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Risk Reduction
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Cincinnati, Ohio 45268

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EPA

Project Summary

Characterization and Treatment of Wastes from Metal-Finishing Operations

The report summarized here details activities associated with characterizing and treating metal-finishing wastes to support the U.S. Environmental Protection Agency's (EPA) development of treatment standards for regulations restricting land disposal of hazardous wastes. It includes information on the waste generators' manufacturing and wastewater treatment plant operations, the chemical composition of the untreated wastes, and performance data generated during bench- and pilot-scale testing. The treatment technologies tested were alkaline chlorination, wet-air oxidation (WAO), ultraviolet light/ozonation (UV/O_3), electrolytic oxidation, stabilization/solidification (S/S), and metals precipitation. WAO bench- and pilot-scale tests indicated significant cyanide destruction; whereas, UV/O_3 provided partial cyanide destruction but essentially no iron cyanide destruction. Cement proved to be the most effective S/S binder for metals.

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

Introduction

The Resource Conservation and Recovery Act (RCRA) Waste Codes F006, F007, F008, F009, F011, F012, and F019 are defined in Table 1. The table also presents a description of each waste, the basis for listing, the waste generator(s) sampled, the technology evaluated, and the scale of the evaluation.

Cyanide Chemistry, Analysis, and Toxicity

The stability and toxicity of the various forms of cyanide and analytical methods for determining cyanide are important to understanding how cyanide compounds respond to treatment. The characterization of cyanide species falls into four general categories: 1. analytical methods, 2. ionic structure, 3. strength of the cyanide-metal complex bond, and 4. compound solubility. Examples of each category are discussed in the full report, along with a brief discussion of the toxicity of free and complexed cyanides and the stability of cyanide-metal complexes.

The various methods used in each of the analytical procedures for cyanide are also explained in the full report. For example, procedures for determining total cyanide include acid reflux/distillation, automated ultraviolet digestion, ligand-exchange, and ion chromatography; free cyanide procedures include absorption spectrophotometry, volumetric titrimetry, ion-selective electrodes, gas chromatography, and ion exchange.

Cyanide Oxidation Treatment

The cyanide oxidation treatment technologies included in this study are alkaline chlorination, WAO, UV/O_3, and electrolytic oxidation.

Alkaline Chlorination

Alkaline chlorination is the method the electroplating industry uses most often to detoxify cyanide. It can be used to destroy

Table 1. *Summary of Metal-Finishing Waste Codes Evaluated Under the Land Disposal Restrictions Program for U.S. EPA's Office of Research and Development*

EPA Hazardous Waste No.	Waste Description	Basis for Listing	Generators Sampled	Evaluation: Technology/Scale
F006	Wastewater treatment sludges from electroplating operations except from the following processes: 1) sulfuric acid anodizing of aluminum; 2) tin plating on carbon steel; 3) zinc plating (segregated basis) on carbon steel; 4) aluminum or zinc-aluminum plating on carbon steel; 5) cleaning/stripping associated with tin, zinc, and aluminum plating on carbon steel; and 6) chemical etching and milling of aluminum	Cadmium, hexavalent chromium, nickel, and cyanide (complexed)	Deere & Company Amerock Corp. Master Lock Co.	• Wet-air oxidation at bench-scale • Stabilization/solidification at bench-scale
F007	Spent cyanide plating-bath solutions from electroplating operations	Cyanide (salts)	Amerock Corp.	• Wet-air oxidation at bench- and pilot-scale
F008	Plating bath sludges from electroplating operations where cyanides are used in the process	Cyanide (salts)	None	Not applicable
F009	Spent strippling and cleaning-bath solutions from electroplating operations where cyanides are used in the process	Cyanide (salts)	Master Lock Co.	• Ultraviolet light/ozonation at bench-scale
F011	Spent cyanide solutions from salt-bath pot cleaning after metal heat-treating operations	Cyanide (salts)	Woodward Governor Co.	• Electrolytic oxidation at full-scale • Stabilization/solidification at bench-scale
F012	Quenching wastewater treatment sludges from metal heat-treating operations where cyanides are used in the process	Cyanide (complexed)	Woodward Governor Co.	• Electrolytic oxidation at full-scale • Stabilization/solidification at bench-scale
F019	Wastewater treatment sludges from the chemical conversion coating of aluminum	Hexavalent chromium and cyanide (complexed)	Ford	• Wet-air oxidation at bench-scale

free dissolved hydrogen cyanide or to oxidize all simple and many complex inorganic cyanides in wastewater. The most commonly used oxidizing agents are chlorine gas or hypochlorite salt.

The full report discusses in detail the treatment processes of three companies that use one- or two-stage alkaline chlorination to treat cyanide-contaminated metal finishing wastewaters. The full report also presents details of the other treatments and processes referred to below.

Wet-Air Oxidation

WAO is the liquid-phase oxidation of organics or oxidizable inorganic components at elevated temperatures and pressures.

Zimpro/Passavant in Rothschild, WI, performed bench-scale WAO testing on F006, F007, and F019, and pilot-scale WAO testing on F007.

Ultraviolet Light/Ozonation

With UV/O_3, the cyanide stream is mixed with ozone before it enters a reaction chamber, where UV radiation enhances oxidation by direct disassociation of the cyanide radical or through excitation of the various species in the waste stream. Some complexed cyanides may be more effectively oxidized by ozone in the presence of UV light.

The Illinois Institute of Technology Research Institute (IITRI), Chicago, IL, conducted bench-scale studies of the UV/O_3 system for the treatment of F009 waste.

Electrolytic Oxidation

Electrolytic oxidation has been used to treat wastes containing high concentrations of cyanide; the full report describes its use to treat residuals from a salt-bath heat-treating operation. The concentrated cyanide waste stream may be subjected to electrolysis for several days. The cyanide gradually decomposes to carbon dioxide and ammonia, with cyanate as an intermediate.

Chemical Precipitation

Precipitation of metal-laden wastewaters involves adding chemicals to alter the physical state of the dissolved or suspended metals and to facilitate their removal through sedimentation. Chemicals used to precipitate metals from aqueous streams include caustic soda, lime, sodium sulfide, phosphoric acid, ferrous sulfide, soda ash, and sodium borohydride. The full report details a phosphoric acid metal precipitation/-alkaline chlorination process.

Stabilization/Solidification

S/S entails mixing a hazardous waste with a binder material to enhance the physical and chemical properties of the waste and the chemical binding of any free liquid. The binder is typically a cement, pozzolan, or thermoplastic.

The U.S. Army Corps of Engineers Waterways Experiment Station (WES) in Vicksburg, MS, conducted S/S testing on F006, F011, and F012 metal-finishing wastes under an interagency agreement. Three different pozzolan binders (lime/fly ash, portland cement, and kiln dust) were tested to determine their application to these wastes.

Testing Results

Of the six technologies discussed above, only WAO, UV/O_3, and S/S were tested to assess their effectiveness in treating cyanide. Bench-scale UV/O_3 testing proved inconclusive in its ability to treat complexed cyanide.

Wet-Air Oxidation: Bench-Scale

The results of the autoclave oxidations of F006, F007, and F019 are presented in Tables 2 through 4. Compared with the dilute wastes, the COD reductions were in the range of 92% to 95% for the F006, 79% to 86% for the F007, and 68% to 83% for the F019. The total cyanide reductions in the filtrates were in the range of 78% to 99% for the F006, 99% to 99.5% for the F007, and 98% to 99.9% for the F019. The ammonia-nitrogen from the cyanide oxidations reached a maximum of about 300 mg/L for the F006 tests at 240° and 280°C, 5000 mg/L

Table 2. *Wet-Air-Oxidation Results for F006*

Parameter*	Autoclave Feed	Oxidized Product Filtrate	Cake	Filtrate	Cake	Filtrate	Cake
Oxidation temp, °C	-	200	200	240	240	280	280
Time at temp, min	-	60	60	60	60	60	60
COD, g/L	3.7	0.166	197	0.269	24	0.311	29
COD reduction, %	-	95.5	-	93	-	92	-
pH	11	9.9	-	9.7	-	10.1	-
NH_3-N, mg/L	-	203.60	-	305.1	-	306	-
Total solids, g/L	17.3	1.92	100%	1.25	100%	1.79	100%
Total ash, g/L	15.9	1.77	85.3%	1.17	86.6%	1.79	87.8%
Cyanide, total, mg/L	122.4	26.3	102 µg/g	0.82	20 µg/g	1.1	81 µg/g
Total cyanide reduction, %	-	78	-	99	-	99	-
Cyanide, amenable, mg/L	73.9	26.3	102 µg/g	0.82	20 µg/g	1.1	81 µg/g
Amenable cyanide reduction, %	-	64	-	99	-	98	-
Sulfides, mg/L	<1	<1	-	<1	-	<1	-
Fluoride, mg/L	3.59	2.12	0.69 mg/g	1.8	0.7 mg/g	3.5	0.63 mg/g
Arsenic, µg/L	<1.2	<5.0	<2400 µg/g	<5.0	<2400 µg/g	<5.0	2400 µg/g
Antimony, µg/L	<5.0	<5.0	72.8 µg/g	<5.0	84.8 µg/g	<5.0	81.4 µg/g
Barium, mg/L	0.54	0.17	40 µg/g	0.17	43 µg/g	0.19	39 µg/g
Beryllium, mg/L	<0.01	0.018	0.28 µg/g	0.014	<0.2 µg/g	0.015	<0.2 µg/g
Cadmium, mg/L	220.5	0.53	241 mg/g	0.25	254 mg/g	0.27	241 mg/g
Chromium (T), mg/L	348.4	44.4	29 mg/g	16.7	31 mg/g	<0.09	32 mg/g
Chromium (+6), mg/L	Interference	33.8	1980 µg/g	15.3	830 µg/g	<0.2	73 µg/g
Copper, mg/L	729.1	25.9	78 mg/g	5.4	85 mg/g	5.9	79 mg/g
Iron, mg/L	1177	0.73	9.5 mg/g	0.07	10.1 mg/g	0.08	9.7 mg/g
Lead, mg/L	1.12	<0.5	48 µg/g	<0.5	103 µg/g	<0.5	127 µg/g
Mercury, mg/L	0.42	2.05	1.1 µg/g	5.14	0.12 µg/g	4.1	0.12 µg/g
Nickel, mg/L	643.9	2.4	62 mg/g	0.12	63 mg/g	0.33	62 mg/g
Selenium, mg/L	<0.2	38	<4000 µg/g	19	<4000 µg/g	36	<4000 µg/g
Silver, mg/L	<0.05	<0.05	<1 µg/g	<0.05	<1 µg/g	<0.05	<1 µg/g
Thallium, mg/L	<5.0	40	<14 µg/g	50	<14 µg/g	40	<14 µg/g
Vanadium, mg/L	<0.05	<0.05	<1 µg/g	<0.05	<1 µg/g	<0.05	<1 µg/g
Zinc, mg/L	355.1	0.44	33 mg/g	0.26	35 mg/g	0.29	33 mg/g

*** Units are specified in this column except as noted elsewhere.**

Table 3. Wet-Air-Oxidation Results for F007

Parameter*	Raw Waste	Dilute Waste**	Oxidized Product					
			Filtrate	Solids	Filtrate	Solids	Filtrate	Solids
Oxidation temp, °C			200	200	240	240	280	280
COD, mg/L	33,370	16,685	3,060	-	2,315	-	3,578	-
COD reduction, %	-	-	81.7	-	86.1	-	78.6	-
Cyanide, total, mg/L	23,667	11,834	117	183 μg/g	86	<1.0 μg/g	58	<1.0 μg/g
Total cyanide reduction, %	-	-	99.0	-	99.3	-	99.5	-
Cyanide, amenable, mg/L	21,750	10,875	114	143 μg/g	86	<1.0 μg/g	55	<1.0 μg/g
Amenable cyanide reduction, %	-	-	99.0	-	99.2	-	99.5	-
Total solids, mg/L	260,770	130,385	110,000	9,500†	86,600	9,000†	76,200	8,800†
Total ash, mg/L	242,300	121,150	103,600	8,300†	83,100	8,100†	66,600	7,800†
pH	10.8	-	9.8	-	9.4	-	9.0	-
NH_3-N, mg/L	134	67	5,000	-	3,104	-	1,187	-
Sulfide, mg/L	1.36	0.68	-	-	-	-	-	-
Arsenic, mg/L	<1.2	<1.2	<1.2	<35	<1.2	<35	<1.2	<32
Barium, mg/L	3.23	1.62	0.017	104	0.012	83.4	0.003	68.0
Cadmium, mg/L	<0.04	<0.04	<0.004	<1.15	<0.004	<1.15	<0.004	<1.07
Chromium (T), mg/L	7.5	3.75	3.24	30.5	3.33	13.5	3.04	13.3
Chromium (+6), mg/L	<0.1	<0.1	0.90	IS††	0.66	<3.4	0.18	<3.9
Copper, mg/L	7663	3832	863	261,440	553	234,600	316	219,450
Lead, mg/L	0.81	0.40	2.3	464	1.4	229	0.80	172
Mercury, mg/L	0.0048	0.0024	0.0095	0.23	0.0106	0.14	0.0106	0.153
Nickel, mg/L	8.46	4.23	0.38	1,305	0.099	408	0.067	337
Selenium, mg/L	31.2	15.6	13.0	90	9.2	89	5.5	116
Silver, mg/L	<0.05	<0.05	<0.05	<1.4	<0.05	<1.4	<0.05	<1.3
Zinc, mg/L	4180	305	305	75,890	159	79,270	29.8	82,565

*Units are specified in this column except as noted elsewhere.

** Concentrations calculated on 1:1 dilution of raw wastewater.

† Concentration of suspended solids/suspended ash filtered from oxidized waste.

†† IS = Insufficient Sample.

for the F007 test at 200°C, and about 760 mg/L for the F019 test at 280°C.

Wet-Air Oxidation: Pilot-Study

The WAO study was performed on the F007 wastes containing total cyanides in excess of 30 g/L (3%). The 24-hr study was conducted in a 5.4-gal pilot unit constructed of titanium. The major oxidation operating parameters for this test were reactor temperature of 454°F, a reactor pressure of 1700 psig, and a reactor residence time of 54 min.

Zimpro's analyses showed a 99.99% cyanide destruction with a residual concentration of 1.57 ppm cyanide in the oxidized liquor.

Stabilization/Solidification

For one source of F006 filter cake, S/S leaching data showed low concentrations of metals in the extracts for all three binders (cement, lime/fly ash, kiln dust). Cadmium was less than 0.003 mg/L, hexavalent chromium ranged from 0.04 to 0.23 mg/L, and nickel was 0.025 to 0.042 mg/L. The cement binder was the most effective in containing copper and zinc.

The second source of F006 waste did not demonstrate the same level of S/S effectiveness for two binder systems. With the kiln dust binder, extracts contained 42.2 to 77.5 mg/L cadmium, 0.054 to 0.078 mg/L hexavalent chromium, 4.63 to 11.3 mg/L nickel, and 106 to 112 mg/L magnesium. The lime/fly ash binder extracts showed 0.031 to 0.17 mg/L cadmium, 0.30 to 0.37 mg/L hexava-

Table 4. Wet-Air-Oxidation Results for F019

		Oxidized Product					
*Parameter**	*Autoclave Feed*	*Filtrate*	*Cake*	*Filtrate*	*Cake*	*Filtrate*	*Cake*
Oxidation temp, °C	-	200	200	240	240	280	280
Time at temp, min	-	60	60	60	60	60	60
COD, g/L	10.5	1.75	73.7	3.04	160	2.12	25.3
COD reduction, %	-	83.3	-	68	-	79	-
pH	8.54	7.95	-	7.9	-	7.8	-
NH_3-N, mg/L	27.7	527.50	-	668	-	766	-
Total solids, g/L	41.7	2.78	98.8%	2.55	100%	2.08	100%
Total ash, g/L	28.1	1.45	83.9%	1.26	79.6%	1.35	89.7%
Cyanide, total, mg/L	293.1	5.07	22.9 μg/g	0.058	142 μg/g	0.133	18 μg/g
Total cyanide from solids, mg/L	-	-	0.91	-	3.07	-	0.57
Total cyanide reduction, %	-	98	-	99.9	-	99.9	-
Cyanide, amenable, mg/L	240.9	5	22.9 μg/g	0.02	142 μg/g	0.02	18 μg/g
Amenable cyanide from solids, mg/L	-	-	0.91	-	3.07	-	0.57
Amenable cyanide reduction, %	-	98	-	>99.9	-	>99.9	-
Sulfides, mg/L	<1	<1	-	<1	-	<1	-
Fluoride, mg/L	38.9	24.7	0.17 μg/g	30.9	0.15 μg/g	38.9	0.23 μg/g
Arsenic, μg/L	80.2	132	114 μg/g	221	135 μg/g	<5.0	109 μg/g
Antimony, μg/L	<5.0	<5.0	465 μg/g	<5.0	460 μg/g	<5.0	469 μg/g
Barium, mg/L	2.7	0.21	138 μg/g	0.35	145 μg/g	0.77	166 μg/g
Beryllium, mg/L	0.007	<0.001	0.32 μg/g	<0.001	0.29 μg/g	<0.01	0.32 μg/g
Cadmium, mg/L	2.11	0.013	102 μg/g	0.007	99 μg/g	<0.04	104 μg/g
Chromium (T), mg/L	1231	1.92	72,267 μg/g	1.86	68,590 μg/g	24	74,072 μg/g
Copper, mg/L	0.355	0.053	48.7 μg/g	0.046	34 μg/g	0.12	66 μg/g
Iron, mg/L	189	0.13	12,000 μg/g	0.08	11,034 μg/g	0.08	15,238 μg/g
Lead, mg/L	14.7	0.003	816 μg/g	0.008	586 μg/g	0.916	584 μg/g
Mercury, mg/L	0.35	1.1	<0.02 μg/g	1.0	<0.02 μg/g	0.8	<0.02 μg/g
Nickel, mg/L	0.875	0.007	46 μg/g	0.011	43 μg/g	0.21	48 μg/g
Selenium, mg/L	50.8	250	<20 μg/g	<5.0	<20 μg/g	<5.0	<20 μg/g
Silver, mg/L	<0.01	<0.005	<0.5 μg/g	<0.005	<0.5 μg/g	0.05	<0.5 μg/g
Thallium, mg/L	<140	9.5	<5 μg/g	5.0	<5 μg/g	5.0	<5 μg/g
Vanadium, mg/L	0.31	0.006	<0.5 μg/g	<0.005	<0.5 μg/g	<0.05	<0.5 μg/g
Zinc, mg/L	4902	4.6	61,000 μg/g	4.6	257,000 μg/g	15.2	279,000 μg/g

** Units are specified in this column except as noted elsewhere.*

lent chromium, less than 0.03 mg/L nickel, and 1.04 to 3.47 mg/L magnesium. The cement binder extracts showed 0.26 to 0.28 mg/L cadmium, 0.023 to 0.074 mg/L hexavalent chromium, less than 0.031 mg/L nickel, and 0.096 to 0.13 mg/L magnesium.

Cement-treated F012 extracts showed average concentrations of 47.5 mg/L magnesium and 2.6 mg/L nickel. Lime/fly ash extracts showed 1.01 mg/L aluminum, 12.9 mg/L magnesium, and 0.034 mg/L nickel. Kiln dust extracts showed concentrations of 46.7 mg/L magnesium and 1.47 mg/L nickel.

Conclusions

Data from the WAO bench-scale test indicated significant destruction of cyanides in F006, F007, and F019 wastes. Similar results were obtained for the F007 pilot-scale tests. The most effective S/S binder system for F006 metals was cement.

The full report was submitted in fulfillment of EPA Contract No. 68-03-3389 by PEI Associates, Inc., under the sponsorship of the U.S. Environmental Protection Agency.

The project was prepared by the staff of PEI Associates, Inc., Cincinnati, OH 45246.
***Ronald J. Turner** is the EPA Project Officer (see below)*
The complete report, entitled "Characterization and Treatment of Wastes from Metal-Finishing Operations," (Order No. PB91-125 732/AS; Cost: $23.00, subject to change) will be available only from:
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