F006: Compositional Characterization A Generation After Listing

By John S. Lindstedt

The Clean Water Act (CWA) of 1972 arguably has had more impact on the metal finishing industry than any other single piece of federal or state legislation since the inception of the industry. This act required the removal of materials used in the finishing process that were not captured on work product and exit the process in wastewater. This resultant generation of wastewater treatment sludges led in 1980 to their becoming a listed (defined) hazardous waste under the Resource Conservation and Recovery Act of 1980 (RCRA) with a waste code F006. The basis of this determination was set forth in a background document for RCRA in November 1980.[1] Final pretreatment regulations requiring concentration based limits on regulated pollutants (primarily metals and cyanide) were promulgated in July, 1986 (40CFR§§413 and 433).

The conclusion of this 1980 listing determination, while valid from the data set evaluated and management practices of that time, has come under an ever increasing criticism from industry. The compositional characteristics of wastewater treatment sludges and their handling procedures have evolved for the better over the last 20 years in response to a variety of environmental regulations. In addition, the industry has responded with technology developments that have eliminated toxins from metal finishing chemistries. Waste from a finishing operation is *different* today than a generation earlier. **There clearly was a need to evaluate the current chemical composition of wastewater treatment sludges and to evaluate that change in relation to the current regulatory framework.**

The task of conducting a scientifically correct compositional characterization study of F006 is a difficult and imposing task for an industry as diverse as the surface finishing industry. A myriad of processing performed on a multitude of basis metals which is entwined in all phases of an industrial economy insure a complex waste product. To help solve this problem, the industry requested the assistance of the U.S. Environmental Protection Agency (EPA).[2,3] The agency responded and initiated the compositional evaluation of present wastewater treatment sludges within its Common Sense Initiative. In late 1996, the work began.

Table 1
National Metal Finishing Performance Goals (By Year 2002)

(1) Improved Resource Utilization ("Smarter")
- (a) 98% of metals ultimately utilized on product.
- (b) 50% reduction in water purchased/used (from 1992 levels).
- (c) 25% reduction in facility-wide energy use (from 1992 levels).

(2) Reduction in Hazardous Emissions and Exposures ("Cleaner")
- (a) 90% reduction in organic TRI emissions and 50% reduction in metals emissions to air and water (from 1992 levels).
- (b) 50% reduction in land disposal of hazardous sludge and a reduction in sludge generation (from 1992 levels).
- (c) Reduction in human exposure to toxic material in the facility and the surrounding community, clearly demonstrated by action selected and taken by the facility. Such actions may include, for example, pollution prevention, use of state-of-art emission controls and protective equipment, use of best recognized industrial hygiene practices, worker training in environmental hazards, or participation in the Local Emergency Planning Committees.

(3) Increased Economic Payback and Decreased Costs ("Cheaper")
- (a) Long-term economic benefit to facilities achieving Goals 1 and 2.
- (b) 50% reduction in costs of unnecessary permitting, reporting, monitoring, and related activities (from 1992 levels), to be implemented through burden reduction programs to the extent that such efforts do not adversely impact environmental outcomes.

(4) Industry-wide Achievement of Facility Goals.
- (a) 80% of facilities nationwide achieve Goals 1–3.

(5) Industry-wide Compliance with Environmental Performance Requirements.
- (a) All operating facilities achieve compliance with Federal, State and local environmental performance requirements.
- (b) All metal finishers wishing to cease operations have access to a government sponsored "exit strategy" for environmentally responsible site transition.
- (c) All enforcement activities involving metal finishing facilities are conducted in a consistent manner to achieve a level playing field, with a primary focus on those facilities that knowingly disregard environmental requirements.

Note: *At facilities where outstanding performance levels were reached prior to 1992, the percentage-reduction targets for Goals 1(b) and (c), and 2(a) and (b) may not be fully achievable, or the effort to achieve them may not be the best use of available resources. In these instances, a target should be adjusted as necessary to make it both meaningful and achievable.*

Background

In 1994, the Administrator of the U.S. EPA, Carol Browner, launched the Common Sense Initiative (CSI), describing it as a "fundamentally different system" to explore industry-specific strategies for environmental protection. The program is designed to promote "cleaner, cheaper and smarter" environmental performance, using a non-adversarial, stakeholder consensus process to test innovative ideas and approaches. Six industry sectors were selected to participate in CSI:

- Petroleum Refining
- Auto Manufacturing
- Iron & Steel
- Metal Finishing
- Printing
- Computers & Electronics

Metal finishing was one of two small business sectors represented.

In January 1995, the Environmental Protection Agency chartered the Metal Finishing Sector Subcommittee of the Common Sense Initiative under the Federal Advisory Committee Act. The Metal Finishing Subcommittee includes representatives of EPA Headquarters and Regional offices, the metal finishing industry and its suppliers, state government, publicly owned treatment works (POTWs), national and regional environmental organizations, the environmental justice community and organized labor.

The CSI Metal Finishing Sector was challenged by Administrator Carol Browner to develop a consensus package of "cleaner, cheaper and smarter" policy actions for the industry as a whole, based on the lessons learned from the Sector's projects and dialogue. Based on this challenge, the Subcommittee established a workgroup to develop a strategic policy and program framework for the industry.

The Metal Finishing Strategic Goals Program, designed by this multi-stakeholder group, is a major product of this effort. It establishes a set of voluntary National Performance Goals for the industry that represent "better than compliance" environmental performance for metal finishers. The Metal Finishing Goals Program, summarized in Table 1, includes facility-based numerical performance targets that track the CSI themes of cleaner, cheaper and smarter performance. The first goal of 98-percent metals utilization is attainable only if metals within the industry's wastewater treatment sludges are returned to use (utilized). The F006 evaluation, therefore, is critical for setting the basis upon which to reuse the metals that are currently designated to a waste stream.

Table 2
Maximum Concentration of Contaminants
For the Toxicity Characteristic

EPA No.	Contaminant	Cas No.	Regulatory Level, ppm
D004	Arsenic	7440-38-2	5.0
D005	Barium	7440-39-3	100.00
D018	Benzene	71-43-2	0.5
D006	Cadmium	7440-43-9	1.0
D019	Carbon Tetrachloride	56-23-5	0.5
D020	Chlordane	57-74-9	0.03
D021	Chlorobenzene	108-90-7	100.0
D022	Chloroform	67-66-3	6.0
D007	Chromium	7440-47-3	5.0
D023	o-Cresol	95-48-7	200.0
D024	m-Cresol	108-39-4	200.0
D025	p-Cresol	108-44-6	200.0
D026	Cresol	—	200.0
D016	2,4-D	94-75-7	10.0
D027	l,4-Dichlorobenzene	106-46-7	7.5
D028	1,2-Dichlorobenzene	107-06-2	0.5
D029	1,1-Dichlorobenzene	75-35-4	0.7
D030	2,4-Dinitrotoluene	121-14-2	0.13
D012	Endrin	72-20-8	0.02
D031	Heptachlor (& its epoxide)	76-44-8	0.008
D032	Hexachlorobenzene	118-74-1	0.13
D033	Hexachlorobenzene	87-68-3	0.5
D034	Hexachlorobenzene	67-72-1	3.00
D008	Lead	7439-92-1	5.0
D013	Lindane	58-89-9	0.4
D009	Mercury	7439-97-6	0.2
D014	Methoxychlor	72-43-5	10.0
D035	Methyl ethyl ketone	78-93-3	200.0
D036	Nitrobenzene	98-95-3	2.0
D037	Pentrachlorophenol	87-86-5	100.0
D038	Pyridine	110-86-1	5.0
D010	Selenium	7782-49-2	1.0
D011	Silver	7440-22-4	5.0
D039	Tetrachloroethylene	127-18-4	0.7
D015	Toxaphene	8001-35-2	0.5
D040	Trichloroethylene	79-01-6	0.5
D041	2,4,5 Trichlorophenol	95-95-4	400.0
D042	2,4,6 Trichlorophenol	88-06-2	2.0
D017	2,4,5TP (Silvex)	93-72-1	1.0
D043	Vinyl chloride	75-01-4	0.2

Background: Hazardous Waste Determination of F006

The U.S. EPA has established two approaches for determining whether a specific waste is hazardous. A waste can be hazardous because it contains a certain hazardous component (*i.e.*, cadmium or cyanide) or exhibits a certain hazardous physical trait (low flashpoint). A waste can also be deemed hazardous simply because it is generated from a process that generally produces hazardous wastes. It does not matter if this waste is tested and determined to be non-hazardous. If the waste is generated from a "listed" process, then it is hazardous. The wastes from these two approaches are defined as "characteristically" hazardous and "listed" hazardous, respectively. Waste that is generated from wastewater treatment of electroplating operations is listed "F006".[4,5]

To classify a waste as characteristically hazardous, forty-five (45) parameters/physical traits are evaluated. These parameters are:

- High/Low pH
- Low Flashpoint
- High Reactive Cyanide Content
- High Reactive Sulfide Content
- High Phenol Content
- High Leachability of Certain Parameters (40 listed parameters as tested by The Toxic Characteristic Leaching Procedure (TCLP)—see Table 2

Of these 45 analyses, 39 are not applicable to F006 waste because those parameters are typically not present in an electroplating shop. The remaining six of the 45 parameters are: pH, Reactive Cyanide, TCLP Chromium, TCLP Cadmium, TCLP Lead, and TCLP trichloroethylene.

The U.S. EPA "listed" wastewater treatment sludges from electroplating operations as a hazardous waste based on four key factors.[6] The Agency's conclusions were:

1. "Wastewater treatment sludges from the listed electroplating operations contain significant concentrations of the toxic metals chromium, cadmium and nickel and toxic complex cyanides."
2. "Leaching tests using the extraction procedure specified in the Extraction Procedure Toxicity Characteristic (EP) have shown that these metals leach out in significant concentrations, with some samples failing the extraction procedure toxicity characteristic. Therefore, the possibility of groundwater contamination via leaching will exist if these waste materials are improperly disposed."
3. "A large quantity of this waste is generated annually with amounts expected to increase substantially when the pretreatment standards for these sources become effective."
4. "Damage incidents (*i.e.,* contaminated wells, destruction of animal life, etc.) that are attributable to the improper disposal of electroplating wastes have been reported, thus indicating that the wastes may be mismanaged in actual practice, and are capable of causing substantial harm if mismanagement occurs."

In addition, there was significant concern over the use of and incomplete treatment of hexavalent chromium plating processes:[7]

"Those electroplating processes using chromium all employ the hexavalent form of their element. Consequently, the raw wastes resulting from this process contain chromium only in the hexavalent form. The efficiency of the removal of hexavalent chromium depends on the extent of its reduction. If reduction is incomplete, or if neutralization and metal precipitation take place too rapidly, hexavalent chromium is likely to be entrained in the precipitation sludges, resulting in their contamination with hexavalent chromium."

The ASTM distilled water leaching test and leaching tests run by the American Electroplaters Society (AES) under an EPA grant demonstrated unsatisfactory levels of leached toxins from electroplating sludges, therby confirming EP results.

Prior to the issuance of RCRA hazardous waste regulations in 1980, there were no federal requirements for management of metal finishing sludges. Disposal practices were diverse and insecure. They included landfilling, lagooning, drying beds and drum burial. These sites frequently lacked leachate and runoff control practices, which increased the risk of percolation of heavy metals and other toxins onto soils, ground and surface waters. Numerous damage incidents attributable to improper electroplating waste disposal were reported. Mismanagement was actual, not perceived. The long-term persistence of heavy metal in the environment increased the potential for risk.

The promulgation of effluent guidelines in 1986 significantly increased the quantities of wastewater treatment sludge generated above pre-1980 levels. In 1993, estimates of the annual amount of F006 generated in the U.S. ranged from 900,000 tons/wet weight to 1,252,072 tons/wet weight.[8] Most of this material is in the physical form of a metal hydroxide sludge. This waste stream is subject to the full set of RCRA hazardous waste regulations (*e.g.,* manifesting, training, emergency response plans).

Reason for Conducting F006 Study

The metal finishing industry believed that many metal finishers have significantly changed the way they operate since 1980, and that the chemical makeup of F006 is more amenable to recycling than it was in 1980. The strengthening of wastewater pretreatment, hazardous waste management and hazardous waste minimization requirements since 1980 have had a positive impact on materials used, process operations and waste management practices in the industry. These improvements have reduced the pollutants contained in F006. The metal finishing industry has responded to the strengthening of wastewater and hazardous waste regulations with improvements in alternative plating chemistries, production management practices, equipment and waste management technology. For example, the installation of countercurrent flow, spray rinsing and dragout reduction methods are examples of techniques that reduce wastewater volumes and the amount of metals and other chemicals used. Metal finishing companies have installed pollution prevention methods that are targeted at further reducing or eliminating the use of specific toxic materials. Some of the more notable efforts have been:

- Substitution of traditional cyanide-based plating solutions (*e.g.*, zinc and copper plating) with alkaline or acid-based plating systems;
- Substitution of trivalent chromium for toxic hexavalent chromium for some applications;
- Replacement of some single metal systems with alloy systems (*e.g.,* replacing cadmium with zinc-nickel)
- Metal "entrapment" methodologies to return metals to the primary plating bath (*i.e.*, use of counterflow rinsing returning rinses to a primary plating bath that operates on an evaporator).
- Metal concentrating techniques (electrodialysis (ED), ion exchange (IX))

The results of a 1993 study by the National Center for Manufacturing Sciences (NCMS) and the National Association of Metal Finishers (NAMF) show that 90 percent of the 318 facilities that responded (16% response rate of 1,971 facilities queried) use pollution prevention methods and have benefitted from them. Water conservation and in-process recycling techniques were noted to be more frequently used than chemical recovery. Approximately 60 percent of respondents attempted material substitution to reduce or eliminate one or more of the following materials: Cadmium, chromium (hexavalent), cyanide and chlorinated solvents.[9]

The economics of waste disposal result in an unacceptable amount of F006 being land-disposed rather than recycled, because recycling is typically more expensive. Most F006—80-90 percent—is treated and disposed of through stabilization and placement in RCRA subtitle C permitted hazardous waste landfills.[10] This means potentially recoverable metals (*i.e.*, those that are land-disposed) no longer available for commerce. Several of the more prominent metals (*e.g.*, nickel and chromium) are strategic metals that are not available in the U.S. If the source of these metals was unavailable for any period of time because of global economic or political uncertainties, the economy and defense of the U.S. may be seriously jeopardized.

National F006 Benchmark Study Approach

The workgroup designed a two-year study methodology. The group focused on three analytical questions to guide its work on characterizing current practices in the metal finishing industry, and the composition and management of F006:

- What are the chemical characteristics of F006?
- What can metal finishers do to make F006 more recyclable, while optimizing pollution prevention? What pollution prevention measures are in place at metal finishing facilities?
- What are the environmental impacts of F006 recycling?

The technical work required for this study was completed by Science Applications International Corporation (SAIC) under contract to the EPA. The contract work was managed by an EPA workgroup member working in close coordination with the workgroup. The workgroup monitored progress and critiqued results throughout the analysis process. The members of the workgroup were:

Diane Cameron (Natural Resources Defense Council)
John Lindstedt (AESF, Artistic Plating Company, Milwaukee, WI)
Bill Sonntag, (AESF, NAMF, MFSA)
Al Collins (AESF, NAMF, MFSA)
Andy Comai (United Auto Workers)
Tom Wallin (Illinois EPA)
Doreen Sterling (U.S. EPA)
Mike Flynn (U.S. EPA)
Jim Lounsbury (U.S. EPA)
Jeff Hannapel (U.S. EPA)
John Lingelbach, facilitator, (Decisions and Agreements, LLC, Denver, CO)

Methodology of Study

The workgroup designed a five-part "benchmarking" study approach to address the three analytical questions identified above. A Quality Assurance Project Plan was developed and approved for this study and is available in a separate report.[11] The five portions of the study are summarized here:

1. A "Regional Benchmarking Study" that involved site visits to 29 metal finishing shops in three cities to gather detailed data on plating processes and pollution prevention practices, and to collect random current F006 samples.
2. A "National Benchmarking Study" that used a mail survey to gather less detailed data on metal finishing operations, pollution prevention practices, F006 characteristics and management practices from a broad range of metal finishers.
3. An analysis that evaluates the extent to which the regional and national benchmarking studies represent the universe of metal finishers.
4. A Survey of Commercial Recycling Companies to gather data on the amount of F006 recycled and the chemical composition of F006 accepted for recycling.
5. A "Community Interest Group Phone Survey" to assess whether community groups in the vicinity of commercial recycling companies believe those companies are good environmental and/or economic neighbors.

Regional Benchmarking Study

The workgroup developed a method for identifying and gathering information from metal finishing companies that are judged to be the "typical" facilities in the metal finishing universe.

The workgroup identified 10 cities known to have high populations of metal finishing facilities. Milwaukee, Chicago and Phoenix were chosen as cities that are representative of the metal finishing industry in terms of the processes they use and the industries they serve.

The workgroup agreed on a list of criteria for selecting facilities and tried to include, as much as possible, a balanced distribution of the following criteria in making facility selections. Selection criteria were:

- Type of shop: captive/job,
- Size: number of employees,
- Type of deposition process in use: zinc, chromium, cyanide copper, etc.,
- Pollution prevention technologies in use,
- F006 treatment technology:
    - alkaline precipitation
    - off-site metals recovery,
    - landfilling of F006.

In all cities, the potential facilities were placed into a "blind" matrix and selected on the basis of the above criteria.

The workgroup developed additional information regarding the third criteria listed above (Type of Deposition Process in Use) for the first sampling city. Five plating processes were identified as among the most frequently used processes in the metal finishing industry. Studying facilities that operate these processes would provide the workgroup with key information about these common processes. The five processes included:

- Zinc plated on steel,
- Nickel/chromium plated on steel,

- Copper/nickel/chromium plated on nonferrous alloys,
- Copper plating/stripping in the printed circuit industry, and
- Chromium plated on steel.

These five processes are among the 25 most common processes identified in the NCMS/NAMF study (1994), and were the main criteria in selecting facilities in Milwaukee. Facility selection in Chicago began using the five processes, but resulted in a principal focus on facilities that operate copper/nickel/chromium electroplate on nonferrous processes—a plating process used by one-half of Chicago platers. Facility selection in Phoenix focused on obtaining data from metal finishers that serviced the printed circuit board and aerospace industries.

A survey was mailed to each facility to gather basic data from facility records. On-site visits were completed to gather detailed data on metal finishing processes, pollution prevention practices, recycling practices, F006 quantities and F006 handling and management practices (handling practices were recorded only in Chicago and Phoenix). The site visit information collection protocol is provided in Table 3.

Forty-six (46) composite samples of F006 were collected from the 29 facilities and transported to an EPA-certified laboratory for chemical analysis and quality assurance methods. Two samples of F006 sludge were collected at some facilities (selected at random) as spot-checks for variability in chemical content. All samples were analyzed for total concentrations of metals, TCLP metals and general chemistry analyses. Four of the samples collected in Milwaukee were also analyzed for total volatile and semi-volatile organic constituents, and TCLP volatile and semi-volatile organic constituents.

The results of the organic analysis in Milwaukee showed undetectable levels in nearly all cases, and therefore, no further organics testing was conducted in the remaining two cities. The laboratory results were reviewed for accuracy and completeness and provided to each facility for review and comment.

Table 3*
Checklist Used to Identify Pollution Prevention Technologies At Metal Finishing Facilities

1. SPENT PLATING SOLUTIONS
   - General Bath Life Extension
     - ❑ Filtration
     - ❑ Carbon treatment
     - ❑ Replenishment
     - ❑ Purified water
     - ❑ Electrolytic dummying
     - ❑ Cyanide bath carbonate freezing
     - ❑ Precipitation
     - ❑ Monitoring
     - ❑ Housekeeping
     - ❑ Drag-in reduction
     - ❑ Purer anodes & bags
   - Hexavalent Chrome Alternatives
     - ❑ Trivalent chrome
     - ❑ Non-chrome conversion coatings
   - Nonchelated Process Chemistries
     - ❑ Continuous filtration
   - Non-cyanide Process Chemicals
   - Solvent Degreasing Alternatives
     - ❑ Hot alkaline cleaning
     - ❑ Electrocurrent
     - ❑ Ultrasonic
   - Alkaline Cleaners
     - ❑ Filtration (Micro/Ultra)
     - ❑ Skimming
     - ❑ Coalescer
   - Caustic Etch Solution Regeneration
   - Acid Purification
     - ❑ Ion exchange
2. DRAG-OUT REDUCTION
   - ❑ Process bath operating concentration & temperature
   - ❑ Wetting agents
   - P2 Technology
     - ❑ Workpiece positioning
     - ❑ Withdrawal & drainage time
     - ❑ Air knives
     - ❑ Spray or fog rinses
     - ❑ Plating baths
     - ❑ Drainage boards
     - ❑ Dragout tanks
3. DRAG-OUT RECOVERY
   - ❑ Evaporation
   - ❑ Ion exchange
   - ❑ Electrowinning
   - ❑ Electrodialysis
   - ❑ Reverse osmosis
   - ❑ Meshpad mist eliminators
4. RINSEWATER
   - Improved Rinsing Efficiency
     - ❑ Spray rinse/rinsewater agitation
     - ❑ Increased contact time/ multiple rinses
     - ❑ Countercurrent rinsing
   - Flow Controls
     - ❑ Flow restrictors
     - ❑ Conductivity-actuated flow control
   - Recycling/Recovery
     - ❑ Rinsewater
     - ❑ Spent process baths
     - ❑ Solvents

**Mark those techniques in use.*

F006 Compositional Data & Results**

The four tenants that the U.S. EPA used as its basis for listing F006, while true in 1980, are no longer accurate or applicable today. The results of the data from this study are conclusive in demonstrating that listing of all wastewater treatment sludge as a group as hazardous is incorrect when evaluated against the 1980 EPA criteria. *Based on the data of the Regional Benchmarking Study the majority of F006 sludge generated (55%) is nonhazardous.* Furthermore, listing sludges as a group is incorrect, and acts as a barrier to additional pollution prevention activities and to engineering innovation within the finishing industry. Because there is no effective exit strategy for F006 from its listing, there is marginal if any incentive to re-engineer treatment systems or to encourage process substitution. Regardless of techniques employed or how a system is engineered, the end product of an electroplating wastewater facility is hazardous, regardless of effort.

"Wastewater treatment sludges from the listed electroplating operations contain significant concentrations of the toxic metals chromium, cadmium and nickel and toxic complex cyanides. Leaching tests using the extraction procedure specified in the extraction procedure toxicity characteristic have shown that these metals leach out in significant concentra-

***All study data is provided in Table 4.*

tions, with some samples failing the extraction procedure toxicity characteristic."

The EPA has stated that the basis for listing the F006 wastewater treatment sludge as hazardous was because of the presence of cadmium, hexavalent chromium and cyanide contents ,and that they have the potential to leach from the waste. The results from this survey, for the most part, parallel the EPA's findings. When a F006 sludge is actually hazardous, it is due to either cadmium, chromium or cyanide. However, the EPA's misconception that all electroplating wastewater treatment sludges from electroplating operations contain cadmium, chromium or cyanide is incorrect. Fifty-five per cent (55%) of the F006 sludge tested (16 out of the 29 samples) did not contain hazardous concentrations of cadmium, chromium or cyanide.

Cadmium

Of the 29 samples that were analyzed, only five (5) were determined to be hazardous per TCLP cadmium characteristics. Based on the samples analyzed and the accompanying facility information, it can be concluded that if a facility conducts cadmium plating, their waste will contain enough cadmium to deem it hazardous per characteristics. This is due to the high toxicity of cadmium and, hence, the low TCLP cadmium limit (1.0ppm).

Of the five sampled facilities that conducted cadmium plating, all five of the wastes had hazardous cadmium levels. These wastes made up 17 percent (5 out of 29) of the total wastes analyzed and 38 percent (5 out of 13) of the wastes that were truly hazardous. If cadmium plating were eliminated from these facilities, however, the total percentage of hazardous F006 waste would be reduced from 45 percent to 27.5 percent.

If F006 could be characterized on the basis of its chemical composition, these facilities would have an incentive with which to help them make their decision whether or not to deposit this metal. Such an incentive (substitution of cadmium with a process which would produce a nonhazardous sludge, *i.e.*, zinc-nickel) could be enough to remove this metal out of the facility's waste stream. The facility under that scenario may continue to plate cadmium as a business decision, but it would have a choice to make. Today, due to listing, there is no other option. **There exists a barrier to cadmium substitution.**

Cyanide

Twenty (20) of the 29 samples had cyanide present in the waste. However, only six of these samples had cyanide that was reactive (via amenable to chlorination testing), and of these six, only three had reactive cyanide in quantities over 30 ppm hazardous. One of these three samples was already deemed hazardous because of TCLP cadmium content. The remaining 17 that had cyanide had either no reactive cyanide or very little reactive cyanide. Most or all of the cyanide present in these wastes was stabilized. The EPA has, in fact, delisted F006 wastes that have tens-of-thousands of ppm of stabilized cyanide and very little reactive cyanide. Therefore, they should consider these 17 samples nonhazardous as well.

If cyanide was replaced with non-cyanide materials and cadmium plating was eliminated, the amount of F006 listed hazardous waste that was truly hazardous would be reduced to 21 percent (6 out of 29).

If the hazard definition of the treatment sludge is based on the leachable chemical composition and not on a 20-year old decision, this would provide an incentive upon which to base the decision of whether or not to use a cyanide process. There currently is an incentive in the regulatory framework that has moved the industry away from cyanide use. This is the land ban. How much more could be accomplished via process substitution if an additional incentive in the form of an exit strategy from RCRA hazard codes were available to the industry?

At the time RCRA regulations were promulgated and F006 waste was designated, the EPA did not have any requirements on maximum cyanide content in the waste (590/30 mg/Kg) as there is today. Currently, the cyanide-bearing F006 sludges are subject to stabilization, if the cyanide content exceeds the 590/30mg limit. F006 waste contained high amounts of cyanide in 1980. Today, F006 waste is subject to cyanide limitations, and those limitations result in a waste that is by necessity a much lower hazard due to cyanide content.

It is generally accepted that an F006 waste that meets the 590/30mg/Kg limit contains cyanide that is complexed by iron.

The EPA is on record, stating that ferri and ferro cyanide complexes do not present a health hazard:

1. "Ferricyanides and ferrocyanides are expected to be extremely stable and insoluble in water."[12]
2. "Constituents of concern (ferri/ferro cyanide) are tightly bound in the waste matrix and thus are not available for leaching."
3. "EPA believes these immobile iron-cyanide complexes do not present a threat to human health via ingestion of contaminated drinking water."[13]

Chromium

Of the 29 samples that were analyzed, only five (5) were determined to be definitely hazardous per TCLP chromium characteristics (11%). Of the 16 sampled facilities that plated chromium, only five generated hazardous waste due to TCLP chromium content. One of the reasons that the EPA listed F006 waste was because there were large quantities of hexavalent chromium in the sludge. This was not found in the study.

The results indicate that the chromium present in the sludge is almost entirely trivalent chromium—**not** hexavalent chromium. The data indicate that nine of 37 sample points (24%) had no detection of hexavalent of chromium. Of the remaining 28 sample points, the wide dispersion between median and mean values of hexavalent chromium—11.0ppm versus 108.9ppm—indicate the presence of outliers, which skews the data. Most of the facilities have a chromium content of their sludge close to the median value of 11.0 ppm. This is indicative of well-functioning waste treatment systems and is not supportive of the EPA's conclusion that improper reduction of the hexavalent state would lead to large amounts of sludge contaminated with hexavalent chromium.

Table 4

Milwaukee F006 Analytical Data

Constituents	# of Samples Included in Calculation* (Percent)	# of Non-Detects (Percent)	# Samples Above Instrument Detection. Below Method Quan. Limit (Percent)	Min	Mean	Med	Max
Total Concentration (mg/kg)							
Aluminum	16(100%)	0(0%)	0(0%)	311.00	8,488.19	3,005.00	31,200.00
Antimony	10(63%)	6(37%)	6(37%)	1.80	43.49	13.85	161.00
Arsenic	14(88%)	2(12%)	2(12%)	3.10	9.27	9.35	18.30
Barium	13(81%)	3(19%)	3(19%)	29.20	175.11	83.40	843.00
Beryllium	2(13%)	14(87%)	0(0%)	0.59	0.64	0.64	0.69
Bismuth	7(44%)	9(56%)	3(19%)	2.10	17.24	3.30	72.50
Cadmium	13(81%)	3(19%)	2(12%)	2.10	4,695.08	10.10	39,300.00
Calcium	16(100%)	0(0%)	0(0%)	855.00	55,947.19	37,800.00	141,000.00
Chromium	16(100%)	0(0%)	0(0%)	193.00	52,685.19	39,600.00	193,000.00
Copper	16(100%)	0(0%)	0(0%)	33.60	16,506.14	14,300.00	41,500.00
Iron	16(100%)	0(0%)	0(0%)	3,350.00	93,421.88	86,450.00	279,000.00
Lead	15(94%)	1(6%)	1(6%)	64.80	604.05	410.00	2,870.00
Magnesium	16(100%)	0(0%)	0(0%)	355.00	14,469.06	12,700.00	44,300.00
Manganese	14(88%)	2(12%)	1(6%)	199.00	956.57	1,024.50	1,710.00
Mercury	6(38%)	10(62%)	4(25%)	0.260	0.700	0.350	2.000
Nickel	16(100%)	0(0%)	0(0%)	57.10	49,295.69	25,300.00	180,000.00
Selenium	10(62%)	6(37%)	0(0%)	1.90	7.86	6.50	16.60
Silver	12(75%)	4(25%)	1(6%)	1.50	130.46	56.20	657.00
Sodium	16(100%)	0(0%)	0(0%)	3,830.00	21,047.50	16,150.00	84,300.00
Tin	16(100%)	0(0%)	0(0%)	9.00	998.73	370.50	8,070.00
Zinc	15(94%)	1(6%)	1(6%)	3,790.00	114,666.00	83,900.00	336,000.00
TCLP (mg/L)							
Arsenic	0(0%)	16(100%)	0(0%)	ND	ND	ND	ND
Barium	4(25%)	12(75%)	12(75%)	0.26	1.25	1.40	2.20
Cadmium	8(50%)	8(50%)	4(25%)	0.04	2.19	0.08	13.30
Chromium	14(88%)	2(12%)	0(0%)	0.20	17.86	12.75	56.20
Lead	4(25%)	12(75%)	0(0%)	0.10	0.45	0.21	1.30
Mercury	3(19%)	13(81%)	0(0%)	0.005	0.006	0.005	0.009
Selenium	1(6%)	15(94%)	1(6%)	0.08	0.08	0.08	0.08
Silver	1(6%)	15(94%)	3(19%)	0.05	0.05	0.05	0.08
General Chemistry (mg/kg)							
Chloride	16(100%)	0(0%)	0(0%)	190.00	8,792.50	6,750.00	30,000.00
Fluoride	15(94%)	1(6%)	1(6%)	1.20	297.75	120.00	1,600.00
Chromium, hex	16(100%)	0(0%)	0(0%)	0.10	67.76	0.63	1,000.00
Total Cyanide	12(75%)	4(25%)	0(0%)	2.00	202.50	60.00	900.00
Cyanide, amen	12(75%)	4(25%)	0(0%)	3.00	438.36	24.00	2,700.00
Percent Solids	16(100%)	0(0%)	0(0%)	14.80	42.96	40.85	77.40

Chicago F006 Analytical Data

Constituents	# of Samples Included in Calculation* (Percent)	# of Non-Detects (Percent)	Min	Mean	Med	Max
Total Concentration (mg/kg)						
Aluminum	15(100%)	0(0%)	153.00	8,920.00	597.00	45,900.00
Antimony	2(13%)	13(87%)	90.00	148.50	148.50	207.00
Arsenic	1(7%)	14(93%)	39.00	39.00	39.00	39.00
Barium	15(100%)	0(0%)	20.00	265.60	76.00	1,080.00
Beryllium	4(26%)	11(74%)	7.00	18.50	15.00	37.00
Bismuth	4(26%)	11(74%)	19.00	43.50	44.50	66.00
Cadmium	12(80%)	3(20%)	9.00	10,652.67	2,264.00	71,300.00
Calcium	15(100%)	0(0%)	4,040.00	30,018.00	18,200.00	83,900.00
Chromium	15(100%)	0(0%)	73.00	26,650.60	18,700.00	83,000.00
Copper	15(100%)	0(0%)	86.00	16,959.67	4,230.00	91,600.00
Iron	15(100%)	0(0%)	1,510.00	86,887.33	56,300.00	257,000.00
Lead	15(100%)	0(0%)	5.00	1,101.67	161.00	10,300.00
Magnesium	15(100%)	0(0%)	1,340.00	71,460.67	27,200.00	336,000.00
Manganese	15(100%)	0(0%)	103.00	1,135.40	799.00	3,300.00
Mercury	5(33%)	10(67%)	0.070	0.160	0.120	0.310
Nickel	15(100%)	0(0%)	106.00	17,888.00	7,390.00	98,800.00
Selenium	0(0%)	15(100%)	ND	ND	ND	ND
Silver	13(87%)	2(13%)	27.00	163.00	112.00	351.00
Sodium	15(100%)	0(0%)	1,060.00	22,019.33	11,600.00	89,200.00
Tin	10(67%)	5(33%)	68.00	16,274.80	10,920.00	41,200.00
Zinc	15(100%)	0(0%)	1,070.00	145,921.33	89,200.00	460,000.00
TCLP (mg/L)						
Arsenic	0(0%)	15(100%)	ND	ND	ND	ND
Barium	1(7%)	14(93%)	0.70	0.75	0.75	0.80
Cadmium	9(60%)	6(40%)	0.02	18.23	1.00	144.00
Chromium	8(53%)	7(47%)	0.02	0.41	0.08	2.80
Lead	0(0%)	15(100%)	ND	ND	ND	ND
Mercury	3(20%)	12(80%)	0.001	0.005	0.002	0.011
Selenium	0(0%)	15(100%)	ND	ND	ND	ND
Silver	4(27%)	11(73%)	0.03	1.00	0.08	3.80
General Chemistry (mg/kg)						
Chloride	15(100%)	0(0%)	322.00	11,669.73	2,380.00	70,100.00
Fluoride	10(67%)	5(33%)	17.50	694.64	254.50	4,210.00
Chromium, hex	13(87%)	2(13%)	1.00	115.07	18.00	1,190.00
Total Cyanide	15(100%)	0(0%)	0.80	1,341.62	373.00	3,920.00
Cyanide, amen	15(100%)	0(0%)	2.60	1,183.31	285.00	5,340.00
Percent Solids	15(100%)	0(0%)	13.50	32.53	32.80	57.00

Phoenix F006 Analytical Data

Constituents	# of Samples Included in Calculation* (Percent)	# of Non-Detects (Percent)	Min	Mean	Med	Max
Total Concentration (mg/kg)						
Aluminum	15(100%)	0(0%)	59.00	23,082.10	2,860.00	76,100.00
Antimony	5(33%)	10(67%)	44.00	7,293.60	221.00	34,800.00
Arsenic	13(87%)	2(13%)	2.00	1,115.31	11.00	8,780.00
Barium	15(100%)	0(0%)	6.00	153.87	67.00	686.00
Beryllium	0(0%)	15(100%)	ND	ND	ND	ND
Bismuth	6(40%)	9(60%)	19.00	95.00	30.50	398.00
Cadmium	6(40%)	9(60%)	3.00	154.00	17.50	806.00
Calcium	15(100%)	0(0%)	682.00	24,505.50	15,100.00	143,000.00
Chromium	15(100%)	0(0%)	10.00	38,595.50	248.00	206,000.00
Copper	15(100%)	0(0%)		135,555.00	11,500.00	631,000.00
Iron	15(100%)	0(0%)	417.00	66,219.60	7,990.00	560,000.00
Lead	14(93%)	1(7%)	80.00	17,074.40	2,125.00	175,000.00
Magnesium	15(100%)	0(0%)	187.00	62,753.10	10,700.00	319,000.00
Manganese	15(100%)	0(0%)	13.00	438.00	183.00	2,080.00
Mercury	4(27%)	11(73%)	0.300	0.380	0.350	0.500
Nickel	15(100%)	0(0%)	51.00	8,254.67	3,080.00	71,900.00
Selenium	0(0%)	15(100%)	ND	ND	ND	ND
Silver	13(87%)	2(13%)	3.00	212.46	23.00	1,190.00
Sodium	15(100%)	0(0%)	25.00	12,135.70	5,660.00	41,600.00
Tin	15(100%)	0(0%)	38.00	45,228.10	2,370.00	467,000.00
Zinc	15(100%)	0(0%)	57.00	6,633.80	672.00	31,600.00
TCLP (mg/L)						
Arsenic	0(0%)	15(100%)	ND	ND	ND	ND
Barium	1(7%)	14(93%)	1.50	1.50	1.50	1.50
Cadmium	4(27%)	11(73%)	0.02	0.04	0.03	0.10
Chromium	5(33%)	10(67%)	0.02	0.53	0.56	1.06
Lead	11(73%)	4(27%)	0.06	155.24	0.13	1,630.00
Mercury	1(7%)	14(93%)	0.003	0.003	0.003	0.003
Selenium	0(0%)	15(100%)	ND	ND	ND	ND
Silver	0(0%)	15(100%)	ND	ND	ND	ND
General Chemistry (mg/kg)						
Chloride	15(100%)	0(0%)	64.00	3,592.50	1,490.00	24,000.00
Fluoride	14(93%)	1(7%)	49.50	1,539.56	793.00	4,240.00
Chromium, hex	8(53%)	7(47%)	5.00	152.63	53.00	548.00
Total Cyanide	7(47%)	8(53%)	1.10	141.37	102.00	579.00
Cyanide, amen	14(93%)	1(7%)	3.90	141.56	30.10	809.00
Percent Solids	15(100%)	0(0%)	20.90	37.09	29.30	94.10

All Cities Combined F006 Analytical Data

Constituents	# of Samples Included in Calculation* (Percent)	# of Non-Detects (Percent)	Min	Mean	Med	Max
Total Concentration (mg/kg)						
Aluminum	46(100%)	0(0%	59.00	13,387.90	1,725.00	76,100.00
Antimony	17(37%)	29(63%)	1.80	2,188.23	67.40	34,800.00
Arsenic	28(61%)	18(39%)	2.00	489.67	10.00	8,780.00
Barium	43(93%)	3(7%)	6.00	199.27	73.70	1,080.00
Beryllium	6(13%)	40(87%)	0.59	12.55	8.50	37.00
Bismuth	17(37%)	29(63%)	2.10	50.86	29.00	398.00
Cadmium	21(46%)	25(54%)	2.10	6,122.32	22.00	71,300.00
Calcium	46(100%)	0(0%)	682.00	37,239.28	17,250.00	143,000.00
Chromium	46(100%)	0(0%)	10.00	39,501.20	13,900.00	206,000.00
Copper	46(100%)	0(0%)	33.60	55,474.35	10,620.00	631,000.00
Iron	46(100%)	0(0%)	364.00	82,420.74	48,980.00	560,000.00
Lead	44(96%)	2(4%)	5.00	85,754.10	346.00	175,000.00
Magnesium	46(100%)	0(0%)	187.00	48,798.09	10,800.00	336,000.00
Manganese	44(96%)	2(4%)	13.00	830.91	563.00	3,300.00
Mercury	15(33%)	31(67%	0.070	0.390	0.300	2.000
Nickel	46(100%)	0(0%)	51.00	23,456.33	5,935.00	180,000.00
Selenium	10(22%)	36(78%)	1.90	7.86	6.50	16.60
Silver	38(83%)	8(17%)	1.50	169.64	87.50	1,190.00
Sodium	46(100%)	0(0%)	25.00	18,458.37	11,000.00	89,200.00
Tin	41(89%)	5(11%)	9.00	20,906.06	1,100.00	467,000.00
Zinc	45(98%)	1(2%)	57.00	88,692.44	24,600.00	460,000.00
TCLP (mg/L)						
Arsenic	0(0%)	46(100%)	ND	ND	ND	ND
Barium	6(13%)	40(87%)	0.26	1.29	1.45	2.20
Cadmium	21(46%)	25(54%)	0.02	8.36	0.11	144.00
Chromium	27(59%)	19(41%)	0.02	9.48	0.92	56.20
Lead	15(33%)	30(67%)	0.06	113.97	0.13	1,630.00
Mercury	7(15%)	39(85%)	0.001	0.005	0.005	0.011
Selenium	1(2%)	45(98%)	0.08	0.08	0.08	0.08
Silver	5(11%)	40(89%)	0.03	0.67	0.06	3.80
General Chemistry (mg/kg)						
Chloride	46(100%)	0(0%)	64.00	8,035.09	2,225.00	70,100.00
Fluoride	39(85%)	7(15%)	1.20	719.06	161.00	4,240.00
Chromium, hex	37(80%)	9(20%)	0.10	108.89	11.00	1,190.00
Total Cyanide	34(74%)	12(26%)	0.80	692.47	114.50	3,920.00
Cyanide, amen	41(89%)	5(11%)	2.60	609.56	51.00	5,340.00
Percent Solids	46(100%)	0(0%)	13.50	37.65	30.80	94.10

"The possibility of groundwater contamination via leaching will exist if these materials are improperly disposed."

The references listed in the 1980 Background Document cite land disposal and mismanagement techniques that date back into the first half of the century.[14] Any land disposal then by today's standards was improper. Lagooning, dry beds and dump burial in sanitary landfills were all that was available. Today's RCRA requirements for land disposal facilities with geological site suitability, multiple containment engineering methodologies, leachate monitoring and run off control all but negate the earlier concern by the agency.

"A large quantity of this waste is generated annually with amounts expected to increase substantially when the pretreatment standards for these sources become effective."

The amount of F006 that was generated annually substantially increased in the early 1980s because of the required implementation of wastewater treatment systems. Today, however, many electroplaters and metal finishers have implemented pollution prevention (P2) techniques in their processes that have significantly reduced the amount of F006 sludge that is generated annually. Most plating facilities implemented P2 techniques to improve compliance with categorical wastewater discharges. As these methodologies removed metal from the discharge stream and returned them to the primary process bath or concentrated them, making on-site recovery possible, the amount of metals in the aqueous phase decreased, as well as the amount of sludge generated.

The amount of sludge generated has dramatically decreased from the initial commencement of effluent guidelines. The EPA estimates indicate 900,000–1,200,000 tons of sludge produced per year. The Surface Finishing Market Research Board (SFMRB) reports that the maximum amount of sludge generated annually within the U.S. is 445,500 tons from a universe of 7,000 job hops and 3,000 captive facilities. The average annual amount of F006 generated by this survey is 213,840 tons.[15] This represents a considerable decrease from earlier estimates. Pollution prevention, as it is embraced by industry, works. There is a need to remove the remaining barriers that limit the implementation of additional P2 practices. Listing of F006 is such a barrier. If removed, more process substitution would be placed in service. Waste stream segregation would occur, which would produce characteristically nonhazardous sludges.

"Damage incidents (i.e. contaminated wells, destruction of animal life, etc.) that are attributable to the improper disposal of electroplating wastes have been reported, thus indicating that the wastes may be mismanaged in actual practice, and are capable of causing substantial harm if mismanagement occurs."

If a hazardous waste or a nonhazardous waste is mismanaged, harm to society can result. Mismanagement is not unique to its hazard code. RCRA regulations stipulate very precise management practices for wastes that are under its jurisdiction. It is not the intent of a possible de-listing of F006 to remove management practices for secure storage, transport manifesting and training, which have significantly reduced damage incidents. The intent is to build on the management success of the last 20 years and to allow for an exit strategy for F006 that encourages resource reclamation and the promotion of additional pollution prevention methodologies. The EPA has the authority within the RCRA regulatory framework to accomplish these dual goals.

Financial Considerations

There is a considerable amount of value in wastewater treatment sludges in the form of precipitated metal hydroxides. The 29 facilities sampled shipped off-site 3,803 tons of F006. This contained:

- Aluminum—40,241 lbs.
- Copper—217,053 lbs.
- Nickel—18,883 lbs.
- Tin—9819 lbs.
- Zinc—395,784 lbs.
- Chromium—68,639 lbs.

The value of this commodity is approximately $750,000! Such a waste of resources ($26,000/facility/year) is difficult to comprehend. A more complete and detailed treatment of the economics and societal costs associated with the current disposal practices of the resource (F006) will be treated in a subsequent paper.

Conclusion

"Command and control" regulations had an immediate and favorable environmental impact on the removal of pollutants from the waters of the U.S. They have, however, run their course. Further environmental improvement will require new strategies that attack the more ubiquitous pollutants in the environment, while more efficiently using our resources to effect their removal. Performance-based systems such as the Strategic Goals Program provide such a strategy. Innovative thought to encourage "beyond-compliance" performance by removing hindrances to improved environmental performance make common sense.

Just as a continuation of command and control methodologies will not improve effluent water quality in the next decade, a continuation of the assignment of an improper hazardous label to wastewater treatment sludges will not promote pollution prevention and the removal of toxins from this product. It will continue the squandering of a societal resource. The U.S. EPA had ample reason 20 years ago to list wastewater treatment sludges generated from electroplating as hazardous. The basis of their reasoning, however, no longer exists for approximately half of all F006 generated in the U.S. today. It is no longer accurate to say that all F006 contains cyanide, cadmium, chromium. *Some does, but not all.* It is no longer accurate to hold the belief that industry management practices are unacceptable. *They are not.* It is no longer accurate to state that the volume of treatment sludges is growing or will continue to increase. *It is not.* Damage incidents are dramatically less from industry-related releases.

Incentives have demonstrated their ability to alter industry performance. The incentive of a land ban on placing cyanide into landfills has caused industry to respond with and use substitute processes. Unlimited liability has caused 40 percent of industry firms to recycle F006 rather than landfills, even though this is economically unsound.[17]

The listing of F006 is a disincentive to further pollution prevention practices and societal reuse of strategic commodities. Listing created the single discharge stream from finishing sites. Why should one engineer have multiple waste streams when by definition all output sludges of those streams are hazardous? If wastewater treatment sludges are evaluated on their chemical content, a significant portion are nonhazardous. If an allowance is made for these to be treated not as a waste but more product-like, a significant barrier to continued environmental improvement and resource utilization will be removed.

Not all sludges are nonhazardous. If a process continues that adds parameters of toxicity and carcinogenicity to the waste, it is hazardous and must be handled as such. But, not all out-falls from all facilities are similar. It is time to rethink a 20-year old policy and make needed performance-based improvements. It is common sense. P&SF

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About the Author

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