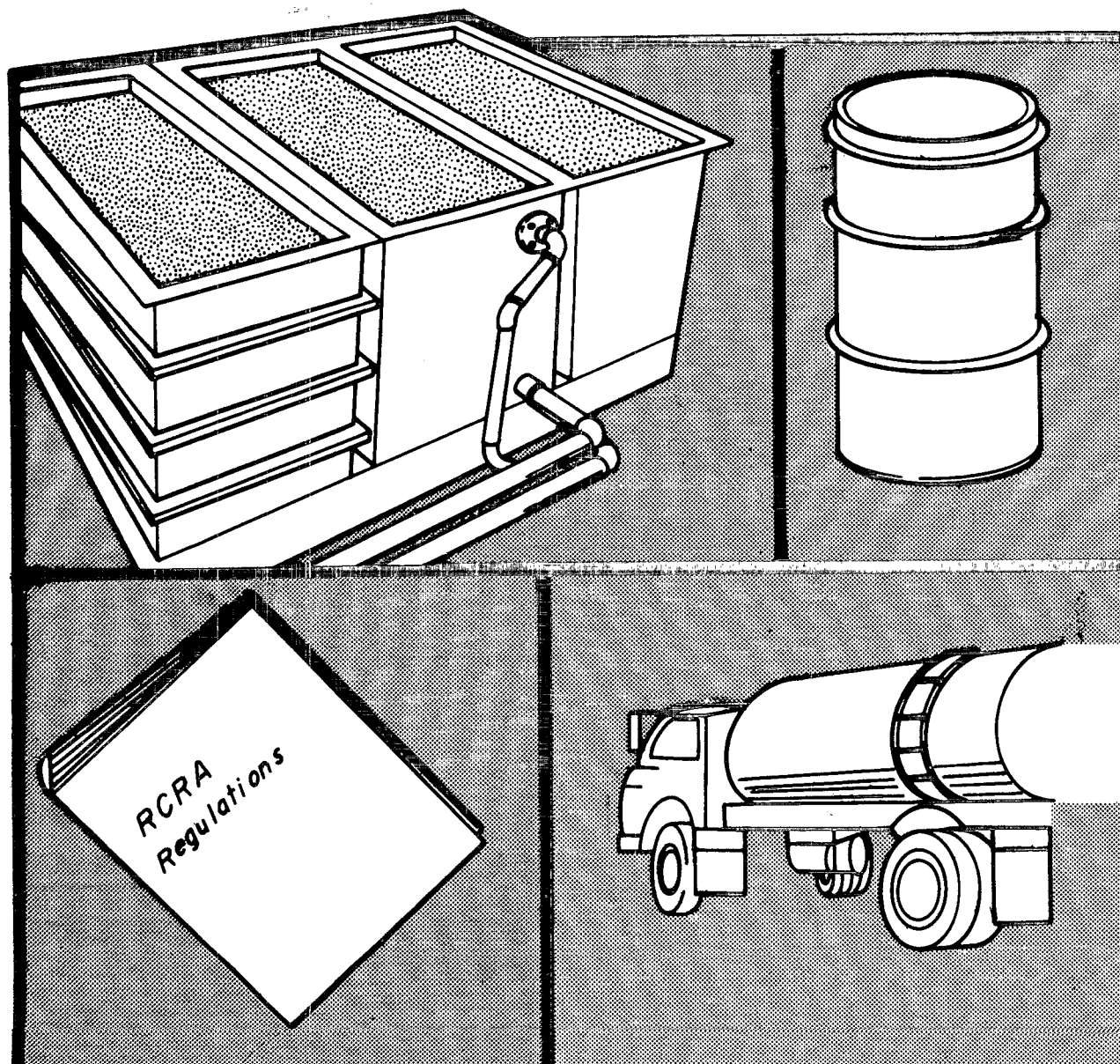
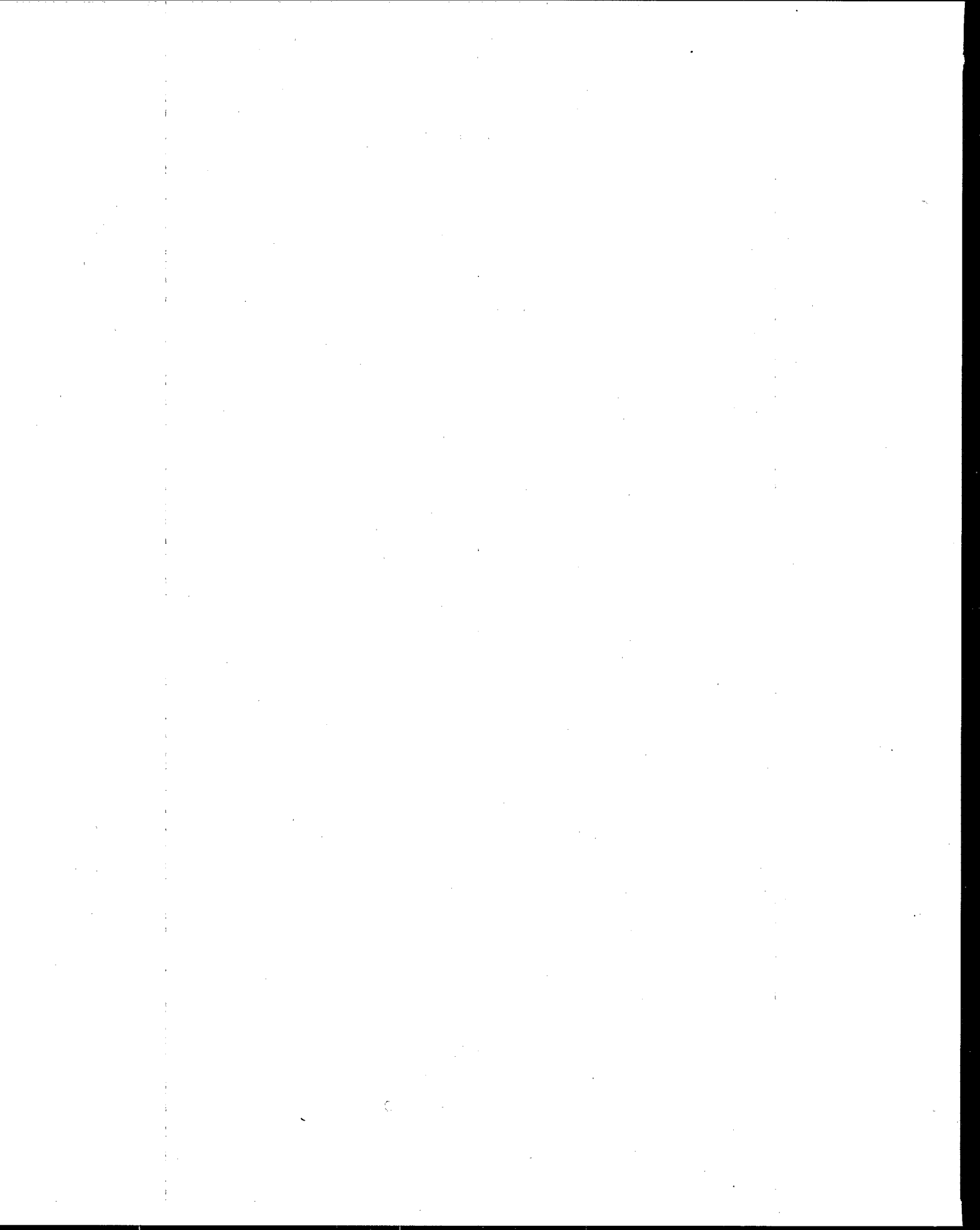


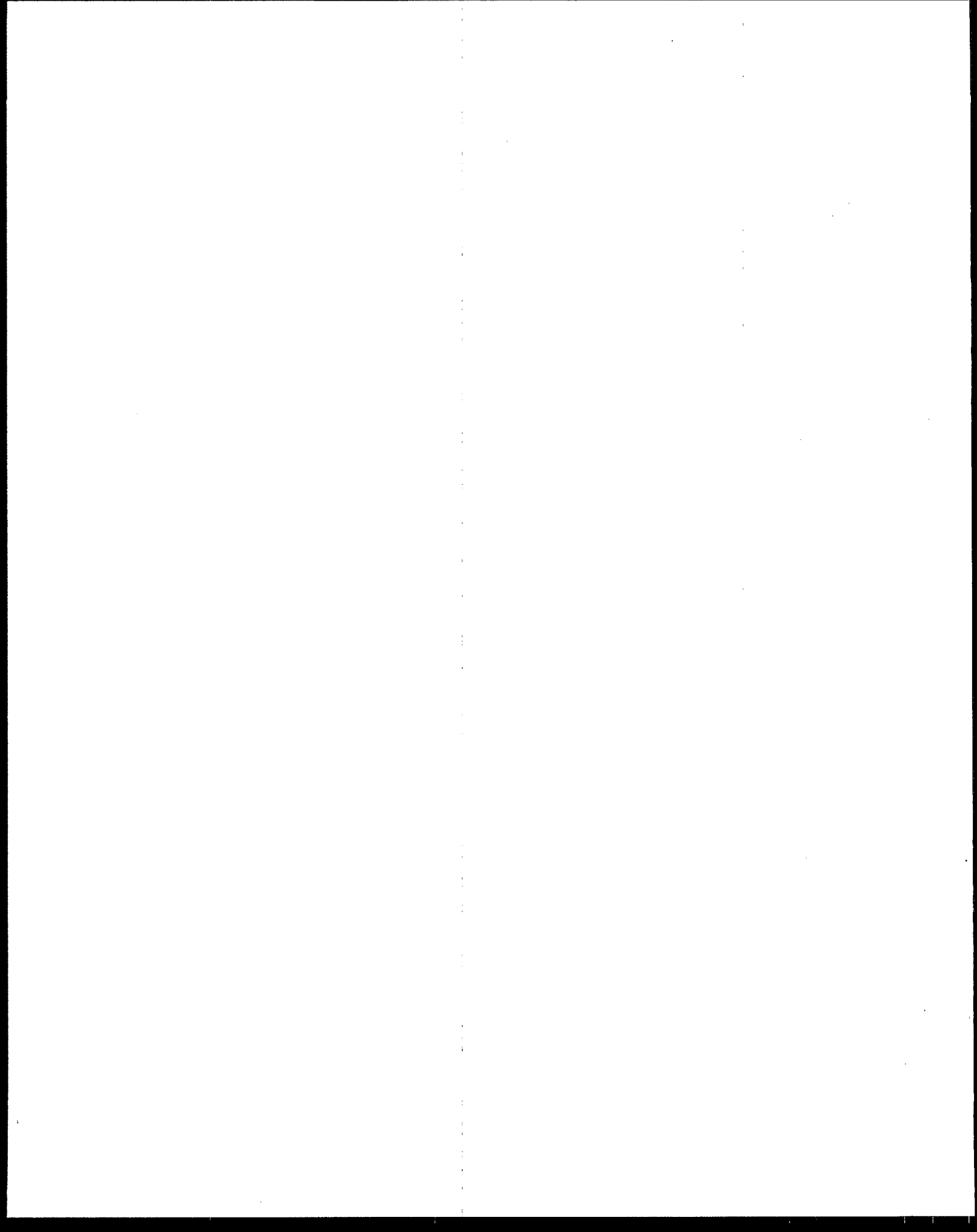


Seminar Publication

Meeting Hazardous Waste Requirements for Metal Finishers







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The following listing indicates the authors whose presentations are summarized in this publication.

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- Chapter Two (Delisting Procedures) — Kenneth Schuster, EPA Office of Solid Waste, Washington, DC.
- Chapter Three (Land Disposal Bans and Procedures for Extensions) — Gwen Porus, EPA Waste Management Division, Boston, MA and Stephen Weil, EPA Office of Solid Waste, Washington, DC.
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This report has been reviewed by the U.S. Environmental Protection Agency and approved for publication. The process alternatives, trade names, and commercial products are only examples and are not endorsed or recommended by EPA. Other alternatives may exist and may be developed. In addition, the information in this document does not necessarily reflect the policy of the EPA, and no official endorsement should be inferred.

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Preface

The metal finishing industry is one of many industries subject to regulation under the Resource Conservation and Recovery Act (RCRA) and the Hazardous and Solid Waste Amendments (HSWA) of 1984. The metal finishing industry has also been subject to extensive regulation under the Clean Water Act (CWA). Compliance with these regulations requires highly coordinated regulatory, scientific, and engineering analyses to minimize costs.

EPA's Office of Solid Waste and Emergency Response has an ongoing outreach program to disseminate information to the community regulated by RCRA and HSWA. Thus, the metal finishing industry was selected under this program as the focus of a series of seminars for the dissemination of regulatory and technology information to aid plant managers and engineers to achieve compliance in the most cost-effective manner.

Three seminars were held in the fall of 1986 in Boston, Chicago, and Los Angeles. Support for the seminars came from the American Electroplaters and Surface Finishers Society, National Association of Metals Finishers, and the Metal Finishing Suppliers Association. This publication contains edited versions of what was presented at each of the three seminars.

Events occurring after the seminars, made some of the regulatory information presented at those meetings obsolete. Wherever possible, information has been updated and revised to take into account recent changes in regulations. For example, the chapter on using hazardous wastes as fuels was updated to reflect regulations proposed in the spring of 1987.

This seminar publication provides information on the regulations affecting hazardous wastes discharged by metal finishers. Chapters are included on topics such as the impact of RCRA regulations on both small and large generators, the "delisting" of a specific facility waste from hazardous waste regulation, land disposal bans on hazardous wastes, the use of used oil and hazardous wastes as fuel, criteria for the use of underground storage tanks for hazardous wastes, the relevance of the Clean Water Act to the hazardous wastes discharged by metal finishers, the selection of a responsible hazardous waste transporter and management facility, the costs and benefits of source reductions in metal finishing, materials reuse and recovery, the treatment and management of organic liquids, and the characterization and treatment of aqueous wastes.

This publication is not a design manual, nor does it include all the latest knowledge about metal finishing; additional sources should be consulted for more detailed information and design criteria. In addition, state and local authorities should be contacted for regulations applicable in local areas.

1. An Overview of RCRA Regulations

Background

In 1976 Congress passed the Resource Conservation Recovery Act (RCRA) to address years of inattention to the problem of hazardous waste disposal. In response, EPA promulgated a body of hazardous waste regulations in 1980 including standards for generators of hazardous waste, for those who transport hazardous waste, and for facilities that treat, store, or dispose of hazardous waste. It was at this time that EPA first defined "small quantity generator" as a facility which generates less than 1,000 kg of hazardous waste per calendar month (roughly 2,200 pounds). These generators were basically exempted from the regulations because of the impracticality of administering a regulatory program for an estimated 500,000 businesses immediately. Instead, the regulatory focus was directed at the larger generators that were estimated to generate well over 90 percent of the country's total hazardous waste, and at permitting the existing treatment, storage, and disposal (TSD) facilities. The small quantity generator issue, including whether 1,000 kg was or was not the most appropriate cut-off, was put on the back burner.

Between 1980 and 1984 EPA began to look at the small quantity generator issue, initiating a two-year study of the types of wastes generated by small quantity generators and how they are managed. As of November 1984, though, no regulations had been proposed, and Congress passed the Hazardous and Solid Waste Amendments, a sweeping overhaul of the hazardous waste program that required EPA to write some 93 different regulations and reports. The use of deadlines known as "hammer provisions" was also initiated to automatically impose requirements if EPA has not acted by specified dates. One hammer provision was the requirement that EPA issue regulations before March 31, 1986 to lower the small quantity generator cut-off from 1,000 kg to 100 kg per calendar month. These regulations became effective September 22, 1986.

By lowering the cut-off to 100 kg per month, companies in virtually every manufacturing and service industry now may be subject to regulation. By far the largest category is vehicle maintenance facilities, including auto body and repair shops, fleet maintenance facilities, and gas stations. Other large groups are dry cleaners and industrial laundries, firms that generate photographic waste, and the metal working industries, including metal finishers.

A recent EPA study addressed the metal working industry, including the types of waste generated and how regulations would affect it. It is estimated there are as many as 11,000 metal manufacturing establishments operating in

the United States that may fall within the new small quantity generator rules. Metal working operations include forging, screw machine products, spring manufacturing, metal stamping, fastener production, heat treating, and electroplating. These processes generate a variety of wastes considered hazardous, including cyanide, ignitable paint, solvent still bottoms, spent solvents, spent plating, strong acids and alkalis, and wastewater sludges containing heavy metals. These last four categories together represent more than 90 percent of metal working waste.

Federal Categories of Generators

In drafting the new regulations EPA was bound by two very specific congressional mandates. One was to impose requirements strict enough to protect human health and the environment; the other was to minimize the burden of regulations on small businesses. In regulating the large quantity generator, the only consideration is the first mandate. The second mandate has the effect of setting apart the small quantity generator from other types of generators. Congress also established certain minimum requirements that have been incorporated into the final small quantity generator rules. Some of these requirements are designed to help small businesses, such as longer storage periods to allow larger, and thus more economical, shipments. Other requirements treat small businesses the same as large hazardous waste generators requiring, for example, that waste be transported via a hazardous waste transporter to a hazardous waste facility.

Table 1.1 lists the three Federal categories of generators. First, there is the conditionally exempt small quantity generator that generates less than 100 kg of hazardous waste in a calendar month and less than 1 kg of certain acutely hazardous waste (generally on the P list in EPA's Part 261 List of Hazardous Wastes). The second category is the small quantity generator, falling within the limits of 100 kg to 1,000 kg per month (or about half of one 55-gallon drum to about five 55-gallon drums of waste). The third category is the large quantity generator that generates more than 1,000 kg per month. There are significant differences between the categories in the way the wastes are managed, but all generators have two requirements in common. First, they must determine if their wastes are hazardous; second, they must determine how much waste they generate.

Identifying Hazardous Waste

In general, waste material comes into the Federal hazardous waste regulatory system in one of two ways. First, the waste or waste components may be specific-

Table 1.1. Steps to Comply with Federal Regulations for Hazardous Waste Generators

Conditionally Exempt Small Quantity Generators (producing no more than 100 kg/mo or less than 1 kg of acute HW)	Small Quantity Generators of 100 - 1,000 kg/mo (and conditionally exempt generators that accumulate more than 1,000 kg on-site)	Large Quantity Generators of more than 1,000 kg/mo (or that generate or accumulate more than 1 kg of acute HW at any time)
<p>Determine if you generate hazardous waste.</p> <p>"Count" your hazardous waste.</p> <p>Send your waste to a facility that is <i>at least</i> approved by a state to manage municipal or industrial solid waste.</p> <p>Avoid accumulating more than 1,000 kg on-site at any one time.</p>	<p>Determine if you generate hazardous waste.</p> <p>"Count" your hazardous waste.</p> <p>"Notify" EPA of hazardous waste activity and obtain a US EPA ID number.</p> <p>Accumulate waste on-site in tanks or containers for no more than 180 days or 270 days if waste must be shipped more than 200 miles. (Other forms of on-site storage require a permit.)</p> <p>Comply with container standards or special SQG tank standards when accumulating waste on-site.</p> <p>Be prepared to respond to emergencies by designating an emergency coordinator and post emergency numbers by the phone. Ensure that employees understand waste management and emergency procedures. Report serious spills or fires to the National Response Center.</p> <p>Your waste may only be disposed of at a facility that has obtained RCRA interim status or an RCRA hazardous waste permit.</p> <p>When shipping hazardous waste off your premises:</p> <ul style="list-style-type: none"> ■ Use only transporters with EPA ID numbers. ■ Comply with DOT requirements for packaging, labeling, and marking. ■ Use the full Uniform Hazardous Waste Manifest. ■ Ship waste only to hazardous waste facilities approved for your waste type. ■ Keep records for 3 years of manifests which are returned by the designated facility. ■ Report missing shipments. Obtain an RCRA permit if you store wastes in other than tanks or containers, dispose of hazardous waste at your site, or conduct certain kinds of treatment. 	<p>Determine if you generate hazardous waste.</p> <p>"Count" your hazardous waste.</p> <p>"Notify" EPA of hazardous waste activity and obtain a US EPA ID number.</p> <p>Accumulate waste on-site for no more than 90 days in tanks and containers. (Other forms of on-site storage require a permit.)</p> <p>Comply with container standards and new tank rules.</p> <p>Prepare and retain a written contingency plan for dealing with emergencies. Prepare a personnel training plan. Report serious spills or fires to the National Response Center.</p> <p>Your waste may only be disposed of at a facility that has obtained RCRA interim status or an RCRA hazardous waste permit.</p> <p>When shipping hazardous waste off your premises:</p> <ul style="list-style-type: none"> ■ Use only transporters with EPA ID numbers. ■ Comply with DOT packaging, labeling, and requirements for marking. ■ Use the full Uniform Hazardous Waste Manifest. ■ Ship waste only to hazardous waste facilities approved for your waste type. ■ Keep records for 3 years of manifests which are returned by the designated facility. ■ File an exception report with the state or EPA Regional Office. <p>Submit a biennial report of your hazardous waste activities during odd-numbered years. Include waste minimization information.</p> <p>Obtain an RCRA permit if you store wastes in other than tanks or containers, dispose of hazardous waste at your site, or conduct certain kinds of treatment.</p>

Check with your state hazardous waste management agency to determine exactly what rules (including state requirements) apply to you.

ly listed as hazardous on EPA's list. There are about 400 materials on the list, including several metal finishing wastes, for example, listed with designated waste ID numbers F06 through F012. The second way a material comes into the hazardous waste regulatory system is by exhibiting at least one of the four following characteristics based on testing or knowledge of its properties. An *ignitable* hazardous waste is flammable or easily combustible; for example, paint wastes and solvents. Waste that corrodes metals or burns the skin is likely to be a *corrosive* waste, such as the strong acids used in metal forming processes. A *reactive* hazardous waste is inherently unstable and can undergo rapid or violent change when it comes into contact with water; for example, the strong oxidizing agents used in metal finishing. *EP* toxic wastes have high concentrations of certain metals or pesticides. To summarize, if it is not a listed hazardous waste and it has not been mixed with a listed hazardous waste, and if it is not exhibiting one of the above characteristics, it is not in the RCRA system (though it may be a material that falls under state regulations). A very important aspect of the rules is this: As a generator, you are responsible for determining whether you generate a hazardous waste.

RCRA was designed to establish a minimum set of requirements, but the states are free to establish regulations that go beyond the Federal in stringency. Therefore, generators must get specific state information in order to know the requirements with which they must comply.

Counting Hazardous Waste

There are four basic principles to counting, or determining the quantity of waste generated. First, material still in the production process is not counted until it is removed from the process; for example, baths being continually used and reused, or a spent solvent still in the production process or in the machine. Second, waste is counted only once in a calendar month. In some cases, for example, a waste may be used more than once a month by recycling it on-site. It used to be that the waste had to be counted every time it was recycled, so theoretically, while the initial quantity might be only five gallons, legally a generator could be responsible for many times that quantity over the course of a month. Under the current rules only the initial quantity is counted. Third, wastes discharged to a publicly owned treatment works, if they are discharged directly and legally, in compliance with the Clean Water Act Pretreatment Standards, are not covered under the RCRA system. Finally, a general guideline for what is counted is any material

that is either a characteristic or a listed hazardous waste, and that is accumulated after its removal from the process before being sent off-site for treatment, storage, or disposal. It is important to understand that this is not a waste-stream-by-stream count, but one combined total of all of the hazardous wastes generated at any individual site, with a site defined as a contiguous geographic property. This is the quantity that determines the category a generator falls under.

A facility meeting the test for a conditionally exempt generator, that is, generating less than 100 kg per month and less than 1 kg of acute hazardous waste, is out of the system provided the waste is sent to a facility that is at least state-approved. That is not necessarily a hazardous waste facility, although the state may insist that it be a hazardous waste facility. It might be a recycling facility or a solid waste facility; but under Federal rules the waste does not have to go to a hazardous waste facility if there is under 100 kg per month total. A conditionally exempt generator that accumulates more than 1,000 kg on-site at any time becomes subject to the small quantity generator standards.

Small quantity and large quantity generators are in the system and must have identification numbers for their facilities. An ID number is obtained by filing a form called Notification of Hazardous Waste Activity, available either through the state or the EPA regional office. This form only has to be filed once.

Facilities with no regular pattern of waste generation, called episodic generators, may move from one category to another in any given month. Though legally they are subject to the more stringent requirements only in the month or months they fall into the higher categories, as a practical matter they will probably want to always be in compliance with the most stringent requirements to minimize paperwork and procedures.

Storage and Transportation Requirements

The allowable storage periods differ between the large quantity generator and the small quantity generator. A large quantity generator gets 90 days to store waste on-site without a permit. In order to accumulate economical shipments, a small quantity generator gets 180 days to accumulate waste on site and an additional 90 days if the waste is shipped farther than 200 miles from the generator's site. The facility is allowed to accumulate up to 6,000 kg of hazardous waste on-site without getting an RCRA permit. When waste is accumulated on-site certain standards must be complied with. Accumulated

wastes must be stored in tanks or containers only; storing accumulated waste in a surface impoundment or pond, for example, is not a generator activity, it is a permit and storage activity requiring a special permit.

The container and tank standards are different for the small quantity generator than for the large quantity generator, largely in regard to paperwork; differences are not substantive except in two cases. First, large quantity generators storing ignitable and reactive wastes in containers are subject to a 50 foot buffer zone requirement — in other words, that material must be stored at least 50 feet from the property line. Small quantity generators are exempt from that requirement, but they must store the material as far from the property line as practical. Second, tank rules have recently been modified for large quantity generators and now require secondary containment for new tanks as well as for leaking tanks or tanks 15 years old or older. The small quantity generator is not subject to the secondary containment rules. The container standards which apply to the small quantity generator say only that the container must not leak, and if it does leak, the material must be transferred to nonleaking containers.

Shipping waste off-site is costly and subject to a considerable number of requirements. First, the transporter must have a U.S. EPA ID number whether the waste comes from a small or large quantity generator. The states have the option of modifying the uniform manifest, so the forms may differ from state to state. Consequently, a generator is required to use the manifest of the destination facility's state. Both large and small generators must also comply with DOT requirements for packaging, labeling, and marking containers. Generators should be able to get help from the transporter, though the generator must sign the manifest and cannot delegate liability.

Both categories of generators must complete a full uniform hazardous waste manifest which basically requires identification of the transporter and the facility to which the waste is being delivered. Other information is required that could be used by the transporter in case of a problem, including the type of waste and its hazard characteristics. This also provides the RCRA tracking mechanism for identifying who had the waste last if the waste does not get to its designated site. There is an exception reporting requirement whereby a large quantity generator is required to notify EPA or the state office if no written confirmation of the shipment is received. The generator must keep these receipts, which are signed copies of the manifests, for three years from the date of the last

shipment. The small quantity generator had been relieved of this exception reporting requirement, but recently EPA adopted a simplified exception reporting system for small quantity generators. Under this system, the generator (in lieu of a formal report) may submit a photocopy of the original manifest along with a handwritten note stating it was not returned by the facility.

Emergency Response Requirement

Changes have also been made in the emergency response regulations. Large quantity generators must now have detailed written contingency plans in their files at all times which explain in detail how they will respond to emergencies and details of their personnel training program. The small quantity generator must post near the telephone a listing of the names of emergency response officials, fire officials, the National Response Center, the emergency coordinator, and other information, and, like a large quantity generator, must designate someone to be called in the case of a fire or spill or other problem at the facility who can get to the facility within 20 minutes. No paper plan is required for the small quantity generator. Similarly, where the large quantity generator must have a formal personnel training system in place, the small quantity generator only has to ensure that his employees understand the waste management and handling techniques that are important to their jobs, but no paper plan is required.

Reporting Requirements

Two waste minimization requirements are now in place under the Federal rules. Waste minimization is considered to be either source reduction or recycling. One requirement is a two-part certification statement to the uniform hazardous waste manifest. The first part certifies the accuracy of the information the generator is providing on the form; the second part states that the generator has a program in place to minimize waste generation to the extent he has deemed economically practicable and has selected the best waste management method that is economical, available, and minimizes potential harm to human health and the environment. For the small quantity generator this statement takes the form of affirming a good faith effort to minimize waste generation and select the best waste management method available and affordable to the generator. So that instead of stating that a program is in place, as a large generator must, this certification simply states that a good faith effort is being made.

Finally, a large quantity generator must file a biennial report detailing the kinds of activities he has conducted, the types of waste he has generated, and where that waste was sent. The biennial report must also contain a narrative description of the generator's waste minimization efforts. The small quantity generator has no biennial report requirement.

2. Delisting Procedures

Introduction

EPA lists hazardous wastes by category (e.g., all inorganic sludges of a certain type), and by whether or not they possess any of the four characteristics of ignitability, toxicity, corrosivity, and leachability. Wastes designated as hazardous because of one or more of the four characteristics cannot be delisted. However, an individual industrial facility's listed waste(s) may not be hazardous despite entire categories of waste having been designated as hazardous. The regulations (40 CFR 260.20 and 260.22) therefore allow for a petition mechanism to delist a specific facility waste from hazardous waste regulation. Delisted wastes from that facility only, can be disposed of in regular solid waste facilities, or otherwise managed as a solid waste. A guidance manual (*Petitions To Delist Hazardous Wastes - A Guidance Manual*, NTIS No. PB85-194488) has been issued to detail the delisting procedures for wastes which do not meet any of the listing criteria, do not exhibit any of the hazardous waste characteristics, or do not contain other toxicants at hazardous levels.

Under Subpart B of Part 261, EPA lists wastes as hazardous if they exhibit the characteristics of ignitability, corrosivity, leachability, or toxicity, are acutely hazardous (fatal to humans in low doses or meet certain oral, inhalation, and dermal LD₅₀ levels for lab animals), or contain one or more of 350 listed hazardous constituents. There are three categories of hazardous wastes: those from non-specific sources, those from specific sources, and specific commercial chemical products.

Required Information and Analyses

The delisting procedures as revised per the Hazardous and Solid Waste Amendments (HSWA), Section 222, require that the EPA consider factors (including additional constituents) other than those for which the waste was listed, as well as the original listing criteria. Information required includes: all raw materials, intermediates, and final products categorized as process materials, discharged process materials, or nondischarged process materials; analytical data or a mass balance demonstration for all hazardous constituents expected to be present in significant levels and a rationale for those constituents not expected to be present at significant levels; and test results for the hazardous waste characteristics of reactivity, ignitability, and corrosivity (or rationale in lieu of); total constituent and leachate analysis; and total oil and grease.

A full year's ground water monitoring data is also required for petitions requiring exclusion of on-site waste disposal units. The ground water monitoring data should include location of monitoring wells, direction of ground water

flow, hydrogeological characteristics of the site, and sampling and analysis procedures. In addition, general administrative information, process information (with schematics), waste stream information (including hazardous waste numbers, generation rates, etc.), and sampling and testing information (including laboratory details; test dates, methods, and equipment; and QA/QC provisions) are required. Also the Oily Waste EP leachate test must be used when the oil and grease content of the petitioned waste exceeds one percent.

There are three major parts to the delisting process. Submitting the petition should be preceded by preliminary consideration of why the waste was listed as hazardous, to whom the petition should be addressed, and the content of the petition. The first section of the petition will contain administrative information relative to the individual or firm, the specific waste-generating facility, the company personnel, and the requested delisting action. The production processes section of the petition requests information on the manufacturing operation or other processes which generate waste. Sufficient information must be submitted to determine what hazardous waste characteristics and toxic constituents might be present. The petition may contain either a list of raw materials or test results for hazardous constituents.

Examples of general process information for operations which produce a listed waste would include descriptions of production lines and equipment including typical stages in the operating cycle(s), description of surface preparation, cleaning, or coating operations, and supportive schematic diagrams for the above. In assessing the hazard of the wastes, two approaches are available.

Generally, Approach A requires test results for hazardous constituents; hazardous waste characteristics; leachate concentration of the (EP) toxic metals, nickel, and cyanide; total concentrations and a mass balance demonstration of the EP toxic metals, nickel, and cyanide; and total oil and grease. A complete list of raw materials, intermediates and end products is required (categorizing each as either discharged into the waste stream or not discharged into the waste stream). Under this first approach, an assessment is required of the likelihood of new waste streams being produced.

Approach B involves the same test results on four representative samples called for in approach A (hazardous waste characteristics; leachate and total tests for EP toxic metals, nickel, and cyanide; Appendix III testing and total organic carbon; and total oil and and grease). In-

stead of supplying lists of raw materials, intermediates, and end products, the petitioner is required to supply explanations for the hazardous constituents not expected to be found.

The waste stream section of the petition calls for a detailed description of the waste stream to be delisted. The specific information used to describe the stream includes EPA hazardous waste numbers, common name, and physical form for each waste. The petitioner is requested to submit average and maximum monthly and annual generation rates as per the operating records, and to describe whether the petitioned wastes are currently being generated, planned to be generated, or are no longer generated. A description of past and current waste management methods is also required along with appropriate schematics, as are names and locations of off-site treatment, storage, or disposal facilities.

An engineering analysis of a waste stream can usually result in the reduction of the list of hazardous constituents that must be included in the demonstration, by employing mass balance techniques and examining likely chemical reactions. Mass balance for a process will show raw materials input, use rates, and likelihood of their presence in the waste stream. Expert chemical judgment must sometimes be applied to predict the by-products of the reactions. Generally, the more detail provided in the engineering analysis the greater the likelihood that the petitioner's mass balance demonstration will be accepted. Mass balance techniques may not be possible for nonprocess applications.

Petition Review Process

The petition review process by EPA first involves an initial review to determine the completeness of the petition. Once the petition is judged to be complete a tentative decision is made to grant or deny. (Denial decisions are often made before a petition is complete, if adequate information is available.) If a decision is made to deny the petition, the petitioner is sent a letter that explains the reasons for the denial decision and presents the option to withdraw the petition. Otherwise, all proposed Agency decisions are printed in the *Federal Register*.

A workgroup of EPA Office of Solid Waste (OSW) members and other staff members evaluates the draft proposed notices, submits comments to OSW, and following review of all comments, sends the proposed notice to the Office of General Counsel for comments. The proposed recommendation is sent to the Assistant Administrator for Solid Waste and Emergency Response who decides whether to approve the Office's decision.

The decision of the Assistant Administrator is published in the *Federal Register* with a request for comments within 30 days. Following the comment period and review of the comments, the decision is reviewed by the workgroup and the above process repeated. The Assistant Administrator's final decision is then published in the *Federal Register* as a final rule.

Of the 698 total petitions received to date, 30 percent were withdrawn, 9 percent passed, 14 percent were denied, 26 percent were "mooted" (i.e., not a hazardous waste by definition), 3 percent were referred to state delisting programs (before HSWA removed authority), and 18 percent are still actively under review.

3. Land Disposal Bans and Procedures for Extensions

Background

When the RCRA Amendments came into effect on November 8, 1984, the scope of RCRA regulations was greatly expanded; many of these new provisions involved restricting wastes from land disposal. The first of these became effective six months after enactment, in May 1985, and banned bulk and noncontainerized hazardous liquids from disposal in landfills. In November 1985, a year after enactment, nonhazardous liquids were banned from disposal in landfills. These two bans remain in effect in addition to the new waste-by-waste restrictions outlined in this discussion.

These new provisions have broadened the definition of land disposal to include placement of hazardous wastes in landfills, surface impoundments, waste piles, injection wells, land treatment facilities, salt domes or salt formations, and underground mines or caves. It is estimated that about 33 billion gallons of untreated hazardous waste now go to these land disposal units, and current thinking is that even properly engineered units with liners and leak detection systems may not be enough to prevent the release of hazardous constituents from these units to ground water, surface water, or air.

National concern has culminated in this congressional mandate that reliance on land disposal must be minimized or eliminated, and that land disposal should be the least favored method for managing hazardous wastes. The expectation is that these land disposal restrictions will eventually lead to an overall reduction in waste generation, and an impetus to recycle rather than just dispose. Treatment of organic wastes is expected to be through such methods as incineration or neutralization, and inorganics through stabilization or fixation techniques. While it is recognized that there will always be some residuals that will have to be land disposed, it is expected this will occur after treatment and that the volume of wastes to be land disposed will be greatly reduced.

Proposed Rules and Regulatory Schedule

The proposed rules discussed here were published in the Federal Register, January 14, 1986. Under the 1984 Amendments to RCRA, land disposal of hazardous wastes is prohibited unless the waste has been treated in accordance with standards set by EPA, or unless it can be shown that continued land disposal of hazardous wastes is protective. EPA has been charged with setting treatment standards for approximately 450 hazardous waste streams. These are the listed wastes and characteristic wastes, identified in 40 CFR 261. HSWA prohibits the wastes from land disposal unless treated to standards set by EPA in a phased approach between Novem-

ber 8, 1986 (solvents and dioxin containing wastes) and May 8, 1990. The treatment standards may be set as performance standards, allowable concentrations of hazardous constituents in a waste extract or in the waste, or as specified technologies. Wastes containing higher levels than the specified treatment standards or not treated by the specified technology, can only be land disposed after these dates by successfully demonstrating that there will be no migration of these constituents from the land disposal unit for as long as the waste remains hazardous.

In promulgating these treatment standards for each waste stream, EPA will in effect determine what can safely be land disposed and at what levels. The obvious objective is to minimize threats to ground water or surface water through leaching and to the air through emissions. This will generally be accomplished by reducing the toxicity and mobility of the wastes before they are land disposed. First, EPA will have to identify and evaluate appropriate treatment technologies in terms of their applicability to specific waste streams, how widespread their uses are, and their overall effectiveness in reducing the toxicity and mobility of wastes.

Treatment standards will be set out in Part 268 of 40 *CFR*. They will be expressed as constituent concentrations in a waste or waste extract or as specified technologies, and land disposal will be allowed when the relevant standards have been met. If the concentration of any of the hazardous constituents in a waste or waste extract as applicable, equals or exceeds the level indicated in the regulations, then the waste must be treated before being land disposed. If concentrations are below these levels, then the waste may be land disposed through normal channels without treatment. In addition, specific technologies that have been shown to be effective in reducing toxicity in certain waste streams will be identified in the preamble to the regulations. However, any method may be used to treat wastes exhibiting concentrations over the allowable limits, except where specific technologies are required.

Congress set up a four-year schedule which started November 8, 1986. This was the first deadline for the first group of wastes to be prohibited—solvents and dioxins, and EPA published its regulations on November 7, 1986. EPA also set out a schedule for ranking and restricting the remaining listed waste streams, putting high volume wastes and high hazard wastes at the top of the list for the earliest bans. This schedule was published on May 28, 1986 (51 *Federal Register* 19300). On the second date, July 8, 1987, the final prohibition for the "Califor-

nia List of Wastes" will be published in the *Federal Register*. The California List is so called because the State of California deemed that these wastes should be banned from land disposal based on their toxicity, mobility, and effects on liners in land disposal facilities. These waste streams include wastes containing cyanide, several metals, acid wastes, PCBs, and halogenated organics.

The last group of wastes will be those that EPA has ranked and divided into three categories. By August 8, 1988 the first third of these ranked listed wastes will be prohibited. By June 8, 1989 the second third of these listed wastes will be prohibited, and by May 8, 1990 the last third of these listed wastes and all characteristic wastes must be banned. If EPA misses these deadlines and fails to set treatment standards for these different groups of wastes, then on the respective dates for solvents, dioxins, the California List, characteristic wastes, and the last third of the listed wastes, land disposal will be banned. There is an "out" for the first and second thirds of the listed wastes; they can continue to be disposed of until 1990 in units meeting the minimum technological requirements of HSWA (double liners, leachate collection, ground water monitoring).

Who Is Affected

How would generators actually go about determining whether or not they are subject to these restrictions? Table 3.1 goes through the steps for such a determination.

First, the generator determines from Part 268 of the regulations if his waste is listed or characteristic hazardous waste. If it is not, then land disposal in nonhazardous waste landfills may be used. If it is a listed or characteristic hazardous waste, the next step is to determine whether any of the hazardous constituents listed in the table in the regulations exceed or equal the allowable concentrations where this is relevant. If the constituents are below the limits shown, then land disposal may continue to be used. If the limits are equalled or exceeded, then the generator is subject to the restrictions. If a specific treatment technology is listed for that waste stream, it must be used to treat that waste until acceptable limits are reached. If a treatment is not specified in the regulations, then any appropriate method can be used that will reduce the levels to the allowable limits. Those treated wastes can then be land disposed.

Exemptions or variances may be granted in certain circumstances. For example, one case-by-case extension

Table 3.1. Land Disposal Restriction Procedures

Generator	RCRA TSD Facility Operating Under Interim Status	RCRA TSD Facility Operating Under a Permit
Procedure 1. Analysis to Determine Constituent Concentrations in Waste or Waste Extract (40 CFR 268.6 and 268.40(b)).		
The generator must determine, through either testing or knowledge of the waste, whether his waste meets the treatment standards under 40 CFR Part 268 Subpart D. If the hazardous constituents in the waste do not exceed the concentrations listed in Table CCWE, ¹ the waste is not subject to further restriction under 40 CFR Part 268 although the generator must designate on the manifest a land disposal facility which is authorized to dispose of the waste (40 CFR 262.20).	The facility must either have documentation of tests conducted by the generator or test the waste to determine that such waste is in compliance with applicable treatment standards. The waste must be tested using the methods described in SW-846 or equivalent methods approved by the Administrator (40 CFR 268.6). The facility must record the result of this testing in its operating record (40 CFR 265.73).	The facility must either have documentation of tests conducted by the generator or test the waste to determine that such waste is in compliance with applicable treatment standards. The waste must be tested using the methods described in SW-846 or equivalent methods approved by the Administrator (40 CFR 268.6). The facility must record the result of this testing in its operating record (40 CFR 264.73).
If the hazardous constituents in the waste extract or waste is subject to the land disposal restrictions and the generator must pursue one or more of the available options under 40 CFR Part 268 (case-by-case extension, petition, or treatment).	If the hazardous constituents in the waste extract or waste do not equal or exceed the 40 CFR Part 268 Subpart D treatment standards, the waste is not subject to further restriction under 40 CFR Part 268, although still a hazardous waste, and may be land disposed at an RCRA facility which has authority to manage the waste.	If the hazardous constituents in the waste extract or waste do not equal or exceed the 40 CFR Part 268 Subpart D treatment standards, the waste is not subject to further restriction under 40 CFR Part 268, although still a hazardous waste, and may be land disposed at an RCRA facility which has authority to manage the waste.

Table 3.1. continued

Generator	RCRA TSD Facility Operating Under Interim Status	RCRA TSD Facility Operating Under a Permit
<p>Procedure 2a. Use of an Identified Technology to Treat a Restricted Waste (40 CFR 268.40(a)).</p> <p>The generator must send its waste to a facility that has the ability to treat the restricted waste using the identified technology found under 40 CFR 268.41.</p>	<p>The treatment facility must be able to apply the identified technology designated for the restricted waste complying with any standards specified for that technology.</p> <p>The treatment facility must provide certification of proper treatment to the land disposal facility receiving the treatment residue.</p> <p>The treatment residue, after treatment by the required technology(ies), must be managed as a hazardous waste² but may be land disposed.</p>	<p>The treatment facility must be able to apply the identified technology designated for the restricted waste complying with any standards specified for that technology.</p> <p>The treatment facility must provide certification of proper treatment to the land disposal facility receiving the treatment residue.</p> <p>The treatment residue, after treatment by the required technology(ies), must be managed as a hazardous waste² but may be land disposed.</p>
<p>Procedure 2d. Use of an Equivalent Treatment Method to Treat a Restricted Waste (40 CFR 268.40(a)).</p> <p>The generator must send its waste to a facility that has the ability to treat the restricted waste using an Equivalent Treatment Method approved by the Administrator.</p>	<p>The treatment facility must petition the Administrator for approval of an Equivalent Treatment Method in accordance with 40 CFR 268.41(b).</p> <p>The treatment facility must provide certification of proper treatment to the land disposal facility receiving the treatment residue.</p> <p>The treatment residue, after treatment by the required technology(ies), must be managed as a hazardous waste² but may be land disposed.</p>	<p>The treatment facility must petition the Administrator for approval of an Equivalent Treatment Method in accordance with 40 CFR 268.41(b).</p> <p>The treatment facility must provide certification of proper treatment to the land disposal facility receiving the treatment residue.</p> <p>The treatment residue, after treatment by the required technology(ies), must be managed as a hazardous waste² but may be land disposed.</p>
<p>Procedure 3. Case-by-Case Extensions of Effective Dates to Allow Continued Land Disposal of a Restricted Waste (40 CFR 268.4).</p> <p>Generators seeking a case-by-case extension must apply to the Administrator. The extension does not become effective until a notice of approval is published in the <i>Federal Register</i> or the generator receives an approval notice from the Administrator. The generator must forward a copy of the approval notice to the land disposal facility receiving its waste before shipping the waste to the facility. The generator must retain the notice of approval in his records (40 CFR 262.40).</p>	<p>Land disposal facilities seeking a case-by-case extension must apply to the Administrator. The extension does not become effective until a notice of approval is published in the <i>Federal Register</i> or the disposal facility receives an approval notice from the Administrator. The facility must have a copy of the approval notice in its operating record and must keep an accounting of the waste disposed under the extension (40 CFR 265.73(b)(8)). This approval notice may be forwarded by the generator or obtained by the disposal facility directly.</p>	<p>Land disposal facilities seeking a case-by-case extension must apply to the Administrator. The extension does not become effective until a notice of approval is published in the <i>Federal Register</i> or the disposal facility receives an approval notice from the Administrator. The facility must have a copy of the approval notice in its operating record and must keep an accounting of the waste disposed under the extension (40 CFR 264.73(b)(10)). This approval notice may be forwarded by the generator or obtained by the disposal facility directly.</p>
<p>Procedure 4. Petitions to Allow Land Disposal of a Restricted Waste (40 CFR 268.5).</p> <p>The generator should have evidence that the facility has an approved petition to land dispose of a specific restricted waste before shipping that waste to the facility for disposal. The</p>	<p>The facility must submit a petition to the Director³ and receive a notice of approval before it can land dispose of a restricted waste. A copy of the approval notice must be kept on file in the operat-</p>	<p>The facility must submit a petition to the Director³ and receive a notice of approval before it can land dispose of a restricted waste. A copy of the approval notice must be kept on file in the operat-</p>

Table 3.1. continued

Generator	RCRA TSD Facility Operating Under Interim Status	RCRA TSD Facility Operating Under a Permit
generator, itself, may also file a petition or be a party to a petition with a treatment, storage, and disposal facility.	ing record. The facility must have interim status (or an approved change under interim status) to manage the restricted waste and to operate the land disposal process. The facility must comply with all conditions of the approval.	ing record. The facility must have a permit which includes (or must modify its permit to include) the restricted waste codes to be managed and the land disposal process. The facility must (through permit conditions) comply with all conditions of the approval.
<p>Procedure 5. Treatment of Restricted Wastes in Certain Surface Impoundments (40 <i>CFR</i> 268.1(ca)).</p> <p>The generator must send its waste to a treatment facility that has an impoundment that meets the minimum technological requirement, i.e., has been constructed with a double liner (with limited exceptions) and is in compliance with ground water monitoring requirements.</p>	<p>The facility must have Interim Status (or an approved change under Interim Status) to manage the restricted waste and operate the treatment process.</p> <p>The impoundments must meet the minimum technology requirements in accordance with 40 <i>CFR</i> 265.221 (a) through (e) and be in compliance with 40 <i>CFR</i> Part 265 Subpart F.</p> <p>The facility must analyze the contents of the impoundments annually in accordance with 40 <i>CFR</i> 268.1(e)(2).</p> <p>Impoundment residue that does not meet the standards found under 40 <i>CFR</i> 268.42 or 268.43 must be removed and managed as a restricted waste, but cannot be further treated in an impoundment.</p> <p>Residue that meets the standards found under 40 <i>CFR</i> 268 Subpart D can remain in the impoundment or can be otherwise land disposed. The residue must be managed as a hazardous waste.</p>	<p>The facility must have a permit which includes (or must modify its permit to include) the restricted waste to be managed and the treatment process to be operated.</p> <p>The impoundments must meet the minimum technology requirements in accordance with 40 <i>CFR</i> 264.221 (a) through (e) and be in compliance with 40 <i>CFR</i> Part 264 Subpart F.</p> <p>The facility must analyze the contents of the impoundments annually in accordance with 40 <i>CFR</i> 268.1(e)(2).</p> <p>Impoundment residue that does not meet the standards found under 40 <i>CFR</i> 268.42 or 268.43 must be removed and managed as a restricted waste, but cannot be further treated in an impoundment.</p> <p>Residue that meets the standards found under 40 <i>CFR</i> 268 Subpart D can remain in the impoundment or can be otherwise land disposed. The residue must be managed as a hazardous waste.</p>
<p>Procedure 6. Land Disposal of Wastes that Meet 40 <i>CFR</i> Part 268 Subpart D Standards</p> <p>The generator must determine, through either testing or knowledge of his waste, that his waste meets the 40 <i>CFR</i> Part 268 Subpart D standards and is, therefore, no longer a restricted waste, before shipping the waste (with accompanying manifest) for land disposal to a facility with Interim Status or an RCRA permit.</p>	<p>The facility must have Interim Status (or an approved change under Interim Status) to manage the waste.</p> <p>The facility must have records and results of waste analysis performed (40 <i>CFR</i> 265.13 and 268.5), documenting in the operating record that the waste meets 40 <i>CFR</i> Part 268 Subpart D standards and may be land disposed without further treatment.</p>	<p>The facility must have a permit which allows (or must modify its permit to allow) management of the waste.</p> <p>The facility must have records and results of waste analysis performed (40 <i>CFR</i> 265.13 and 268.6), documenting in the operating record that the waste meets 40 <i>CFR</i> Part 268 Subpart D standards and may be land disposed without further treatment.</p>

¹Constituent Concentration in a Waste Extract, 40 *CFR* 268.41.²Unless the residue has been delisted (40 *CFR* 260.22) or the residue is the result of treating a waste that is hazardous solely because it exhibits one or more hazardous waste characteristics (40 *CFR* Part 261 Subpart C) and the residue no longer exhibits the characteristic(s).³Director is as defined under 40 *CFR* 270.2.

requires that the generator demonstrate that there is no alternate capacity for his wastes; then an extension can be granted for up to two one-year periods from the date that waste would be banned. In order to get this extension the generator must show a binding contractual commitment to provide or construct this alternate treatment capacity by the end of the extension period. Another type of variance is an actual petition to continue disposal of a particular waste in a particular unit. To do that is much more complicated because the generator must demonstrate that waste and site-specific factors such as hydrogeology or other special considerations allow for degradation or immobilization of the waste so that there is no migration of hazardous constituents from the unit for as long as the waste remains hazardous. This demonstration must also take into account any receptors of the leachate or the constituents as they migrate and show that they would not be affected at levels that would endanger human health. When the final ruling for the first group of wastes comes out for solvents and dioxins, it is expected that a draft petitioner's guidance manual will be issued.

Summary

The *Federal Register* notice dated July 8, 1987 contains the final ruling for the (California List) wastes covering metals and cyanides. There is a 60-day comment period allowed. Also, Headquarters has indicated that the standards coming out for the California Wastes will be those listed in the actual statute; that is, the California Wastes as they are defined. EPA may attempt to set lower limits in a separate rulemaking. In any case, the limits in the proposed rule will eventually end up being meaningless because treatment standards will be set under another category — the listed wastes.

4. Used Oil and Hazardous Wastes as Fuel

Background

The November 29, 1985 major rule pertaining to the use of used oils and hazardous waste as fuels consisted of one final set of interim regulations and two proposed regulations, related to the HSWA amendments. The ruling placed most of its emphasis on the marketers and burners, and represented EPA's first attempt to regulate the burning of used oil as fuel under RCRA. Interpretation of the ruling is highly dependent on the understanding of the definitions of the following concepts and terms: marketer, burner, generator, waste fuel, hazardous waste fuel, used oil fuel, used oil, characteristic waste, nonindustrial burner, beneficial recycling, and on-spec/off-spec used oil fuel. The term "waste fuel" encompasses both hazardous waste fuel and used oil fuel. These definitions are distributed throughout the following text.

The major impact of the ruling is that the burning of hazardous waste fuel or off-specification used oil fuel in non-industrial boilers is prohibited. The specifications for used oil fuel are arsenic (5 ppm), cadmium (2 ppm), etc. Used oil fuels not meeting these specs are considered off-spec. Only specification (on-spec) oil can be burned in nonindustrial boilers.¹ Any on- or off-spec used oil mixed with listed hazardous wastes becomes a listed hazardous waste and cannot be burned in nonindustrial burners. The same holds true for used oil/characteristic hazardous mixtures that continue to exhibit a hazardous waste characteristic. Nonindustrial boilers include residences and commercial facilities such as laundries, hotels, office buildings, and service stations. Notably, greenhouse boilers are classified as industrial boilers. The burning of these materials can only be for energy recovery and not for destruction, i.e., the material must have a heat value greater than approximately 5,000 Btu per pound. The burning of eligible fuels is permitted only in industrial boilers, industrial furnaces, utility boilers, space heaters, and hazardous waste incinerators. The two proposed regulations included listing used oil as a hazardous waste² and also hazardous waste recycling standards.

The remaining concerns of the rules lie in the administrative requirements which include notification, tracking, and recordkeeping requirements. The notification requirements apply to all marketers of waste fuels, any generator

who ships waste fuels directly to a burner, and all burners of hazardous waste fuels and off-spec used oil fuel. Marketers and burners who have previously notified EPA and have an ID number must renotify in order to complete an expanded fuel information section.

The party that first claims that a used oil fuel meets EPA burning specifications as well as marketers of used oil fuel that process off-spec used oil fuel to produce on-spec used oil fuel must also notify EPA. Generators of used oil are generally exempt from notification procedures unless they market directly to an eligible burner, thus bypassing the marketer who would normally notify EPA.

Tracking Requirements

The tracking requirements of the rule state that all hazardous waste (including characteristic waste) fuel shipments must be accompanied by a manifest. For purposes of tracking, off-spec used oil fuel marketers and burners are now required to implement an invoice system. The invoice prepared by the marketer is kept on file for at least three years and includes such information as name, address, and ID number of the marketer and burner, quantity of waste being shipped, and a statement on the invoice indicating that the waste is a EPA regulated substance under 40 CFR Part 266.

All off-spec used oil marketers and burners must keep on file for three years copies of all invoices as well as certifications (which, briefly, is a notice from the burner to the marketer stating that EPA has been notified, an ID number issued, and that the burner will not use any nonindustrial type boilers). Certifications are generally made on the date of the initial shipment of a waste fuel. The marketer and burner are required to keep a copy of the certification for three years after the date of the final shipment of a waste fuel. A marketer must keep copies of any used oil fuel analysis that was performed to show that a used oil is on-specification.

Hazardous Waste Fuel Defined

EPA has taken the position that any used oil in which the total halogen content was found to be greater than 1,000 ppm will be presumed to be a hazardous waste fuel. A generator can rebut this presumption by proving that the high halogen levels were not the result of mixing with a listed hazardous waste. It is important to realize that if a listed hazardous waste is knowingly mixed with used oil *in any concentration* (even if the final halogen content did not exceed 1,000 ppm), the mixture remains

¹The regulations do allow non-industrial boilers to burn hazardous waste fuel and off-spec used oil if they are in compliance with the hazardous waste incinerator (Subpart O of 40 CFR) requirements.

²In a November 17, 1986 Federal Register notice, EPA published their intent not to list used oil as a hazardous waste. Used oil remains subject to the November 29, 1985 management standards, however.

a hazardous waste unless delisted.³ The so-called "re-buttable presumption" merely places the burden of proving hazardous waste adulteration on EPA in cases where the halogen limit is not exceeded.

A used oil mixed with a characteristic hazardous waste is a hazardous waste unless it no longer exhibits that characteristic, e.g., flash point of 140°F. Blending of a characteristic hazardous waste/used oil mixture to render it nonhazardous is considered treatment and may require a hazardous waste treatment permit. Off-spec used oil, however, can be blended to meet specification without a treatment permit.

An important implication of these regulations is the need to carefully segregate all waste. The contamination or mixing of used oil fuel with any of the listed solvents may render the product a hazardous waste fuel and the mixture will be subject to all of the regulatory requirements, resulting in increased handling and removal costs.⁴

³At this time, used oil mixed with small quantity general (SQG) hazardous waste is regulated as a used oil. As a practical matter, however, such mixing is strongly discouraged because many marketers will not accept used oil mixed with hazardous wastes.

⁴a) States like California can declare all used oil as a hazardous waste subject to all the requirements for storing, treating, transporting, and disposing of hazardous wastes.
b) Future EPA regulations are expected on the burning of hazardous waste as fuel and off-spec oil.

5. Underground Storage Tank and Hazardous Waste Requirements

Background

Underground storage tanks (USTs) became prevalent when industry and the public found they save space, provide protection from the environment, and prevent hazards such as fires and explosions, especially for fuels, oils, and chemicals. However, placing tanks underground does not eliminate such problems as corrosion, structural damage, and loss of product waste through leakage; thus, improvements have been made in tank construction and installation and in systems that measure tank inventory loss. These improvements have not been universally adopted. Nor have they ensured that tanks are consistently installed properly, that safety standards are met and maintained, and that loss of inventory and damage to the environment are prevented. A recent EPA survey showed that the major causes of tank failure are: 1) structural, 2) piping, 3) ancillary equipment, 4) operator error, 5) external corrosion, and 6) improper installation. Of the UST failures, 74 percent resulted in ground water contamination.

In Europe and in many states, these problems were recognized early on and programs were developed to regulate commonly used tanks such as those to store gasoline and other petroleum products. The Federal government began regulating tanks storing hazardous waste products as early as 1981 under Subtitle C of the Resource Conservation and Recovery Act of 1976 (RCRA). However, it wasn't until November 1984 that a Federal program was established to regulate USTs under Subtitle I of RCRA when the Hazardous and Solid Waste Amendments (HSWA) were promulgated.

Estimates of USTs in the United States range from 1.5 to 2.5 million tanks. It is known that many USTs are leaking or are on the verge of leaking into the environment — specifically, into our nation's ground water.

To limit or control the enormous potential risks from leaking USTs, Congress directed EPA to enforce two provisions of the HSWA:

- (1) The requirement that owners of existing USTs notify the states of the age, size, type, location, and uses of their USTs.
- (2) An interim prohibition on the installation of new USTs.

The RCRA Subtitle I UST Program

As defined by EPA, a tank is a stationary device constructed primarily of nonearthen materials (e.g., wood, concrete, steel, plastic) which provide structural support. An UST as defined in Subtitle I is any tank or combination of

tanks, including underground piping, used to contain an accumulation of regulated substances, the volume of which, including underground piping, is 10 percent or more underground. Under Subtitle I, regulated substances include all substances defined as hazardous under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and all petroleum products, including crude oil, and refined products, such as antifreeze. Tanks which store hazardous wastes as defined in RCRA are regulated under the RCRA Subtitle C hazardous waste program. Exemptions to the Subtitle I UST definition include:

- Farm or residential tanks storing less than 1,100 gallons of motor fuel for noncommercial purposes.
- Tanks storing heating oil at the premises where it is consumed (Numbers 2, 4, and 6 oil used for noncommercial purposes).
- Septic tanks.
- Pipelines regulated under other laws.
- Surface impoundments, pits, ponds, or lagoons.
- Stormwater or wastewater collection systems.
- Flow-through process tanks.
- Liquid trap or associated gathering lines directly related to oil or gas production and gathering operations.
- Storage tanks situated on or above the floor of underground areas such as basements, shafts, and tunnels.

EPA has stated that most other types of containers (for example, small metal boxes, underground sumps, dump tanks, hydraulic lifts, possibly even coffins and burial vaults), could be considered USTs and as such, subject to notification requirements.

Interim Prohibition

The interim prohibition on the installation of new tanks applies to any tank, new or used, which was installed for use as a UST after May 7, 1985. Tanks installed after May 7, 1985 must be:

- Designed to prevent releases due to corrosion or structural failure.
- Cathodically protected against corrosion, constructed of a noncorrosive material, steelclad with noncorrosive material or its equivalent, or designed in a manner to prevent the release or threatened release of any stored substance.
- Constructed or lined with a material which is chemically compatible with the material stored.

These requirements may increase the total installed cost of a tank from 20 to 100 percent over that of an unpro-

tected steel tank; the installed cost of a double-walled tank may be even higher.

Notification

State and Federal notification provisions were published in the November 8, 1985 *Federal Register*. These provisions apply to all tanks regulated under RCRA Subtitle I program:

- If a tank was taken out of operation on or before January 1, 1974 but not removed from the ground, the owner does not have to notify the state; if a tank was taken out of operation after January 1, 1974 but not removed from the ground, the owner must notify the state by May 8, 1986.
- Owners who bring any tank into operation after May 8, 1986 must notify the appropriate state or local agency within 30 days of installation of the age, size, type, location, and use of such tanks.
- Anyone who deposits a regulated substance in an UST after December 8, 1985 must advise the owner or operator of the notification requirements.
- Starting 30 days after EPA issues new tank performance standards, anyone who sells an UST must advise the purchaser of the owner's notification requirements.

Some states have regulations which are more stringent than the Federal requirements; tank owners must conform to both state and Federal requirements.

The other requirements listed in RCRA Subtitle I have not yet gone into effect. Although Congress required EPA to have such regulations in effect by February 1987, only draft regulations will be available at that date for public review and comment; final regulations will be available by early 1988. These regulations will include:

- Leak detection and leak detection records.
- Tank technical standards (the interim prohibition will be eliminated on promulgation).
- Performance standards on design, construction, installation, release detection, and compatibility standards.
- Corrective action for releases from tanks.
- Financial responsibility for the tank, damages from releases, and corrective action
- Inspections, monitoring, and testing.

The CERCLA reauthorization legislation may also affect this schedule and the contents of the final regulations.

State UST Programs

EPA intends to authorize the states to administer the UST program in lieu of the Federal program. Once the final regulations are promulgated, states may apply to EPA for approval of their programs. The state program must be at least as stringent as the existing Federal program and must provide for adequate enforcement. Some states have already developed UST programs, although Federal regulations for authorization are not yet in place. RCRA's Subtitle I UST program provides for temporary authorization of such programs even though their requirements are less stringent. If regulatory amendments only are needed to fully comply with the Federal program, the temporary authorization will last one year after the Federal authorization regulations go into effect. If legislative amendments are necessary, the temporary authorization may last up to two years. If both regulatory and legislative amendments are required, temporary authorization may be extended up to three years.

Federal Enforcement of the UST Program

Section 9006 of RCRA Subtitle I provides EPA with both administrative and judicial enforcement authority. EPA may issue a compliance order for any violation of the provisions of the UST program. Failure to comply could result in the issuance of an order which may include the following penalties:

- \$10,000 per tank per day for violation of the notification and interim prohibition requirements.
- \$10,000 for noncompliance with requirements of Section 9003.
- \$25,000 per day for noncompliance with an administrative order (including Section 9003(h) orders).

Additional enforcement is also available under Sections 3013 and 7003 of Subtitle C of RCRA to compel investigations and to clean up spills or leaks; Section 9005 of Subtitle I allows EPA to request information, tank testing, etc. Citizen suits may be brought under Section 7002 of RCRA. There are no criminal penalties for violations under Subtitle I.

Regulatory Development

New regulations will affect many industrial plants, gasoline stations, and municipalities. The most difficult aspect of this program is informing the regulated community and the public of the UST program and its requirements. It is important that the development of this program be monitored by those it affects to ensure that the requirements are met. A carefully and effec-

tively implemented program will assist in the protection of the nation's ground water resources, especially its critical drinking water supplies.

The RCRA Subtitle C UST Program

Existing regulations for hazardous waste tanks under RCRA Subtitle C, Title 40 *CFR* Parts 264 and 265 were amended in July 1986 and became effective in January 1987. If the amended regulation is listed in Title 40 *CFR* Part 271.1(j) it becomes effective in all states on its effective date, regardless of whether the state is authorized to operate its own program. If the regulation is not listed, it is not effective in the authorized state until the state amends its regulations and receives authorization from EPA.

The regulations under Subtitle C apply as follows:

- Large quantity generators (generating over 1,000 kg of hazardous waste per month) effective January 12, 1987.
- Small quantity generators (generating between 100 and 1,000 kg of hazardous waste per month, storing more than 180 days, or having greater than 6,000 kg in storage), effective March 24, 1987.
- Small quantity generators (generating between 100 and 1,000 kg of hazardous waste per month, storing less than 180 days, and not having greater than 6,000 kg in storage), exempt but expected to be added.
- All other generators are exempt.

Secondary containment can consist of an external liner, vault, double-walled tank, or an equivalent approved device — attachments that often cannot be visually inspected. All must contain the wastes. Secondary containment and monitoring requirements and their effective dates are:

- New tanks — before they are placed into service.
- Leaking tanks — before they are returned to service.
- For existing tanks of known age, secondary containment and monitoring are required by January 12, 1989 or when the tank becomes 15 years old, whichever is later.
- For existing tanks of undocumented age, secondary containment and monitoring are required by January 12, 1989 if the facility is 15 years old or less. If the facility is more than 15 years old, secondary containment and monitoring are required by January 12, 1992.

- For tanks storing chlorinated phenols, secondary containment and monitoring are required by January 12, 1989.
- For tanks storing newly regulated wastes, add two years to the date when the waste becomes regulated.

Secondary containment requirement variances are possible. The petition for variance must be either technology- or risk-based; the petitioner must demonstrate that an alternate design will detect leaks and prevent migration of any hazardous waste beyond secondary containment. Or, the petitioner must demonstrate that if a release occurs from an existing tank, there will be no substantial actual or potential hazard to human health and the environment.

Leak Detection and Closure Requirements

The leak detection system under Subtitle C must be able to detect failure of the primary or secondary containment system or the presence of waste or liquid. Responses to leaks and spills must include:

- Prevention of further releases.
- Removal of the released waste.
- Notification to EPA.
- Repair or closure of the system.
- Certification of repair (by a professional engineer) prior to reuse.

Under Subtitle C closure requirements require that the tank must be removed and all wastes and residues decontaminated, or the hazardous waste landfill must be closed, and financial assurance must be provided.

Tank Assessments

The Subtitle C regulatory scheme for tanks is one of containment, detection, and response through secondary containment, interstitial monitoring, and clean up. Assessments of existing tanks include a mandatory leak test or other examination, and a written assessment of tank integrity. Assessments of new tanks include a written assessment of integrity, an installation inspection, and testing prior to use.

6. Clean Water Act Update

This discussion highlights recent changes in the Clean Water Act (CWA) Reauthorization. Though the reauthorization is not totally defined, this summarizes what is likely to be enacted in areas significant to industry.

Penalties

The most substantial change in compliance enforcement will be higher penalties for conviction of criminal violations. Congress is requiring a two- to three-year jail term and an increase in the per day penalty from \$25,000 to \$50,000. Civil penalties will be increased from \$10,000 to \$25,000 per day, and up to \$125,000 per violation. EPA will be empowered to administer civil penalties subject to hearings, thus removing the need to go to court every time the CWA is violated.

Hazardous Waste and the CWA

In the 1986 Domestic Sewage Study, EPA estimated that approximately 70 to 80 percent of all the hazardous wastes that RCRA would normally control are discharged to publicly owned treatment works (POTWs) rather than put into landfills. Under the Domestic Sewage Exemption Act, hazardous waste mixed with domestic sewage is not treated as hazardous waste but as domestic sewage. Hazardous wastes can be discharged to the sewer directly at the plant or in more extreme cases, trucked to the front of the plant and dumped down a manhole. This has been an area of concern for Congress because of the potential for uncontrolled discharge of hazardous waste. The CWA will concentrate on efforts to control RCRA substances that end up in POTWs through more stringent pretreatment standards and by promoting the effective operation of POTWs. Congress could decide to modify the domestic sewage exemption if EPA and the municipalities do not take action. Modification could have significant impact on RCRA and CWA management and how amenable municipalities are to treating industrial waste in the future.

The major emphasis in the pretreatment program is now on toxics. Initiatives are being considered that would allow EPA to impose biomonitoring requirements and permit additional chemical monitoring if there were suspected toxic pollutants in a particular discharge. Pretreatment prior to discharge into a sewage system may be required for more parameters, particularly metals, since POTWs traditionally have not been built to handle large amounts of toxics.

Industrial pretreatment requirements and discharge limits will be enforceable by EPA authorities even when the

local ordinances are more stringent than Federal standards.

Under the CWA amendments, EPA is now required to reopen permits at any time for cause. For example, EPA is required to reissue a POTW's permit with amended controls if the facility's effluent is found to contain a sophisticated toxic material. Previously, EPA had to wait until the permit expired unless the permittee requested modifications. The new procedure will allow EPA greater flexibility in permitting.

Section 309F of the CWA includes a provision that allows EPA to require POTWs to cut off an industrial user whose discharge is interfering with the POTW's treatment system. The statute also authorizes EPA to ask the courts to terminate the connection if necessary. This approach has not been used often, but could also prove to be an effective method for controlling disposal of industrial waste.

CWA and Municipalities

The National Municipal Policy, aimed at encouraging municipalities to comply with the final requirements in their permits, could be altered under the CWA reauthorization. Most municipalities have not complied with their final current limits. Previously EPA would provide funding to aid the municipalities with compliance, but it is now believed that the cost of managing and administering the pretreatment program, including laboratory analyses, monitoring, and field personnel, should be borne by the municipality. Their funding could come from increased rates or fines imposed on out-of-compliance industries. For example, if EPA requires that a municipality build or improve a POTW to meet its final permit limits, each industrial discharger could be approached to supplement the municipality's funds. The municipality may also request that industry reduce its daily output, thus encouraging industry to develop its own pretreatment systems.

Stormwater Regulations

The requirement that EPA promulgate regulations governing stormwater runoff resulted from a lawsuit filed by the Natural Resources Defense Council several years ago. Since then two sets of regulations have been issued. Current stormwater regulations became operative in 1984; they were slightly amended in 1985.

EPA must permit discharges; regulations are currently being developed based on two groups of stormwater

discharges. Group I, the major and most common category, involves stormwater generated from industrial and manufacturing areas, including parking lots and access roads leading to the manufacturing facility. Stormwater transferred off the property into surface water via pipe or other drainage system is included, and stormwater transferred into a municipal storm sewer is likely to be included in the proposed regulations. Group I dischargers in existence prior to August 1979 now have until October 1, 1990 to comply with the regulations. Dischargers that came into existence after August 1979 must submit an application to EPA prior to commencing discharge. The Group I application requires submittal of EPA Form 1. The second part of the form requires analysis of stormwater from every discharge point for the 126 EPA priority pollutants.

The Group II category includes discharges of stormwater from parking lots of office buildings, commercial buildings, and institutions. The deadline for these applications has been extended to October 1, 1992.

7. Selecting a Responsible Transporter and Waste Management Facility

Background

There can be little doubt that the Resource Conservation and Recovery Act (RCRA) of 1976 places the responsibility for the effects of hazardous waste disposal squarely on the generator. The much touted "cradle to grave" philosophy of RCRA assures that the generator is responsible for the safe storage, transport, and ultimate disposal of his hazardous waste. Although he will probably contract for removal and disposal, the generator cannot assign liability for the effects of his waste on others.

If RCRA established cradle to grave liability, then the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) of 1980 extended liability beyond the grave. Under this legislation, past contributors of wastes to sites deemed hazardous by EPA and slated for remediation are held liable for the cleanup costs. The liability is joint and several, so that it is conceivable that a minor contributor could be saddled with a large fraction of the remedial costs for a particular site. Furthermore, CERCLA imposes the potential for treble damages in cases where responsible parties do not effectuate a timely remediation of a site. Thus, a sobering picture is painted for the hazardous waste generator. It depicts a relatively high risk situation in which the penalties for malfeasance can be very high. So it is imperative that the hazardous waste generator do all in his power to ensure that his waste materials are properly handled, tracked, and disposed.

Although the risks to the generator can never be totally removed, they can be managed and reduced to an acceptable level by exercising due care in the selection of the hazardous waste transporter and the ultimate disposal facility. This chapter discusses the selection of the transporter and hazardous waste management facility and hopefully gives the reader some insight into the ramifications of these important decisions.

First consider the selection of a hazardous waste transporter. Companies that offer hazardous waste transportation services range from very small local contractors to large national corporations, and, as might be expected, equipment and staff sophistication vary greatly. The generator then is faced with the problem of evaluating the capability and reliability of candidate transporters to fill his need. The tools he has available to do this include certain governmental programs and services, waste transporter directories, professional consultants, metal finishing industry trade associations, and his own judgment.

Licensing

Hazardous waste transportation is regulated to some extent by the Federal government, and to a greater extent, by some states. There is no Federal licensing system for hazardous waste transporters. Under the RCRA regulations a transporter is required to obtain an EPA identification number. But the transporter does not have to demonstrate capabilities to obtain that number. Rather, he must simply submit a form to EPA indicating his intent to transport hazardous wastes. Most regulation at the Federal level is through the Department of Transportation (DOT), which regulates transportation of hazardous materials in general, not specifically hazardous wastes. Many hazardous wastes listed under RCRA or parallel state listings would not necessarily be classified as hazardous under DOT regulations. Also, DOT is concerned primarily with acute hazards such as flammability, explosivity, and release of toxic gases; problems that would be a direct threat to public health if an accident or spill were to occur. The longer term or chronic environmental hazards such as surface water or ground water contamination may not be adequately covered by DOT provisions.

State licensing programs covering hazardous waste transporters tend to be more responsive to the need to establish qualifications before allowing transporters to operate. Of course licensing procedures vary among states and the generator is encouraged to contact the environmental and/or transportation regulatory agencies in his state to: a) find out what protective measures are ensured through licensing provisions, and b) obtain a listing of licensed hazardous waste transporters. Not all states have licensing in place, but those that do typically cover such areas as equipment type and condition, operator training, waste handling, recordkeeping, routing, emergency response, contingency planning, tariffs, and financial responsibility or insurance. Therefore, the fact that a transporter carries a state license gives some assurance that his equipment meets certain standards, that his operators are properly trained, and that he has a contingency plan to respond to unforeseen emergencies. Again, however, the generator should investigate the requirements for licensing in his particular state rather than assume the license itself affords adequate protection.

Although there is no licensing at the Federal level, RCRA does impose certain transporter requirements. The most important of these involve the transporter's obligations under the manifesting system. The manifest must be completed for each shipment of hazardous waste by the

generator. This is essentially the "chain of custody" document that traces the waste from its point of generation through its ultimate disposal. The transporter is required to carry the manifest, deliver the manifest with the shipment to the disposal facility, and maintain a copy of the manifest for three years. RCRA requires the transporter to meet delivery standards in that he is required to transport the waste material to a properly permitted hazardous waste management facility. RCRA further requires that the transporter provide safe vehicle operation, have a spill and accident reporting procedure, and that he use appropriate materials and handling techniques for the hazardous waste being shipped.

Selection Criteria for Transporters

Given that the Federal regulations require certain standards for transporters, there really is no direct enforcement. Therefore, the generator must thoroughly investigate and evaluate candidate transporters to maximize his protection. What, then, are the factors to consider in such an evaluation? One should begin by ascertaining that the candidate transporter holds an EPA identification number. Next, one should look carefully at what licenses and/or certifications the transporter carries. If the state in which the generator is located has a hazardous waste transporter licensing system, then the candidate transporter should at least hold that license.

It is also desirable for the transporter to carry the licenses of the state in which the ultimate disposal facility is located and any states he must pass through. This may be required in some states. It is also advised that the generator check with the issuing department to determine what level of competence must be demonstrated to obtain the license.

The transporter's familiarity with the manifest system is important. This should be evaluated by checking his recordkeeping procedures, specifically that manifests are kept on file and are readily accessed for verification of transportation. Also, while checking company records the accident and spill contingency plan should be inspected. The plan should outline emergency procedures to be followed in the event of a spill and indicate specific individuals and agencies to be contacted to provide quick response and minimize potential environmental or public health impacts.

A factor to be considered is the transporter's experience in handling wastes from the metals finishing industry. As a group these wastes tend to have certain characteristics such as a high level of corrosivity, high toxic met-

als concentrations, and possibly trace concentrations of certain toxic organic compounds, primarily solvents. The wastes occur both in concentrated liquid form and in solid form as dewatered sludges. It is important that the transporter be familiar with these characteristics as they relate to his selection of equipment, worker protection procedures, and spill contingency planning. The generator should inspect the transporter's equipment to be sure that it is well maintained and suited to the type of waste to be transported.

An experienced hazardous waste transporter who has worked with the metal finishing industry probably has direct knowledge of the designated disposal facility. His knowledge of that facility's practices and requirements can be quite helpful in assuring, for example, that all necessary waste testing has been done and that the material is compatible with the particular facility's scope of services. This is not to say that the generator should rely on the transporter to evaluate the disposal facility, but the transporter's direct experience with the designated facility is a plus.

Two final factors to consider in evaluation of transporters are reputation and cost. The transporter's reputation can best be established by asking for a list of references and following through by contacting each one. In addition, the state environmental agency should be questioned concerning any reportable accidents that the transporter may have had or any notices of violation he may have received. Hazardous waste management facilities (HWMF) may also be able to comment on the reputation of certain transporters.

Transportation of hazardous waste is expensive. This is the result of a combination of factors including specialized equipment needs, worker training, licensing costs, and insurance and bonding requirements. Also, hazardous waste transportation is somewhat of a seller's market as many smaller firms are being eliminated by their inability to meet substantial financial responsibility regulations imposed by state government. Nevertheless there is some competition and the generator should solicit competitive bids after he has prequalified transporters to his satisfaction.

There are several sources the generator may use to develop a list of hazardous waste transporters. Published listings of hazardous waste management firms, such as that published by Environmental Information Ltd., list such firms for each state. State environmental agencies and the regional EPA offices may be accessed for lists of licensees and firms that have been issued EPA trans-

porter identification numbers. Another source is metal finishing and chemical industry trade journals where firms in the hazardous waste handling business frequently advertise. The solid/hazardous waste industry also has trade publications which list such firms. Finally, consulting engineering firms are able to work with the generator to provide possible transporters and to assure that the transporter meets the generator's specific needs.

Selection Criteria for HWMFs

The hazardous waste generator is faced not only with arranging for safe transportation but also for the proper ultimate disposal of the waste. Selection of a hazardous waste management facility (HWMF) is similar in many ways to selection of a transporter, but longer term consequences must be considered. The generator must be satisfied that the waste will remain secure indefinitely. Consequently, the viability of the HWMF as a business and its ability to maintain proper operational supervision over the long term is very important.

The RCRA permitting regulations provide much more stringent coverage for HWMFs than for transporters. Therefore, the permitting process offers a fairly high degree of assurance as to the suitability of the HWMF. All hazardous waste treatment storage or disposal facilities must carry an RCRA permit. This permit is issued by the EPA, or through state environmental agencies where the authority has been delegated by EPA. Thus the first logical place to look when developing a list of potential HWMFs is the state environmental agency and/or regional EPA office where lists of permitted facilities should be available.

The fact that an HWMF holds an RCRA permit may not be an absolute guarantee against future problems, but it does indicate certain standards set forth in the regulations have been met. The permit covers design, operation, and closure of the facility. The generator should look carefully at all three when considering a facility.

The HWMF must be designed and constructed to equal or exceed numerous criteria. For example, a secure landfill must be sited in a proper geological setting such that it is adequately isolated from an underlying aquifer. This usually means at least 20 feet of low permeability clay must be in place under the landfill. The secure landfill must be lined with an impervious liner and be equipped with a leak detection system. A leachate collection and treatment system must be in place. Groundwater monitoring wells must be installed around the landfill perimeter. The landfill must provide separated

areas with positive barriers or different types of wastes. Gas venting and control to prevent off-site migration is also required. In the case of incinerators, combustion efficiency and trial burning procedures are definitely established.

The HWMF permit also stipulates certain management and operational practices. Testing and complete analysis of all waste material entering the facility is required. Waste handling, appropriate segregation, and worker health and safety practices are prescribed. Extensive recordkeeping is required including filing copies of all manifests. A record of where wastes were placed in a landfill and when they were placed must be maintained so that such wastes could be accessed in the future if necessary. Contingency plans to cover emergency response and remediation of problems must be prepared and kept readily available. Finally, ongoing ground water monitoring, at least on a quarterly basis, is required.

A third aspect of the HWMF permit that is quite important from the perspective of the generator's long term security is the closure/postclosure plan. If the HWMF facility is a secure landfill, it will have a finite life. It is important at the termination of that life, that it be properly closed to preclude the possibility of long term environmental impairment. This means at least the placement of a proper RCRA approved cover, surface drainage, revegetation, slope stability, leachate treatment, and ground water monitoring. Financial responsibility for postclosure coverage must be established.

Special Considerations

With respect to the metals finishing industries, there are some special considerations in choosing an HWMF. Liquids are banned from landfill disposal. Since many metal finishing wastes are liquid they must be solidified before they may be disposed of in a landfill. There are various fixation and cementation processes that will solidify liquid wastes and immobilize the inorganic constituents such as the heavy metals. In some cases the solidified material is sufficiently inert that it may qualify for delisting, a formal procedure under which the material is removed from the hazardous waste listing by EPA. The material may then be disposed of in any permitted municipal landfill. Some hazardous waste processors have obtained a generic delisting whereby they process hazardous liquid wastes from numerous generators and produce a solid product which may be disposed of at a conventional landfill. If presented with this option the generator is advised to evaluate it as any other HWMF, that is, with diligence. The processor's operation, phys-

ical plant, records, and history should be carefully examined. Results of laboratory tests of the solidified product using the generator's actual waste material should be examined.

Candidate HWMFs should be evaluated on the basis of physical facilities, operation, reputation, geographical location, and cost. If possible the generator should visit the facility to investigate the design and operational considerations cited above and to review facility records. The reputation of the HWMF, and especially any past violations of Federal or state regulations, should be checked. Geographical location is not the overriding factor but it is important. A nearby facility reduces the transportation costs and decreases the possibility for problems such as an accidental release occurring in transit. Finally, cost must be considered. Once candidate sites have been "prequalified" to the generator's or his consultant's satisfaction, the least cost alternative is selected. Transportation and disposal cost must be looked at together since it may be advantageous to pay a higher HWMF fee to dispose closer to home. The generator should bear in mind that basing the selection solely on cost is risky since a short term saving in disposal fees could result in a long term environmental impairment liability of much greater magnitude.

Summary

In conclusion, it is appropriate to reiterate that Federal and state laws place the responsibility for safe disposal of hazardous wastes squarely on the generator. As a first step the generator is well advised to do everything feasible to minimize the amount of waste produced. Raw material substitutions, process modifications, reclamation and recycle should be employed to the extent practicable. When faced then with selection of a hazardous waste transporter and HWMF, the evaluation should be thorough and should be conducted by properly qualified professionals. Representations should not be taken at face value, but rather first-hand investigation should be performed at every opportunity. The generator must proceed with the understanding that the risk inherent in the disposal of his waste material is his and cannot be transferred. After implementing waste minimization the best way he can reduce and manage that risk is through proper screening and selection of all parties involved in handling and disposing of his hazardous wastes.

8. The Costs and Benefits of Source Reduction in Metal Finishing

Introduction

It is not currently feasible to achieve a zero discharge of chemical pollutants from metal finishing operations. However, substantial reductions in the type and volume of hazardous chemicals wasted from most metal finishing operations are possible. Because end-of-pipe waste detoxification is costly for small- and medium-sized metal finishers, and the cost and liability of residuals disposal have increased for all metal finishers, management and production personnel may be more willing to consider production process modifications to reduce the amount of chemicals lost to waste.

This chapter provides guidance for reducing waterborne wastes from metal finishing operations in order to avoid or reduce the need for waste detoxification and the subsequent off-site disposal of detoxification residuals. Waste reduction practices may take the form of:

- Chemical substitution.
- Waste segregation.
- Process modifications to reduce drag-out loss.
- Capture/concentration techniques.

Each is discussed below.

Chemical Substitution

The incentive for substituting process chemicals containing nonpolluting materials has only been present in recent years with the advent of pollution control regulations. Chemical manufacturers are gradually introducing such substitutes. By eliminating polluting process materials such as hexavalent chromium and cyanide-bearing cleaners, and deoxidizers, the treatments required to detoxify these wastes are also eliminated. It is particularly desirable to eliminate processes employing hexavalent chromium and cyanide, since special equipment is needed to detoxify both.

Substituting nonpolluting cleaners for cyanide cleaners can avoid cyanide treatment entirely. For a 2 gal/min rinsewater flow, this means a savings of about \$12,000 in equipment costs and \$3.00/lb of cyanide treatment chemical costs. In this case, treatment chemical costs are about four times the cost of the raw sodium cyanide cleaner.

There can be disadvantages in using nonpolluting chemicals. Before making a decision the following questions should be asked of the chemical supplier:

- Are substitutes available and practical?

- Will substitution solve one problem but create another?
- Will tighter chemical controls be required of the bath?
- Will product quality and/or production rate be affected?
- Will the change involve any cost increases or decreases?

Based on a survey of chemical suppliers and electroplaters who use nonpolluting chemicals, some commonly used chemical substitutes are summarized in Table 8.1.

Table 8.1 Chemical Substitutes

Polluting	Substitute	Comments
Fire Dip (NaCN)	Muriatic Acid with additives	Slower acting than + H ₂ O ₂ traditional fire dip.
Heavy Copper Cyanide Plating Bath	Copper Sulfate	Excellent throwing power with a bright, smooth, rapid finish. A copper cyanide strike may still be necessary for steel, zinc, or tin-lead base metals. Requires good pre-plate cleaning. Noncyanide process eliminates carbonate build-up in tanks.
Chromic Acid Pickles, Deoxidizers, & Bright Dips	Sulfuric Acid and Hydrogen Peroxide	Nonchrome substitute. Nonfuming.
Chrome Based Anti-Tarnish	Benzotriazole (0.1-1.0% solution in methanol) or water-based proprietaries	Nonchrome substitute. Extremely reactive, requires ventilation.
Cyanide Cleaner	Trisodium-Phosphate or Ammonia	Noncyanide cleaner. Good degreasing when hot and in an ultrasonic bath. Highly basic. May complex with soluble metals if used as an intermediate rinse between plating baths where metal ion may be dragged into the cleaner and cause wastewater treatment problems.
Tin Cyanide	Acid Tin Chloride.	Works faster and better

The chemical supplier can also identify any regulated pollutants in the facility's treatment chemicals and offer available substitutes. The federally regulated pollutants are cyanide, chrome, copper, nickel, zinc, lead, cadmium, and silver. Local and/or state authorities may regulate other substances, such as tin, ammonia, and phosphate.

Waste Segregation

After eliminating as many pollutants as possible, polluting streams should be segregated from nonpolluting streams. Nonpolluting streams can go directly to the sewer, although pH adjustment may be necessary. The segregation process will likely require some physical re-layout and/or repiping of the shop. These potentially nonpolluting rinse streams represent about one-third of all plating process water. Caution must be exercised to make certain that so-called nonpolluting baths contain no dissolved metal. The cost savings in segregating polluting from nonpolluting streams is realized through wastewater treatment equipment and operating costs. The remaining polluting sources which require some form of control include all dumped spent solutions, including tumble finishing and burnishing washes, cyanide cleaner rinses, plating rinses, rinses after "bright dips," and aggressive cleaning solutions.

Process Modifications to Reduce Drag-Out Loss

Plating solution which is wasted by being carried over into the rinsewater as a workpiece emerges from the plating bath is defined as drag-out, and is the largest volume source of chemical pollutant in the electroplating shop. Numerous techniques have been developed to control drag-out; the effectiveness of each method varies as a function of the plating process, operator cooperation, racking, barrel design, transfer dwell time, and plated part configuration.

Wetting agents and longer workpiece withdrawal/drainage times are two techniques which significantly control drag-out. These and other techniques are discussed below.

Wetting Agents

Wetting agents lower the surface tension of process baths. To remove plating solution dragged out with the plated part, gravity-induced drainage must overcome the adhesive force between the solution and the metal surface. The drainage time required for racked parts is a

function of the surface tension of the solution, part configuration, and orientation. Lowering the surface tension reduces the drainage time and also minimizes the edge effect (the bead of liquid adhering to the part edge); thus there is less drag-out. Plating baths such as nickel and heavy copper cyanide also use wetting agents to maintain grain quality and provide improved coverage. The chemical supplier should be asked if the baths he supplies contain wetting agents and, if not, whether wetting agents can be added. In some baths the use of wetting agents has the potential to reduce drag-out by 50 percent.

Longer Drain Times

With slower withdrawal rates and/or longer drain times, drag-out of process solutions can be reduced by up to 50 percent. Where high-temperature plating solutions are used, slow withdrawal of the rack may also be necessary to prevent evaporative "freezing," which can actually increase drag-out. In the extreme case, too rapid a withdrawal rate causes "sheeting," where huge volumes of drag-out are lost to waste. Figure 8.1 shows the drain-

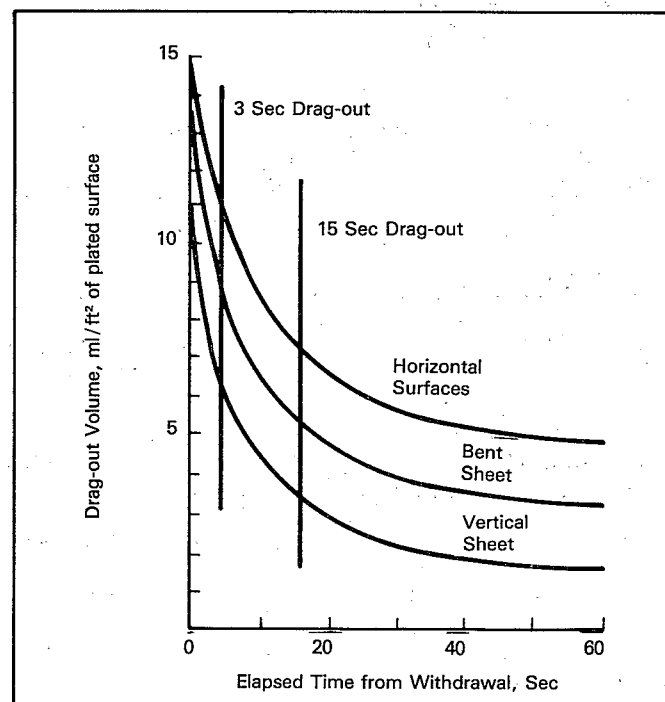


Figure 8.1. Typical drag-out drainage rates (from Beckman Rinse Tank Control Handbook).

age rates for plain and bent-shaped pieces. Drainage for all shapes is almost complete within 15 seconds after withdrawal, indicating that this is an optimum drain time for most pieces.

One of the best ways to control drag-out loss from rack plating on hand lines is to provide drain bars over the tank from which the rack can be hung to drain for a brief period. Hanging and removing the racks from the drain bars ensures an adequate drain time. Slightly jostling the racks helps shake off adhering solution.

In barrel plating, the barrel should be rotated for a time just above the plating tank in order to reduce the volume of dragged-out chemical. Holes in the barrels should be as large as possible to improve solution drainage while still containing the pieces. A fog spray directed at the barrel or its contents can also help drag-out drainage. Deionized water is recommended to minimize bath contamination.

The combined application of wetting agents and longer withdrawal/drainage times can significantly reduce the amount of drag-out for many cleaning or plating processes. For example, a typical nickel drag-out can be reduced from 1 liter per hour to ¼ liter per hour by these techniques.

Other Drag-Out Reduction Techniques

Rinse Elimination. The rinse between a soak cleaner and an electrocleaner may be eliminated if the two baths are compatible.

Low Concentration Plating Solutions reduce the total mass of chemicals being dragged-out. The mass of chemicals removed from a bath is a function of the solution concentration and the volume of solution carried from the bath. Traditionally, the bath concentration is maintained at a midpoint within a range of operating conditions. With the high cost of replacement, treatment, and disposal of dragged-out chemicals, the economics of low concentration baths are favorable.

As an illustration, a typical nickel plating operation with five nickel tanks has an annual nickel drag-out of about 2,500 gallons. Assuming the nickel baths are maintained at the midpoint operating concentration, as shown in Table 8.2, the annual cost of chemical replacement, treatment, and disposal are about \$13,500. If the bath is converted to the modified operating condition as shown in the table, the annual cost of chemical replacement, treatment, and disposal are approximately \$12,200, a savings of about \$1,300 per year. Generally, any percent de-

Table 8.2. Standard Nickel Solution Concentration Limits

Chemical	Concentration Range (oz/gal)	Midpoint Operating Condition (oz/gal)	Modified Operating Condition (oz/gal)
Nickel Sulfate			
NiSO ₄ ·6H ₂ O	40-50	45	41
As NiSO ₄	-	26.5	24.2
Nickel Chloride			
NiCl ₂ ·6H ₂ O	8-12	10	8.5
As NiCl ₂	-	5.5	4.6
Boric Acid (H ₃ BO ₃)	6-6.5	6.25	6.1

crease in bath chemical concentration results in the same percent reduction in the mass of chemicals lost in the drag-out. The disadvantage of low concentration baths may be lowered plating efficiencies, which may require higher current densities and closer process control. The reduction in plating chemical replacement, treatment, and disposal costs could be partially offset by the added labor and power costs associated with the use of the lower concentration baths.

Clean Plating Baths. Contaminated plating baths, for example carbonate buildup in cyanide baths, can increase drag-out as much as 50 percent by increasing the viscosity of the bath. Excessive impurities also make the application of recovery technology difficult, if not impossible.

Low Viscosity Conducting Salts. Bath viscosity indexes are available from chemical suppliers. As the bath viscosity increases, drag-out volume also increases.

High Temperature Baths reduce surface tension and viscosity, thus decreasing drag-out volume. Disadvantages to be considered are more rapid solution decomposition, higher energy consumption, and possible dry-on pattern on the workpiece.

No Unnecessary Components. Additional bath components (chemicals) tend to increase both viscosity and drag-out.

Fog Sprays or Air Knives may be used over the bath to remove drag-out from pieces as they are withdrawn. The spray of deionized water or air removes plating solution from the part and returns as much as 75 percent of the drag-out back to the plating tank. Fog sprays, located just above the plating bath surface, dilute and drain the adhering drag-out solution, thus reducing the concentration and mass of chemicals lost. Fog sprays are best when tank evaporation rates are sufficient to accommo-

date the added volume of spray water. Air knives, also located just above the plating bath surface, reduce the volume of drag-out by mechanically scouring the adhering liquid from the workpiece. The drag-out concentration remains constant, but the mass of chemicals lost is reduced. Air knives are best when the surface evaporation rates of the bath are too low to allow additional spray water. In some cases, use of supplementary atmospheric evaporators may be justified by economic considerations.

Air knives can be installed for about \$500 per bath if an oil-free, compressed air source is available. Fog sprays can be installed for about \$500 per bath if a deionized water source is available. The spray should be actuated only when work is in the spraying position. Properly designed spray nozzles distribute the water evenly over the work, control the volume of water used, and avoid snagging workpieces as they are withdrawn from the tank.

Proper Racking. Every piece has at least one racking position in which drag-out will be at a minimum. In general, to minimize drag-out:

- Parts should be racked with major surfaces vertically oriented.
- Parts should not be racked directly over one another.
- Parts should be oriented so that the smallest surface area of the piece leaves the bath surface last.

The optimum orientation will provide faster drainage and less drag-out per piece. However, in some cases this may reduce the number of pieces on a rack, or the optimum draining configuration may not be the optimum plating configuration. In addition, the user should maintain rack coatings, replace rack contacts when broken, strip racks before plating buildup becomes excessive, and ensure that all holes on racks are covered or filled.

Capture/Concentration with Full Reuse of Drag-Out. The pioneer in simple, low-cost methods of reducing waste in the plating shop was Dr. Joseph B. Kushner. In *Water and Waste Control for the Plating Shop* (1972), he describes a "simple waste recovery system" which captures drag-out in a static tank or tanks for return to the plating bath. The drag-out tanks are followed by a rinse tank which flows to the sewer with only trace amounts of polluting salts and is often in compliance with sewer discharge standards. A simplified diagram of this reuse system is shown in Figure 8.2. It is not difficult to automate the direct drag-out recovery process and commercial units are available.

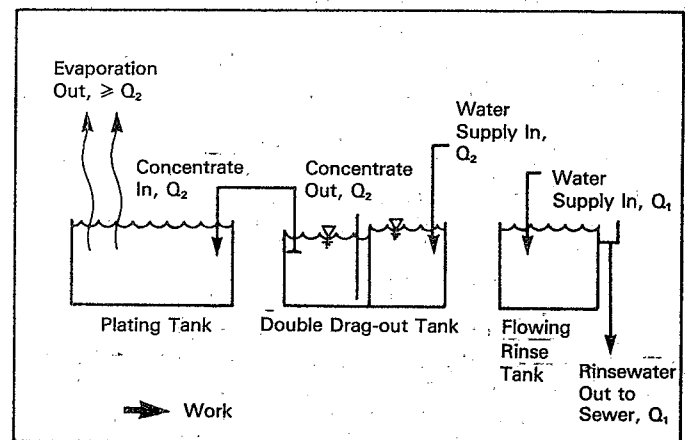


Figure 8.2. Kushner method of double drag-out for full reuse.

The Kushner concept is easily applicable to hot plating baths where the bath evaporation rate equals or exceeds the pour-back rate, Q_2 . The drag-out concentration depends on the bath drag-out rate, the number of drag-out tanks, the rinsewater flow rate, Q_2 , the plating bath evaporation rate, and drag-out return rate. The number of drag-out tanks must be based on the available space. The higher the number of counterflowed drag-out tanks, the smaller will be the return rate necessary to obtain good rinsing. The Kushner multiple drag-outs are not feasible if there is no room for the required drag-out tanks. If there is little or no evaporation from the bath, supplementary evaporation should be considered. Bath contamination must be minimized by using purified (1X or RO) water for Q_2 .

Capture/Concentration with Partial Reuse of Drag-Out. By adding a trickling water supply and drain, Q_3 , to the drag-out tank, the application of Kushner's concept can be extended to other metal finishing processes which may not be amenable to full reuse but can allow partial reuse. Figure 8.3 depicts the partial reuse scheme. The trickle concentrate can also be batch treated in a small volume on-site, recycled at a central facility, or mixed with Q_1 , for discharge, if the combined metal content is below sewer discharge standards.

Waste Reduction Costs and Benefits

Benefits of waste reduction in the metal finishing shop include:

- Reduced chemical cost.

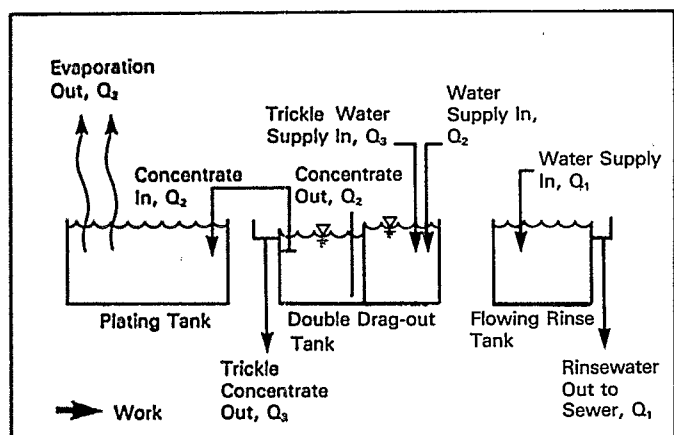


Figure 8.3. Modified method of double drag-out for partial reuse.

- Reduced water cost.
- Reduced volume of "hazardous" residuals.
- Reduced pretreatment cost.

The benefits of saving valuable chemicals and water and reducing sludge disposal costs can best be illustrated by an example. An electroplating operation discharges 26,000 gal/d of wastewater containing 2 pounds of copper, 2.5 pounds of nickel, and 2 pounds of cyanide. The shop can reduce its generation of cyanide and copper waste by about 50 percent by eliminating cyanide cleaners and utilizing pour-back of copper cyanide solution; generation of nickel waste can be reduced 90 percent by pour-back of the nickel solution. Reducing wasted salts also allows a reduced rinsewater flow rate, thus saving water and sewer use fees. Annual dollar savings are shown in Table 8.3.

Table 8.3. Illustration of Cost Savings for Waste Reduction

Process chemical savings ¹	
Copper	\$ 1,250
Cyanide	250
Nickel	4,000
Treatment chemical savings ²	
Copper	160
Cyanide	1,030
Nickel	360
Reduced treatment sludge disposal ²	
Copper	390
Cyanide	0
Nickel	880
Water and sewer use fee reduction ³	
	2,250
Total annual savings	\$10,570

¹From Figure 8.4

²From Table 8.4 and Figure 8.4

³\$1.50/1,000 gal

Table 8.4. Chemical Costs of Treatment and Disposal (1980 Prices)

Pollutant	Chemical Cost (\$/lb)	
	Treatment ¹	Disposal ²
Nickel	0.64	1.57
Copper	0.64	1.57
Cyanide	4.13	NA

¹Cost of NaOH @ \$0.235/lb and NaOCl @ \$0.55/lb

²Cost of disposal @ \$0.43/lb of sludge (\$200/drum) @ 30% solids content

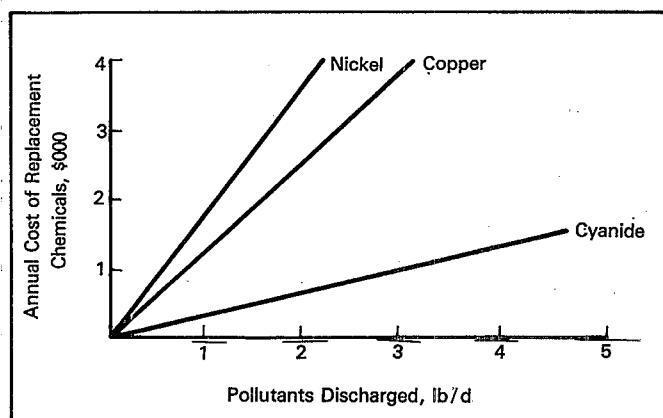


Figure 8.4. Annual replacement cost of chemicals (1980 prices).

9. Materials Reuse and Recovery

What Is Reuse/Recycling?

Direct reuse involves the reuse of a waste material without processing either as a feedstock in a production process or as a substitute for a commercial product. Reclamation or recovery removes impurities and recovers raw materials or by-products.

Recycling is related to the RCRA definition of solid waste (40 CFR 261.2 (e)), i.e., materials are not RCRA solid wastes when they can be shown to be recycled by being:

- Used or reused in an industrial process to make a product, if the materials are not being reclaimed.
- Effective substitutes for commercial products.
- Returned to the original process from which they were generated without first being reclaimed.

Waste streams must be physically and economically amenable to recycling. Examples of waste streams generated by the metal finishing industry not physically amenable to recycling include:

- F006—Wastewater treatment sludges from electroplating operations.
- F008—Plating bath residues from the bottom of plating baths in electroplating operations where cyanides are used in the process.

Examples of waste streams generated by the metal finishing industry currently considered not economically amenable to recycling include:

- F007—Spent cyanide plating bath solutions from electroplating operations.
- F009—Spent stripping and cleaning bath solutions from electroplating operations where cyanides are used in the process.
- F019—Wastewater treatment sludges from chemical conversion coating of aluminum.

Waste stream-specific factors also determine the feasibility of recycling and fall into two basic categories:

- (1) Uniformity.
 - Mixed wastes are difficult and costly to recycle.
 - Segregation of wastes at the plant site is an advantage.
- (2) Constituent concentrations.
 - High concentrations of known constituents increase the probability of recycling as a waste management option.

Technologies used for reclaiming are dictated by the type of waste and nature of contamination, and fall into two basic categories:

- (1) Physical separation makes use of differences in physical properties.
 - Density and particle size (filtration, settling, flocculation).
 - Boiling point (evaporation).
 - Freezing point (crystallization).
 - Solubility (solvent extraction).
- (2) Chemical separation makes use of chemical reactions to effect removal of certain chemical constituents.
 - Precipitation.
 - Oxidation-reduction.
 - Ion exchange.
 - Electrolytic recovery (electrochemical reactions).

Wastes Produced in Metal Finishing Operations

Primary wastes are derived mainly from two sources:

- (1) Dumping of process baths and related materials (cleaners, activators, etc.).
- (2) Rinse waters used to wash off process solutions on product surface or trapped in the crevices due to the shape of the product piece.

Primary wastes and process sources are listed in Table 9.1.

A summary of raw waste data for a metal finishing operation (printed circuit board manufacturer) is shown in Table 9.2.

Incentives for Recycle/Reuse

Case A

A plant with an existing, adequate waste treatment system should evaluate a given recycle/reuse technology. Savings are based on the purchase of chemical raw materials, associated waste treatment chemicals, and sludge handling and disposal costs. If a reasonable pay-back period on the recycle technology investment (three years or less) is available based on these savings, then the new system should be installed.

Case B

A new plant, or one with an inadequate treatment system, may present a viable economic situation for a new recycle/reuse system. In this case an additional economic benefit is available in not spending money for unnecessary waste treatment capacity.

Case C

Minimizing or eliminating generation of sludge. Justification for recycle/reuse system is supported by possible

Table 9.1. Metal Surface Finishing Wastes

Waste Description	Process Origin	Composition	RCRA Code
Spent Bath Solution	Dumping of the process solutions after depletion or loss of activity.	Cyanides, cyanide complexes, hexavalent chrome, copper, nickel, zinc, cadmium, and other metals and their salts in water.	F007
Waste Rinse Water	Rinsing treated objects, equipment cleaning, quenching of case hardened steel.	Same as spent bath solution.	F007
Filter Waste	Filtration of process solution, spent baths, and treated waste rinse water.	Metal hydroxide sludges, used filter cartridges.	F006
Spills and Leaks	Overflows and leaks from various process equipment.	Same as spent bath solution.	F007
Stripping Waste	Removal of coatings from improperly treated objects.	Cyanides, other materials.	F009

elimination of hazardous waste residuals and therefore minimizing long-term liability. A definitive economic analysis is difficult in this case.

Areas of Metal Finishing Operations Where Reuse/Recovery Technologies are of Interest:

- Recycling concentrates to process baths through rinse tanks (most recovery schemes focus on this area because of dragout to rinse waters).
- Nonrecycle recovery of metals or concentrates (decoupling of recovery process from basic finishing process).
- Selling by-product sludges.
- Regenerating process baths.
- Recycling treated wastewaters.

Some Reuse and Recovery Technologies

More Commonly Used in Metal Finishing Industry

- Electrolytic Recovery
- Evaporation
- Ion Exchange
- Reverse Osmosis

Less Commonly Used in Metal Finishing Industry

- Carbon Adsorption
- Crystallization
- Electrodialysis

Electrolytic Recovery

This is a technology that uses special electroplating equipment to lower the concentration of dissolved metals in discarded process baths and rinse waters. Benefits of this technology are:

- There is no metal sludge after downstream wastewater treatment.
- The process destroys cyanide via oxidation.
- The process permits recovery of usable metals.
- The process permits regeneration of ammoniacal or chloride etch solutions during metal recovery.

There are three variations of electrolytic recovery in use in the metal finishing industry:

- (1) Methods primarily for removing metals from re-

Table 9.2. Summary of Raw Waste Data - Printed Circuit Board Manufacturing

Constituent	Range (mg/l)
Total Suspended Solids	0.998-408.7
Cyanide, Total	0.002-5.3
Cyanide, Free	0.005-4.6
Copper	1.582-535.7
Nickel	0.027-8.4
Lead	0.044-9.7
Chromium, Hexavalent	0.004-3.5
Chromium, Total	0.005-38.5
Fluorides	0.648-680.0
Phosphorus	0.075-33.8
Silver	0.036-0.2
Palladium	0.008-0.10
Gold	0.007-0.19

covery rinse with minimal resulting by-product value.

- (2) Recovery of metals on high-surface area substrate with good potential for metal by-product recovery.
- (3) Electrowinning produces sheets/slabs of high purity metals with high market value.

Schematics of these three process variations are shown in Figures 9.1, 9.2, and 9.3.

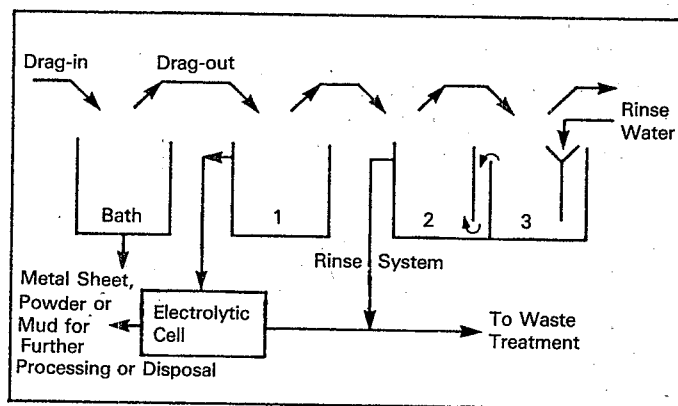


Figure 9.1. Electrolytic metal recovery — general purpose extractive cell (from Lancy International, 1986).

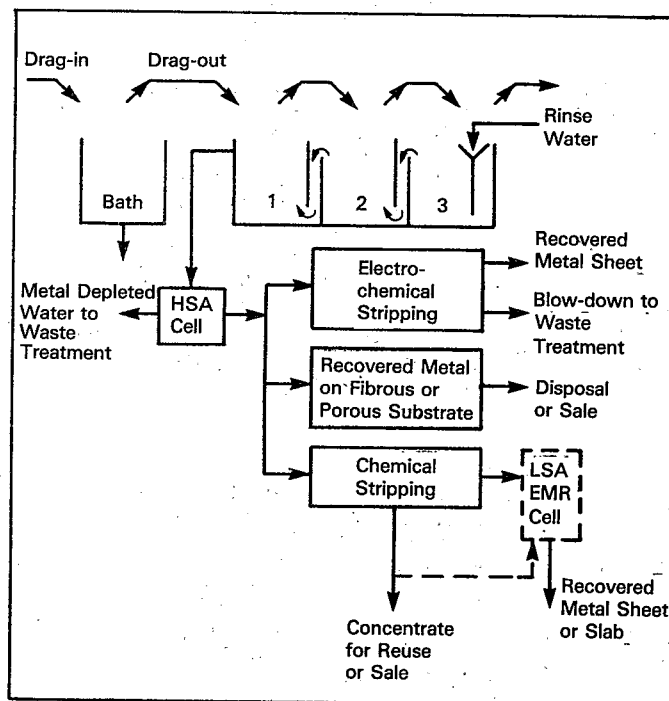


Figure 9.2. Electrolytic metal recovery — high surface area cell (from Lancy International, 1986).

Applications in the Metal Finishing Industry

Small electrolytic units for gold and silver recovery from dragout rinse water have been on the market for a number of years. Only recently have these units been used for copper, cadmium, and zinc dragout rinse water (from cyanide baths) for base metal recovery.

New applications for this type of unit are for use on dragout rinse water from acid copper, platinum, and zinc by substituting a platinized titanium cathode for the stainless steel cathode normally provided with the unit. The metal clad titanium cathode may be subsequently used as an anode in the electroplating process.

A commercially available unit with a 550 gph rating is claimed to be capable of recovering gold, silver, cadmium, tin, lead, zinc, and copper from cyanide bath rinse waters. Metal recovery efficiencies are claimed to be in the 99+ percent range. The units cost approximately \$2,000 each. These units are claimed to be easy to work with, reasonable in cost, easy to maintain, and compact and economical to operate for small job shops.

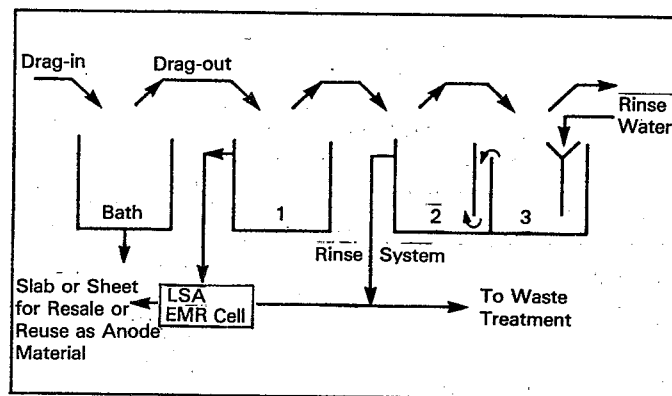


Figure 9.3. Electrolytic metal recovery — low surface area cell (from Lancy International, 1986).

Another electrolytic unit is described by the vendor as follows:

- Electrolytic recovery unit in operation over one year processes 350 gal batches of spent plating baths.

- Unit requires floor space of 36 inches by 20 inches.
- Has 15 to 20 square feet of area for metal recovery and 50 or more square feet of area when used for cyanide destruction.
- Unit costs about \$6,000.
- Stainless steel anode is used in recovering cadmium and zinc from spent cyanide baths.
- Platinized titanium anode is used for acid baths.
- Unit operates on 110 V; minimal electrical operating cost.
- Typical cycle of three weeks treatment on 17 oz/gal cyanide bath containing 6 oz/gal of cadmium metal; achieves 2 ppm residual cyanide suitable for discharge to local POTW.

Evaporation

Evaporation involves the vaporization of liquid from a solution, slurry, or sludge using an energy source. It can also take place without an energy source under the right set of conditions. Evaporation is a practical process if one component is minimally volatile (i.e., in electroplating, evaporating water concentrates the nonvolatile metal salts). Evaporation is applicable for dragout recovery from nickel, chromium, zinc, and cadmium plating.

Small atmospheric and vacuum evaporators are available for use in plating shops. Atmospheric evaporation application involves removal of excess water from counterflow rinse water before returning drag-out to the plating tank. The heat for the evaporation process can be recovered from the plating bath when atmospheric evaporators are used to increase evaporative losses from the bath. Partial recovery (with lower evaporation rates) results in reduced heat energy cost and slower accumulation of rinse water impurities in plating tank. If all the water needed for good rinsing can be evaporated, then the system can be a "closed loop" with no water or dragout going to the drain (as high as 90-99 percent recovery is possible with evaporation).

A schematic of the atmospheric evaporation process adapted to plating operations is shown in Figure 9.4.

Evaporation Processes:

Single Effect Unit:

A single effect unit usually uses steam to heat the liquid to its boiling temperature. The steam is passed through a steam coil or jacket, and the vapors produced by the boiling liquid are drawn off and condensed. The concen-

trated liquid is then pumped from the bottom of the vessel. The process requires energy of about 1200 Btu/lb of water evaporated. The process is illustrated in Figure 9.5.

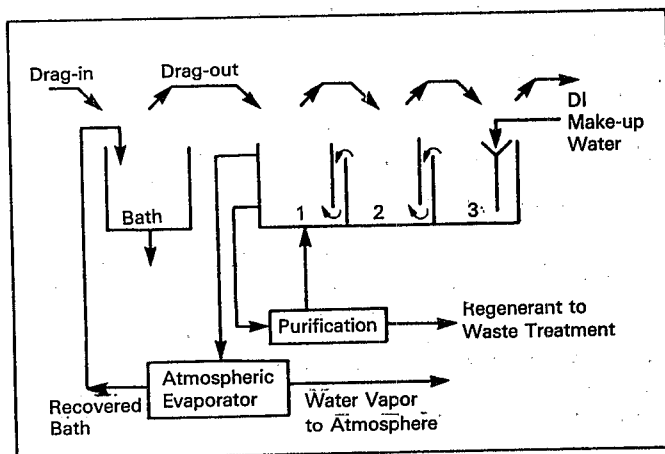


Figure 9.4. Atmospheric evaporation schematic (from Lancy International, 1986).

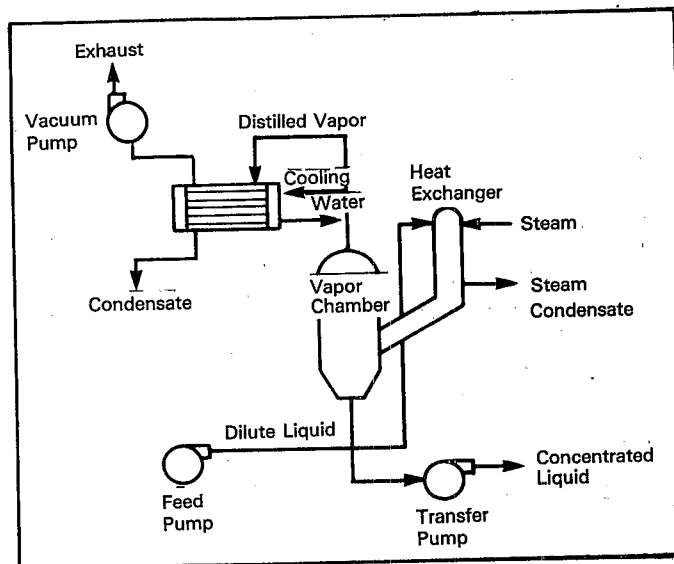


Figure 9.5. Typical single-effect evaporator — falling film type (from Metcalf and Eddy, 1985).

Multiple Effect Unit:

A multiple effect unit consists of a series of single-effect evaporators. Vapor from the first evaporator is used as the heat source to boil liquid in the second evaporator. Boiling is accomplished by operating the second evaporator at lower pressure than the first. The process can continue for several evaporators (effects). Depending on the number of effects, a multiple effect unit may require as little as 200 Btu/lb of water evaporated. The process is illustrated in Figure 9.6.

Vapor Recompression Evaporation:

The vapor recompression evaporation process uses steam to initially boil the liquid. The vapor produced is compressed to a higher pressure and temperature. The compressed vapor is then directed to the jacketed side of the evaporator instead of using more steam, and is thus used as a heat source to vaporize more liquid. The vapor recompression evaporation process requires as little as 40 Btu/lb of water evaporated. The process is illustrated in Figure 9.7.

Operating Parameters

Operating costs consist of electrical power for mechanical equipment on a unit (i.e., blower and pump) and heat

for evaporation. The heat needed for evaporation is 626 watts per liter or 2,371 watts per gallon.

It is necessary to minimize buildup of rinse water impurities. For example, if a high percentage of chrome dragout is returned, then Cr^{+3} must be removed (cation exchange) and rinse water purified by reverse osmosis, or deionization.

Metal Finishing Applications**Atmospheric evaporation:**

Auto bumper recycler—The process consists of two units used to recover bright nickel and hexavalent chromium dragout. The brightener consumption was reduced by 50 percent, and the chromic acid addition was reduced by 90 percent.

Cart maker—Process used one evaporation unit 24 hours per day, six days per week. Chromic acid additions were reduced by about 95 percent and the use of sodium metabisulfite for waste treatment was eliminated.

Vacuum evaporation:

Cadmium plater—The use of a cadmium cyanide plating system was able to continue with minimal use of a

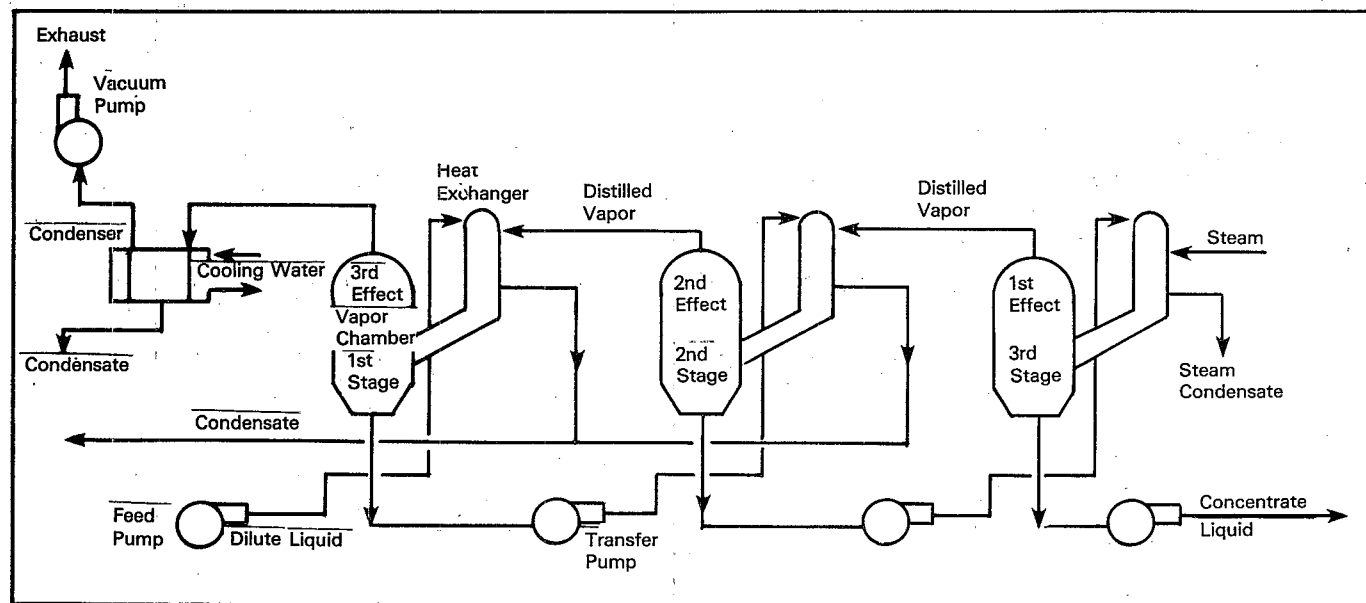


Figure 9.6: Typical multi-effect (triple effect) evaporator — falling film type (from Metcalf and Eddy, 1985).

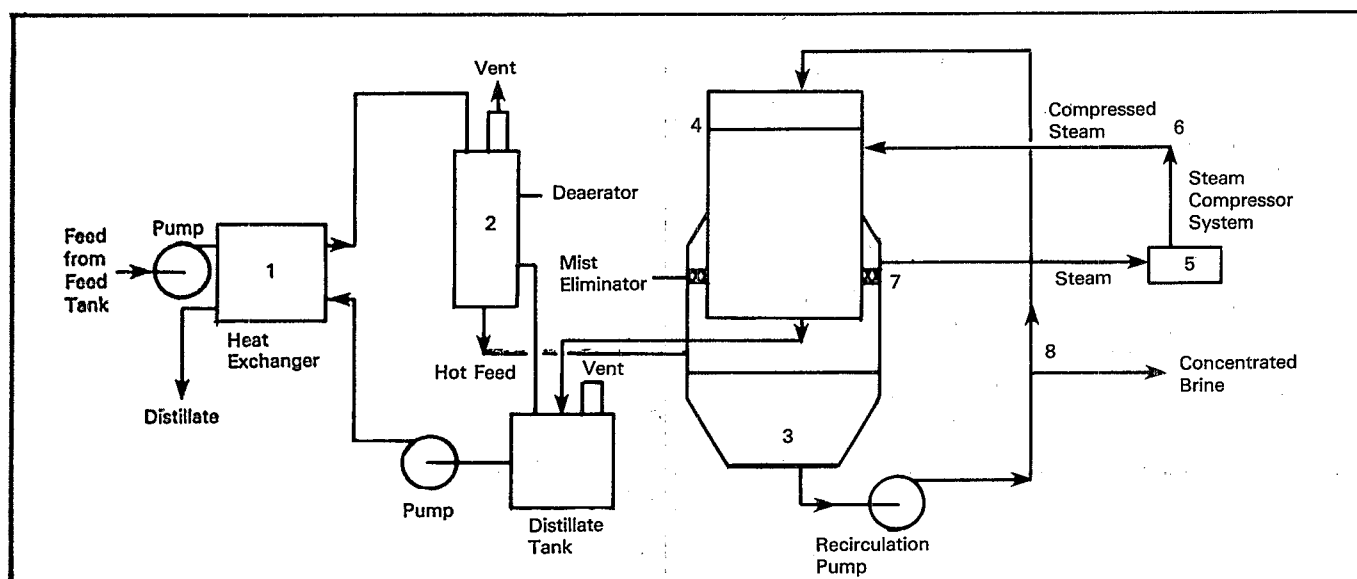


Figure 9.7: Vapor recompression application — brine concentration (from Resource Conservation Corporation, 1986).

cyanide destruct system. The anticipated payback is less than three years.

Vapor recompression:

Electronic industry metal finisher—Able to concentrate waste rinse water from electroplating copper foil. A 10-fold concentration was achieved and was used as a plating bath make up.

Advantages

Evaporation is an uncomplicated, rugged, reliable, and widely applicable process. In addition, it is comparatively maintenance-free.

Disadvantages

Disadvantages include relatively high energy consumption for older units. Newer designs use two stages or heat pumps to achieve higher efficiencies. In addition, the entire bath is recycled, including undesirable constituents, and the flow rates of rinse waters must be kept to a minimum to keep investment and energy costs down.

Ion Exchange

Ion exchange (IX) has been a useful process in the metal finishing industry for several decades. The most widespread application is the use of cation exchange resins to capture metal ions from a waste stream allowing their recycle or recovery. The process is one which reversibly exchanges ions in solution with ions retained on a reactive solid material called resin.

A typical IX system in metal finishing application has a fixed bed of resin with the ability to exchange or remove metallic cations or anions (chromate) from rinse waters. Unlike other metals recovery systems, IX is almost totally unaffected by dilution of the water being fed to the recovery unit. However, high concentrations should be avoided. An extremely high metal capture rate is typical, since metal discharge from the column can be less than 0.1 mg for a freshly regenerated column. Rinsing with relatively high flow rates can be used effectively when IX recovery of metals is utilized.

Schematics of the generic IX system for metals recycle and nonreturn to the plating bath are shown in Figures 9.8 and 9.9.

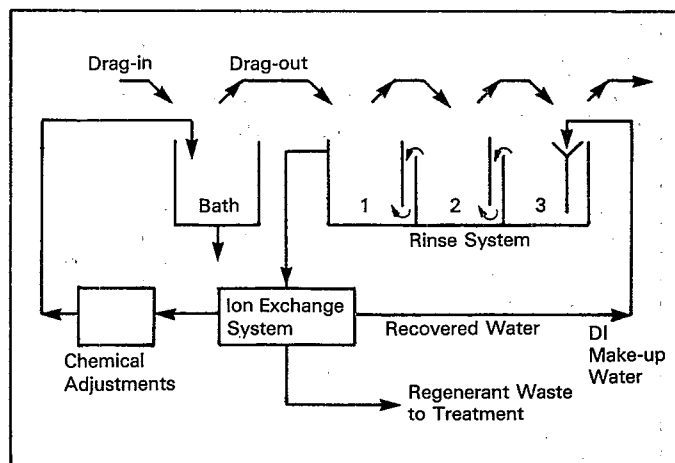


Figure 9.8. Ion exchange schematic — metals recycle (from Lancy International, 1986).

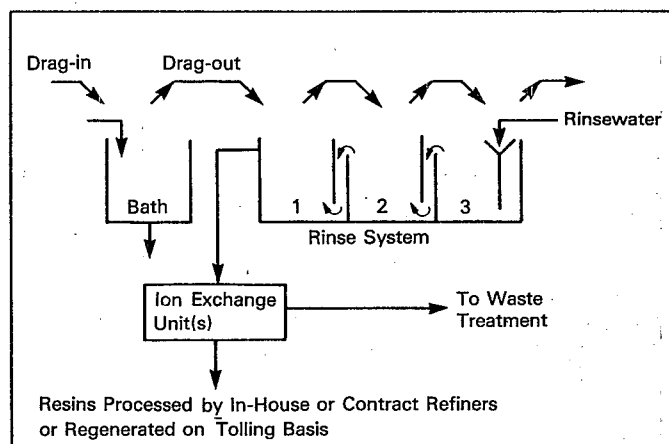


Figure 9.9. Ion exchange schematic — metals nonrecycle (from Lancy International, 1986).

Process Description

The IX resins used for metals (cations) recovery are typically copolymers consisting of styrene and divinylbenzene in a cationic form. The IX resins for anions (chromate) recovery are anionic form of styrene-divinylbenzene resin.

Generally, divalent and trivalent ions have higher affinity for ion exchange than monovalent ions, i.e., divalent

cadmium, nickel cations and divalent chromate and selenate anions are selectively removed by IX. When useful capacity of cation exchange resins is exhausted, they are regenerated with dilute acid solution. Metals from the waste stream are concentrated in spent regenerant.

A typical process schematic of a basic two step cation-/anion IX system including series treatment with separate cation and anion exchange systems is shown in Figure 9.10.

Process Hardware

Pressure vessels for IX typically range in size from two to six feet in diameter for prepackaged modular units (i.e., to handle 25 gpm to 300 gpm flow rates) on up to a maximum custom size of a 12 foot diameter (maximum of 1150 gpm flow rates). The vertical height of these vessels varies from six to 10 feet, providing adequate resin storage, distribution nozzle layout, and freeboard capacity for bed expansion during backwashing. The nominal surface loading of IX vessels typically ranges from 8 to 10 gpm/ft².

Steady progress has been made in developing rugged, reliable instruments for detection of the breakthrough of metal ions, but even the best may be too sophisticated for many metal finishing shops. (Reliable instrumentation is the key for producing high quality effluent for dis-

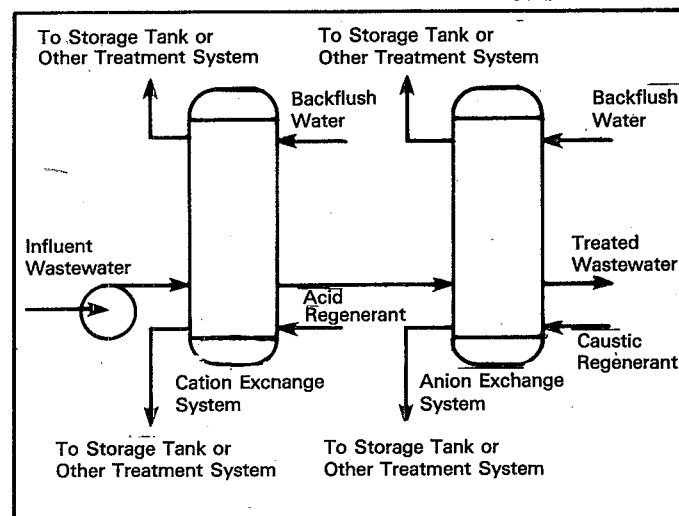


Figure 9.10. Schematic of ion exchange (from Metcalf and Eddy, 1985).

charge.) Close control of pH of feed to the IX unit is required, since lower pH tends to reduce capacity and performance, and slightly higher values cause metal precipitation and plugging of IX unit or its filter. Calcium ions may cause bed plugging when sulfuric acid is used for regeneration.

Metal Finishing Applications

Where IX is applicable for metal salt recovery, the optimum approach to its use in metal finishing is to recycle as much as possible and either sell, discard, or electrolytically recover that portion of the metal that cannot be recycled to the original process.

Case Histories

Case A—Recovery of copper, nickel and chromium at a small job shop in Montreal, Canada: IX recovery equipment consists of preassembled, skid-mounted automatic units. Results of the first 10 months of operation are summarized in Tables 9.3 through 9.7. Details of operating experience with the IX system are given in the April 1986 issue of *Plating and Surface Finishing* magazine.

Table 9.3. Performance of Recovery System Concentrations in mg/l

Item	CrO ₃	Ni	Cu
Bath	260,000	84,000	82,000
First Rinse	170	460	260
Third Rinse	10	17	6
Recovered Product	53,000	22,000	35,000
Unit Effluent	20	1.3	0.9
Effluent Flow (Avg.)	1.6 l/min	15 l/min	10 l/min

Table 9.4. Final Plant Effluent (mg/l)

Item	Actual	Limit
Cr	0.2	5
Ni	1.9	5
Cu	1.4	5
Cn	0.1	1
pH	6.8	6-8
Flow	—	33-45 l/min = 11.89 gal/min

Table 9.5. Economics of Chromic Acid Recovery

Item	Consumption	Unit Cost	Cost/kg, \$
Sulfuric Acid (93%)	2.8 kg	0.11/kg	0.31
Caustic Soda (50%)	4.3 kg	0.22/kg	0.95
Di Water	173 l	0.54/1000 l	0.09
Barium Carbonate	0.07 kg	0.88/kg	0.06*
Electricity	2 Kw-hr	0.05/Kw-hr	0.10
	Total		\$1.51/kg

*Wastewater treatment and disposal of the very toxic barium chromate could significantly increase cost shown.

Table 9.6. Economics of Nickel Sulfate Recovery

Item	Consumption	Unit Cost	Cost/kg, \$
Sulfuric Acid (93%)	0.69 kg	0.11/kg	0.07
Caustic Soda (50%)	1.06 kg	0.22/kg	0.23
Di Water	478 l	0.54/1000 l	0.26
Electricity	1 Kw-hr	0.05/Kw-hr	0.05
	Total		\$0.61/kg

Table 9.7. Economics of Copper Sulfate Recovery

	Consumption	Unit Cost	Cost/kg, \$
Sulfuric Acid (93%)	1.1 kg	0.11/kg	0.12
Caustic Soda (50%)	1.7 kg	0.22/kg	0.37
Di Water	981 l	0.54/1000 l	0.53
Electricity	1 Kw-hr	0.05/Kw-hr	0.05
	Total		\$1.07/kg

Advantages

Ion exchange is capable of extracting essentially all of the metal from a relatively dilute feed stream; therefore, it is the only usable recovery technology for certain applications. It can produce effluent suitable for discharge without further treatment. Regenerants and resin rinses must be treated. In addition, it has low capital and operating costs at a given loading rate (i.e., lb metal/hr and gallons per minute) compared to other recovery technologies. Costs increase, however, when regenerant chemicals and wastewater treatment are considered.

Disadvantages

Ion exchange is not capable of producing a highly concentrated stream for recycle (in actual practice, about 15-30 gm/l vs 50 gm/l ideally). It is difficult to select the proper split between recovered metal salts (stripped from IX resin) and excess regenerant acid (latter is undesirable in plating bath). In addition, waste containing excess regenerant must be handled.

Ion exchange is a chemically driven process (i.e., increases plant chemical consumption and quantity of salt in aqueous discharge). Sophisticated controls are required if IX resin capacity is not to be exceeded. Reliable instrumentation to readily detect metal breakthrough is both costly and expensive to maintain.

Reverse Osmosis

Reverse osmosis (RO) is the recovery process with the second longest history of operation in metal finishing

(after evaporation). RO is used to separate water from inorganic salts (metal salts). Pressure (typically 200 to 1200 psi) is used to force water from a solution through a semipermeable barrier (membrane) which will pass only certain components of a solution (permeate), but is impermeable to most dissolved solids (both inorganic and organic).

To prevent fouling of the RO membrane, feed solutions must be pretreated to remove oxidizing materials (including manganese, calcium, lead, and iron salts); to filter out particulates; to remove oil, grease and other film formers; and to destroy microorganisms. RO produces a concentrated stream for recycle to the plating bath (including all undesirable impurities). RO performs most efficiently on dilute rinses.

Test data on RO removal efficiencies for some metals are shown in Table 9.8. Schematic of RO use in plating bath recycle mode is shown in Figure 9.11.

Table 9.8. Laboratory Studies of RO Removal Efficiencies for Metals Used in Metal Finishing

Description of Study						
Metal	Study Type	Waste Type	Influent Concentration	Effluent Concentration ¹	Removal Efficiency	Membrane Type ²
Chromium	Batch	Pure compound	12.5 ppm	0.25-1.12	91-98%	C-PEI
			0.94 ppm	0.028	97%	CA
			8.65 ppm	0.06	93%	CA
			9.35 ppm	1.4	85%	CA
Copper	Batch	Pure compound	12.5 ppm	0.0125	99.9%	C-PEI
			0.7 ppm	0.035	95%	CA
			6.5 ppm	0.065	99%	CA
Lead	Batch	Pure compound	12.5 ppm	0	100%	C-PEI
			0.95 ppm	0.005	99.5%	CA
			9.3 ppm	0.205	97.8%	CA
Nickel	Batch	Pure compound	12.5 ppm	0.87	93%	C-PEI, pH 8
				0.25	98%	C-PEI, pH 11
Zinc	Batch	Pure compound	12.5 ppm	0.375	97%	C-PEI, pH 8
				0	100%	C-PEI, pH 11
			10.0 ppm	0.14	98.6%	CA
			32.8 ppm	0.16	99.5%	CA
Cadmium	Batch	Pure compound	0.10 ppm	0.001	90%	CA
			1.0 ppm	0.013	98.7%	CA
Chromic Acid	Lab, Continuous Flow	Industrial	200 ppm	30	85%	PB

¹Effluent concentration derived from influent concentration and removal efficiency.

²CA - cellulose acetate membrane; C-PEI - cross-linked polyamide membrane;

AP - aromatic polyamide membrane; PB - polybenzimidazole membrane.

Source: Metcalf and Eddy, 1985

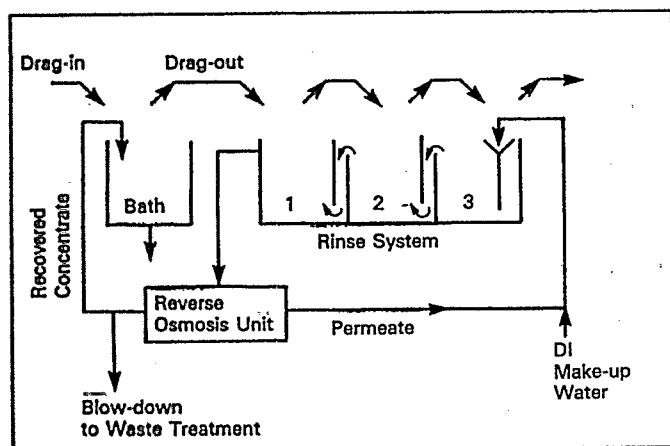


Figure 9.11. Reverse osmosis schematic — recycle mode (from Lancy International, 1986).

Process Technology

The basic components of an RO unit include:

- Membrane.
- Membrane support structure.
- Containing vessel.
- High pressure pump.

Reverse osmosis can be arranged either in parallel to provide adequate hydraulic capacity, or in series to effect the desired degree of removal. A wide range of flows can be accommodated depending on the number of modules used.

Membrane Technology

Commonly used membranes include tubular membranes, spiral-wound membranes, and hollow fiber membranes.

The tubular membrane consists of a membrane which is inserted onto or into the surface of a porous tube. This type of membrane is primarily used for low-volume operations.

Spiral-wound devices usually use the membrane as a flat film. Sheets of the flat membrane film are separated by a mesh spacer and are spiral wound to form a cartridge or module. A number of spiral tubes are usually connected together and inserted into a pressure vessel.

Hollow fiber membranes consist of millions of aramid or cellulose acetate fibers formed into the tube bundle or module. The hollow fiber device permits very large membrane areas per unit volume, making this the most compact device in terms of surface area.

Membrane materials include cellulose acetate, aromatic polyamides, and cross-linked polyamides. The three types of commercial membranes are shown in Figures 9.12, 9.13, and 9.14.

Metal Finishing Applications

The largest single application of reverse osmosis is in the recovery of nickel from nickel plating operations (99.5 percent of RO applications in plating shops).

Factors making RO attractive for nickel recovery include:

- Valuable metal and high volume use.
- Nickel plating baths are warm, allowing for evaporation, thus permitting recycle of RO concentrate.
- pH and chemical characteristics of nickel plating baths are favorable for RO use.

The installed cost for RO units in the plating industry ranges from \$25,000 to over \$100,000. Generally, paybacks have been in one to two years. Maintenance usually is not a problem, providing membranes are cleaned regularly.

Advantages

Reverse osmosis has a long-term operational history. It uses considerably less energy than evaporation for the same rinse water flow rate, and produces medium to high concentrations of metal salts for recycle to plating bath.

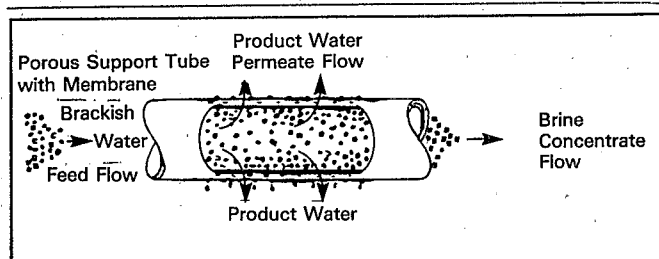


Figure 9.12. Reverse osmosis — tubular module (from Metcalf and Eddy, 1985).

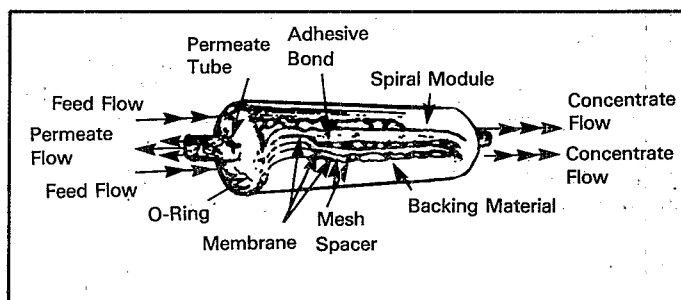


Figure 9.13. Reverse osmosis — spiral membrane module (from Metcalf and Eddy, 1985).

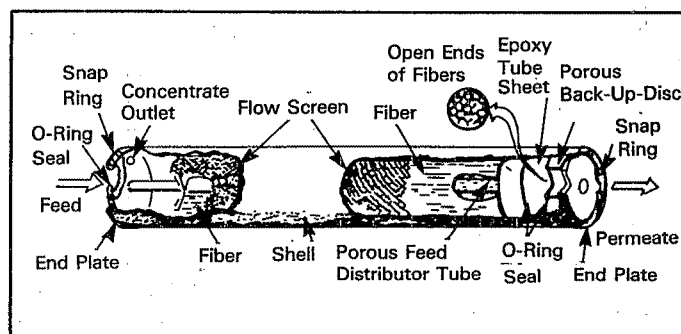


Figure 9.14. Reverse osmosis — hollow fiber module (from Metcalf and Eddy, 1985).

Disadvantages

Reverse osmosis product cannot be highly concentrated because of inherent technology limitations (unlike evaporation). Dragout impurities may be returned to the plating bath, which can be deleterious. There may not be sufficient evaporation from the plating bath to accommodate the volume of RO concentrate returned, and incompatible materials must be removed from or chelated in the feed solution prior to RO treatment.

Carbon Adsorption

Carbon adsorption is a separation technology used to remove and/or recover dissolved organics and certain inorganics from single-phase fluid streams. The material used is granular activated carbon (GAC). Activated carbon includes any amorphous form of carbon that has been specially treated (i.e., activated) to increase the surface area/volume ratio of the carbon.

In the metal finishing industry, carbon adsorption would be used as a polishing technology for wastewater cleanup and recycle. In combination with optimal use of water in plating shop, segregation of different types of plating bath dragout, and rinsewater cleanup with activated carbon as part of treatment system, a potential for 90 to 100 percent of water reuse is available.

Carbon Adsorption Technology

The majority of carbon adsorption systems use cylindrical pressure vessels which contain the activated carbon. The stream to be treated can flow through the vessel in an upward or downward flow design mode. The velocity of the upward flowing stream can be set so that the carbon bed is expanded and fluidized or so that it is not expanded. The bed expansion configuration in the GAC system upward flow design mode allows the GAC unit to handle influents which contain suspended solids without appreciable pressure drop. The GAC system downward flow design mode develops high pressure drop with suspended solids accumulation and typically requires upstream filtration as a pretreatment step. In addition, the stream can flow through the beds in series or in parallel.

The activated carbon used in the carbon adsorption process eventually reaches a point where it will no longer adsorb material. This spent activated carbon must then be either regenerated or discarded. The most common form of regeneration is thermal regeneration, although various types of chemical regeneration are used. Chemicals used for regeneration include acids, bases, and solvents.

The amount of material removed in carbon adsorption systems will depend on the characteristics of the process stream and its constituents. Most carbon treatment efficiencies are greater than 99 percent with influent concentrations below 1,000 ppm. At higher concentrations, removal efficiencies can reach 99 percent. A schematic for a carbon adsorption system for chromium polishing is presented in Figure 9.15. This schematic illustrates a parallel configured carbon adsorption system.

Crystallization

Crystallization is the formation of solid particles within a homogeneous phase. It occurs in a supersaturated solution where very small particles of a new phase are

formed. This formation of small particles is referred to as nucleation. The driving force behind crystallization is the difference between the concentration of the feed and the solubility of the solute at equilibrium temperature.

Crystallization Technology

Crystallization technology is economical when the influent stream has a relatively high concentration of salts to be crystallized. In the metal finishing industry, the rinse water contains relatively low concentrations of the salts. Therefore, the rinse rate must be lowered so that the salt concentration is raised. This process change may have an effect on the product quality and must be evaluated in detail. In the instances in which crystallization is feasible, the end product is typically a reusable caustic or acid solution, and a potentially reclaimable metal salt or sludge. The recovery of the pickle or alkali solution is the primary objective. However, the fact that the reclaimed sludge may be resaleable, thus resulting in no discharge of hazardous material, is particularly attractive.

Commercial crystallizers may be either batch or continuous operation. The main objective of crystallization

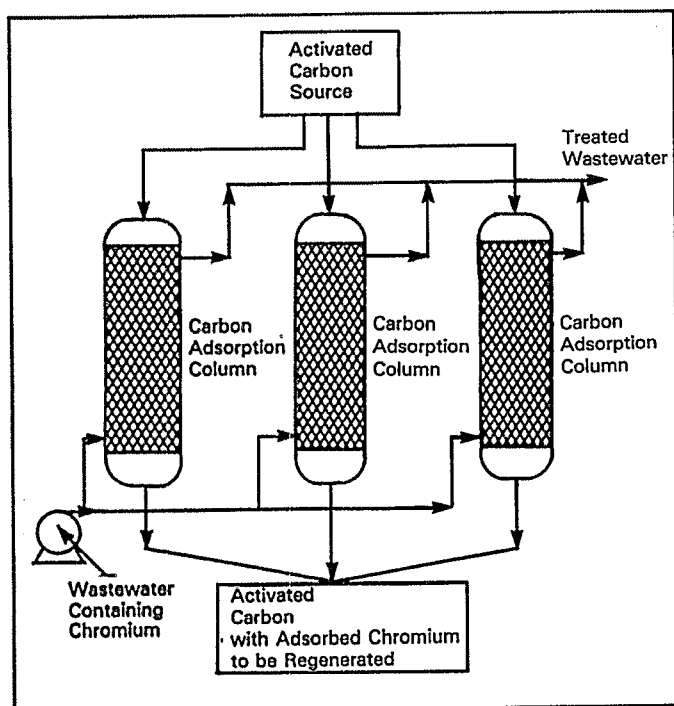


Figure 9.15. Carbon adsorption schematic (from Metcalf and Eddy, 1985).

equipment is to produce a supersaturated solution. Crystallization units may range from 10 to 40 feet in length, and have diameters of four to 15 feet.

A schematic of a typical caustic etch regeneration system is presented in Figure 9.16.

Applications in the Metal Finishing Industry

Fuji Sash Process

A process developed by Fuji Sash Industries of Japan for the recovery of caustic soda (NaOH) from aluminum etching solutions has been commercially available in the U.S. since about 1980.

Caustic soda is recovered by continuously pumping the etchant to a crystallization tower, where $\text{Al}(\text{OH})_3$ is precipitated in a controlled manner. The recovered caustic soda is then returned to the etching tank. The $\text{Al}(\text{OH})_3$ crystals withdrawn from the bottom of the crystallizer are dewatered by means of a centrifuge, and the centrifugate is returned to the etching tank for reuse.

The recovery operation can reduce caustic soda purchases by 80 percent. The hydrated alumina crystals produced are equivalent to commercial grade and can be a source of income provided a market is found. However, this operation is not widely used in the U.S.

Regeneration of an acid solution for copper cleaning is commonly accomplished by crystallization of copper sulfate and removal of the crystals. This process is used by printed circuit manufacturers and metal finishers. The value of the recovered copper salts justifies use of the process.

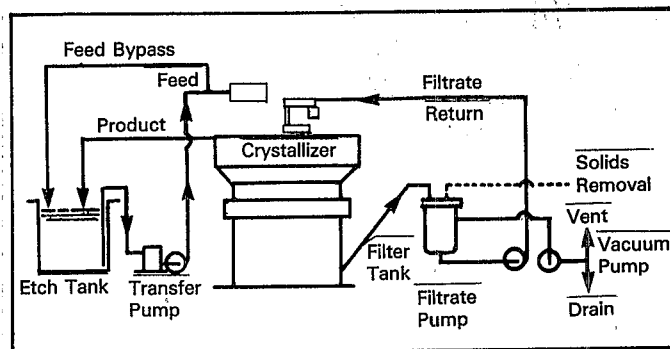


Figure 9.16. Recovery of caustic soda from spent caustic etch (from Metcalf and Eddy, 1985).

EFCO Crystallization Process

The EFCO Corporation in Monett, MO uses a crystallization process to remove dissolved aluminum from their etch solution which can then be recycled rather than discharged to a wastewater treatment plant. The system operates continuously, producing a potentially saleable alumina sludge (70 to 80 percent alumina) and free caustic, which is reused.

Electrodialysis

Electrodialysis (ED) is a process which uses a "stack" of closely spaced ion exchange membranes through which ionic materials are selectively transported. The driving force for the process (provided by voltage from a rectifier) is imposed on electrodes at the two ends of the stack.

In a plating operation, the ionic materials are extracted from the relatively dilute recovery rinse, and accumulated in a highly concentrated stream. Concentration of product is limited only by the volume of water transported through the membrane with the ions. The ED concentrate can either be recycled to the process bath or processed separately for recovery.

A schematic of ED use in the recycle mode is shown in Figure 9.17.

Applications in Metal Finishing

ED is being used successfully for recovering concentrates of gold, silver, nickel, and tin from rinse waters. It can be used in bright nickel plating, where the bath is slowly circulated through the ED unit. This provides continuous removal of organic impurities and essentially eliminates the need for batch purification (with associated major losses in nickel).

Advantages

Because of the high metal ion concentration available from ED, the volume and concentration of product is seldom the limitation on its capability of being returned to the bath. Electrodialysis requires minimal amounts of energy. Since only ionic materials are recovered, many undesirable impurities are rejected.

Disadvantages

Because conductivity of recovery rinse must be reasonably high, losses to subsequent rinsing would typically be higher than those associated with RO or IX, but lower than evaporation.

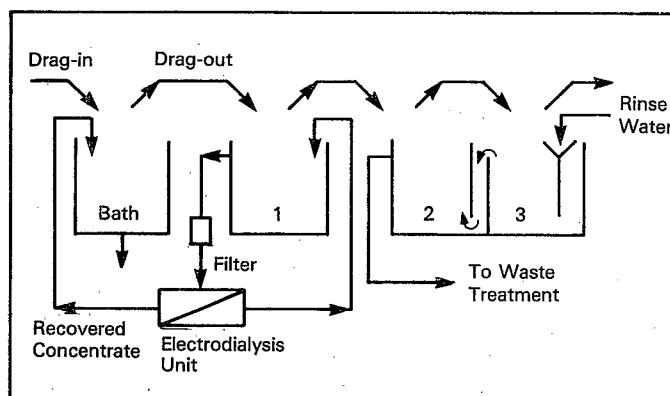


Figure 9.17. Electrodeialysis schematic — recycle mode (from Lancy International, 1986).

Electrodialysis is a membrane process which requires careful operation (including pretreatment) and periodic maintenance to avoid damage to the membrane stack. The stack is usually reconditioned by the manufacturer.

Comparison of Evaporation, RO, IX and ED Summary of Basic Parameters for Alternate Recovery Systems

Parameter	Evaporation	RO	ED	IX
Feed Concentration	High	Low	Medium	Very Low
Product Concentration	Very High	Low	High	Medium
Capture Efficiency	Highest	High	Medium	Very High
Energy Requirement	High	Medium	Low	Very Low

Conclusions

A number of recycle/reuse technologies are available to the metal finisher which offer the ability to reduce, if not eliminate, hazardous waste generation, as well as offer the potential for reasonable payback. Any recycle/reuse scheme installed by a metal finisher will not necessarily eliminate long-term liability for hazardous waste disposal. Each technology will generate some form of waste with its own disposal problems/requirements. Any investment made in recycle/reuse technologies by the metal finisher should be based (to the extent possible) on a definitive economic analysis.

10. Organic Liquids: Treatment and Residues Management

This discussion focuses on general guidance to assist the metal finisher in planning an organic liquids management program. While site specific concerns can have an important impact on any hazardous waste management program, they will be left to the development of the facility's process team.

Why Treat?

With increasing waste disposal costs, the minimization of hazardous materials, specifically organic liquids, is becoming a critical issue in facility management. Only 21 states currently have hazardous waste disposal (HWD) sites that accept hazardous waste materials. As of August 1986 only three new licensed commercial disposal facilities were under construction. Existing licenses for hazardous waste facilities are in jeopardy because of increased public pressure to eliminate disposal sites from their backyard. The impending ban on solvent disposal at HWD landfills makes it imperative that a facility implement treatment/recycle methods to minimize solvent wastes requiring incineration. Finally, the long term environmental liability and potential impact on the firm's future is crucial. Hazardous waste materials improperly disposed of, even if the generator acted properly, still bear liability to the generator.

Regulatory Overview

U.S. EPA has become increasingly concerned with the total waste management of hazardous materials. Solvents are an important concern since they affect all media; their usage is regulated under major environmental legislation including the Clean Water, Clean Air, and Resource Conservation and Recovery (RCRA) Acts. For example, EPA is concerned with site management where ground water has been contaminated with organic materials.

Ground water contaminated with volatile organic compounds (VOC) may be contained on site by pumping it from the ground to an above-ground treatment system such as an air stripping tower. Here the air flows countercurrent to the ground water and the VOC are stripped by the air flow. The treated water is then reinjected into the ground or discharged to surface water or a sanitary sewer system. The VOC-laden air may then be passed through an activated carbon column, which adsorbs the organic compounds from the air, thus placing it back into the solid phase (i.e., the carbon). The carbon contaminated with the VOC can then be regenerated for reuse by steam-stripping (placing the VOC into the liquid phase) or disposed of via incineration, thereby oxi-

dizing and destroying the VOC. Note that all media are affected by the VOC remedial action plan. The EPA is concerned that we do not simply move contaminants from one medium to another, e.g., ground water to air, but rather look at a pollutant's *total* environmental impact.

Organic Liquid Waste Management Program

A basic organic liquid waste management program may consist of three steps:

- (1) Assessing process wastes (chemical audit).
- (2) Identifying waste management concerns.
- (3) Developing waste management options.

The purpose of the process waste assessment, or chemical audit, is to provide sufficient engineering data to evaluate various organic waste liquid management options in light of management limitations. The process waste assessment tabulates such information as the physical form of the organic chemical(s) involved, the chemical nature of the material and possible reaction(s) that can occur to promote or inhibit treatment, and the process specifics on waste generation such as quantities, generation time, and temperature during time of generation.

While this discussion deals with organic liquids, the solid and gaseous phases that typically accompany liquid waste management should also be considered. For example, while a degreaser may contain a volatile organic liquid compound such as 1,1,1-trichloroethane, the degreaser also contains chemical vapors and solids such as metal particulates in the sump of the degreaser.

Possible reactions that the organic liquid can undergo either in storage prior to treatment or during treatment itself must be assessed. Typically, solvent mixtures have beneficial reactions in that they can be separated by distillation or evaporation. On the other hand, certain organic liquids generate flammable or hazardous vapors, and potentially explosive reactions can occur.

A complete process waste assessment must also characterize each waste to the extent that its characteristics affect treatability. Typically, the following items need to be reviewed:

- Solids content.
- Flammability.
- Viscosity.
- pH.

- Temperature.
- Volatility.
- Solubility.
- Molecular weight.
- Polarity.
- Toxicity.

Metal Finishing Process Operations

Process operations involving organic compounds should be reviewed as a starting point for determining whether chemical substitution and/or process modifications can be introduced. Such operations, as identified by EPA studies, include:

- Machining—buffing compounds, rustproofing compounds and machining oils.
- Cleaning and Degreasing Operations — organic solvents (depending on the oils/greases to be removed and the substrate material processed).
- Laminating — organic resins and solvents.
- Hot Dip Coating — organic lacquers and organic coating materials.
- Painting/Electroplating — coating systems.
- Stripping — organic and hot alkaline materials (with organic additives).

Chemical Substitution

The audit may indicate areas where less harmful process chemistries or those that offer recycle opportunities can be substituted to minimize hazardous waste disposal costs. Chemical substitution to minimize toxic concerns with organic solvents was initiated 50 years ago when chlorinated solvents, with their higher solvency and nonflammable nature, began to replace hydrocarbon solvents such as gasoline, benzene, and kerosene. Recently, "compliance" solvents such as 1,1,1-trichloroethane and methylene chloride, which are exempt from many of the State Air Quality Implementation Plans under the Clean Air Act, are being substituted for compounds such as perchloroethylene which contribute to photochemical ozone/oxidant problems in the urban atmosphere. Other chemicals such as the fluorinated compounds are replacing certain of the chlorinated solvents due to their higher level of acceptability under OSHA standards.

Clean air regulations are also forcing the switch from low-solids to high-solids organic coating systems, and from organic solvent-based to water-based coating sys-

tems. Hazardous waste disposal costs are also encouraging a second look at alkaline versus solvent paint stripping systems.

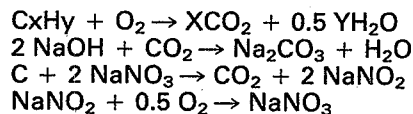
Process Modifications

A 1981 EPA study reviewed vapor degreaser process equipment modifications for minimizing solvent loss. Conclusions reached were that the degreaser should be operated in an area of relative calm, not subject to drafts, that the freeboard ratio should be increased to 75 percent from 50 percent, that a refrigerated freeboard chiller could reduce emission rates by 40 percent, and that an automated lid or lid adjustment mechanism would minimize solvent vapor layer disturbance and reduce solvent loss.

Other studies by EPA (September 1986) evaluated alternatives to organic paint strippers commonly utilized in military applications (epoxy stripper, MS-111, which contains both methylene chloride and phenol at 85 percent and 10 percent concentrations by volume, respectively). Chemicals containing less toxic organic materials were successful in stripping enamels and polyamide paint coating systems, but the two successful alternatives to MS-111 still contained methylene chloride, although at lower concentrations.

Other process changes for painting or coating systems that have gained increased acceptance in the metal finishing industry include electropainting or electrocoating. These methods yield better coverage of irregular parts including recessed areas and sharp edges, and use nearly 100 percent of available coating solids, thereby minimizing organic waste liquid disposal. These systems can use aqueous-based coatings rather than halogenated or solvent-based coatings.

The solvent and organic wasteload from stripping improperly painted or coated parts and stripping racks used to hold the parts is usually greater than from the painting/coating process itself. Molten salt bath and cryogenic processes can eliminate use of solvents in this area. The molten salt bath process uses high temperature (650° to 900°F) inorganic salts without generating toxic solvent stripping wastes. The chemical formulas involved are:



In these formulas the organic compound (CxHy) is converted into carbon dioxide (CO₂) and water (H₂O) with

subsequent carbonate (Na_2CO_3) formation and return of the nitrite salt (NaNO_2) to the nitrate (NaNO_3) form by adsorption into the bath of oxygen from the atmosphere. The only waste from this process is the carbonate precipitate formed, which may contain some paint pigments. However, the waste is typically nonhazardous since the organic carriers have been converted to carbon dioxide and water.

Another method to remove organic coating finishes without generating solvent waste is to use very low temperatures. The cryogenic process utilizes liquid nitrogen at -15°F to freeze and embrittle the organic finish so it can be easily removed from the basis metal by either wire brushing or tumbling. Residual waste consists solely of the organic finish, i.e., no added solvent chemical or stripping agent, and is typically nonhazardous.

Waste Management Concerns

After accumulating process waste data through an assessment and, if possible, minimizing the quantity of organic liquids generated by either modifying the process equipment or the process chemical, waste management concerns should be considered. These include:

- **Cost**—both capital and operation and maintenance costs.
- **Complexity**—different treatment systems require different technical skill levels depending on equipment involved. Complexity can be adjusted to the level of the employees, from a manual to a fully automated "fail-safe" system.
- **Space Requirements**—for the treatment system as well as the storage of hazardous wastes prior to transportation of either treatment residues or the raw waste liquids.
- **Regulations Impacted**—local, state and Federal.
- **Treatment, Storage, Disposal Facility (TSDF) Applicability**—Part B forms needed?
- **Long Term Environmental Liability**—the firm's potential exposure under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) should be assessed.
- **Effluent Quality Requirement**—according to forthcoming EPA treatment standards for hazardous waste treatment facilities.
- **Acceptability-Public Relations**—the impact of the treatment (recycle) or storage of hazardous wastes at the facility must be considered in light of public/neighborhood concerns.

Waste Management Options

The data accumulated from the process waste assessment/audit and the various site-specific and general concerns of the facility can be used in assessing options available to manage the hazardous organic liquids. The three main options include off-site disposal, off-site treatment/reclamation, and on-site treatment/reclamation.

Option 1: Off-Site Disposal. Off-site disposal is the least favored option by U.S. EPA, although it is the easiest to implement from the point of view of management time. From the standpoint of long term environmental impact and potential liability to the firm, however, it is the least favored choice. There are no economic or regulatory incentives to dispose of organic liquids. The chapter on "How to Select a Responsible Transporter and Waste Management Facility" should be closely reviewed if this or the next option is chosen.

Option 2: Off-Site Treatment/Reclamation. Many facilities that generate hazardous organic liquids use off-site treatment and reclamation facilities for those liquids. The advantages and disadvantages of off-site treatment and reclamation are:

- Low capital investment.
- Chemical reuse/chemical purchase credit.
- Quality control if raw virgin chemical rather than reused solvent is necessary for product quality.
- Waste transportation/storage regulatory requirements.
- Potential liability for transport of hazardous waste materials over public roads to the treatment site and residues from the off-site reclamation or treatment process.

Option 3: On-Site Treatment/Reclamation. More facilities are turning to on-site treatment/reclamation techniques to recycle organic liquids, leaving only treatment residues for off-site disposal. Factors include:

- Initial capital funding requirements.
- Cost-benefit ratio.
- Quality control to obtain the quality of solvent or organic liquid needed for the facility's product quality processing needs.
- Storage/treatment regulatory requirements.
- Potential liability.
- Treatment methods.

Four methods typically used in recycling, both off-site and on-site, include solids separation, distillation, evaporation, and incineration.

Solids Separation

Particle filtration is often used in the metal finishing industry to treat and extend the life of various process electroplating baths. Similar technology can extend the life of certain organic liquids. Particle filtration typically removes particles of 0.5 to 100 microns. If finer particles are affecting the reuse of the organic liquid, ultrafiltration techniques can be used to remove particles from 1 micron down to 0.001 micron.

In a particle filter, the liquid passes through a wound filter element and particles larger than the pore size are retained by the filter element. As the filter element becomes clogged with particles, the pressure needed to force or drive the organic liquid through the filter increases until the pressure loss is too great for the pumping system to maintain without forcing solids through the filter. Then the filter must be replaced. Two major types of particle filters are the fiber-wound element and the fixed-pore size element.

The fiber-wound element is the standard choice for use in recycling process baths in electroplating operations. The pore size of the element, rated in microns, is an "average" pore size. Since there are the same number of diamond-shaped openings (pores) on each layer, the openings on the outer layers must be larger due to the increased circumference. During filtration, larger particles are therefore retained on the outer layers where the openings are largest, while smaller particles are retained selectively on succeeding inner layers of smaller openings. The rated size of the element therefore is an average of the largest to smallest size.

Fiber-wound elements are manufactured from various materials at relatively low cost and are meant to be disposable. The low replacement cost of the element must take into account, however, that if it is contaminated with a hazardous waste, it becomes a hazardous waste itself and disposal costs will increase accordingly. That price should be taken into account in the cost-benefit analysis.

The fixed-pore particle filter is not used as frequently by the electroplater. The pore size is not an average, but relatively consistent throughout the filter's depth, hence the name "fixed-pore." This filter is manufactured by sintering (fusing), near the temperature of the alloy be-

ing used, a metal under pressure and in a reducing atmosphere. This causes the metal particles to bond together and form a coherent matrix which has interconnected equal porosity. It is a relatively expensive manufacturing process when compared to fiber-wound filters. However, one advantage is that there is a controlled pore size, not an average, and therefore it has better solids retention for a particular size. Since it is a metal filter it is also suitable for most solvents, and the rigid structure of the metal matrix prevents collapse of the openings due to high pressure applications. The fixed-pore filter can be backwashed; therefore, there is no need to dispose of the filter element. This minimizes the quantity of hazardous waste generated and, over the long term, may make it more economical than a fiber-wound element filtration system. The cost benefit analysis must be performed on the specific hazardous waste and facility requirements.

Ultrafiltration can be used when submicron particles must be removed from the liquid waste stream. The membranes that make up the ultrafilter separate the particles on the basis of size, as rated by the Molecular Weight Cut Off (MWCU). Membranes can retain from 1,000 to 1 million molecular weight compounds—roughly from glucose to proteins.

The ultrafilter separates the feed stream into the permeate (the liquid which passes through the filter), and the retentate (the concentrated solids which are rejected by the filter). In the case of electropainting or electrocoating systems, the permeate is the water or solvent based carrier, while the retentate would be the solid or coatings material returned to the bath for reuse in the coating system.

The flux is the flow of permeate passed through the membrane rated in gallons per square foot per day. The concentration polarization factor is an important factor in membrane performance affecting the flux. For an acceptable cost-benefit ratio on an ultrafilter, a high proportion of flux to feed must be maintained. However, as the solids build up at the membrane surface they cause increased local pressures and decreased flows or flux. Cross-flow fluid management can help to minimize the effect of the concentration polarization by sweeping away the accumulated layer of retained particles at the membrane surface. Relatively high pressures are used in cross-flow fluid management, but it is effective in separating solids and retaining relatively high flux rates.

Ultrafilters are used in the industry for reconcentrating paint resins and pigments in spray booth washwater and for particle separation in electrocoating systems.

They are also used to remove oils from alkaline cleaning solutions in order to reuse those solutions. Manufacture of ultrafilter membranes usually includes both the plate and frame or porous tube techniques. Porous tubes are bound together to form bundles in a fabricated ultrafilter module, while the plate and frame membranes are rolled to form a spiral module construction.

Distillation

Distillation is one means of reclaiming organic liquids such as solvents. Organic solvents contaminated with oils and greases from the degreasing process will exhibit a wide boiling point differential between the solvents and the contaminants. Distillation uses this differential to separate the compounds; i.e., the solvent vaporizes at a relatively low temperature compared to the oil/grease contaminants.

Although considerable energy is required for distillation, solvents do vaporize at a relatively low temperature compared to water (100 Btu/lb versus 980 Btu/lb). Therefore, the energy required to evaporate water-based liquids is significantly lower, and the cost balance is usually favorable. Where large volumes of solvents require distillation, vacuum systems may also be applied to further decrease the energy requirements.

Distillation is applicable to a wide variety of spent solvents used in the metal finishing industry—both halogenated and nonhalogenated compounds, such as the spent methyl ethyl ketone solvent mixture from a paint line clean-out. Continuous distillation columns which contain trays, packing, plates, etc. can be used to increase the liquid vapor contact area for larger volume requirements. Smaller units very similar in construction to the familiar vapor degreaser are typically used in the metal finishing industry. The main difference between a solvent still versus a vapor solvent degreaser is the higher temperature needed to operate the still. These smaller batch stills typically allow for on-site recycling for all but the smallest volume users. (State regulations should be closely checked to insure that recycling is properly permitted at the state level.) A recent EPA project summary identified a distillation unit capable of handling as little as 14 to 35 gallons of a solvent per batch. Others have indicated that solvent usage of only 5 gallons per batch could be handled. These smaller units can even be table top mounted, while most larger units can be mounted within 10 to 20 square feet of floor space.

Of concern in distillation are azeotropic mixtures, i.e., liquid mixtures that exhibit a maximum or minimum

boiling point relative to the boiling points of the surrounding mixture composition. The boiling points of the pure components must be sufficiently close to permit the formation of an azeotrope. These mixtures are not formed when dealing with the typical solvent and oil/grease mixtures encountered in the metal finishing industry. Solids in feed, another concern, may plug the packing in a larger distillation column and need to be filtered prior to off-site reclamation. Solids are not a problem on the smaller on-site batch units since they will remain in the bottom residue of a still.

A batch still at a metal finishing facility which has a feed stock of spent solvents contaminated with oils, condensed water, and solids can satisfactorily recycle solvents back to the metal finishing process vapor degreaser. A typical example:

- Feed Stock - solvent 90-95%/oils, water 5-10%/solids 0-1%.
- Distillate - solvent 95-99%/oils, water 1-5%.
- Bottoms - oils, water 85-95%/solids 5-10%/solvents 1-5%.

Evaporation

In distillation all or most of the liquid phase components have an appreciable vapor pressure and therefore appear in the overhead vapors. In evaporation the overhead vapor is primarily solvent (e.g., water), contaminated only by smaller amounts of liquid phase material (organic or inorganic solids with very low vapor pressures at the temperature of evaporation), which are called entrainments.

In wiped film evaporation (WFE) a rotating arm wipes a thin film of solvent across the evaporative surface. There is very little hydraulic head to impede equilibrium vapor pressures, and therefore a high heat efficiency is achieved. WFE is also useful to reclaim solvents that contain a higher quantity of solids since the mechanical wiping action of the rotating arm moves the solids across, rather than allowing them to adhere to the evaporative surface. While WFE is relatively expensive compared to batch stills, because of the critical machining involved in the wiped film surface, they are considered state-of-the-art technology and useful for gaining the higher recovery of solvents.

A WFE can typically handle higher solids content in the feed stock as indicated in the example:

- Feed Stock - solvent 70-95%/oils, water 5-15%/solids 0-35%.

- Distillate - solvent 97-99%/oils, water 0-3%.
- Bottoms - solids 30-65%/oils, water 35-65%/solvent 0-5%.

Incineration

Incineration is used to detoxify and sterilize compounds. While there is energy to recover from certain organic liquids, spent halogenated solvents usually do not yield sufficient quantities to make them marketable. Incineration is primarily used with degreaser and still bottom sludges which may require mixing with a high heating value fuel oil to be effective. Organic wastes composed of carbon and hydrogen have a relatively high heating value. However, when halogenated compounds are added to the organic wastes, their energy content drops significantly. For example, carbon has 14,000 Btu/lb of energy content, while hydrogen has 61,000 Btu/lb energy content. Ethane contains about 22,000 Btu/lb, and the heating value drops when chlorine atoms are added. Subsequent heating values of the compound are:

- Dichloroethane - 5,400 Btu/lb.
- Trichloroethane - 3,600 Btu/lb.
- Tetrachloroethane - 2,500 Btu/lb.

Certain organic liquids contain significant heating factors such as methyl ethyl ketone (20,000 Btu/lb), toluene (18,000 Btu/lb), and various phenol based stripping compounds (13,000 to 15,000 Btu/lb).

The heat content of the fuel is important in determining whether EPA considers it a hazardous waste fuel that is burned for energy recovery in a boiler or industrial furnace. The EPA "rule of thumb" is that it must have greater than 5,000 Btu/lb. Currently a hazardous waste fuel is exempt from regulations when burned in an industrial furnace. However, hazardous wastes, if burned, are regulated under RCRA hazardous waste incineration standards. Therefore, the fuel content is an important factor in regulatory involvement. It is important to keep in mind that chlorinated solvents generally fall below this 5,000 Btu/lb value and therefore are not considered hazardous waste fuel.

Treatment Process Residuals

Solids separation. Particle filtration as well as ultrafiltration removes solids from hazardous organic liquids. If any of the organic liquids are retained on the solids, or if the solids themselves constitute hazardous waste according to EP toxicity testing or similar characterization under RCRA, these residuals may require further off-site

treatment. In the case of particle filtration, the spent filter elements could increase this volume significantly.

Distillation. The bottoms—the resultant oil/water mixture that is removed from the solvent during distillation—are considered hazardous and must be handled appropriately. Typically these wastes are incinerated.

Evaporation. Similar to the distillation column, the wiped film evaporator will generate bottoms which are considered hazardous when dealing with organic liquids.

Incineration. The incinerator ash generated from combustion may contain hazardous constituents. EP toxicity testing to determine the leachate values of the metals coming from the ash will depend on the content in the feed steam to the incinerator. While organic solvents will typically be burned with no residual, contributors to the incinerator may make the resultant "mixed" ash hazardous.

In the case of the residuals discussed, potential environmental liability is still incurred by management even if the waste has been sent off-site for reclamation. Therefore, the feasibility of additional treatment operations should be investigated with the specific hazardous waste treatment facility.

Management options for treatment process residuals include:

- Incineration.
- Off-site disposal in secure landfills (depending on the outcome of the recent EPA provision).
- Additional treatment to reduce volumes, such as redistillation of the bottoms from a distillation column by using steam stripping techniques.

11. Characterization and Treatment of Aqueous Wastes

This chapter provides an overview of technologies applicable to treatment and management of residues resulting from metal finishing. It is based on experience over the past five years in over 100 facilities processing metals from the point at which they are mined to the point at which they are sold as finished products.

Regulatory History of RCRA

It is first appropriate to review the regulatory history of RCRA to develop a proper framework under which appropriate management and treatment of residues will occur. In November 1984, Congress amended the Resource Conservation and Recovery Act (RCRA) of 1976 by passing the Hazardous and Solid Waste Amendments (HSWA). Central to these amendments was a hierarchy of waste management (see Figure 11.1). It was Congress' intent to place an emphasis on source reduction, material reuse and recovery, and treatment and to strongly de-emphasize land disposal.

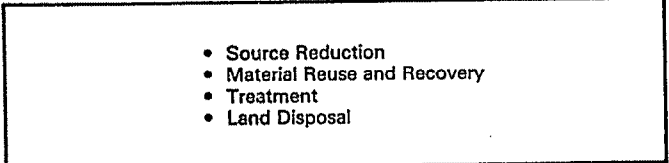
- 
- Source Reduction
 - Material Reuse and Recovery
 - Treatment
 - Land Disposal

Figure 11.1. HSWA hierarchy.

Earlier chapters of this document reviewed effective control technologies for source reduction and material reuse and recovery. In chapter 10, applicable technologies were presented for treatment of organic and spent solvent wastes. The emphasis of this chapter is on three other types of wastes generated by metal finishers. These are:

- Corrosive wastes.
- Cyanide containing wastes.
- Metal containing wastes.

The emphasis of the hierarchy created by Congress under HSWA will yield:

- More concentrated wastes.
- Wastes with a varied array of constituents.
- Wastes with a greater degree of complexation.

One obvious consequence of the emphasis on source reduction and material reuse and recovery is that the wastes generated for treatment will be more concentrated.

As these wastes are concentrated, constituents present at non-detectable concentrations in dilute wastes will be present at elevated, treatable concentrations. Likewise, the degree of complexation will become greater as the wastes become more concentrated.

Waste Characterization

One of the most critical steps in ensuring proper selection of source reduction, material reuse and recovery, and treatment alternatives is effective waste characterization. Specifically, this means full characterization of each source of waste generated in a facility and documentation of the rate at which each waste is generated. Additionally, for each constituent that is present at elevated concentrations, it is important to understand the reasons for their presence. Detailed characterization will yield a better basis for design, a better basis for operation, and better data for use in negotiating permit conditions with regulatory authorities.

Many of the technologies which are applicable to the residues of metal finishing processing have their roots in wastewater treatment. There are many fine descriptions of these technologies when applied to wastewater in the literature. The emphasis of this chapter will be on the applicability of these technologies to the treatment of wastes.

Waste Segregation

The first step to be taken in establishing a treatment system design or modification is to determine which wastes require segregation. The objective of segregation is to minimize the amount of reagent required for treatment and the size of treatment vessels, and to maximize treatment removal effectiveness.

This chapter will concentrate on four categories of wastes requiring segregation:

- Cyanide containing wastes.
- Chromium (VI) containing wastes.
- Arsenic and selenium containing wastes.
- Other metals containing wastes.

Segregation must be viewed in conjunction with neutralization. The most effective means of treating a corrosive waste is through neutralization. Neutralization is the reaction of an acid or base with a corrosive waste to reduce or eliminate the corrosivity. The definition of a corrosive waste under RCRA is a waste with a pH less than or equal to 2.0 or a pH greater than or equal to 12.5 (note: it is also defined as a waste that corrodes steel).

(SAE 1020) at a rate in excess of 6.35 millimeters per year). As such, neutralization in the context of treating a RCRA waste means the addition of a base to raise the pH to above 2.0 or an acid to lower the pH to below 12.5.

Neutralization

One technique used in a number of facilities that utilize molten salt for metal surface treatment prior to pickling, is to take advantage of the alkaline values generated in the molten salt bath in treating other wastes generated in the plant. When the bath is determined to be spent, it is in many instances manifested, hauled off-site, and land disposed. One technique is to take the solidified spent molten salt (molten salt is sold at ambient temperatures) and circulate acidic wastes generated in the facility over the material prior to entry to the waste treatment system. This in effect neutralizes the acid wastes and eliminates the requirements of manifesting and land disposal.

Cyanide Containing Wastes

There are six methods applicable to the treatment of cyanide wastes for metal finishing:

- Alkaline chlorination.
- Electrolytic decomposition.
- Ozonation.
- UV/Ozonation.
- Hydrogen peroxide.
- Ferrous sulfate precipitation.

Alkaline chlorination is the most widely applied in the metal finishing industry. A schematic for cyanide reduction via alkaline chlorination is provided in Figure 11.2. This technology is generally applicable to wastes containing less than one percent cyanide, generally present as free cyanide. It is conducted in two stages; the first stage is operated at a pH greater than 10 standard units and the second stage is operated with a pH in the range of 7.5 to 8 standard units. Alkaline chlorination is performed using sodium hypochlorite and chlorine.

Electrolytic decomposition technology was applied to cyanide containing wastes in the early part of this century. It fell from favor as alkaline chlorination came into use at large-scale facilities. However, as wastes become more concentrated, this technology may find more wide spread application in the future. The reason being that it is applicable to wastes containing cyanide in excess of one percent. The basis of this technology is electrolytic decomposition of the cyanide compounds at an elevated

temperature (200°F) to yield nitrogen, CO₂, ammonia, and amines (see Figure 11.3).

Ozonation treatment can be used to oxidize cyanide, thereby reducing the concentration of cyanide in wastewater. It has not found widespread application in the metal finishing industry, however, because it generally has higher capital and operating costs than alkaline chlorination. Additionally, in most instances ozonation is no more effective in reducing cyanide concentrations than alkaline chlorination.

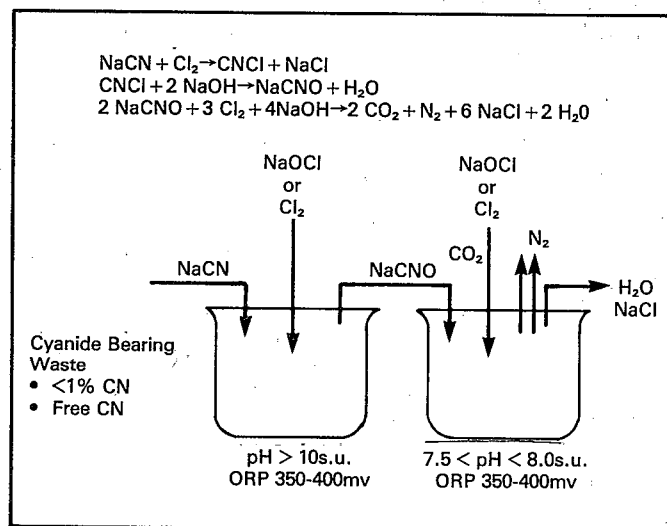


Figure 11.2. Cyanide reduction via alkaline chlorination.

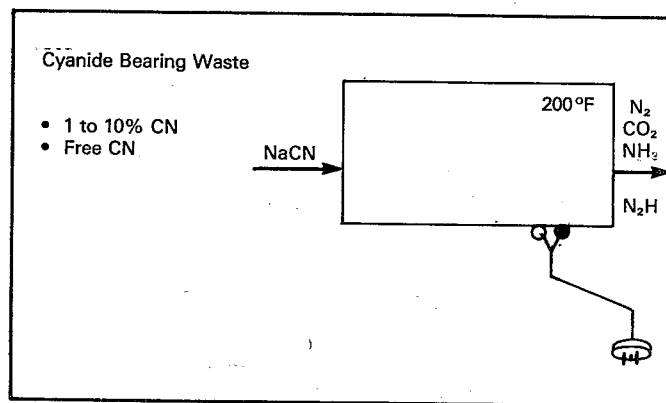
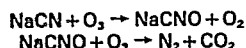


Figure 11.3. Cyanide reduction via electrolytic decomposition.

One interesting variation on ozonation technology is augmentation with UV radiation. This is a technology that has been applied on wastes in the coke by-product manufacturing industry. A significant development has been made that has resulted in significantly less ozone consumption through the use of UV radiation (see Figure 11.4).

Cyanide reduction with hydrogen peroxide is effective in reducing cyanide. It has been applied on a less frequent basis within this industry, due to the fact that there are high operating costs associated with hydrogen peroxide generation. The reduction of cyanide with peroxide occurs in two steps and yields CO_2 and ammonia (see Figure 11.5).

Each of the technologies described above is effective in treating wastes containing free cyanides; that is, cyanides present as CN^- in solution. There are instances in metal finishing facilities where complex cyanides are present in wastes. The most common are complexes of iron, nickel, and zinc. A technology that has been applied to remove complex cyanides from aqueous wastes is ferrous sulfate precipitation. The technology involves a two-stage operation in which ferrous sulfate is first added at a pH of 9 to complex any trace amounts of free cyanide. In the second stage, the complex cyanides are precipitated through the addition of ferrous sulfate or ferric chloride at a pH range of 2 to 4.



Ozonation with UV Radiation

UV Absorption — Ozone and Cyanide Are Raised
to Higher Energy States
— Free Radicals Are Formed
— More Rapid Reaction
— Less Ozone Required

Figure 11.4. Cyanide reduction via ozonation.

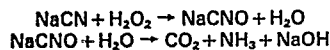


Figure 11.5. Cyanide reduction via hydrogen peroxide.

Chromium Containing Wastes

There are three treatment methods applicable to wastes containing hexavalent chromium. Wastes containing trivalent chromium can be treated using chemical precipitation and sedimentation, which is discussed below. The three methods applicable to treatment of hexavalent chromium are:

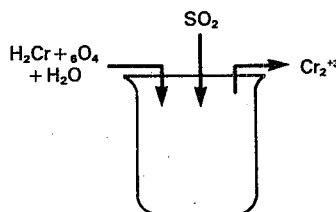
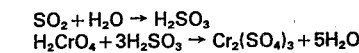
- Sulfur dioxide.
- Sodium metabisulfite.
- Ferrous sulfate.

Hexavalent chromium reduction through the use of sulfur dioxide and sodium metabisulfite has found the widest application in the metal finishing industry. It is not truly a treatment step, but a conversion process in which the hexavalent chromium is converted to trivalent chromium. The hexavalent chromium is reduced through the addition of the reductant at a pH in the range of 2.5 to 3 with a retention time of approximately 30 to 40 minutes (see Figure 11.6).

Ferrous sulfate has not been as widely applied. However, it is particularly applicable in facilities where ferrous sulfate is produced as part of the process, or is readily available. The basis for this technology is that the hexavalent chromium is reduced to trivalent chromium and the ferrous iron is oxidized to ferric iron.

Arsenic and Selenium Containing Wastes

It may be necessary to segregate waste streams containing elevated concentrations of arsenic and selenium, especially waste streams with concentrations in excess



pH 2.5-3.0s.u.
30 Minutes Retention

Figure 11.6. Hexavalent chromium reduction.

of 1 mg/l for these pollutants. Arsenic and selenium form anionic acids in solution (most other metals act as cations) and require special preliminary treatment prior to conventional metals treatment. Lime, a source of calcium ions, is effective in reducing arsenic and selenium concentrations when the initial concentration is below 1 mg/l. However, preliminary treatment with sodium sulfide at a low pH (i.e., 1 to 3) may be required for waste streams with concentrations in excess of 1 mg/l. The sulfide reacts with the anionic acids to form insoluble sulfides which are readily separated by means of filtration.

Chemical Precipitation and Sedimentation

The most important technology in metals treatment is chemical precipitation and sedimentation. It is accomplished through the addition of a chemical reagent to form metal precipitants which are then removed as solids in a sedimentation step. The options available to a facility as precipitation reagents are: lime ($\text{Ca}(\text{OH})_2$), caustic (NaOH), carbonate ($\text{Ca}(\text{CO}_3)_2$ and $\text{Na}(\text{CO}_3)_2$), sulfide (NaHS and Fe_2S), and sodium borohydride (NaBH_4) (see Figure 11.7).

- Lime ($\text{Ca}(\text{OH})_2$)
- Caustic (NaOH)
- Carbonate ($\text{Ca}(\text{CO}_3)_2$ and $\text{Na}(\text{CO}_3)_2$)
- Sulfide (NaHS and Fe_2S)
- Sodium Borohydride (NaBH_4)
- Combined

Figure 11.7. Metal wastes chemical precipitation and sedimentation.

The advantages and disadvantages of these reagents are summarized in Figure 11.8. Lime is the least expensive reagent, however it generates the highest volume of residue. It also generates a residue which cannot be resold to smelters and refiners for reclaiming because of the presence of the calcium ion. Caustic is more expensive than lime, however it generates a smaller volume of residue. One key advantage to caustic is that the resulting residues can be readily reclaimed. Carbonates are particularly appropriate for metals where solubility within a pH range is not sufficient to meet a given set of treatment standards. The sulfides offer the benefit of achieving effective treatment at lower concentrations due to

- Lime
 - Least Expensive Precipitation Reagent
 - Generates Highest Sludge Volume
 - Sludges Generally Can Not Be Sold to Smelter/Refiners
- Caustic
 - More Expensive than Lime
 - Generates Smaller Volume of Sludge
 - Sludges Can Be Sold to Smelter/Refiners
- Carbonates
 - Applicable for Metals where Solubility within a pH Range Is Not Sufficient to Meet Treatment Standards

Figure 11.8. Applicability of reagents.

lower solubilities of the metal sulfides. Sodium borohydride has application where small volumes of sludge that are suitable for reclamation are desired.

It is appropriate to look at reagent use in the context of the current regulatory framework under HSWA. Historically, lime has been the reagent of choice. It was relatively inexpensive and simple to handle. The phrase "Lime and Settle" refers to the application of lime precipitation and sedimentation technology. In the 1970s, new designs made use of caustic as the precipitation reagent because of the reduction in residue volume realized and the ability for reclamation. In the 1980s, a return to lime and the use of combined reagent techniques have come into use.

One obvious question is why return to lime as a treatment reagent, given that caustic results in a smaller residue volume and a waste that can undergo reclamation? The answer lies in the three points discussed above, that result from the implementation of the HSWA hierarchy. As source reduction and material reuse and recovery techniques are applied, facilities will be generating:

- More concentrated wastes.
- Wastes with a varied array of constituents.
- Wastes with a greater degree of complexation.

Complexation

Complexation is a phenomenon that involves a coordinate bond between a central atom, the metal, and a ligand, the anions (refer to Figure 11.9). In a coordinate bond, the electron pair is shared between the metal and the ligand. A complex containing one coordinate bond is

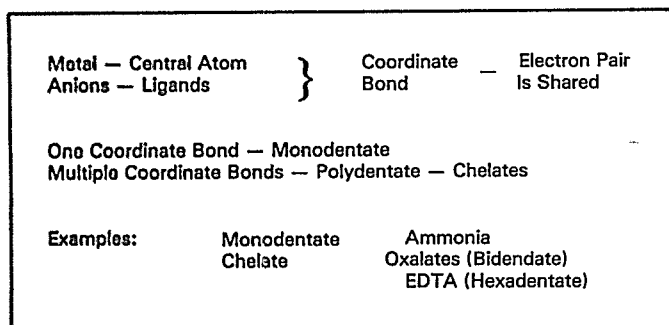


Figure 11.9. Complexation.

referred to as a monodentate complex. Multiple coordinate bonds are characteristic of polydentate complexes. Polydentate complexes are also referred to as chelates. An example of a monodentate forming ligand is ammonia. Examples of chelates are oxalates (bidentates) and EDTA (hexadentates).

The reason for the return to lime is due to the calcium ion present in lime. The calcium ion present in solution through the addition of lime is very effective in competing with the ligand for the metal ion. The sodium ion contributed by caustic is not effective. As such, lime dramatically reduces complexation and is more effective in treating complexed wastes. The term "high lime treatment" has been applied in cases where excess calcium ions are introduced into solution. This is accomplished through the addition of lime to raise the pH to approximately 11.5 or through the addition of calcium chloride (which has a greater solubility than lime).

The use of combinations of precipitation reagents has been most effective in taking advantage of the attributes of caustic as well as the advantages of lime. As an example, a system may use caustic in a first stage to make a coarse pH adjustment followed by the addition of lime to make a fine adjustment. This achieves an overall reduction in the sludge volume, through the use of the caustic and more effective metal removal through the use of lime. Sulfide reagents are used in a similar fashion in combination with caustic or lime to provide additional metal removal, due to the lower solubility of the metal sulfides. Sulfides are also applicable to wastes containing elevated concentrations (i.e., in excess of 2 mg/l) of selenium and arsenic compounds.

Other Metals Wastes

There are three techniques applicable to managing solids generated in metal finishing. These are:

- Dewatering.
- Stabilization.
- Incineration.

There are four dewatering techniques that have been applied in metal processing. The most widely applied techniques are vacuum and belt filtration. They have a higher relative capital cost but generally have a lower relative operating cost. Plate and frame filter presses have experienced less wide spread application. Belt filters generally have a lower relative capital cost and have higher relative operating costs. The higher operating costs are due to the fact that the units are more labor intensive. Centrifuges have been applied in specific instances, but are more difficult to operate when a widely varying mix of wastes is treated.

Experience has shown that companies are most successful in applying a dewatering technique that they have successfully designed and operated in similar applications within the company. As an example, many companies operate plate and frame filter presses as a part of metal manufacturing operations. The knowledge gained in metal processing had been successfully transferred to treatment of metal finishing wastes.

There are six stabilization techniques currently available, however, only two of them have found wide spread application. These are cementation and stabilization through the addition of lime and fly ash. There is currently developmental work being undertaken to make use of bitumen, paraffin, and polymeric materials to reduce the degree to which metals can be taken into solution. Encapsulation with inert materials is also under development.

