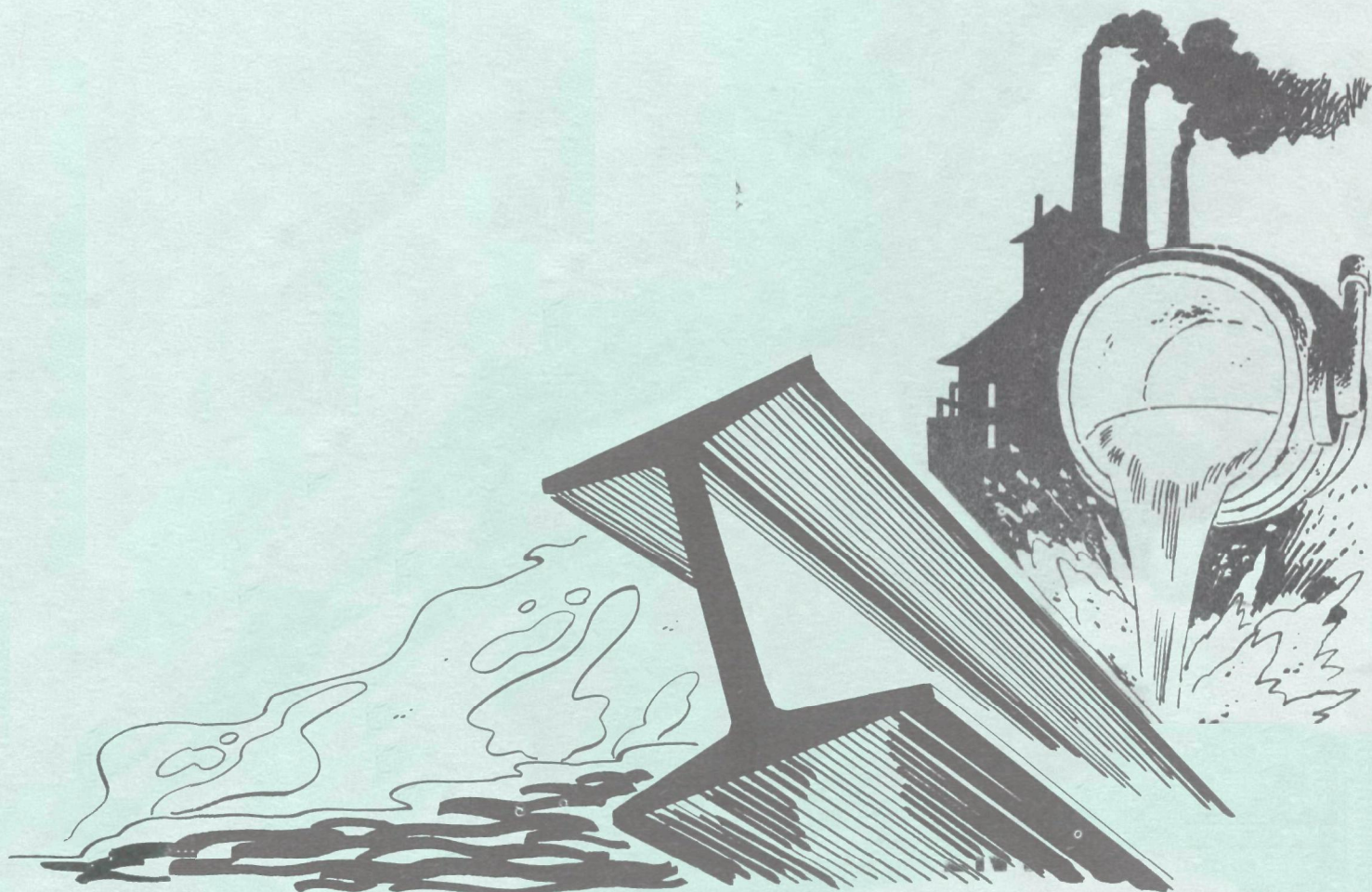




A STATE -of-the- ART REVIEWTM of METAL FINISHING WASTE TREATMENT



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A STATE -of-the- ART REVIEW of METAL FINISHING WASTE TREATMENT

**Sponsored by
FEDERAL WATER QUALITY ADMINISTRATION
U.S. DEPARTMENT OF THE INTERIOR
and
METAL FINISHERS FOUNDATION**

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ABSTRACT

This state-of-the-art survey discusses information in the open literature pertaining to waste treatment in the metal-finishing industry during the last 25 years. The survey emphasizes such aspects as the nature of electroplating and metal-finishing wastes; their impact on sewers, sewage treatment plants, and natural water bodies; current restrictions on their disposal; and conventional methods available for treatment of these wastes.

The review of conventional treatment methods was intended to provide facts for the guidance of the smaller plater in the selection of a waste treatment process. It should be pointed out, however, that these methods were developed more or less for use in larger electroplating plants having large volumes of wastewater. The use of these methods for treating low volumes of wastewater would certainly be feasible, but could be impractical or uneconomical for the smaller plater. An evaluation of these methods from this standpoint will be a major objective in subsequent phases of the program.

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Key Words: Electroplating wastes
Restrictions
Waste treatment

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INTRODUCTION AND SUMMARY

There are between 15,000 and 20,000 metal-finishing facilities in the United States. These include several thousand small-job shops, some larger independent shops, and a larger number of captive facilities. The captive shops are associated with manufacturing concerns producing specific end products, e.g., the automobile industry.

Electroplating and metal finishing waste streams are significant contributors to stream pollution, either directly, owing to their content of toxic and corrosive materials, such as cyanide, acids, and metals, or indirectly, owing to the deleterious effect these components exert on sewage treatment systems. Federal, state, and municipal regulations fixing the allowable concentrations of the harmful components of these wastes already have been established. The restrictions are fairly rigorous at present. There is indication that they will, in many places, be made more rigorous in the future. Enforcement of regulations may be expected to become increasingly strict.

At the present time it appears that most of the smaller plating plants are discharging rinse waters from chromium and cyanide operations directly, with little or no in-plant treatment. Eventually, these plants may be forced by Government agencies to treat rinse waters.

There is an ample technology available for treating chromium and cyanide rinse waters to any required degree of detoxification. The problem facing the smaller plater who may be forced to treat rinse waters before disposal is not expressed by the question "Can the job be done?" but by the question "What is the best and cheapest way for my particular plant to do the job?"

A valid answer to this question must be based on a set of facts. These are

- (1) The volume and composition of the rinse waters to be treated
- (2) The requirements set by Government agencies for an acceptable waste effluent
- (3) Capital costs for rinse water treatment facilities
- (4) Operating costs for the treatment process
- (5) Installation costs for the waste treatment facilities
- (6) Credits from the recovery of metals, cyanide, or rinse water or the decrease in sewage rental fees that might accrue to the selected process.

One phase of this program is designed to provide such facts for the guidance of the small plater. This state-of-the-art survey is an initial effort to do so. It summarizes pertinent information appearing in the open literature. The open literature, however, does not give ample

coverage to the smaller plater. Additional information is being obtained by such means as the circulation of questionnaires, by the sampling and analyses of rinse water from many plating shops, and by the accumulation of cost and some engineering data on the existing processes. Such information will be assembled and presented in a later report.

Another and possibly more important phase of the program is devoted to the investigation and development of new processes. This phase has just begun.

ELECTROPLATING AND METAL FINISHING
IN THE OVERALL WASTE PICTURE

The waste streams that are continuously flowing into our natural waters may be classified as natural, domestic, and industrial. Natural wastewaters are those resulting from rain or melting snow. They carry silt, sediment, soluble salts, small amounts of organic material and atmospheric gases, and floating pollution. Most of the natural wastewaters discharge directly to natural water bodies without benefit of intermediate treatment. Some enter sanitary sewer systems as runoff after storms through leaks, manholes, and seepage to dilute the normal waste burden of the sewers. The polluting effects of natural wastewaters, as such, are generally insignificant and transient. Natural waste streams can and do, however, pick up and transport domestic and industrial wastes when they are in the flow path, and these wastes may be deposited in streams or sewer systems. For example, the runoff from farm lands may contain unusually large amounts of soil and silt, and such materials as phosphate and nitrate, residual insecticides, herbicides, etc. The runoff from the vicinity of certain industrial plants may dissolve or physically transport toxic materials from land or lagoon disposal sites. For this reason, the land disposal of spent electroplating baths can be an undesirable and possibly hazardous practice.^{(1,2)*}

Domestic waste streams are those generated in the kitchens, toilets, bathrooms, noncommercial laundry rooms, and garages of the nation. Their obnoxious characteristics and disease-producing potential have always impelled mankind to do something about them, with the fortunate consequence that adequate technologies have been developed to treat them.

The degree of treatment given domestic waste depends on a number of factors. These factors include the quantity of the sewage, the characteristics of the natural water body that receives the treated effluent, and population distribution along receiving streams, in most cases legally set standards, and in a few regrettable cases mere expediency. Municipal sewage treatment plants are primarily designed to treat domestic waste. They are effective--sometimes with minor modifications--on many industrial wastes as well, particularly those in which the pollutants are organic. Some of the components of industrial wastes, however, are incompatible with the processes used in domestic sewage treatment plants. If their concentration exceeds certain low limits, they can seriously impair or completely destroy the functioning of the plant.

Industrial waste streams are those arising from man's commercial activities. Unlike domestic waste streams, which are reasonably constant in composition and relatable to population in volume, industrial waste streams cover the gamut of composition and volume. This variability makes it necessary to consider each waste stream as a separate problem. Solution of this problem requires basic data on the volume and composition of the waste and on the volume and composition of an effluent that

*References are listed on page 45.

can be tolerated by a receiving stream, sewer, or treatment plant. This is particularly true for the electroplating and metal finishing industry, which emits highly toxic and sometimes corrosive wastewaters.

The Nature of Electroplating and Metal Finishing Wastes

Wastes from an electroplating and metal finishing plant may range from virtually nontoxic to highly lethal and/or corrosive. Innocuous effluents are achieved only by the use of thorough in-plant waste treatment methods. Highly lethal or corrosive effluents are generally the result of the accidental or intentional discharge of concentrated solutions. The incidence of accidental or intentional discharge is minor in the metal finishing field.

The wastewaters from the bulk of the plating plants in this country are of low to medium toxicity, and they might be generally described in such terms as noncatastrophic, presently tolerable, and borderline. Nevertheless, they are undesirably high in toxic and corrosive components, and are not quite adequately controlled.

What is this typical, intermediate-grade waste that is emitted from the majority of plants in the industry? Qualitatively, it is a dilute solution of toxic and corrosive chemicals such as hexavalent chromium, cyanides, metals, mineral acids, and alkalies. The dilution of the effluent --as it leaves the plant--is almost never enough to render the solution innocuous.

In a later section of this report, an attempt is made to characterize this wastewater quantitatively.

Where Wastewaters End Up

Wastewaters from plating and metal finishing plants always end up in some natural body of water; most of these are surface bodies, but some are possibly subterranean. However, the routes to these natural bodies of water are different. A large majority of establishments run their wastes to municipal sanitary sewers. Once in the sewage system, the industrial wastes are diluted with domestic wastes, carried along with them to a sewage treatment plant, and then to some natural body of water. In the sewage system, the toxicity of the plating waste is decreased by such mechanisms as dilution, mixing, neutralization, and precipitation, with dilution exerting the greatest effect.

There are many metal finishing establishments situated in areas where there is no municipal sewage system. The wastes from these plants must take a more direct route to natural water bodies. These plants must provide their own treatment before disposal; the extent of this treatment will depend on the composition of the waste and on the levels of pollutants permissible in the stream or lake.

The Impact of Waste on Sewers

If sufficiently diluted and nearly neutral, plating wastes are only mildly--if at all--corrosive to sewer structures. But serious structural damage from corrosion has occurred from concentrated and acidic wastes not adequately diluted or neutralized before disposal.⁽³⁾

Plating wastes can create toxic conditions directly in sewers. Sewer workers have been poisoned by cyanide gases generated from relatively small accumulations of concentrated plating wastes in sewer systems.⁽⁴⁾ Even relatively dilute cyanide solutions in sewers can be dangerous. Experimentation has shown that a solution containing as little as 50 ppm of cyanide can generate lethal concentrations of cyanogen in sewer atmospheres. A maximum of 20 ppm of cyanide in sewer waters is considered a safe level by some, but other investigators state that 20 ppm of cyanide in small sewers is dangerous and that as low as 10 ppm can be harmful in large sewers where men may work for long hours.⁽³⁻⁵⁾

Plating wastes may also exert indirect toxic effects in sewers by promoting the anaerobic decomposition of domestic sewage in sewer lines. Anaerobic decomposition gives rise to the formation of methane (sewer gas) which has been known to suffocate sewer workers and which may cause fires or explosions. Fortunately, there are few instances of these phenomena.

Plating wastes also can cause the blockage of sewers by solids, although this occurs rarely when wastes are sufficiently dilute.

The Impact of Waste on Sewage Treatment Plants

The general objective of sewage plants is to produce a treated effluent that will meet specifications set by state regulatory bodies. Specific objectives may be any one or combination of the following.

- (1) To render the sewage inoffensive with respect to appearance, odor, etc.
- (2) To reduce the disease-producing potential of the sewage to a point consistent with the subsequent usage of the water
- (3) To avoid creating conditions that may kill the normal population of aquatic life in the receiving stream or lake.

The size, nature, and subsequent usage of the receiving stream has a great deal to do with the degree of sewage treatment required. Communities on the seacoast, near large lakes, or on the banks of large streams may simply screen their sewage and pump the untreated effluent into the natural body of water. Federal and state regulations, mostly formulated since about 1948, have done much to eliminate instances of serious and growing pollution arising from this "no-treatment" practice. Prior to 1948, for example, less than 1 percent of the population in the Ohio

River Basin was served by sewage treatment plants. By 1960 the percentage of the sewered population which operated or was constructing treatment facilities had risen to 84 percent.⁽⁶⁾

Communities discharging their sewage effluents into reasonably large streams or lakes may practice what is called "primary" treatment. The "primary" process is outlined in Figure 1. This amounts simply to screening to remove floating materials, grit and sand separation for the protection of plant equipment, and sedimentation (or settling) to remove solid organic sewage. Primary treatment produces a more or less clear effluent, but one that is still contaminated with oxygen-consuming components and, possibly, disease-producing bacteria. Many municipalities disinfect the final effluent from primary treatment plants by chlorination to eliminate any possible disease-producing organisms. In the sedimentation or settling step of primary treatment processes, inorganic chemicals such as iron or aluminum compounds and lime may be added to improve settling characteristics and the clarity of the effluent. Plating wastes are seldom harmful to the primary treatment plants. Excessively large volumes of plating waste could, however, overtax the capacity of the sedimentation tanks with the result that the sewage would not receive the intended or necessary degree of treatment. Large amounts of acidic wastes can corrode equipment and pipes, and will increase the lime consumption of the plant. The metal content of plating wastes adds to the volume of sediment or sludge produced and may interfere with the subsequent "digestion" of the sludge, if this is practiced by the primary treatment plant.

Many communities, owing to the volume of their sewage effluent and the nature and size of the receiving stream, are forced to practice what is called "secondary" treatment. In this process, the sewage is screened, freed of sand and grit, and subjected to sedimentation as in the "primary" treatment method. The effluent from the primary sedimentation tank is then given an additional or secondary treatment. This secondary treatment amounts to aerating the solution in the presence of aerobic bacteria. The aeration step provides oxygen for the bacteria and other forms of microscopic life to feed upon and destroy most of the organic soluble or colloidal pollutants that remain in the effluent from the primary treatment. After these bacteria have done their job and the pollutants have been ingested, the treated sewage again is subjected to sedimentation where a secondary sludge settles out and the treated effluent is discharged.

The aeration step can be accomplished in a number of ways with different types of equipment. The two major processes of secondary treatment are the trickling filter process and the activated sludge process. These are outlined in Figures 2 and 3.

It is with plants using the secondary treatment that plating wastes can wreak the most damage. This is because the chemicals and metals occurring in these wastes may, if sufficiently concentrated, be toxic to the bacterial colonies which make the process operate. There have been numerous instances where the efficiency of secondary treatment plants

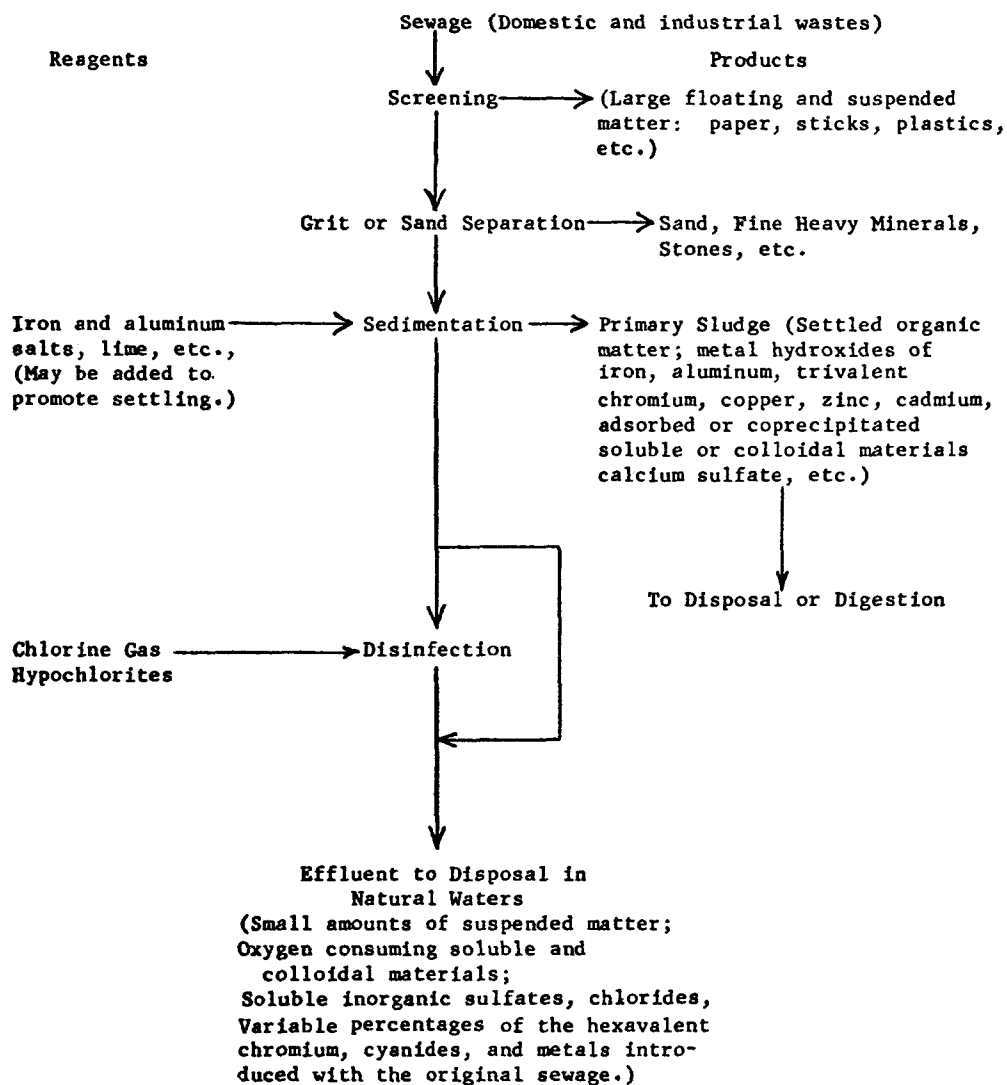


FIGURE 1. PRIMARY SEWAGE TREATMENT

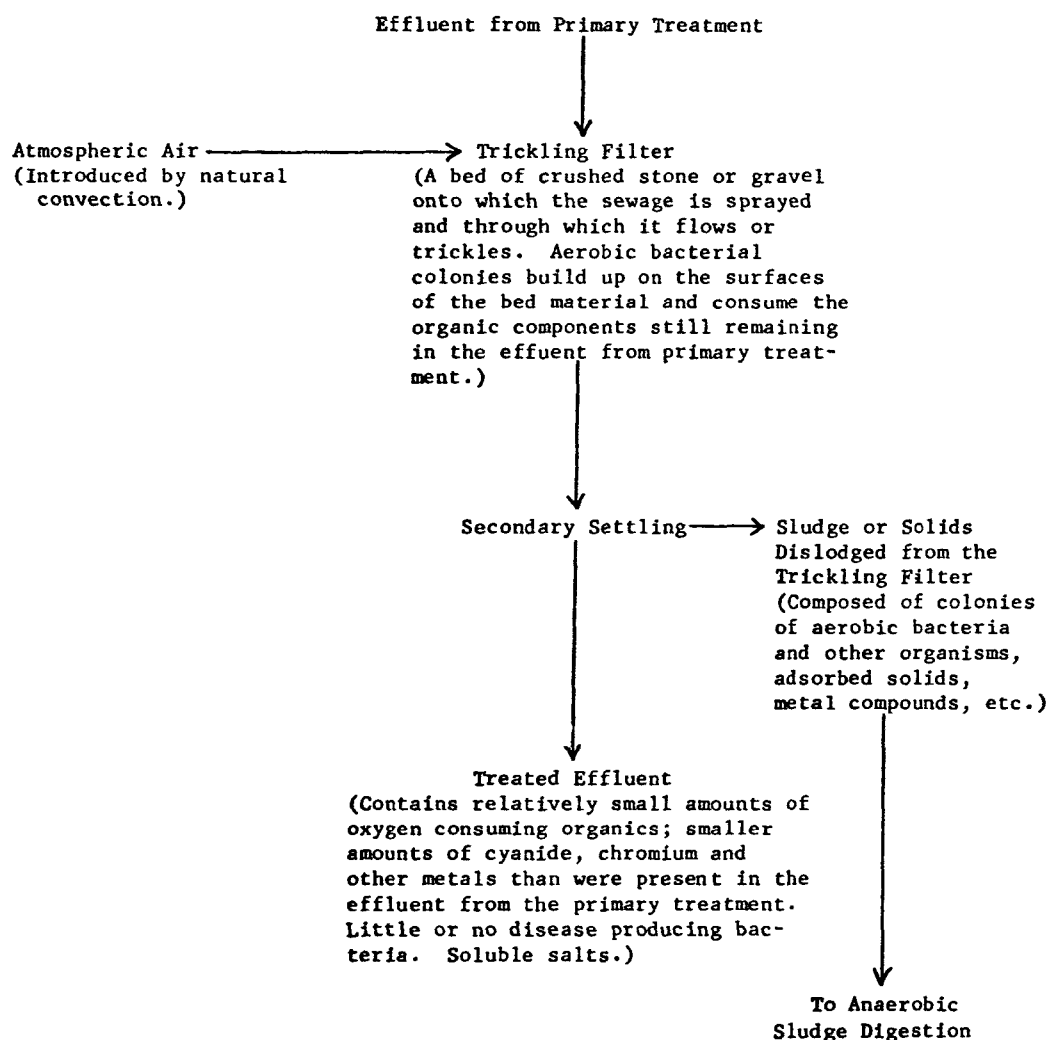


FIGURE 2. TYPICAL TRICKLING FILTER SECONDARY TREATMENT PLANT

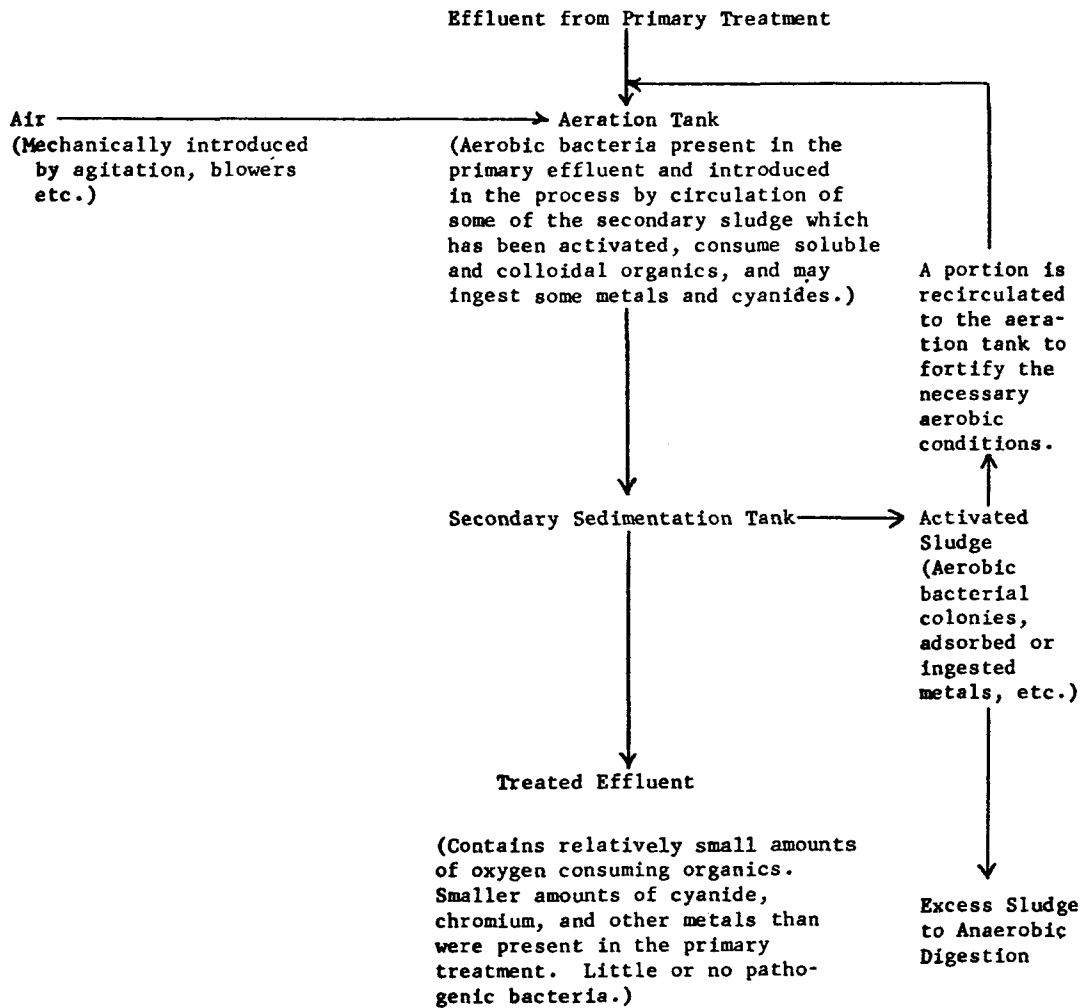


FIGURE 3. TYPICAL ACTIVATED SLUDGE SECONDARY TREATMENT PROCESS

have been grossly or completely impaired by slugs of concentrated wastes.⁽⁷⁻¹⁵⁾ Table 1 lists some of the important troublemaking components of plating waste and shows their reported effects on primary and secondary treatment plants.

There is another unit operation--practiced by both the primary and secondary types of plants--in which the metals in plating wastes can be and sometimes are harmful. This is in the so-called "sludge digestion" step in which primary sludge, either alone or mixed with secondary sludge, is subjected to treatment by anaerobic bacteria. In this process the concentrated sludge, still offensive and toxic, is converted to an innocuous, readily disposable material. Digestion is carried out in the absence of air in large, closed, heated tanks. The digestion process produces a mixture of methane, hydrogen, and carbon dioxide which frequently is burned to supply heat for the sewage plant.

The metal components of the plating wastes concentrate in the settled sludge from primary and secondary treatment and become concentrated even more in the sludge digestion tanks. Instances have been reported where sludge digestion processes were completely halted due to the accumulation of metals (such as copper) in the digestion tanks.⁽¹⁶⁾ It has been estimated that when the total concentration of chromium, copper, nickel, zinc, and cadmium exceeds 400 ppm in digesters, failure can occur.⁽¹⁷⁾ Such concentrations could be produced by raw sewage containing 1.5 to 3 ppm of these metals.

Cyanide does not concentrate in sludges and, in fact, largely decomposes in secondary treatment. However, if the cyanide content of the raw sewage exceeds certain levels, enough may be transferred to the digesters to cause trouble.⁽¹⁸⁾ A steady feed of raw sewage containing 5 ppm of cyanide is capable of disrupting digester operation.⁽¹⁹⁾

The Impact of Waste on Streams, Lakes, Etc.

One of the benefits of plating wastes disposal via municipal sewers is that the wastes become highly diluted and mixed with other wastes; the toxic components are then removed in the sewage treatment process. This is not true for plants that dispose of their wastes directly into natural streams and lakes. Restrictions on the effluents from these plants are significantly tighter than on effluents destined for municipal sewage systems.

There always is some danger that the components of plating wastes in streams can be harmful to man. Cases have been reported where plating wastes were fed to a stream and caused fatalities to livestock.^(20,21) The major and most frequent danger, however, is the destruction of aquatic life. This can occur with extremely low concentrations of cyanides and metal salts.⁽²²⁻²⁴⁾ The data in Table 2 provide some concept of the lethal nature of these compounds to fish. These data show the lowest concentrations which have been demonstrated to be lethal. The lethal concentration will vary with the type of fish, the pH and hardness of the water, temperature, etc.

TABLE 1. EFFECTS OF COMPONENTS OF PLATING WASTES ON SEWAGE TREATMENT PLANT

	Partially Precipitated With or Adsorbed by Sludge	Corrosive to Equipment or Structures	Tolerable Concentration at Steady Flow, ppm	Concentration with Appreciable Effect at Steady Flow, ppm	Concentration of "Slugs" Causing Temporary Impairment, ppm	Increases Toxicity of Metals	May Cause High Sludge Volumes	Concentration of Slugs Causing Considerable Impairment	Affects Oxidizing Ability of Sludge	Partially or Largely Consumed
<u>Hexavalent Chromium</u>										
Primary	x									
Trickling filter			1-4	10						
Activated sludge	x		2-8	5-10	10-50			100-500	x	
<u>Trivalent Chromium</u>										
Primary	x									
Trickling filter	x									
Activated sludge	x									
<u>Copper</u>										
Primary	x									
Trickling filter	x			1-3						
Activated sludge	x		1	4(a)	50				x	
<u>Zinc</u>										
Primary	x									
Trickling filter	x			1-3						
Activated sludge	x			5-10					x	
<u>Cadmium</u>										
Primary	x									
Trickling filter	x									
Activated sludge	x								x	
<u>Nickel</u>										
Primary	x									
Trickling filter	x									
Activated sludge	x			1-3						
<u>Cyanide</u>										
Primary										
Trickling filter			2		30	x				x
Activated sludge			1-2	9(a)		x				x
<u>Acid</u>										
Primary		x								
Trickling filter		x								
Activated sludge		x								
<u>Solids</u>										
Primary							x			
Trickling filter							x			
Activated sludge							x			

(a) Combination of 9 ppm CN^- and 4 ppm Cu adversely affected sludge flocculation.

TABLE 2. EFFECT OF PLATING WASTE COMPONENTS
ON FISH LIFE⁽²⁵⁾

Component	Levels of Concentration Fatal to Some Fish, ppm
Hexavalent chromium	5
Trivalent chromium	about 5
Cyanide	0.05
Ferrocyanide	1.45
Copper	0.02
Zinc	0.3
Cadmium	0.6
Nickel	5

Restrictions

Water pollution by domestic and industrial wastes has been recognized as a threat to the health and welfare of the country for many years. Prior to the 1940's many individuals, associations, Government agencies, and communities fought isolated battles against pollution; many more did substantially nothing. It was not until after World War II that public officialdom became generally aware that water pollution had already reached a serious level and that with the accelerating growth of population and industry the problem could become catastrophic.

In 1948, the Congress of the United States passed the Water Pollution Control Act which was to have the effect of unifying and implementing a nationwide battle against water pollution. This act was extended in scope and sanctioned by additional legislation in 1956, 1961, 1965, and most recently the 'Clean Water Restoration Act of 1966'.

Federal legislation is aimed primarily at maintaining the quality of federally controlled interstate and other natural waters as they may affect the public health and welfare. The laws allocate the authority and responsibility for maintaining water quality to the individual states and, in the case of interstate waters, to associations of states. Jurisdiction over intrastate waters is left to the individual association of states with the provision that Federal intervention is possible upon the request of a governor.

The role of the Federal Government is largely advisory and coordinating. It provides guidelines for the states and interstate associations to follow, reviews criteria and enforcement procedures set by the states, determines their suitability for achieving the aims of the Federal water quality laws, and adjudicates disputes or differences that may crop up between states. The basic regulations for water quality are therefore laid down by the individual states or by associations of states which

either directly or indirectly determine the quality of all wastewater generated within their jurisdictional area, industrial and domestic alike.

Direct control by states or state associations applies when effluents are sent directly to state or interstate waters. Such is the case for municipal sewage treatment plants discharging into streams or lakes, or rurally located industries discharging their waste directly to some body of natural water. Indirect control by the states is exerted through municipalities that operate the sewage treatment plants. These municipalities are answerable to the state for the quality of their sewage plant effluents. It also is left to these municipalities to ascertain--by proper regulation and enforcement--that industrial plants using their sewers and sewage plants do not discharge wastes that would impair the quality of the sewage treatment effluent.

The intent of various Federal and State agencies charged with the abatement of stream pollution is to improve or maintain the quality of surface waters at levels commensurate with the anticipated use for these waters. A comprehensive guideline which sets forth the standards for the five basic uses of water recently has been developed by the Federal Water Pollution Control Administration. This guideline has been published as a report entitled Water Quality Criteria.(135) . The five basic uses of water outlined in that publication are

- (1) Recreation (including aesthetic uses)
- (2) Fish, aquatic life, and wildlife
- (3) Public water supply
- (4) Agriculture
- (5) Industry.

Since the majority of plating shops in the country are located in or near highly urbanized areas, the restrictions placed upon their effluents are influenced by the standards set for public water supply. These standards are set by the U. S. Department of Health, Education, and Welfare and are to some extent tentative; periodically they are revised.(27) The following tabulation is an abridgement of specifications set up in 1962 (listing only the specific components likely to be found in plating plant effluents)

<u>Component</u>	<u>Recommended Maximum Level, ppm</u>	<u>Levels for Rejection, ppm</u>
Arsenic	0.01	0.05
Barium	--	1.0
Chlorine	250	--
Copper	1.00	--
Cyanide	0.01	0.2
Iron	0.3	--
Cadmium	--	0.01
Nickel	2.0	--
Sulfate	250	--

<u>Component</u>	<u>Recommended Maximum Level, ppm</u>	<u>Levels for Rejection, ppm</u>
Tin	1.0	--
Zinc	5.0	--
Hexavalent chromium	--	0.05
Trivalent chromium	--	1.0
Lead	--	0.05
Silver	--	0.05

The "drinking water" specification is more or less a guideline based on the toxic potential of the above components to humans. If the stream, stream segment, or lake is used for fishing, restrictions on some components (such as cyanide, barium, copper, and zinc) are much tighter; the permissible levels are based on such conditions as the type of fish involved, alkalinity, and hardness of the water.

Each state and association of states has adopted its own route to satisfying the objectives and intent of the overall Federal legislation. One state, Pennsylvania, requires that all effluents meet the "Drinking Water" standards except for chlorides, sulfates, and nitrates. It further requires that hexavalent chromium and cyanides in wastes be kept below detectable levels. (26)

The majority of state agencies and interstate associations have adopted a different approach. These agencies first determine the usage to which the water in a stream, stream segment, pond, or lake is to be put and then, employing various terminologies, classify the water according to this usage. Each class is assigned maximum limits for the concentration of pollutants by considering the dilution afforded by the stream itself and by tributary streams, the naturally occurring "self" purification of the stream, etc. Table 3 shows the regulations imposed by the states.

Municipalities also are obliged to produce sewage plant effluents that meet the standards of the states or group agencies. They in turn apply their own regulations to industries contributing to their sewerage systems.

Municipal regulations are based on such factors as the volume of the waste in relationship to the total volume of sewage waste; the type of sewage treatment employed; limitations imposed on the sewage plant's own effluent; the number, size, and type of industry discharging to the sewers; and, in some cases, the materials of construction and the engineering details of the sewers or the treatment plants. Their specifications will require in-plant treatments ranging from "complete" to none. Table 4 shows typical restrictions on flows to municipal sewers.

The disposal of concentrated wastes such as stripping or anodizing solutions often is not specifically regulated, but these must be treated by dilution, neutralization, and detoxification procedures to the point where concentration of harmful components (acids, alkalies, cyanides, metals) meets the requirements of the municipalities or states. In some

TABLE 3. STATE REGULATIONS RE: WASTE WATER CRITERIA

STATE	Date of letter, law, or public act	Classi- fication	CHEMICAL CONSTITUENTS - PPM														SOLIDS CONTENT				California per 100 ml				COMMENTS							
			Acidity	Alkali	pH Range	Heavy Metals	Cd	Cu	Zn	Cr	NH ₃	CO ₂	Cl	SO ₄	CN	CND	FeCN	Insoluble Solids	Dissolved Solids	Total	Oil	Insoluble Solids	BOD	Coliform					Phenol	Color	Odor	Taste
ALABAMA	6-14-54																												No established limits (1) and (7) for guidance			
ARIZONA	9-18-54																												(8)			
ARKANSAS	5-3-54																												(8) No toxic limits established			
CALIFORNIA	Members (1) 6-9-54 (2)																												No fixed effluent or stream standards (2)			
COLORADO	6-10-54 Pub. 131-10-54 Member (8)				5.0								0.5					0.5 ml APHA		15ppm	30			0.02					Ph. 0.1 ppm, As 0.05 ppm, Se 0.05 ppm, (5)			
CONNECTICUT	6-2-54																												Survey of drainage basins and water usage underway			
DELAWARE	12-10-54																												(8) Use (2) for guidance			
FLORIDA	5-28-54																												Consider individual cases on own merits			
IDAHO	6-8-54 Member (7)	a Water Supply b Recreation c Fish and Wild Life d Navigation e Industrial			6.5-8.5																											
					6.5-8.5																											
					6.5-8.5																											
					6.5-8.5																											
					6.0-9.0																											
ILLINOIS	6-14-54																													(8)		
INDIANA	6-10-54 Pub. 131-10-54																														(8)	
IOWA	12-7-54 Member (4)																														(8)	
KANSAS	6-10-54				6.0-9.0																										(8)	
KENTUCKY	6-15-54																														(8) No limits of general applicability	
LOUISIANA	Member (2)																														(A) - Water supply (B) - Bathing and Recreation (C) - Fish (D) - Sewage and Ind. waste	
MAINE	6-10-54 Pub. 131-10-54																														Threshold odor No. 80	
MARYLAND	6-10-54 Pub. 131-10-54				5.5-8.5													1500 ppm	400 ppm	1900 ppm	30 ppm	100ppm			400 ppm						Threshold odor No. 80	
MASSACHUSETTS	6-2-54 Member (6)																														(8)	
MICHIGAN	7-6-54 Pub. 131-10-54																														(8)	
MINNESOTA	6-2-54 Pub. 131-10-54																														(8)	
MISSISSIPPI	12-13-54 Pub. 247				6.5-8.6																										(8)	
MISSOURI	6-10-54 Member (4)																														Toxic substances including Metallic ions, Phenols, Oils, Alkalies, Acids should be virtually eliminated from effluents.	
MONTANA	7-7-54 Pub. 131-10-54																															
NEBRASKA	6-1-54 Member (5)																														No refuse harmful to Aquatic life may be pumped	
NEVADA	12-10-54 Pub. 131-10-54																															
NEW HAMPSHIRE	12-10-54 Pub. 131-10-54				5.0-8.3																										(A) Water Supply (B) Bathing and Recreation (C) Sewage	
NEW JERSEY	6-3-54				5.0-8.5	0								0	0						0				40 ppm		0				(B) Water for potable uses, shell fish culture, bathing & recreation on	
NEW MEXICO	6-10-54 Pub. 131-10-54																														(8)	
NOTES: (1) United States Public Health Standards (2) "Water Quality Criteria" of California Publication #3 (1952) (3) S.W. Mississippi Basin Comm. (4) Missouri Drainage Basin (5) Radioactive Materials Alpha, Beta and Gamma Radiation-1x10 ⁻⁶ Micro-Curies each (6) New England Interstate Water Pollution Control Comm. (7) Pacific NW Pollution Control Council (8) Consider Individual Cases on Own Merit (9) None Making Water Unavailable for Use Indicated (10) Toxic Substances Per (1) (11) None Attributable to Sewage or Industrial Wastes (12) None After Reasonable Dilution in Receiving Body																																

TABLE 3. STATE REGULATIONS RE: WASTE WATER CRITERIA (continued)

STATE	Date of Letter, Law or Public	Classification	Acidity	Alkali	pH Range	CHEMICAL CONSTITUENTS - PPM														SOLIDS CONTENT			Coliform per 100 ml	Phosphorus	Color	Odor	Taste	COMMENTS																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																													
						As	Cu	C ¹³	Zn	Cd	NH ₃	CrO ₃	Cl	SO ₄	CN	CNO	FeCN	Residual	Total	OH	Residual	BOD																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
NEW YORK	6-28-54	Surface water			6.5-8.5	(7)	0.2		0.3	0.3	2 at pH 8	(7)			0.1		0.4	(11)		(11)	5.0 ppm																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				

Taken from Finishers' Management (June, 1968)

TABLE 4. SOME RESTRICTIONS ON PLATING AND METAL FINISHING
WASTES DISCHARGED TO SEWERS

	pH	CN	Cu	Cr ⁶	Cd	Zn	Ni	Ba	Other Heavy Metals	Total Dissolved Solids	Suspended Solids	Ref.
Typical Limits	6-10	0	0.3	0.05	0.4	0.3	2.0	--	--	--	--	28
Typical Range	5-10	0.2	0.4	0-10	0-5	0-5	2-10	--	0-50	2000-5000	200-1000	21
Examples of Limits:												
New Jersey	6-10	1	1	3	3	3	10			Avg. 1500	Avg. 500	29
Conneaut, Ohio (1951)	5.5-9.5		3	5		2						30
Canadian	--	2	1								350	31
New York (1963)	--	0.2	5.0	0.5	0.5	5.0	3.0					12
Kentucky City Ord.	5.5-9.0	<2(a)		<5							<20	32
Connecticut	6.5-8.5	0.05	3.0	3.0		3.0	3.0					33
Said to be gen- erally acceptable				5								34

(a) As NaCl.

cases, associations of platers have adopted the policy that such wastes should never be sent to municipal sewers or streams, but must be disposed of by other means, such as sale to outside salvage organizations. In some cases municipalities permit the disposal of concentrated wastes to sewers with ample dilution and/or neutralization, but only after notifying municipal officials. The direct disposal of concentrated toxic or highly acidic wastes to natural waters is practically never permitted.

CHARACTERISTICS OF ELECTROPLATING AND METAL FINISHING WASTES

Sources

Waterborne wastes generated in the electroplating and metal finishing industry include the following.

- (1) Rinse waters from plating, cleaning, and other surface finishing operations.
- (2) Concentrated plating and finishing baths that are intentionally or accidentally discharged.
- (3) Wastes from plant or equipment cleanup.
- (4) Sludges, filter cakes, etc., produced by naturally occurring deposition in operating baths or by intentional precipitation in the purification of operating baths, chemical rinsing circuits, etc., when flushed down sewers.
- (5) Regenerants from ion exchange units.
- (6) Vent scrubber waters.

From the viewpoint of the smaller plater, by far the most important of these wastes is the rinse water. It is the constantly flowing, production-connected stream that is generally so large in volume that it cannot be economically impounded for treatment before disposal; this stream is usually concentrated enough to be toxic. Under present restrictions and enforcement procedures, rinse water disposal may not present much of a problem to many platers. With more stringent regulations and more rigorous enforcement, it could become an acute problem.

It is a chief aim of this review to present to the smaller plater the currently available conventional processes which can be applied to rinse water wastes. It is an aim of the current research program (for which this review is a preliminary phase) to investigate several possible new approaches and, eventually, to present an evaluation of all the processes available.

The other wastes (concentrated sludges, cleanup water, filter cakes, regenerants, and scrubber waters) are not believed to be of great concern to the smaller plater because they are not so vitally connected to production and can be handled as isolated, more or less individual problems.

Quantities and Composition

Much of the information in the literature on the volumes and composition of electroplating and metal finishing wastes refers to the large- or intermediate-size plants that do routine plating. Table 5 presents a cross section of this information. As will be seen from the data, there

TABLE 5. VOLUMES OF CHROMIUM AND CYANIDE-BEARING WASTES
FROM TYPICAL PLATING OPERATIONS IN THE ELECTRO-
PLATING INDUSTRY

Type of Work Plated	Chromium-Bearing Waste				Cyanide-Bearing Waste					Ref.
	Volume, gal.	Analyses, ppm ^(a)			Volume, gal.	Analyses, ppm ^(a)				
		Cr	Ni	Cu		CN	Cu	Zn	Cd	
Aircraft engines and parts	440,630/day	--	--	--	293,760/day	--	--	--	--	35
Automobile bumpers	480,000/day	--	--	--	--	--	--	--	--	36
Automobile grills	100,000/day	700	--	--	--	--	--	--	--	37
Missile parts	80,000/day	1	--	--	32,000/day	80	--	--	--	38
Office furniture	24,000/day	--	--	--	--	--	--	--	--	39
Typewriters and office machines	50,000/day	16	39	--	--	39	--	--	--	40
Instrumentation and control equipment	--	--	--	--	13,000/day	--	--	--	--	41
Electronic hardware	828,000/day	--	--	--	259,200/day	200-1500	--	--	--	42
Home appliances	43,200/day	--	--	--	108,000/day	--	--	--	--	20
Television antennae	--	--	--	--	11,000/day	--	--	--	--	43
Silverware	40,000/day	5	33	135	165,000/day	172	18	11	--	44
Instrument motors and electric clocks	112,000/day	--	--	--	--	--	--	--	--	45
Automobile manufacture	620,000/day	30	80	70	410,000/day	204	--	113	--	46
Unspecified	--	--	--	--	250-400/hr	40-130	--	--	--	47
Metal fastener plant	89,000/day	52	302	--	--	--	--	--	--	48

(a) Analyses not shown are not available.

are wide variations in both the volume and composition from plant to plant. This is because the waste streams from these plants are the product of local plant conditions and practices such as dragout, rinsing techniques, recovery methods employed, and the admixture of other waste streams, such as those from machine shops.

There is little or no information on the volume and composition of wastes that might be encountered in the smaller shops that do general plating. It must be assumed, however, that the rinse waters from the smaller establishments are extremely variable from shop to shop, and perhaps from day to day or hour to hour within a specific shop. As an example of the variability that may be expected, one article indicates that "typical" rinse waters from general plating operations may contain from 2 to 76 ppm hexavalent chromium, 0.5 to 32 ppm copper, 0.1 to 2 ppm of nickel, and 21 to 68 ppm zinc.⁽⁴⁹⁾

Methods for Treating Rinse Waters

The technology of plating and metal finishing waste treatment has been thoroughly developed and has been the subject of numerous excellent publications.^(1, 50-63) There are at most about a dozen unit processes which are basic to the technology as a whole. Each does a specific job with varying degrees of effectiveness, simplicity of application, and cost. These unit operations are listed in Table 6 and are discussed in the following sections.

TABLE 6. CHEMICAL METHODS FOR DETOXIFYING WASTES

Conventional Methods for Cyanide Rinses

- Complete cyanide destruction by chlorine gas
- Complete cyanide destruction by hypochlorites
- Conversion of cyanide to cyanate by chlorine gas
- Conversion of cyanide to cyanate by hypochlorites
- Conversion of cyanide to ferrocyanide by ferrous sulfates

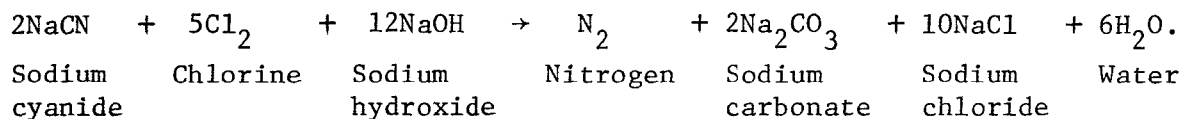
Conventional Methods for Chromium Rinses

- Reduction of hexavalent chromium by sulfur dioxide
- Reduction of hexavalent chromium by sulfites, etc.
- Reduction of hexavalent chromium by ferrous sulfate
- Precipitation of hexavalent chromium by barium compounds

Conventional Methods for Cyanide Rinses

Complete Cyanide Destruction by Chlorine Gas. Cyanide in rinse waters can be completely destroyed by treatment with chlorine gas in an alkaline solution at room temperature. The cyanide radical, CN, is disrupted with

the carbon fragment being converted to carbonate and the nitrogen to nitrogen gas. The reaction involved is



The process is carried out by adding chlorine gas and an alkaline compound, such as caustic soda or hydrated lime, to the solution. Special equipment is required for the safe and efficient addition of chlorine. Some form of agitation is also necessary to obtain adequate mixing and reaction rates. The overall reaction is fairly slow, possibly requiring hours for the complete destruction of cyanide--particularly if the solution contains heavy metals which may form cyanide complexes.

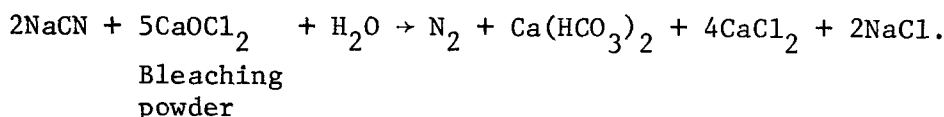
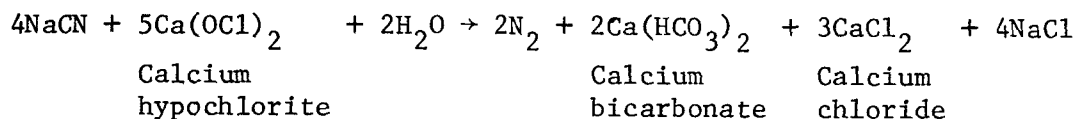
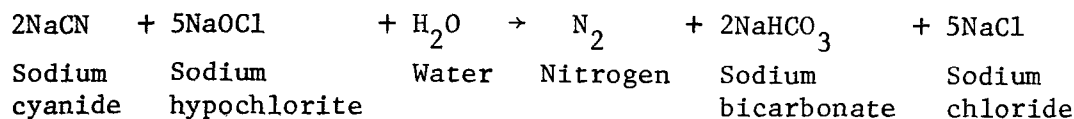
The process can be carried out on a batch or continuous basis. If done batchwise, it requires the installation of rather large tanks for storing the rinse waters before treatment. It has been recommended that duplicate tankage be provided--each capable of undergoing treatment while the other is filling. Recommended tank sizes vary, ranging in capacities corresponding to from 4 to 24 hours of operation.^(64,65,66) If done continuously on a flow-through basis, this process requires some instrumentation to control the reagent additions and the quality of the effluent.

In the chlorination step, which is conducted under highly alkaline conditions, most of the heavy metals that accompany cyanide in the rinse waters precipitate as hydroxides, or possibly as ferro or ferricyanides. These latter respond slowly to the chlorine treatment and, if permitted to settle out, probably receive little or no treatment. This is one of the basic reasons for the vigorous agitation required in the process.

Sludge formation nearly always accompanies the chlorination process. The sludge is composed of the precipitated metal hydroxides and, if lime is used to provide the alkalinity, the sludge also contains calcium carbonate and possibly calcium sulfate. In some cases the volume of sludge produced may be too great for disposal to sewers. If so, provisions for permitting the sludge to settle before disposal of the liquid phase must be incorporated in the plant.

The suitability of this process for the smaller plater has been questioned by some authorities, primarily because of the potential hazards and difficulty in handling, metering, and distributing the chlorine gas⁽⁶⁷⁾ and in maintaining the proper conditions of alkalinity in the solution to prevent formation and evolution of poisonous cyanogen chloride. Commercial application of this process is described frequently in the literature.⁽⁶⁸⁻⁷⁵⁾

Complete Cyanide Destruction by Hypochlorites. Cyanide also may be completely destroyed by hypochlorites such as sodium hypochlorite (NaOCl), calcium hypochlorite [$\text{Ca}(\text{OCl})_2$], or bleaching powder (CaOCl_2). The probable reactions, analogous to the reactions with chlorine gas in an alkaline medium, are shown below



The process is relatively simple and consists essentially of adding the hypochlorite, either as a solution or as a solid to the rinse water. No additional alkalinizing agent, such as sodium hydroxide or hydrated lime, is required, as in the chlorine gas process.

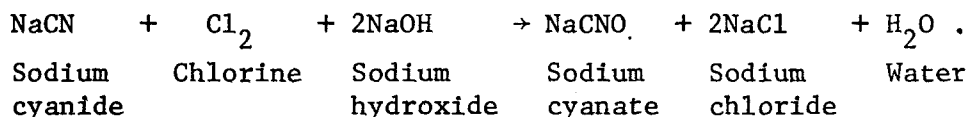
Agitation also is required with hypochlorites to effect proper mixing. The process with hypochlorites may be conducted batchwise or continuously. This process probably is best suited to the needs of the smaller plater who is faced with the necessity for complete destruction of cyanide.

Advantages of hypochlorite processes over the chlorination process are

- (1) If sodium hypochlorite or calcium hypochlorite are used, the theoretical chlorine consumption is only half as great as that if chlorine gas is used. If bleaching powder is used, the theoretical chlorine consumption will be the same as for the chlorine gas process.
- (2) Handling and metering of the hypochlorites is relatively simple and nonhazardous.
- (3) The reaction is more rapid than that with chlorine.
- (4) If sodium hypochlorite is used, sludge production is minimized.

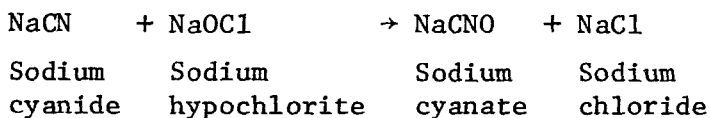
This process is also used commercially. (14,76,77,78)

Conversion of Cyanide to Cyanate by Chlorine Gas. The cyanate radical (CNO) is only about one-thousandth as toxic as cyanide⁽⁴⁹⁾, and many regulatory agencies will accept rather high cyanate concentrations in effluents. The conversion of cyanide to cyanate by chlorine gas is a rapid reaction, requiring only minutes. The reaction is, in fact, an intermediate stage in the process for the complete destruction of cyanide by chlorine. The chemical equation involved is



It is carried out in the same fashion and type of equipment as the process involving the complete destruction of cyanide by chlorine. It may be conducted batchwise or continuously. Sludge formation also occurs in this process and provisions for separating sludge from treated liquor may be required.

Conversion of Cyanide to Cyanate by Hypochlorites. The hypochlorites also are capable of converting cyanides to the relatively nontoxic cyanates by a similar reaction



Other hypochlorites, such as calcium hypochlorite or bleaching powder can be used in place of sodium hypochlorite. The process is straightforward and rapid.

For the smaller plater aiming at the partial destruction of cyanide, i.e., the conversion of cyanide to cyanate, the hypochlorite method is more suitable than the chlorine method. This process has also been applied practically using either chlorine or one of the hypochlorites. (68,79-84)

Conversion of Cyanide to Ferrocyanide by Ferrous Sulfate. The formation of less toxic cyanide complexes such as ferro and ferricyanides also has been used as a method for disposing of cyanide wastewaters. This process involves the use of iron salts to form complex compounds with the free cyanide in the wastes. Eventually these cyanide complexes are precipitated and removed as a sludge. The use of ferrous sulfate, for example, produces the characteristic dark blue sludge or Prussian blue.

The major advantage of this treatment method is that it is relatively inexpensive where waste ferrous sulfate is available. However, considerable quantities of sludge may be formed and the treated solutions are strongly colored. There also is evidence that ferrocyanides may be decomposed to free cyanide by sunlight. The regeneration of the cyanide under these conditions would contaminate the receiving stream. (61)

This method has received very little acceptance by the industry in this country, but appears to be used in Europe. (64-74) The complexing process apparently does not completely destroy cyanide under practical operating conditions. Cyanide levels in treated solutions may be as great as 5 to 10 ppm. (85,86)

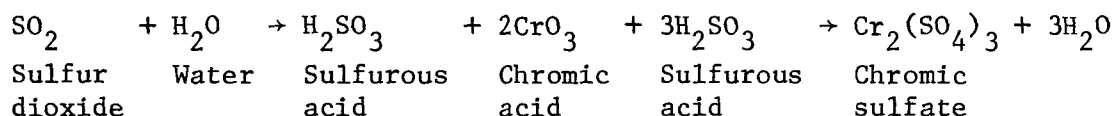
Conventional Methods for Chromium Rinses

Reduction of Hexavalent Chromium by Sulfur Dioxide, Sulfites, and Ferrous Sulfate. Chromium-bearing wastes often are disposed of by processes involving the reduction of chromium to the trivalent form and the subsequent precipitation of the reduced chromium with alkali. This general

process is employed extensively by intermediate and large plating plants for treatment of chromium wastewaters. (37,65,81,87-92)

Methods for reduction of hexavalent chromium vary with each particular plant. Common reducing agents are gaseous sulfur dioxide; sodium bisulfite, metabisulfite, or hydrosulfite; and ferrous sulfate.

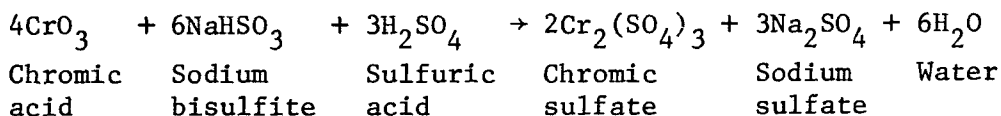
Reduction with SO_2 is the method most commonly employed by many large plating plants. Basic equipment for this method consists of sulfonators for combining sulfur dioxide with water and agitated tanks for conducting the reduction. During reduction sulfuric acid is normally added to maintain an acid solution with a pH range of 2.0-3.0. Under these conditions, the reactions which occur are



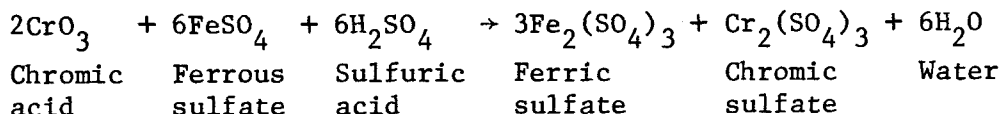
The approximate chemical usage is 1 pound of SO_2 per pound of chromic acid (CrO_3) in the waste solution.

A recent development in this treatment method is the utilization of the sulfur dioxide contained in waste flue gases from boiler plants. (93) This novel technique involves the use of scrubbers for adsorption of the sulfur dioxide in the waste chromium solutions. If complete reduction is not obtained in the adsorption column, sodium bisulfite or some other reducing agent is added for final treatment of the waste solution. One such plant employing this technique reports that enough sulfur dioxide is available from the boiler flue gases to completely treat the total volume of waste chromium solution from the plating plant.

Other reducing agents, such as bisulfites or ferrous sulfate, also are used by plating plants for treatment of chromium wastewaters. The reaction with bisulfites is



The bisulfite may be added as a solid or as a solution. As with sulfur dioxide, the addition of sulfuric acid is required to maintain a pH of about 2 to 3 to obtain rapid and complete reaction. The anhydrous form of sodium bisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) or sodium metabisulfite also may be used. The reaction with ferrous sulfate is



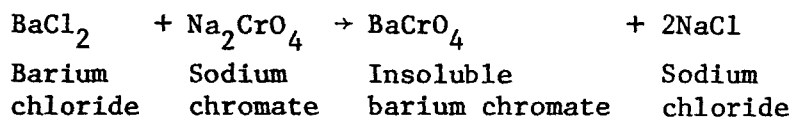
With ferrous sulfate, however, larger quantities of sludge are produced than with sulfur dioxide or bisulfites. Some economic advantage for

reduction with ferrous sulfate may be realized if quantities of waste pickle liquor are readily available at the plating plant.

After reduction, the solution is acidic and contains the chromium and other metals that may have accompanied the chromium rinse waters (copper, nickel, etc.). If ferrous sulfate is used, the solution also will contain relatively large amounts of iron. If this solution is discarded directly to the sewer, it is sufficiently acid to be corrosive. Neutralization, therefore, generally is required. This is done in various ways. The acidic wastes may be combined with alkaline wastewaters, such as treated cyanide wastes, or they may be treated with alkalies such as sodium hydroxide or hydrated lime. The precipitates from the neutralization step are composed of the hydroxides of the metals (chromium, nickel, copper, etc.). If ferrous sulfate has been used for reduction, they also will contain relatively large amounts of iron hydroxide. If neutralization has been carried out with lime, the precipitates will contain excess lime and calcium sulfate. It may therefore be necessary to provide a settling tank to permit separation of the precipitates from the effluent before their disposal.

After reduction it may be possible to dispose directly of the effluent. The effluent may, however, require neutralization and precipitation of the now trivalent chromium (and other metals) before disposal to reduce its corrosiveness and whatever toxicity it may possess from such metals as nickel, copper, etc. If the precipitated solids after neutralization are too high or too potentially toxic to meet local regulations, the neutralized effluent may have to be given some sort of solids-liquids separation, such as sedimentation or filtration, prior to disposal.

Precipitation of Hexavalent Chromium by Barium Compounds. Removal of toxic chromium from wastewaters also can be effected by precipitation as hexavalent chromium.^(5,94) This method of treatment usually involves the use of barium salts for precipitation of insoluble barium chromate. With barium chloride, for example, the following reaction takes place



The major disadvantage of this method is that the additions of barium chloride must be strictly controlled, as this chemical is highly toxic. The sludges produced also are toxic and may result in an additional disposal problem.

The process involving the precipitation of highly insoluble barium chromate generally will require a solids-liquid separation step before the effluent is disposed. Relatively few plants employ this process.

Miscellaneous Methods for Treating Rinse Water

In addition to the previously outlined conventional processes for treating rinse waters, other methods described in the literature have been used. These include the formation of cyanide complexes by the use of polysulfides to form relatively nontoxic sulfocyanates^(61,66), the destruction of cyanide by potassium permanganate⁽⁹⁵⁾, the conversion of cyanide to cyanate by ozone^(58,96), the conversion of cyanide to cyanate by hydrogen peroxide⁽⁹⁷⁾, the complexation of cyanide by nickel salts to form the highly stable nickel cyanide complex⁽⁹⁸⁾, the biological destruction of cyanide on trickling filters^(99,100), the destruction of cyanide by irradiation⁽¹⁰¹⁾, the use of techniques such as dialysis and reverse osmosis to purify both chromium and cyanide rinse waters⁽¹⁰²⁻¹⁰⁴⁾, the electrolytic reduction of hexavalent chromium, and the use of scrap metal to reduce chromium⁽¹⁰⁵⁻¹⁰⁶⁾.

These processes are in various stages of development. Some, such as the use of polysulfides to complex cyanides, or the use of permanganate to destroy cyanides, have been reduced to commercial practice. Some have been merely suggested, i.e., the complexation of cyanide by nickel. Reverse osmosis and dialysis as methods for treating electroplating wastes are in early stages of development. Little is known about the electrolytic reduction of hexavalent chromium in rinse waters at this time because the only reference to this process encountered was in Japanese and a translation was not available.

The fact that these approaches have not been included in the discussion of conventional methods should not be interpreted to mean that they are being dismissed from consideration. Any one or several of them may prove to have some merit as a means for treating rinse waters. They will be evaluated during the course of the current research program.

Physical Methods for Treating Rinse Water

In addition to the chemical operations discussed in the foregoing sections, there are two commonly used physical methods that have been used in the treatment of rinse waters. These are ion exchange and evaporation.

The technological and engineering aspects of ion exchange processes for treating chromium solutions have been thoroughly developed. These processes have been widely used in the treatment of chromium wastes and mixed wastes not only for detoxification but also for the recovery of chromium, water, and, in the case of hot rinses, of heat^(43,56,57,107-121). Numerous applications of ion exchange to chromium wastes are reported in the literature for the treatment of dilute rinse waters, more concentrated rinse waters as might be produced in countercurrent rinsing, and for the regeneration of plating baths.

Among the specific applications of ion exchange techniques in chromium plating are

- (1) The purification of contaminated plating baths by using cationic exchangers to remove iron, trivalent chromium, etc.
- (2) The recovery of chromic acid from reclaim rinsing systems by the use of cationic exchangers for the removal of impurities followed by the concentration of the purified rinse solution by evaporative procedures.
- (3) The detoxification of rinse waters containing chromium by using both cationic and anionic exchangers to effect the removal of both trivalent and hexavalent chromium as well as other impurities.

In the second of the applications cited above, it has been demonstrated that a plant of size sufficient to produce about 1000 gallons of still rinse solution containing about 7 oz/gal. of CrO_3 every 48 hours of operation was able to recover CrO_3 at a total cost--including depreciation--of 8 cents per pound where CrO_3 was selling for 28 cents per pound. Recovery operations of this type are generally batch in nature.

Very little has been published on the applicability of anionic exchange processes to the treatment of very dilute rinse waters containing 10 to 100 ppm of hexavalent chromium. The potentiality of such a process for the smaller plater will be discussed in the final phase report on this project.

Although laboratory and pilot-plant work have indicated the feasibility of using ion exchange for straight cyanide rinse waters, the process has found little use. The most frequently cited difficulties are 'poisoning of the resin' by the irreversible adsorption of complex metal cyanides such as those of nickel and iron, the production of hydrogen cyanide within the equipment during adsorption, etc.

Ion exchange has been successfully applied, however, to mixed wastes (chromium metals and cyanides) by a dual bed process in which the mixed waste is first passed through a cationic exchanger to adsorb metals, help break up complex metal cyanides and generate free hydrogen cyanide, and then through an anionic exchanger to adsorb the liberated cyanide. The published literature on the treatment of mixed wastes by the dual bed ion exchange process cautions against the presence of too great a concentration of cyanide in the mixed waste, one reference stating that the cyanide should not exceed 4 to 5 percent (presumably of the total waste components) and another stating that with increased cyanide some modifications of the exchanger would be required.

Regeneration, which amounts to removing the load of cyanide or metals that the resins have absorbed, must be done periodically. This is accomplished by passing sulfuric acid and/or sodium hydroxide through the resins to redissolve the metals or cyanides. The regenerated solutions are greatly concentrated, but they are still toxic. If they are to be discharged to waste, then they require the chemical treatments previously discussed, but because they are concentrated and relatively low in volume compared to the original rinse waters, treatment can be carried out batchwise in small tanks. Recovery of cyanides, chromium, and other metals from the regenerating solutions also is a possibility; however,

its economic feasibility for the smaller plater would require study. Water recovery for reuse in rinsing is a built-in feature of the ion exchange process. A typical ion exchange application is shown in Figure 4.

Evaporative processes have found some use for both chromium and cyanide rinse waters.(43,105,122-124) Generally, evaporative processes are economical only on concentrated rinses, such as those produced in still tanks or multistage countercurrent rinsing. If the smaller plater employs such rinsing techniques, evaporation processes may be worth consideration not only for the recovery of plating chemicals but also of rinse water. As with the ion exchange process the evaporative processes have been thoroughly developed for both chromium and cyanide waste streams. A typical evaporative process is shown in Figure 5.

Other Approaches

Other approaches to the detoxification of plating and metal finishing effluents are described in the literature. The so-called "integrated" approach is the most widely used of these. It is not strictly a method for treating rinse waters so much as a method for eliminating toxic components early in the rinsing operation. The theory, practice, application, and cost factors associated with the integrated approach are presented in a number of articles.(125-130)

Other approaches which may be classified as rinse water treatments are also described in the literature. In general, these are of the pre-engineered "package type" and embody the known chemical or physical unit operations discussed in this report. Typifying these is a recent foreign development said to be particularly suitable for the smaller plater.(131)

Waste Reduction by In-Plant Control Measures

The cost of waste treatment for the plater is directly proportional to the amounts of materials such as chromium and cyanide which have to be treated and proportional through some coefficient to the volume of the waste solution. In-plant control measure can reduce both the amounts of toxic materials and the volume of flow.

These measures include

- (a) The reduction of drag-in to the rinsing circuit by such means as increasing draining time, the installation of drip boards or drip tanks, air jetting, tumbling, or vibrating the pieces
- (b) The curtailment in water usage by such expedients as countercurrent rinsing, the use of sprays, better control of water flow, proper racking and proper maintenance of racks, tanks, etc.

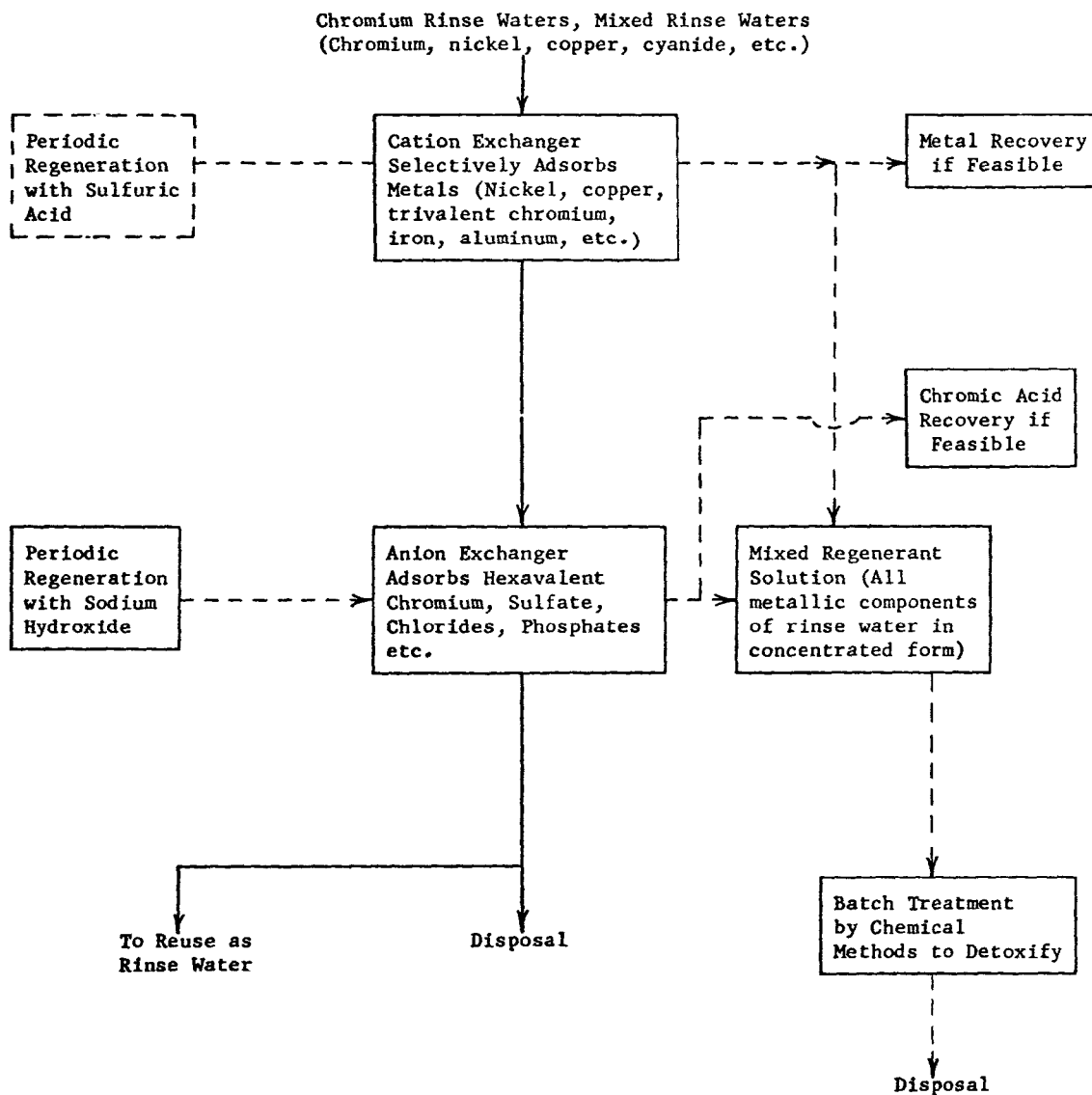


FIGURE 4. ION EXCHANGE METHOD OF TREATING CHROMIUM RINSE WATERS OR MIXED RINSE WATERS

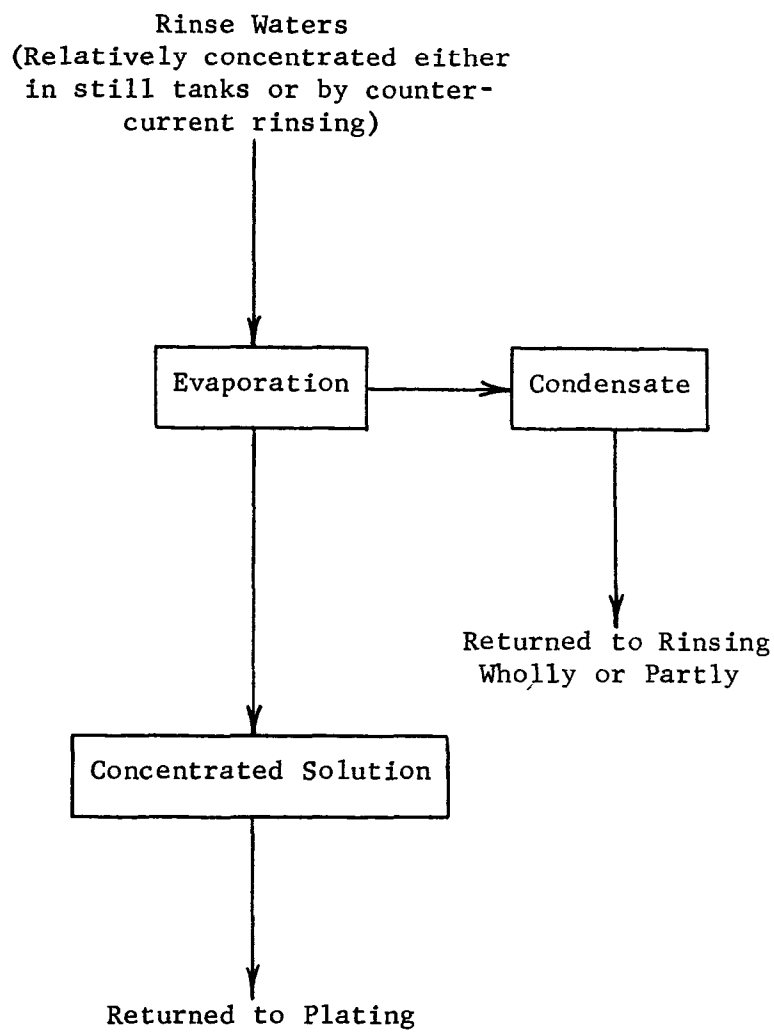


FIGURE 5. EVAPORATIVE TREATMENT OF RINSE WATERS⁽¹²²⁾

- (c) The segregation of nontoxic wastewaters from the normal toxic waste stream
- (d) The prevention of leaks, overflows, and spills
- (e) Provisions for impounding these if they should occur by standby tanks, sumps, etc.

Space limitations and the cost of installing the equipment for many of the techniques used for in-plant waste control preclude their use in the majority of small plating shops. It is certain, however, that many of the waste disposal problems encountered in these shops could be eliminated or diminished and made less costly by the adoption of such measures where this is possible.

Selection of a Process

Conventional unit processes available for the treatment of rinse waters have been described in the foregoing sections of this report. To determine which of the unit processes to use and their sequence in a complete waste treatment facility requires a careful review of the technical, practical, and economical factors. These factors are

- (1) Rinse water volume and flow variations
- (2) Physical and chemical characteristics of the rinse waters
- (3) Regulations on effluent quality
- (4) Plant facilities such as space, layout, etc.
- (5) The feasibility of separating various waste streams within the plant for separate treatment
- (6) The feasibility of altering rinsing circuits to reduce the volume of rinse water
- (7) The feasibility of reducing dragout
- (8) The feasibility of the recovery of metals, cyanide, or rinse water
- (9) The suitability of existing equipment for waste treatment and the cost of new equipment that may be required
- (10) The cost of chemicals to carry out a given process
- (11) Labor requirements
- (12) Other operating expenses, such as power and maintenance and costs incurred for solids disposal.

Various flowsheets that could be followed for the separate treatment of cyanide rinse waters are outlined in Figure 6. Three of the commonly used treatments are shown

- (1) Complete destruction of cyanide by treating alkaline rinse waters with chlorine gas, sodium hypochlorite, or calcium hypochlorite
- (2) Partial destruction of cyanide, i.e., by converting it to the considerably less toxic cyanate form, by milder treatment with the same chlorine chemicals (these processes, requiring less time and fewer chemicals, are frequently used)

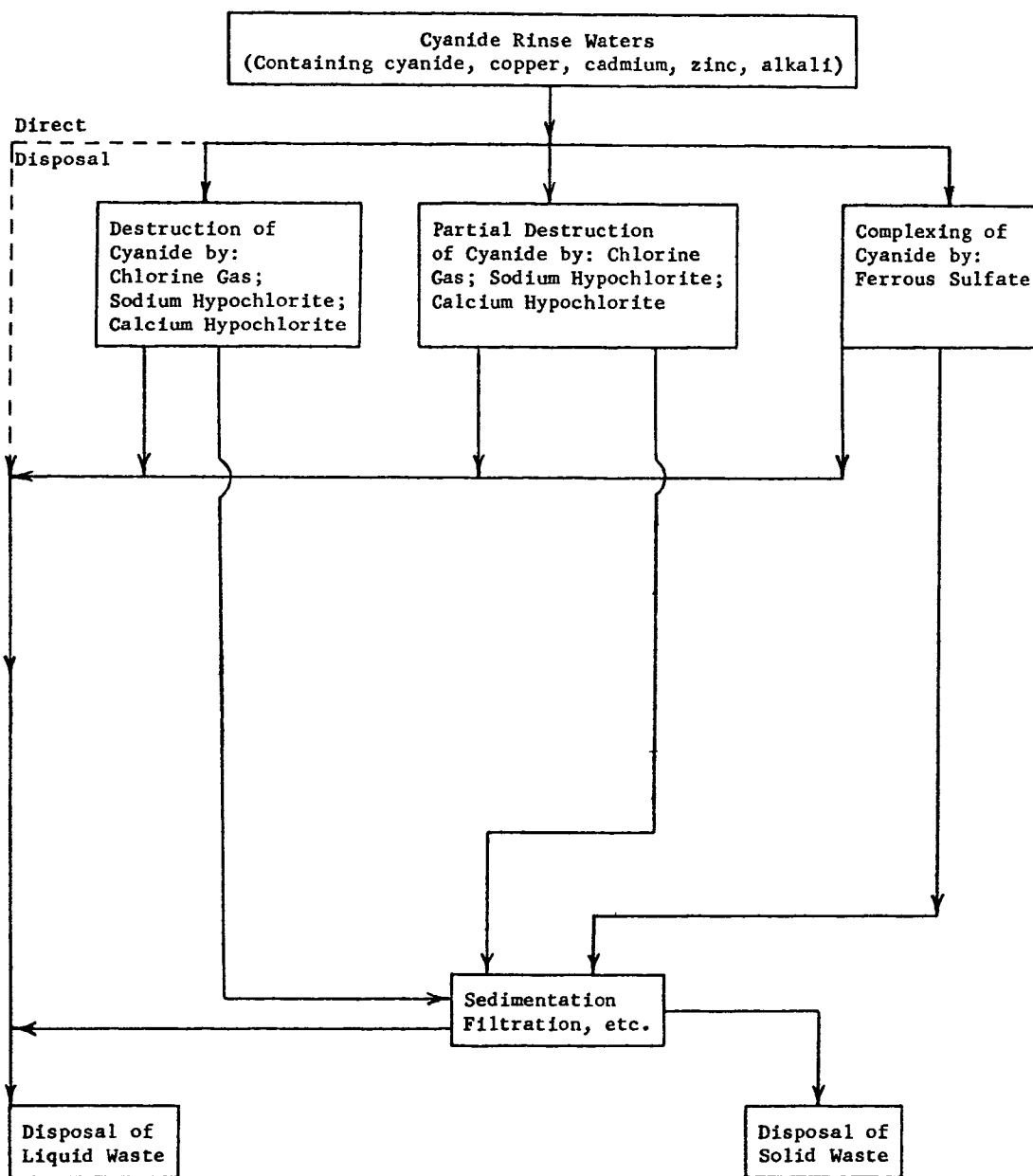


FIGURE 6. CHEMICAL TREATMENT OF CYANIDE WASTE

(3) The complexing of cyanide by ferrous salts to convert it to a stable ferrocyanide complex which is relatively nontoxic.

As is shown in Figure 6, after each of these primary treatments, various paths may be taken before eventual disposal. The simplest path and one that is frequently followed at the present time is to dispose directly the treated effluent. All of these treatment processes result in the formation of solids, including metal hydroxides, probably calcium sulfate, and precipitated complex cyanides. It is possible, therefore, that restrictions on solids or potentially toxic metal hydroxides may make additional treatment mandatory. This could involve separation of the solids by sedimentation or settling, filtration, etc., before sending the effluent to waste. It also would involve periodic separate disposal of the solids.

Figure 7 is a diagram of the chemical methods for the separate acidic chromium-bearing wastes. As with cyanide, direct disposal often is used as depicted by the line at the left side of the diagram. Simple neutralization of the generally acidic chromium wastes is practiced to some extent but largely to reduce the corrosiveness of the usually acidic solutions. Neutralization will precipitate any trivalent chromium, copper, or nickel that may accompany the waste but will have little or no effect on the hexavalent chromium. Neutralized chromium wastes may be disposed of directly or, if precipitated solids are too high for acceptance by authorities, some form of solids-liquids separation (sedimentation, filtration, etc.) may be employed.

The sequential arrangements of unit operations in Figures 6 and 7 apply to instances where chromium and cyanide rinse waters are treated separately. In cases where chromium and cyanide rinses are mixed, the same chemical treatments would be applicable as unit operations, but optimum sequences for this operation would have to be decided and many factors would enter into the decision. Sequential arrangements of unit operations which have been employed in the treatment of mixed rinse waters are shown in Figure 8.

Costs

Published information on waste treatment costs for the plating industry falls into two categories

(1) That pertaining to large or intermediate size plants (mostly captive) doing what amounts to production line plating, with waste streams reasonably constant in volume and composition and with carefully designed, engineered, and operated treatment facilities

(2) That supplied by engineering or equipment companies in the business of designing and installing waste treatment plants (This is usually general in nature and is almost always--and quite justifiably--accompanied by statements or implications that specific plant surveys are required for firm estimates of capital and operating costs. It is

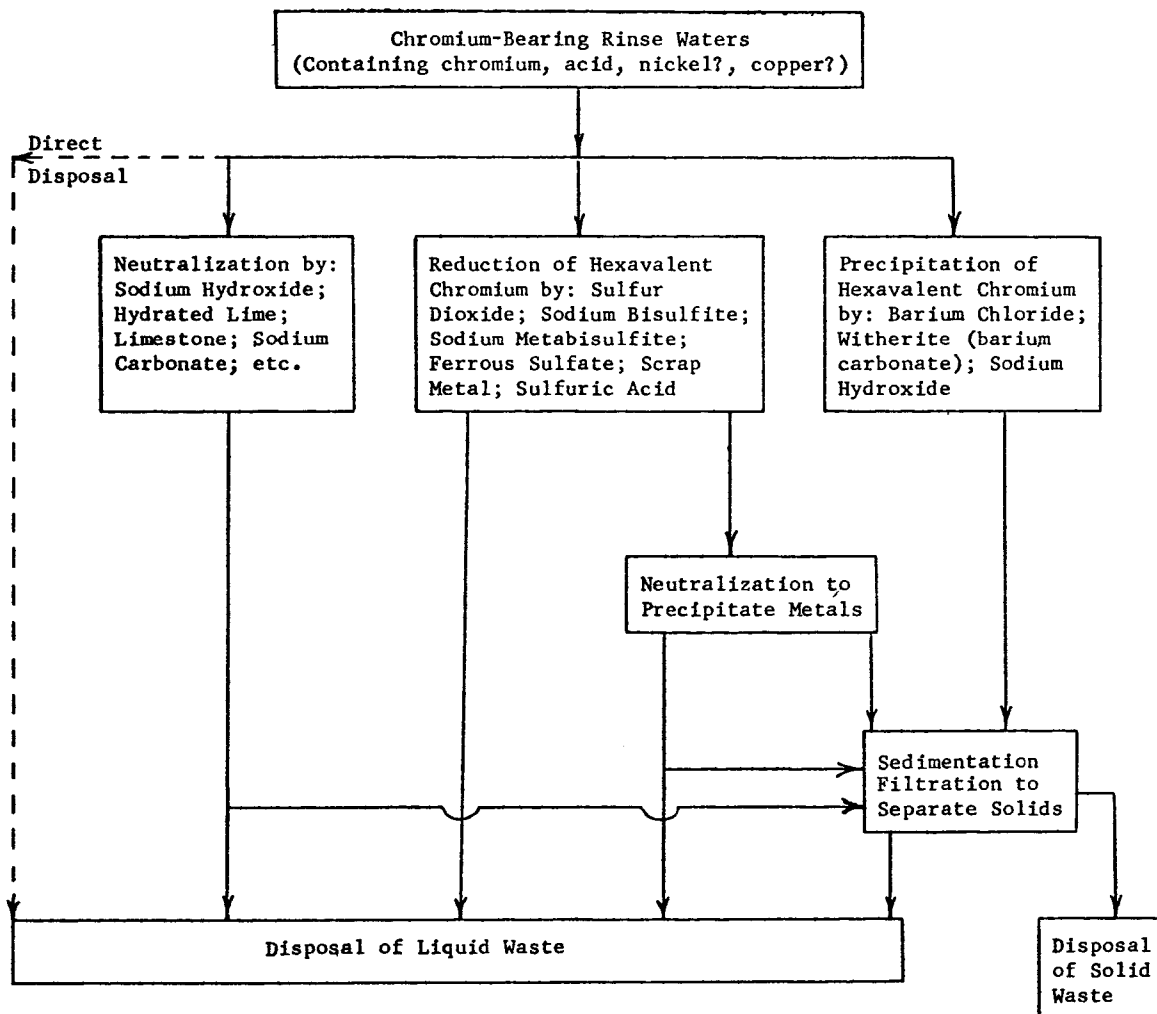


FIGURE 7. CHEMICAL TREATMENT OF CHROMIUM WASTE

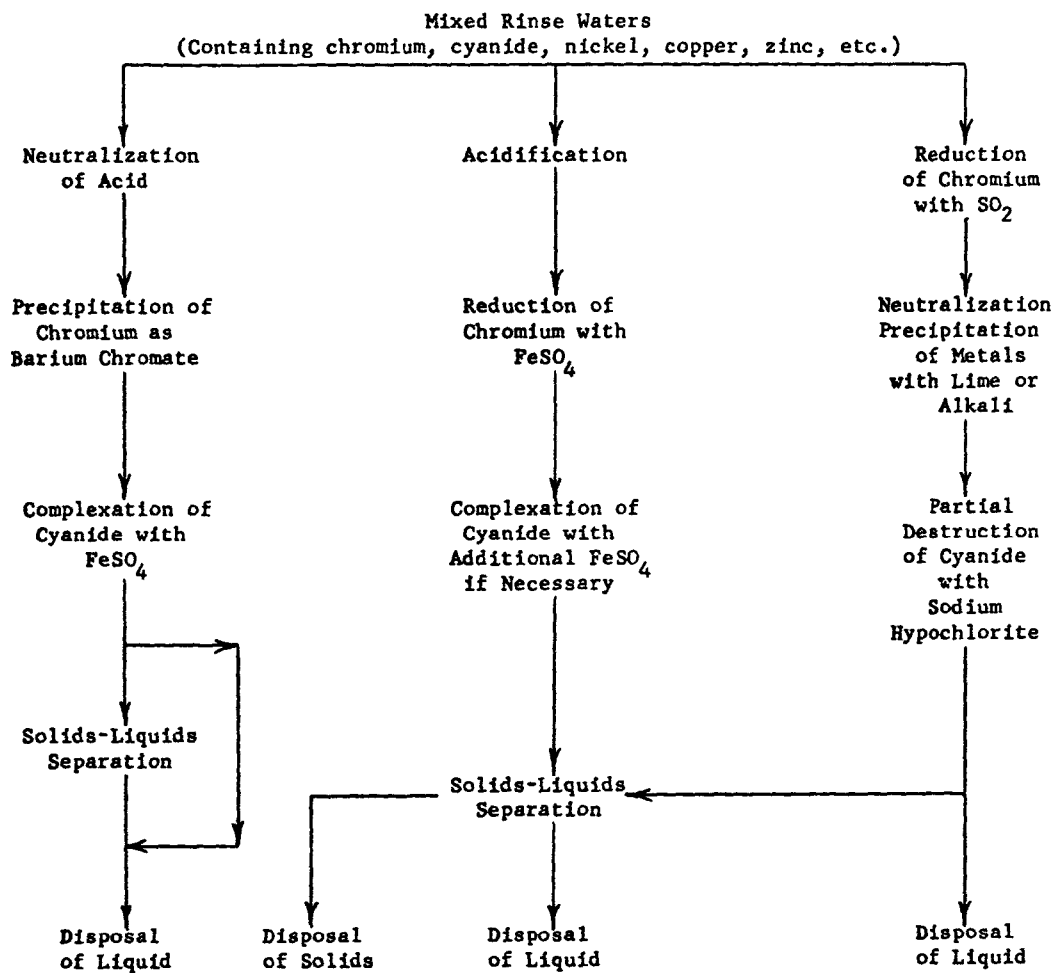


FIGURE 8. PROCESSES APPLICABLE TO MIXED CHROMIUM
AND CYANIDE RINSE WATERS

probable that most of these firms can provide approximate estimates based on their experience but whatever rule of thumb they employ is not published.).

Capital costs of waste treatment plants for the small plater will depend on a number of factors which include the type of waste; its volume and composition; the degree to which it must be treated to produce an acceptable effluent; the treatment process selected; whether the recovery of metals, chemicals, or water is an objective; and the availability of space, buildings, and utility services.

It is therefore impossible at this time to suggest any guidelines for estimating capital costs to the smaller company contemplating waste treatment on the basis of what has been learned from the open literature. As this project continues, an effort will be made to gather more information. Hopefully, useful guidelines that will permit at least "ball-park" estimates can be developed. Recently published examples of capital costs for waste treatment are shown in the following tabulation.

<u>Waste Stream</u>	<u>Flow Rate, gpm</u>	<u>Concentration, ppm</u>	<u>Treatment</u>	<u>Capital Cost, dollars</u>
Chromic acid rinse	100	40	Reduction	39,000
Chromic acid rinse	100	40	Ion exchange with recovery	45,000
Chromic acid and cyanide rinse	50	--	Chromium recovery	40,000
			Cyanide oxidation	
			Integrated treatment	15,000

The situation is almost as uncertain for operating costs. These will depend on many of the factors listed above for capital costs. The components of operating costs are chemicals, labor, maintenance, utilities, overhead, and amortization. Only the first, i.e., chemical costs, can be predicted with any certainty from known conditions.

One engineering firm has published some broad guidelines which the job-shop plater may find useful in attempting to predict the chemical costs of treating rinse water wastes.⁽¹²⁶⁾ These are shown in the following tabulation

	<u>Basis for Estimating Costs of Chemicals to Detoxify</u>
Chromium Wastes	3 to 4 cents/100 square feet of chromium plated surface 2-1/2 to 5 cents/pound of chromic acid purchased
Cyanide Wastes	5 to 7 cents/100 square feet of surface plated 70 cents to \$1/1000 pounds of barrel plated material 25 to 50 cents/pound of sodium cyanide purchased.

The author stresses that these costs are for the "average" plant which probably does not exist. They are based primarily on average dragout

rates* and on average oxidation of cyanide during plating. At best, they may provide some basis for further investigation to the company interested in or faced with the requirement of waste treatment. Specific costs of chemicals for waste treatment can only be predicted after a careful plant survey and the selection of the best technical and economic treatment method.

When these two steps have been taken, the amount of chromium to reduce, the cyanide to destroy, and the acid or alkali to neutralize will be known. From these data one can calculate the amount of chemicals that theoretically will be required. Chemicals generally used in waste treatment, the quantities required per pound of contaminant, and the approximate unit costs of these chemicals are listed in Table 7.

TABLE 7. CHEMICAL CONSUMPTION IN WASTE TREATMENT

Chemical	Amount Required per Pound of Component, lb	Approximate Unit Cost of Chemical, \$/lb
<u>Chromium Wastes</u>		
Sulfur dioxide (SO ₂)	1.9	0.11
Sodium bisulfite (NaHSO ₃)	3.0	0.02
Sodium metabisulfite (Na ₂ S ₂ O ₅)	2.8	0.06
Ferrous sulfate (FeSO ₄)	8.8	0.01
Barium chloride (BaCl ₂)	4.0	0.10
<u>Cyanide Wastes</u>		
Chlorine gas (Cl ₂)	2.7-6.8	0.035-0.18 ^(a)
Sodium hypochlorite (NaOCl)	2.9-7.2	0.37-0.49 ^(b)
Calcium hypochlorite [Ca(OCl) ₂]	2.8-6.9	0.425
Ozone (O ₃)	1.8-4.6	0.20
Ferrous sulfate (FeSO ₄)	2.3	0.01
<u>Combined Wastes</u>		
Sulfuric acid	--	0.02

*Dragout rates may be estimated from "typical" data shown in the following tabulation. (132-134)

Type of Material	Dragout Rate
Vertical, well drained	0.4-1.0 gal/1000 ft ²
Vertical, poor drainage	2-3 gal/1000 ft ²
Vertical, very poor drainage	4-5 gal/1000 ft ²
Horizontal, well drained	0.8-2.0 gal/1000 ft ²
Horizontal, very poor drainage	10 gal/1000 ft ²
Cup shaped work, very poor drainage	24 gal/1000 ft ²
Barrel--angle	2-9 fluid ounces per load
Barrel--horizontal	5-30 fluid ounces per load

TABLE 7. (Cont.)

Chemical	Amount Required per Pound of Component, lb	Approximate Unit Cost of Chemical, \$/lb
<u>Combined Wastes (Cont.)</u>		
Sodium hydroxide	--	0.03
Sodium carbonate	--	0.25
Hydrated lime	--	0.01

(a) Depending on quantity purchased, location, etc.

(b) Depending on form of sodium hypochlorite (granule, tablet) solution. Cost shown is per pound of available chlorine.

Note: Costs shown in this table are approximate and may be expected to vary, possibly within wide limits depending on quantities purchased, freight costs, location, etc. Most of the costs shown have been taken from a current issue of Oil, Paint, and Drug Reporter. In a few cases cost information has been obtained from specific articles.

Sewer Rentals

Any discussion of costs should cover the topic of sewer rentals, and other special charges made by municipalities for treating electroplating and metal finishing wastes because these are definite cost items and must be considered when evaluating the economics of waste treatment. There is very little information in the open literature on these costs, and they naturally vary from place to place and perhaps from one plant to another. Those plating shops which incur such costs no doubt are aware of them.

In some cases, these sewer rental fees or "penalty charges" for unusual wastes, which amount to credits for waste treatment operations, may be sufficiently great to justify some waste reduction or waste treatment method.

Recovery

The recovery of chromium, cyanide, metals, and water might be important factors in justifying the installation of waste treatment facilities for a job-shop plater. Because of the variability of conditions existing in individual plants, a decision on the merits of installing recovery systems can only be determined by a specific plant study in which such factors as dragout rate, water costs, utility costs, sewer rental costs, and the advantages of modifying rinsing techniques must be weighed.

DISCUSSION

This state-of-the-art review has shown that there are many ways to treat rinse waters. It has not shown that any given method or combination of methods is clearly the most suitable for the requirements of the smaller plater, or on the other hand, that any can be ruled out from consideration. It is probable that any of the cited methods or combinations thereof could turn out to be the most feasible for a given metal finishing plant.

As pointed out previously, the selection of an optimum method depends on many factors, one of the most important of which is the volume and composition of the rinse waters.

One of the objectives of this study is to provide information on this factor. This is being done by questionnaire and by the sampling and analyses of rinse waters from many smaller establishments.

An additional objective of the study is to assemble as much information as possible on the other factors that must be considered in the selection of a process. These include present restrictions on effluent quality, possible future restrictions, capital and operating costs, etc.

It is hoped that this information assembled in a final report will provide more positive guidance to the smaller plater than does this preliminary review.

Some of the factors which might influence the selection of a process are purely local. These include the space utilities and equipment available for installation of a treatment facility. Probably the best that this study can do to assist the smaller plater is to provide information on the spatial equipment, labor, and utility requirements for the various processes.

The foregoing discussion applies to existing processes which may well turn out to be the most satisfactory for the smaller plater.

However, the program, as originally proposed to the Metal Finishers Foundation and as is being carried out, involves an additional and equally important objective. This is to investigate and, if indicated, to develop new techniques and unit processes which might prove to be simpler and more economic for smaller plants than the existing methods.

Work has already begun on three such approaches--solvent extraction, ion flotation, and adsorption on relatively inexpensive materials. The results obtained within the first few weeks of the experimental program have been positive, but are still far from delineating technically and economically feasible processes. As the experimental work continues, these new approaches will be continuously appraised from the viewpoint of their applicability to the problems of the smaller plater.

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APPENDIX A

BIBLIOGRAPHY OF FOREIGN LITERATURE ON CYANIDE AND HEXAVALENT CHROMIUM WASTEWATER TREATMENT AND ANALYSIS

The bibliography which follows is supplemental to the references listed previously in this report. This bibliography contains only foreign references, some of which already have appeared in the aforementioned list of references. The search was confined to papers concerned with methods for treatment of analysis of wastewaters containing cyanides and/or hexavalent chromium. The search was made using the indexes of Chemical Abstracts because this is by far the most comprehensive abstract journal available.

The search included the 1969 abstracts and went back through the year 1957. As the search continued backwards through the cumulative indexes, it was apparent that the foreign references became less in number and the number of American references increased.

The references in the bibliography below are grouped into several classifications to make it easier for the user to locate the desired references. The latest references appear first. In most cases the Chemical Abstracts (C.A.) reference is given. Where the C.A. reference is omitted, the reference originated in the previous bibliography.

An explanation is appropriate here as to what is included under the various headings. In the treatment section, the term "chemical means" refers to oxidation by chlorine, hypochlorites, permanganates, etc., and to reduction by sulfur dioxide, ferrous sulfate, etc. The groupings under electrolysis and ion exchange are self explanatory. The "miscellaneous" treatment section contains references to biological degradation, adsorptive processes, water reuse, etc. There is a section listing review articles. These would be useful for a relative newcomer to the field for obtaining a quick study of the methods for treating cyanide or hexavalent chromium wastewaters.

The search included analytical titles because in wastewater problems analysis plays such an important role. These references also were divided up and placed under appropriate headings. Again the term "chemical" is used and here it refers to methods in which a quantitative determination is made by titration. The other headings are easily interpreted. In some cases the abstracts described analyses in which a combination of methods are used and these are grouped separately.

Finally a section on patents is included. For an appreciable number of these, the abstracts gave little or no detail.

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