID Number - The identification number of the visited plant. Duplicate numbers indicate different sampling days at the same plant.

2. Effluent Concentration - The measured concentration of the final effluent after treatment. At this point, cyanide wastes are mixed with other wastewaters.

3. Dilution Factor - This number represents the amount of dilution of the cyanide raw waste stream by other raw waste streams and is determined by dividing the total effluent stream flow by the cyanide stream flow.

4. Adjusted Cyanide Effluent Concentration - These concentrations are calculated by multiplying the effluent cyanide concentrations by the dilution factor applicable in each individual case.

The data contained in Table 7-52 were arranged in the following manner:

1. For each plant data set (CN_A) the concentrations were listed in decending order.

2. The plant data sets were listed in ascending order using the first value in each plant data set as the basis for ordering (the first value in each plant data set represents the highest concentration).

Ordering the data in this fashion facilitates identification of poorly operated treatment systems. As illustrated in the table, a break occurs between plant 20080 and 04045. The highest concentration at plant 20080 is 0.416 mg/ℓ and at plant 04045 the highest concentration is 2.2 mg/ℓ. Since alkaline chlorination is capable of reducing amenable cyanide concentrations to levels approximating zero, plants listed after plant 20080 exhibit poor control and excessive effluent concentrations. These plants have been deleted from the data base used to determine performance for cyanide oxidation.

Table 7-53 presents amenable cyanide data after deletions to remove plants with poorly operated treatment systems. The entire plant data set (both CN_A and CN_T) was deleted if any cyanide amenable concentration for that plant exceeded the breakpoint between 0.416 mg/ℓ and 2.2 mg/ℓ. Plants which were deleted from both the amenable and total cyanide data bases are listed in Table 7-54.

Total cyanide data (after deleting the plants listed in Table 7-54) are presented in Table 7-55. These data correspond to the amenable cyanide data remaining in the data base from which performance is determined. In Table 7-55 two data points, 105.0 mg/ℓ and 5.69 mg/ℓ were deleted from the calculation of the mean effluent concentration for total cyanide. The 105.0 mg/ℓ was deleted because it was a high outlier although the corresponding cyanide amenable value did not indicate a high level. The 5.69 mg/ℓ was deleted as a high outlier and because there was no corresponding cyanide amenable value. Plant data sets which were deleted from the total cyanide data base are listed in Table 7-56.

The edited data sets (presented in Tables 7-53 and 7-55) were used to determine performance for cyanide oxidation. The adjusted mean effluent concentrations from the edited data base are presented below.

Parameter	Adjusted Mean Effluent Concentration (mg/ℓ)
Cyanide, Total	0.18
Cyanide, Amenable	0.06

TABLE 7-52
AMENABLE CYANIDE DATA BASE

PLANT ID	CN_A EFFLUENT CONCENTRATION (mg/l)	DILUTION FACTOR	ADJUSTED CN_A CONCENTRATION (mg/l)
12065	0	10.0	0
21051	0	1.0	0
	0	1.0	0
	0	1.0	0
38051	0	19.9	0
06075	0.005	5.0	0.025
	0.005	4.8	0.024
36623	0.005	5.1	0.025
	0.005	4.9	0.024
	0.005	4.3	0.021
19050	0.005	6.2	0.031
20079	0.005	7.9	0.039
	0.005	6.2	0.031
	0.005	6.1	0.030
	0.005	5.6	0.028
	0.005	5.0	0.025
	0.005	4.8	0.024
05021	0.005	8.0	0.04
	0.005	4.8	0.024
	0.005	4.8	0.024
20078	0.01	6.6	0.066
	0.005	7.4	0.037
	0.005	7.0	0.035
	0.005	6.9	0.034
	0.005	5.7	0.029
	0.005	5.6	0.028
15070	0.02	3.4	0.068
	0.005	2.8	0.014
	0.005	2.5	0.012
33073	0.027	5.5	0.147
	0.008	5.1	0.041
09026	0.06	2.6	0.156
	0.01	2.4	0.024
	0.005	3.8	0.021

TABLE 7-52(CON'T)
AMENABLE CYANIDE DATA BASE

PLANT ID	CN_A EFFLUENT CONCENTRATION (mg/l)	DILUTION FACTOR	ADJUSTED CN_A CONCENTRATION (mg/l)
31021	0.05	3.2	0.16
	0.05	3.2	0.16
	0.05	3.0	0.150
33024	0.04	5.1	0.204
20080	0.104	4.0	0.416
	0.005	5.8	0.029
	0.005	4.5	0.023
	0.005	4.5	0.023
	0.005	4.5	0.023
04045	2.2	1.0	2.2
	1.0	1.0	1.1
	0.25	1.0	0.25
06089	1.14	3.5	3.99
	0.285	3.0	0.855
	0.163	2.9	0.478
36041	0.4	10.4	4.16
	0.1	11.5	1.15
	0.1	10.1	1.01
06381	0.751	6.5	4.88
	0.089	8.7	0.733
	0.096	6.3	0.609
06085	1.08	5.0	5.4
	0.56	4.8	2.69
	0.06	5.4	0.323
20082	3.0	1.8	5.4
	1.08	2.1	2.23
	0.945	2.0	1.88
	0.625	2.1	1.32
	0.056	2.0	0.147
	0.034	2.0	0.064
06084	1.97	3.6	7.19

TABLE 7-52(CON'T)
AMENABLE CYANIDE DATA BASE

PLANT ID	CN_A EFFLUENT CONCENTRATION (mg/l)	DILUTION FACTOR	ADJUSTED CN_A CONCENTRATION (mg/l)
20081	0.49	15.6	7.64
	0.348	16.3	5.68
	0.075	17.6	1.32
	0.017	17.7	0.3
	0.005	15.9	0.079
	0.005	14.4	0.072
11103	3.37	3.0	10.0
	2.91	2.4	6.98
02033	4.2	2.6	11.1
20077	3.0	5.9	17.7
	2.1	7.8	16.4
	0.78	9.7	7.58
	0.1	6.5	0.65
	0.005	9.7	0.049
	0.005	7.1	0.036
06090	5.27	4.3	22.5
20086	5.25	4.5	23.6
	0.36	4.5	1.62
	0.005	4.5	0.023
06037	11.6	6.4	73.7
	0.408	6.4	2.59
	0.122	6.4	0.775
21066	11.75	7.4	86.9
	6.57	10.2	66.9
	8.83	4.7	41.5

TABLE 7-53
DATA USED FOR AMENABLE CYANIDE PERFORMANCE

PLANT ID	CN_A EFFLUENT CONCENTRATION (mg/l)	DILUTION FACTOR	ADJUSTED CN_A CONCENTRATION (mg/l)
12065	0	10.0	0
21051	0	1.0	0
	0	1.0	0
	0	1.0	0
38051	0	19.9	0
06075	0.005	5.0	0.025
	0.005	4.8	0.024
36623	0.005	5.1	0.025
	0.005	4.9	0.024
	0.005	4.3	0.021
19050	0.005	6.2	0.031
20079	0.005	7.9	0.039
	0.005	6.2	0.031
	0.005	6.1	0.030
	0.005	5.6	0.028
	0.005	5.0	0.025
	0.005	4.8	0.024
05021	0.005	8.0	0.04
	0.005	4.8	0.024
	0.005	4.8	0.024
20078	0.01	6.6	0.066
	0.005	7.4	0.037
	0.005	7.0	0.035
	0.005	6.9	0.034
	0.005	5.7	0.029
	0.005	5.6	0.028
15070	0.02	3.4	0.068
	0.005	2.8	0.014
	0.005	2.5	0.012
33073	0.027	5.5	0.147
	0.008	5.1	0.041
09026	0.06	2.6	0.156
	0.01	2.4	0.024
	0.005	3.8	0.021

TABLE 7-53 (CON'T)
DATA USED FOR AMENABLE CYANIDE PERFORMANCE

PLANT ID	CN_A EFFLUENT CONCENTRATION (mg/l)	DILUTION FACTOR	ADJUSTED CN_A CONCENTRATION (mg/l)
31021	0.05	3.2	0.16
	0.05	3.2	0.16
	0.05	3.0	0.150
33024	0.04	5.1	0.204
20080	0.104	4.0	0.416
	0.005	5.8	0.029
	0.005	4.5	0.023
	0.005	4.5	0.023
	0.005	4.5	0.023

TABLE 7-54

PLANTS DELETED FROM CYANIDE DATA BASE
DUE TO POOR PERFORMANCE

04045
06089
36041
06381
06085
20082
06084
20081
11103
02033
20077
06090
20086
06037
21066

TABLE 7-55
DATA USED FOR TOTAL CYANIDE PERFORMANCE

PLANT ID	CN_T EFFLUENT CONCENTRATION (mg/l)	DILUTION FACTOR	ADJUSTED CN_T CONCENTRATION (mg/l)
12065	0.014	10	0.14
21051	0	1.0	0
	0	1.0	0
	0	1.0	0
38051	0	19.9	0
06075	0.005	4.8	0.024
	0.005	5.0	0.025
	0.014	4.8	0.067
36623	0.01	4.3	0.043
	0.02	4.9	0.098
	0.033	5.1	0.167
19050	0.005	6.2	0.031
20079	0.005	4.8	0.024
	0.005	6.1	0.031
	0.005	6.2	0.031
	0.005	7.9	0.039
	0.02	5.6	0.112
	21.0	5.0	105.*
05021	0.005	4.8	0.024
	0.005	4.8	0.024
	0.007	8.0	0.056
20078	0.005	5.6	0.028
	0.005	5.7	0.029
	0.005	7.0	0.035
	0.005	7.4	0.037
	0.01	6.9	0.069
	0.04	6.6	0.266
20080	0.005	4.5	0.023
	0.005	4.5	0.023
	0.005	4.5	0.023
	0.005	5.8	0.029
	0.1	4.1	0.41
	0.111	4.0	0.444
	1.23	4.6	5.69*

* Not used in calculation of mean effluent concentration.

TABLE 7-55(CON'T)
DATA USED FOR TOTAL CYANIDE PERFORMANCE

PLANT ID	CN_T EFFLUENT CONCENTRATION (mg/l)	DILUTION FACTOR	ADJUSTED CN_T CONCENTRATION (mg/l)
15070	0.02	2.5	0.05
	0.03	3.4	0.102
	0.29	2.8	0.818
33073	0.013	5.5	0.071
	0.129	5.1	0.66
	0.254	5.5	1.39
09026	0.03	2.4	0.072
	0.02	3.8	0.076
	0.08	2.6	0.208
31021	0.16	3.2	0.512
	0.16	3.2	0.512
	0.35	3.1	1.1
33024	0.04	5.1	0.204

TABLE 7-56
PLANT DATA DELETED FROM TOTAL CYANIDE DATA BASE

PLANT ID	CN_T EFFLUENT CONCENTRATION (mg/l)	DILUTION FACTOR	ADJUSTED CN_T CONCENTRATION (mg/l)
02033	10.0	2.6	26.0
04045	6.4	1.0	6.4
	8.7	1.0	8.7
	15.2	1.0	15.2
06037	0.53	6.3	3.37
	0.591	6.3	3.75
	12.6	6.4	80.6
06084	0.027	2.9	0.078
	0.435	4.3	1.86
	2.8	3.6	10.2
06085	0.96	4.8	4.61
	0.92	5.4	4.95
	1.8	5.0	9.0
06089	0.285	2.9	0.835
	0.428	3.0	1.28
	2.42	3.5	8.47
06090	2.81	4.3	12.1
	6.73	4.3	28.7
	10.8	4.3	46.1
06381	0.089	8.7	0.773
	0.25	6.3	1.58
	0.981	6.5	6.38
11103	10.0	2.4	24.0
	9.37	3.0	28.1
20077	0.005	7.1	0.036
	1.5	9.7	14.6
	2.5	6.5	16.2
	3.0	5.9	17.7
	2.5	7.8	19.5
	2.4	9.7	23.3

TABLE 7-56 (CON'T)
PLANT DATA DELETED FROM TOTAL CYANIDE DATA BASE

PLANT ID	CN_T EFFLUENT CONCENTRATION (mg/l)	DILUTION FACTOR	ADJUSTED CN_T CONCENTRATION (mg/l)
20081	0.035	17.7	0.618
	0.023	14.4	0.331
	0.068	15.9	1.08
	0.911	17.6	16.0
	1.16	16.3	19.0
	3.82	15.6	59.6
20082	0.034	2.0	0.068
	0.635	2.1	1.34
	0.722	2.0	1.47
	0.945	2.0	1.88
	3.09	1.8	5.63
	3.31	2.1	6.85
20086	0.73	4.5	3.28
	1.13	4.5	5.08
	5.25	4.5	23.6
21066	16.38	4.7	76.9
	12.15	10.2	123.9
	20.65	7.4	152.8
36041	0.25	11.5	2.87
	0.4	10.1	4.04
	0.6	10.4	6.24

Self-monitoring data for total cyanide and amenable cyanide are shown in Table 7-57. For each plant, this table shows the number of data points, the mean effluent concentration, and the calculated variability factors plus the total number of points, the overall mean effluent concentration, and the median variability factors.

	CN_T	CN_A
Mean Effluent Concentration (mg/ℓ)	0.18	0.06
Variability Factors (Daily/10-day)	6.68/3.61	14.31/5.31
Daily Maximum Concentration (mg/ℓ)	1.20	0.86
Maximum Monthly Average Concentration (mg/ℓ)	0.65	0.32

The percent of plants with cyanide levels below the cyanide daily maximum effluent concentration limitations are as follows:

Parameter	EPA Sampled Plants Daily Maximum	Self-Monitoring Data Daily Max.	Self-Monitoring Data 10-Day Ave.
Cyanide, Total	97.8	79.2	62.9
Cyanide, Amenable	100.0	92.8	78

The percent compliance for the self-monitoring data for the cyanide total daily maximum and for the cyanide total and cyanide amenable 10-day averages is relatively low compared to the EPA samples plants. When examining the EPA sampled data, the Agency excluded numerous plants that had high cyanide levels after correcting for dilution. Apparently many plants are relying on dilution of treated cyanide wastes rather than performing alkaline chlorination to its capability. Self-monitoring data are insufficient to examine the adequacy of the treatment system because both cyanide amenable and cyanide total results are generally not available for the same plants. Two plants have both cyanide amenable and cyanide total values; however, the cyanide amenable results are indicative of inadequate treatment. This appears to indicate that there is a need for additional control of cyanide by many of the plants that submitted self-monitoring data. This is illustrated in Table 7-58 which shows the adjusted mean and maximum concentrations for cyanide total and cyanide amenable for plants with self- monitoring data for which dilution factors were available.

Demonstration Status

The oxidation of cyanide wastes by chlorine is a widely used process in plants using cyanide in cleaning and plating baths. There has been recent attention to developing chlorine dioxide generators and bromine chloride generators. A problem that has been encountered is that the generators produce not only the bromine chloride and chlorine dioxide gas, but chlorine gas is also formed simultaneously. Both of these gases are extremely unstable, corrosive, and have low vapor pressure, which results in handling difficulties. These generators are in the development stages and as advances are made in their design, they may become competitive with chlorine.

Oxidation by chlorine is used in 206 plants in the present data base, and these are identified in Table 7-59.

TABLE 7-57

EFFLUENT TOTAL CYANIDE SELF-MONITORING PERFORMANCE DATA
FOR PLANTS WITH OPTION 1 SYSTEMS

Plant ID	Number OF Points	Mean Effluent Concentration (mg/ℓ)	Variability Factor Daily	Variability Factor 10-Day
1067	230	0.041	1.92	1.46
3043	89	0.154	10.02	4.75
6051	13	0.07	--	--
6107	10	2.20	25.01	--
11008	179	0.09	6.10	4.15
11125	54	1.21	3.64	1.35
15193	12	0.053	3.23	3.68
20080	268	0.001	--	--
20082	246	0.132	7.25	3.55
31021	119	0.533	11.16	7.67
36082	121	0.043	4.23	3.33
44045	50	0.008	--	7.68
47025	138	0.057	7.92	2.57
OVERALL	1529(Total)	0.156(Mean)	6.68(Median)	3.61(Median)

EFFLUENT AMENABLE CYANIDE SELF-MONITORING PERFORMANCE DATA
FOR PLANTS WITH OPTION 1 SYSTEMS

Plant ID	Number OF Points	Mean Effluent Concentration (mg/ℓ)	Variability Factor Daily	Variability Factor 10-Day
31021	28	0.196	14.32	3.18
38223	235	0.0004	--	5.31
47025	243	0.007	--	5.77
OVERALL	529(Total)	0.016(Mean)	14.31(Median)	5.31(Median)

TABLE 7-58

ADJUSTED EFFLUENT TOTAL CYANIDE SELF-MONITORING DATA

Plant ID	Number OF Points	Adjusted CN,T Mean Concentration (mg/ℓ)	Adjusted CN,T Maximum Daily Concentration (mg/ℓ)
3043	89	0.57	3.11
11008	179	0.35	8.40
11125	54	10.11	33.32
15193	12	1.75	5.33
20080	268	0.01	0.46
20082	246	0.66	7.0
31021	119	1.48	15.29
36082	121	0.21	5.0
44045	50	0.83	15.0
47025	138	2.26	12.32
LIMITATION COMPARISON		0.18 (EPA Sample Data Mean)	1.20 (Daily Max.)

ADJUSTED EFFLUENT AMENABLE CYANIDE SELF-MONITORING DATA

Plant ID	Number OF Points	Adjusted CN,T Mean Concentration (mg/ℓ)	Adjusted CN,T Maximum Daily Concentration (mg/ℓ)
31021	28	0.54	3.89
38223	235	0.06	1.43
47025	243	0.28	6.80
LIMITATION COMPARISON		0.06 (EPA Sample Data Mean)	0.86 (Daily Max.)

TABLE 7-59

METAL FINISHING PLANTS EMPLOYING CYANIDE OXIDATION

01007	05029	06090	08008	13039	19104	21066	30096
01067	05033	06094	08074	13040	20001	21074	30097
01068	06002	06101	09026	15042	20005	21078	30109
02033	06006	06107	09060	15045	20017	22028	30111
02037	06037	06111	10020	15047	20073	22656	30162
20240	06050	06113	11008	15048	20077	23039	30967
03042	06051	06115	11096	15070	20078	23059	31021
03043	06052	06119	11098	15193	20079	23061	31037
04045	06053	06120	11103	16033	20080	23074	31040
04076	06002	06122	11125	16035	20081	23076	31047
04114	06072	06124	11118	18050	20082	23337	31070
04178	06073	06129	11174	18055	20084	25001	33024
04199	06075	06141	11177	18534	20086	25030	33043
04124	06079	06146	11184	19050	20087	25031	33065
04227	06078	06147	12005	19051	20158	27044	33070
04236	06079	06152	12065	19063	20162	27046	33071
04263	06081	06358	12078	19069	20172	28082	33073
04277	06084	06360	12087	19084	20243	28105	33113
04279	06085	06381	12709	19090	20708	30011	33120
04182	06087	06679	13033	19099	21003	30022	33137
05021	06089	08004	13034	19102	21062	30090	33146

33184	36041	36151	40037	47005
33187	36082	36154	40047	47025
33275	36083	36156	41116	
34041	36084	36623	42830	
34042	36090	37042	43052	
35061	36091	38031	44037	
35963	36102	38038	44040	
36036	36112	38051	44045	
36040	36113	38223	45035	

ALTERNATIVE CYANIDE TREATMENT TECHNIQUES

Alternative treatment techniques for the destruction of cyanide include oxidation by ozone, ozone with ultraviolet radiation (oxyphotolysis), hydrogen peroxide and electrolytic oxidation. These techniques are presented in the following paragraphs.

Oxidation By Ozonation

Ozone may be produced by several methods, but the silent electrical discharge method is predominant in the field. The silent electrical discharge process produces ozone by passing oxygen or air between electrodes separated by an insulating material. The electrodes are usually stainless steel or aluminum. The dielectric or insulating material is usually glass. The gap or air space between electrodes or dielectrics must be uniform and is usually on the order of 0.100 to 0.125 inches. The voltage applied is 20,000 volts or more, and a single phase current is applied to the high tension electrode.

Ozone is approximately ten times more soluble than oxygen on a weight basis in water, although the amount that can be efficiently dissolved is still slight. Ozone's solubility is proportional to its partial pressure and also depends on the total pressure on the system. It should be noted, however, that it is the oxidizable contaminant in the water that determines the quantity of ozone needed to oxidize the contaminants present. A complete ozonation system is represented in Figure 7-26.

Thorough distribution of ozone in the water under treatment is extremely important for high efficiency of the process. There are four methods of mixing ozone with water; these are: (1) diffusers, (2) negative or positive pressure injection, (3) packed columns whereby ozone-containing air or oxygen is distributed throughout the water, and (4) atomizing the aqueous solution into a gaseous atmosphere containing ozone.

Application

Ozonation has been applied commercially for oxidation of cyanides, phenolic chemicals, and organo-metal complexes. It is used commercially with good results to treat photoprocessing wastewaters. Divalent iron hexacyanato complexes (spent bleach) are oxidized to the trivalent form with ozone and reused for bleaching purposes. Ozone is used to oxidize cyanides in other industrial wastewaters and to oxidize phenols and dyes to a variety of colorless, nontoxic products.

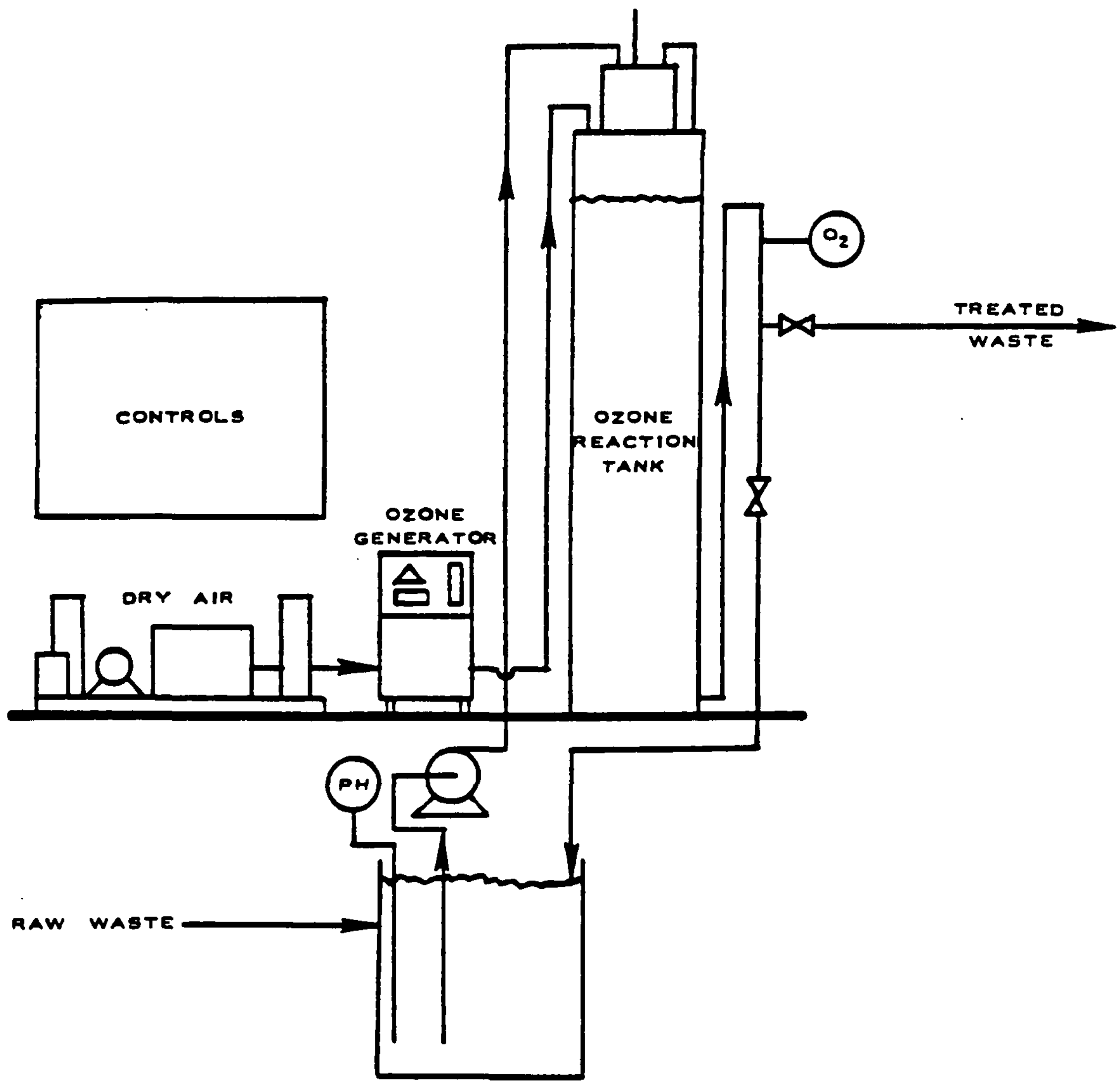

FIGURE 7-26

TYPICAL OZONATION PLANT FOR WASTE TREATMENT

Oxidation of cyanide to cyanate is illustrated below:

$$CN^{-1} + O_3 = CNO^{-1} + O_2$$

Continued exposure to ozone will convert the cyanate formed to carbon dioxide and ammonia if the reaction is allowed to proceed; however, this is not economically practical, and cyanate can be economically decomposed by biological oxidation at neutral pH.

Ozone oxidation of cyanide to cyanate requires 1.8 to 2.0 pounds of ozone per pound of CN^- and complete oxidation requires 4.6 to 5.0 pounds of ozone per pound of CN^-. Zinc, copper, and nickel cyanides are easily destroyed to a nondetectable level, but cobalt cyanide is resistant to ozone treatment.

The first commercial plant using ozone in the treatment of cyanide waste was installed by a manufacturer of aircraft. This plant is capable of generating 54.4 Kg (120 pounds) of ozone per day. The concentration of ozone used in the treatment is approximately 20 mg/l. In this process the cyanate is hydrolyzed to CO_2 and NH_3. The final effluent from this process passes into a lagoon. Because of an increase in waste flow the original installation has been expanded to produce 162.3 Kg (360 pounds) of ozone per day.

Some advantages of ozone oxidation for handling process effluents are that it is well suited to automatic control, on-site, generation eliminates treatment chemical procurement and storage problems, reaction products are not chlorinated organics, and no dissolved solids are added in the treatment step. Ozone in the presence of ultraviolet radiation or other promoters such as hydrogen peroxide and ultrasound shows promise of reducing reaction time and improving ozone utilization. Some limitations of the process are high capital expense, possible chemical interference in the treatment of mixed wastes, and an energy requirement of 15 to 22 kwh per kilogram of ozone generated. Cyanide is not economically oxidized beyond the cyanate form.

Performance

An electroplating plant (ID 30022) that serves the electronics industry plates gold, silver, copper, and nickel. Ozone was selected for treatment of cyanide bearing waste, and the results were as follows:

A. Optimum operating conditions were determined to be 1 to 1.5 moles of ozone/mole CN at a pH of 9.0-9.5 in the ozone contactor.

B. It was established that ozone dosage is the most critical operating parameter, with 1.0 to 1.5 moles O_3/mole CN found to be optimum at low CN concentrations (20 mg/l) and 1.8 to 2.8 moles O_3/mole CN at levels greater than 40 mg/l.

C. Cost data based on plant experience were obtained. Treatment operating cost was $1.43/100 gallons of influent cyanide bearing waste water and $1.03/1000 gallons total waste water. Total capital costs were $66,613 for this installation but are estimated at $51,200 for an optimized, non-research installation.

D. The results of three days of sampling are shown below:

PLANT ID 30022 (mg/l)

Parameter	Day 1 In	Day 1 Out	Day 2 In	Day 2 Out	Day 3 In	Day 3 Out
Cyanide, Total	1.4	.113	.30	.039	2.4	.096
Cyanide, Amenable	1.4	.110	.30	.039	2.389	.096

Demonstration Status

Ozone is useful for application to cyanide destruction. There are at least two units presently in operation in the country (Plant ID's 14062 and 30022), and additional units are planned. There are numerous orders for industrial ozonation cyanide treatment systems pending.

Ozone is useful in the destruction of wastewaters containing phenolic materials, and there are several installations in operation in the United States.

Research and development activities within the photographic industry have established that ozone is capable of treating some compounds that are produced as waste products. Solutions of key ingredients in photographic products were composed and treated with ozone under laboratory conditions to determine the treatability of these solutions. It was found that some of these solutions were oxidized almost completely by ozonation and some were oxidized that were difficult to treat by conventional methods. Ozone breaks down certain developer components that biodegrade slowly, including color developing agents, pheniodone, and hydroxylamine sulfate. Developing agents, thiocyanate ions, and formate ions degrade more completely with ozone than when exposed to biological degradation. Thiosulfate, sulfite, formalin, benzyl alcohol, hydroquinone, maleic acid, and ethylene glycol can be degraded to a more or less equal degree with either biological treatment or ozone. Silver thiosulfate complexes were also treated with ozone resulting in significant recovery of the silver present in solution. Ozone for regeneration of iron cyanide photoprocessing bleach and treatment of thiosulfate, hydroquinone, and other chemicals is currently being utilized by the photoprocessing industry. There are 40 to 50 installations of this nature in use at the present time.

Oxidation By Ozonation With UV Radiation

One of the modifications of the ozonation process is the simultaneous application of ultraviolet light and ozone for the treatment of wastewater, including treatment of halogenated organics. The combined action of these two forms produces reactions by photolysis, photosensitization, hydroxylation, oxygenation and oxidation. The process is unique because several reactions and reaction species are active simultaneously.

Ozonation is facilitated by ultraviolet absorption because both the ozone and the reactant molecules are raised to a higher energy state so that they react more rapidly. The energy and reaction intermediates created by the introduction of both ultraviolet radiation and ozone greatly reduce the amount of ozone required compared with a system that utilizes ozone alone to achieve the same level of treament. Figure 7-27 shows a three-stage UV/ozone system.

A typical process configuration employs three single stage reactors. Each reactor is a closed system which is illuminated with ultraviolet lamps placed in the reactors, and the ozone gas is sparged into the solution from the bottom of the tank. The ozone dosage rate requires 2.6 pounds of ozone per pound of chlorinated aromatic. The ultraviolet power is on the order of five watts of useful ultraviolet light per gallon of reactor volume. Operation of the system is at ambient temperature and the residence time per reaction stage is about 24 minutes. Thorough mixing is necessary and the requirement for this particular system is 20 horsepower per 1000 gallons of reactor volume in quadrant baffled reaction stages. A system to treat mixed cyanides requires pretreatment that involves chemical coagulation, sedimentation, clarification, equalization, and pH adjustment. Pretreatment is followed by a single stage reactor, where constituents with low refractory indices are oxidized. This may be followed by a second, multi-stage reactor which handles constituents with higher refractory indices. Staging in this manner reduces the ultimate reactor volume required for efficient treatment.

Application

The ozonation/UV radiation process was developed primarily for cyanide treatment in the metal finishing and color photoprocessing areas, and it has been successfully applied to mixed cyanides and organics from organic chemicals manufacturing processes. The process is particularly useful for treatment of complexed cyanides such as ferricyanide, copper cyanide and nickel cyanide, which are resistant to ozone alone, but readily oxidized by ozone with UV radiation.

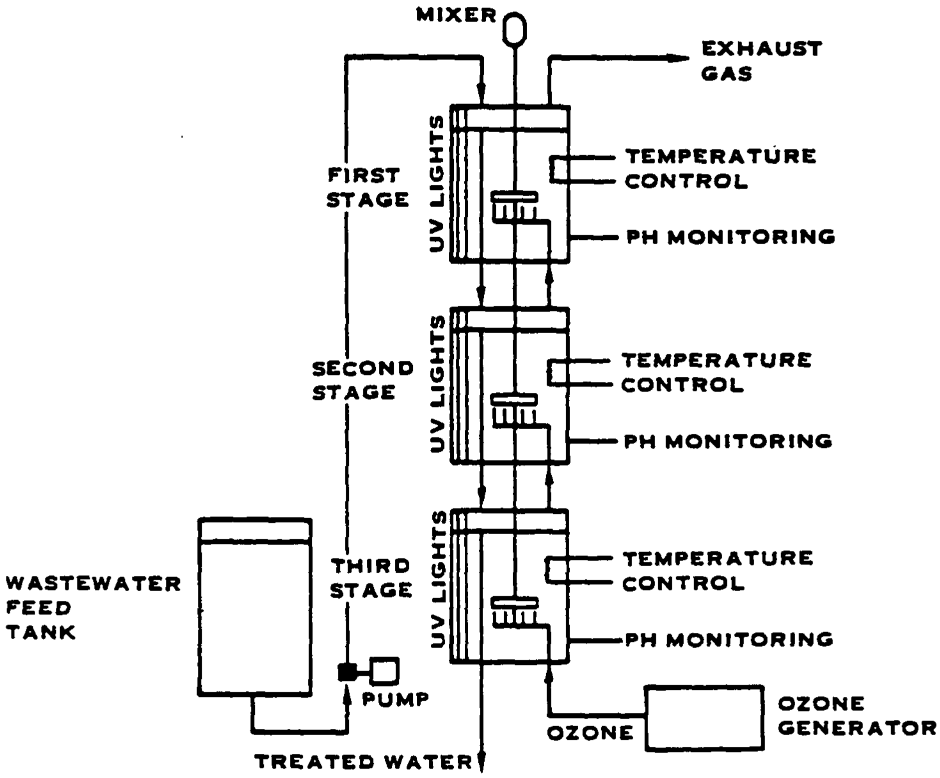

FIGURE 7-27

UV/OZONATION

Performance

For mixed metal cyanide wastes, consistent reduction in total cyanide concentration to less than 0.1 mg/l is claimed. Metals are converted to oxides, and halogenated organics are destroyed. TOC and COD concentrations are reduced to less than 1 mg/l.

Demonstration Status

A full scale unit to treat metal complexed cyanides has been installed in Oklahoma, while a large American chemical company in France has installed an on-line unit for the treatment of cyanides and organics and a similar design is scheduled for installation by the same company in the United States. There are also two other units known to be in service, one for treating mixed cyanides and the other for treatment of copper cyanide.

Oxidation By Hydrogen Peroxide

The hydrogen peroxide oxidation treatment process treats both the cyanide and metals in cyanide wastewaters containing zinc or cadmium. In this process, cyanide rinse waters are heated to 49-54°C (120-130°) to break the cyanide complex, and the pH is adjusted to 10.5-11.8. Formalin (37% formaldehyde) is added, while the tank is vigorously agitated. After 2-5 minutes, a proprietary formulation (41% hydrogen peroxide with a catalyst and additives) is likewise added. After an hour of mixing, the reaction is complete. The cyanide is converted to cyanate and the metals are precipitated as oxides or hydroxides. The metals are then removed from solution by either settling or filtration.

The chemical reactions which take place are as follows:

$$CN + HCHO + H_2O = HOCH_2CN + OH^-$$

The hydrogen peroxide converts cyanide to cyanate in a single step:

$$CN + H_2O_2 = NCO + H_2O$$

The formaldehyde also acts as a reducer, combining with the cyanide ions:

$$Zn(CN)_4^{-2} + 4\ HCHO + 4H_2O = 4\ HOCH_2CN + 4\ OH^- + Zn^{+2}$$

The metals subsequently react with the hydroxyl ions formed and precipitate as hydroxides or oxides:

$$Zn^{+2} + 2\ OH^- = ZnO + H_2O$$

The main pieces of equipment required for this process are two holding tanks. These tanks must be equipped with heaters and air spargers or mechanical stirrers. These tanks may be used in a batch or continuous fashion with one tank being used for treatment while the other is being filled. A settling tank or a filter is needed to concentrate the precipitate.

Application

The hydrogen peroxide oxidation process is applicable to cyanide bearing wastewaters, especially those from cyanide zinc and cyanide cadmium electroplating. The process has been used on photographic wastes to recover silver and oxidize toxic compounds such as cyanides, phenols and "hypo" (sodium thiosulfate pentahydrate). Additions of hydrogen peroxide are made regularly at a large wastewater treatment plant to control odors and minimize pipe corrosion by oxidizing hydrogen sulfide.

Chemical costs are similar to those for alkaline chlorination and lower than those for treatment with hypochlorite, and all free cyanide reacts and is completely oxidized to the less toxic cyanate state. In addition, metals precipitate and settle quickly, and they are recoverable in many instances. However, the process requires energy expenditures to heat the wastewater prior to treatment. Furthermore, the addition of formaldehyde results in treated wastewater having relatively high BOD values. Although cyanates are much less toxic than cyanide, there is not complete acceptance of the harmlessness of cyanates.

Performance

In terms of waste reduction performance, this process is capable of reducing the cyanide level to less than 0.1 mg/l and the zinc or cadmium to less than 1.0 mg/l.

Demonstration Status

This treatment process was introduced in 1971 and is being used in several facilities.

Peroxide oxidation is used in three plants in the present data base: 08061, 21058, and 30009.

Electrochemical Cyanide Oxidation

Electrochemical cyanide oxidation is used to reduce free cyanide and cyanate levels in industrial wastewaters. In this process, wastewater is accumulated in a storage tank and then pumped to a reactor where an applied DC potential oxidizes the cyanide to nitrogen, carbon dioxide and trace amounts of ammonia. The gases generated are vented to the atmosphere. The oxidation reaction is accomplished if concentrations are not greater than 1000 mg/l. If reaction time is critical, the process can be accelerated by augmenting the system with a chemical (hypochlorite) treatment as long as the cyanide concentration level is less than 200 mg/l. The process equipment consists of a reactor, a power supply, a storage tank and a pump.

Another electrochemical oxidation system employs a low voltage anode with a metallic oxide coating. Upon application of an electrical potential several oxidation reactions occur at the anode. These reactions include the oxidation of chloride (from common salt) to chlorine or hypochlorite and the formation of ozone, as well as direct oxidation at the anode. Although untested on cyanide-bearing wastewaters, this system shows good potential in that area.

Application

The electrochemical cyanide oxidation system has been used commercially only for heat treating applications; however, it should be equally appropriate for other cyanide bearing wastes. Its application for plating and photographic process wastewaters is still in the development stage. The process can also be applied to the electrochemical oxidation of nitrite to nitrate.

Electrochemical cyanide oxidation has the advantage of low operating costs with moderate capital investment, relative to alternative processes. There is no requirement for chemicals, thereby eliminating both their storage and control, and there is no need to dilute or pretreat the wastewater as the process is most efficient at high cyanide concentration levels. However, the process is less efficient than chemical destruction at cyanide concentrations less than 100 mg/l, and it is relatively slow when not accelerated by addition of treatment chemicals. Moreover, it will not work well in the presence of sulfates.

Performance

Performance has been demonstrated on a commercial scale and shown to result in a reduction in the cyanide concentration level from 3500 mg/l to less than 1.0 mg/l in 160 hours. The process emits no noticeable odor with adequate ventilation.

Demonstration Status

There is currently a unit in operation which is handling the cyanide bearing wastewater generated by a heat treating operation. The manufacturer claims that there is a potential for future use of the process in both the electroplating and photographic industries. However, despite a variety of experimental programs, industry has not been enthusiastic about the electrolytic approach to cyanide oxidation.

Electrochemical cyanide oxidation is used at plants 04224, 18534, 19002, and 30080.

Chemical Precipitation

Chemical precipitation is a classic waste treatment process for metals removal as described under the "Treatment of Common Metal Wastes" heading. The precipitation of cyanide can be accomplished by treatment with ferrous sulfate. This precipitates the cyanide as a ferrocyanide, which can be removed in a subsequent sedimentation step. Waste streams with a total cyanide content of 2 mg/l or above have an expected waste reduction of 1.5 to 2 orders of magnitude. These expectations are substantiated by the following results from plant 01057:

CONCENTRATION OF TOTAL CYANIDE (mg/l)

Raw Waste	Final Effluent
2.57	0.024
2.42	0.015
3.28	0.032

Evaporation

Evaporation is another recovery alternative applicable to cyanide process baths such as copper cyanide, zinc cyanide, and cadmium cyanide and was described in detail for common metals removal.