May 17, 1973

To the Graduate Council:

I am submitting herewith a thesis written by Inho Nam entitled "A Review of Current Practice of Treatment and Recovery of Industrial Wastewaters Containing Metallic Compounds." I recommend that it be accepted for nine quarter hours of credit in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

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A REVIEW OF CURRENT PRACTICE OF TREATMENT AND RECOVERY OF INDUSTRIAL WASTEWATERS CONTAINING METALLIC COMPOUNDS

A Thesis

Presented to

the Graduate Council of

The University of Tennessee

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

---

by

Inho Nam

August 1973

ACKNOWLEDGMENTS

The writer wishes to express his appreciation to those who have been of assistance in the writing of this thesis. Particular gratitude is extended to Dr. J. Clement Burdick III, whose advice and guidance helped make this thesis possible.

Appreciation is extended to the other members of the committee who studied and approved this thesis: Dr. William A. Drewry and Dr. Kenneth E. Noll.

Finally, the writer wishes to thank his mother and his wife, without whose encouragement and financial assistance, the writer could have never finished his graduate study.

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ABSTRACT

Since numerous studies have revealed the potentially disastrous effects of metallic pollutants in the water environment, increasing efforts have recently been directed toward their control. Industry is the major source of the metallic pollutants and regulations setting the allowable concentrations of toxic metallic ions have already been established in many cases. It is likely that these regulations will become more stringent in the future.

This review summarizes current information available in the literature pertaining to metallic ion treatment and recovery in industrial wastewaters. During the past decade, the progress of treatment techniques has been rapid; versatile methods have been developed using sophisticated systems. At present, reverse osmosis, evaporation, and ion exchange processes are most widely used in the economical treatment and recovery systems for industrial wastewaters containing metallic ions, though chemical precipitation has been widely used in the past.

Recently developed closed loop recycle systems seem to be an ideal method for the recovery of waste materials and reuse of water, which is highly acceptable not only from pollution control but also from economical point of view.

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CHAPTER I

INTRODUCTION

Numerous metallic compounds are currently used by various kinds of industry and are discharged in wastewater streams in varying chemical forms and concentrations. The concentrations of metals which cause pollutional effects in water environment depend upon their specific chemical form, but most metals have very significant effects even at extremely low concentrations. At present, the concentrations of seven metals (arsenic, barium, cadmium, chromium, hexavalent, lead, selenium, silver) are restricted, and the limiting concentrations of additional four metals (copper, iron, manganese, zinc) are recommended by the U. S. Public Health Service (USPHS) drinking water standards [1] as shown in Table 1.

Also, the Federal Water Pollution Control Administration (FWPCA) established extensive water quality criteria for various uses and published them in the "Water Quality Criteria" [2]. The FWPCA criteria on metals for public water supply, farmstead use, livestock use, and farm animals water supply are shown in Table 2, and for irrigation use in Table 3. The criteria on metals for industrial uses vary widely according to the uses ranging from cooling water to process water.

It should be pointed out, however, that there are other metals which are not fully reflected in USPHS drinking water standards or in FWPCA water quality criteria but frequently require water quality

TABLE 1

USPHS LIMITATIONS ON METAL IONS
FOR PUBLIC WATER SUPPLIES [1]

Metal Component	Recommended Maximum Level, ppm	Levels for Rejection, ppm
Arsenic	0.01	0.05
Barium	-	1.0
Cadmium	-	0.01
Chromium, hexavalent	-	0.05
Copper	1.0	-
Iron	0.3	-
Lead	-	0.05
Manganese	0.05	-
Selenium	-	0.01
Silver	-	0.05
Zinc	5.0	-

TABLE 2

FWPCA WATER QUALITY CRITERIA ON METALS FOR THE USES OF PUBLIC WATER SUPPLY, FARMSTEAD, LIVESTOCK, AND FARM ANIMALS WATER SUPPLY [2]

unit mg/l

	Public Water Supply		Farmstead		Farm Animal	
	Permissible	Desirable	Allowable	Recommended	Water Supply	Livestock
Arsenic	0.05	Absent	0.05	-	0.05	0.05
Barium	1.0	do	1.0	-	-	-
Cadmium	0.01	do	0.01	-	0.01	0.01
Chromium, hexavalent	0.05	do	0.05	-	0.05	0.05
Copper	1.0	Virtually Absent	-	1.0	-	-
Iron	0.3	do	-	0.3	-	-
Lead	0.05	Absent	0.05	-	0.05	0.05
Manganese	0.05	do	-	0.05	-	-
Selenium	0.01	do	0.01	-	0.01	0.01
Silver	0.05	do	0.05	-	-	-
Zinc	5.0	Virtually Absent	-	5.0	-	-

TABLE 3

TRACE ELEMENT TOLERANCES FOR IRRIGATION WATERS [2]

Element	For Water Used Continuously on all Soils	For Short-Term Use on Fine Textured Soils Only
	mg/l	mg/l
Aluminum	1.0	20.0
Arsenic	1.0	10.0
Beryllium	0.5	1.0
Boron	0.75	2.0
Cadmium	0.005	0.05
Chromium	5.0	20.0
Cobalt	0.2	10.0
Copper	0.2	5.0
Fluorine	([1])	([1])
Iron	([1])	([1])
Lead	5.0	20.0
Lithium	5.0	5.0
Manganese	2.0	20.0
Molybdenum	0.005	0.05
Nickel	0.5	2.0
Selenium	0.05	0.05
Tin	([1])	([1])
Tungsten	([1])	([1])
Vanadium	10.0	10.0
Zinc	5.0	10.0

[1]Variable.

abatement. For example, such metals as cobalt, mercury, nickel, antimony, tin, bismuth, molybdenum, titanium, uranium, etc. require regulation.

The metal ions in the water environment originate from industrial, agricultural, and natural sources. Especially certain industrial wastewaters contain extremely high concentration of metallic ions causing serious pollution problems in the streams into which they are discharged.

This survey includes the industrial sources, nature, and effects of each metal ion in the water environment, though the main objective of the study is to discuss their treatment.

Conventional municipal sewage treatment plants generally do not provide effective removal of the metal ions, because the metal ions are biologically nondegradable and persistent in the water. Such metal ions are not only slightly removed by biological treatment but also hinder the effective operation of the plant by their high toxicity to the microorganisms which carry the process.

Regulations restricting the discharge of the metal ions to municipal sewers have been established in many cases. Some of the typical restrictions are shown in Table 4. Current regulations are likely to become more stringent in the future with increasing enforcement on the industrial units leading to suitable in-plant treatment.

The treatment technology has been steadily developed to meet the regulations. Various unit processes have been studied using laboratory and pilot scale plants. There have been about a dozen unit processes studied for metallic wastewaters; chemical treatment, ion exchange,

TABLE 4

SOME RESTRICTIONS ON METALS DISCHARGED TO SEWERS [3]

Unit: mg/l

	pH	Cu	Cr^{+6}	Cd	Zn	Ni	Other Heavy Metals	Total Dissolved Solids	Suspended Solids
Typical Limits	6-10	0.3	0.05	0.4	0.3	2.0	--	--	--
Typical Range	5-10	0.4	0-10	0-5	0-5	2-10	0-50	2000-5000	200-1000
Examples of Limits:									
New Jersey	6-10	1	3	3	3	10		Avg. 1500	Avg. 500
Conneaut, Ohio (1951)	5.5-9.5	3	5		2				
Canadian	--	1							350
New York (1963)	--	5.0	0.5	0.5	5.0	3.0			
Kentucky City	5.5-9.0		<5						<20
Connecticut	6.5-8.5	3.0	3.0		3.0	3.0			
Said to be generally acceptable			5						

freezing, solvent extraction, ion flotation, reverse osmosis, electrodialysis, carbon adsorption, evaporation, eutectic freezing, etc.

Among the various processes, the most feasible at present are ion exchange, reverse osmosis, and evaporation, which are currently being incorporated into practice. Chemical precipitation has been most widely used in the past, though its use is decreasing due to economic factors and the inability to obtain the required effluent concentrations. This study discusses the basic theory of each unit process and its practical application and effectiveness in metallic wastewater treatment.

At present, it is considered that the removal of metallic ions from wastewaters can be technically achieved to any required degree. However, the current problem facing the industrial units who must do the job is now "know-how", but "cost".

The recently developed recovery systems, however, have made a great stride for an economical resolution of the problem. The so-called closed loop recovery system provides the recycle of waste materials and reuse of water, ideally eliminating any loss of materials as wastes. The economical evaluation of this recovery system is discussed in comparison with nonrecovery treatment system.

CHAPTER II

METALLIC POLLUTANTS IN THE WATER ENVIRONMENT

Although most of the elemental forms of metals are insoluble in water, many of their salt forms are soluble and appear in the form of ions. Metallic ions in natural water body are very stable, and are not readily removed by natural processes. Therefore, a characteristic feature of metal pollution is its persistence in time as well as in space after the pollution operations have ceased.

Considerable interest currently exists concerning the concentrations of metals in the nation's surface waters. A U. S. Geological Survey Report [4] was made on the distributions of seven metals (arsenic, cadmium, chromium, cobalt, lead, mercury, zinc). According to the report, small amounts of these metals are widely distributed in streams and lakes throughout the United States. In spite of the widespread occurrence of these metals, the concentrations normally do not exceed current USPHS drinking water standards except in a few samples among more than 720 collected samples [4].

The majority of the metal ions are considered to originate from industries. Industrial wastewaters discharged to sewers or to other routes join the natural water body, mostly surface streams, eventually ending up in the sea. The metal ions in the streams influence directly the water quality when the stream waters are drawn for various uses.

Also, the metal ions affect the aquatic life in the streams and in the sea, causing possible deleterious effects.

An extensive discussion of the physiological action of metal ions is found in the Water Quality Criteria [2]. According to the report, one of the characteristics of living cells is their ability to take up elements from a solution against a concentration gradient. The cells have high affinity for metals which are chelated by organic molecules [2].

An element is said to be toxic if it injures the growth or metabolism of an organism when supplied above a certain concentration. All elements are toxic at too high concentrations and some are notorious poisons even at low concentrations. For example, the essential micronutrient, copper, which is a necessary constituent of all organisms, is highly toxic at quite small concentrations. The other essential micronutrients are also toxic when supplied in excess, though not all in such striking fashion [2].

The toxicity of a metal is known to be a function of the temperature, pH, the species of organisms exposed, the ionic form of the metal, and synergistic action with other substances [2].

In this chapter, the industrial sources, nature, effects, and regulatory impacts of the metals, which are usually subject to water quality abatement, are discussed for each metal respectively.

I. ARSENIC

Industrial Sources

Major source of arsenic waste is the manufacturing of calcium arsenate and lead arsenate for pesticide uses [5]. The manufacture of Paris green and calcium meta-arsenate, both insecticides, was reported to produce wastewaters containing 362 mg/l of arsenious oxide [6]. Other industrial sources less significant include metal finishing, glassware and ceramic production, power plant, petroleum refining, rare-earth industry, dye, tannery, pharmaceutical industry, etc. [6,7]. Although arsenic is widely associated with various industrial wastewaters, little information was encountered on current levels of arsenic in industrial wastes. High arsenic levels, however, have been encountered in raw municipal water supplies, necessitating arsenic removal by the water treatment industry [6]. According to the previously mentioned U. S. Geological Survey Report [4], about 21 percent of the surface water samples contained detectable amounts of arsenic (more than 10 µg/l), but 2 percent of the samples exceeded the 50 µg/l upper limit set by USPHS.

Nature and Effects

In the water, arsenic occurs in various forms of ions and compounds as shown in Table 16 in the Appendix. Neither trivalent nor pentavalent arsenic is known to be an essential or beneficial element, and the body is not known to be dependent on a daily intake [1]. But the toxicity of arsenic is well-known and the ingestion of as little as 100 mg.

usually results in severe poisoning [1]. The toxicity of the pentavalent form is believed to be due to its reduction to the trivalent form [1]. Arsenic concentrations of from 2 to 4 mg/l are reported not to interfere with the self-purification of streams, nor have arsenic concentrations of 3 to 14 mg/l been harmful to mayfly nymphs and 10 to 20 mg/l to dragon and damsel flies [1]. Bass have tolerated 6 mg/l for 232 hours [1]. Concentrations of 15 mg/l proved toxic to crappies and blue gills, and 20 mg/l (as sodium arsenite) proved harmful to minnows after 36 hours exposure [1].

The widespread uses of arsenic in pesticides and its presence in animal foods, tobacco, and other sources, make it necessary to set a limit in drinking water and in other uses (Tables 2 and 3, pages 3 and 4).

II. BARIUM

Industrial Sources

Barium, as sulfate salt, is used as a white pigment for paint [6]. Barium is used in metallurgy, glass, ceramics and dyes manufacture, and in vulcanizing of rubber [7]. Barium has been also reported present in explosives manufacturing wastewater [6].

Very little information is available in the literature on concentrations of barium in industrial wastes.

Nature and Effects

Barium is recognized as a general muscle stimulant, including especially the heart muscle [1]. The fatal dose for man is from

0.8-0.9 g as the chloride [1]. Barium can cause nerve block and small or moderate dose produces transient increase in blood pressure by vasoconstriction [1].

Barium is reflected in USPHS drinking water standards to limit to 1 mg/l; but no limitation on barium is made in the 1961 WHO European Standard for Drinking Water (Table 17 in the Appendix).

III. CADMIUM

Industrial Sources

Industrial sources of cadmium wastewaters include electroplating, pigment works, plastic stabilizers, metallurgical alloying and cadmium batteries; all of which amount to 90 percent of total industrial cadmium use [6]. The sulfate salt of cadmium is a by-product in lead mines and the chloride salt is widely used in printing and dyeing of textile [8]. Other sources are ceramics, photography, rubber curing agents, nuclear reactor shields and rods, etc. [6].

The high concentrations of cadmium occur from electroplating. Cadmium plating baths may contain cadmium concentration of 23,000 mg/l [9]; the rinse water of which may contain cadmium of 48-240 mg/l [9]. Other high concentration of cadmium in wastewater was reported as 1,000 mg/l from a lead mine acid drainage [7].

According to the previously mentioned U. S. Geological Survey Report [4], about 42 percent of the surface water samples contained cadmium of 1 to 10 µg/l, and 4 percent in excess of the 10 µg/l upper limit set by USPHS.

Nature and Effects

Cadmium occurs largely as the sulfide which is often an impurity in zinc ores [2]. The chloride, nitrate, and sulfate of cadmium are highly soluble in water [2]. The carbonate and hydroxide are insoluble, thus cadmium will be precipitated at high pH values [2].

As far as known, cadmium is biologically a nonessential, nonbeneficial element, which has a high toxic potential [1]. Most quantitative data on the toxicity of cadmium are based on the specific salts of the metal. The acute lethal level for fish varies from about 0.01 to about 10 mg/l depending on the test animal, the type of water, temperature, and time of exposure [2].

A study, to determine the effects of cadmium in drinking water, concludes that the content of cadmium in the kidney and liver increased in direct proportion to the dose at all levels ranging from 0.1 to 10 mg/l [1].

USPHS drinking water standards provide the basis for rejection of the supply for the cadmium concentration in excess of 0.01 mg/l [1]. Some municipalities have established restrictions on cadmium discharged to sewers: New Jersey limits to 3 mg/l and New York to 0.5 mg/l [3].

IV. CHROMIUM

Industrial Sources

Extremely high concentrations of chromium ions occur from metal plating. Cooling water systems may use high quantities of chromates to reduce corrosion [8]. Other industrial uses are chrome tanning, textile,

dyeing, aluminum anodizing, stainless steel manufacturing, explosives, paints, glass, ceramics, etc. [6].

The following is a measure of typical untreated chromium concentrations [8]:

Metal plating - bright dip	10,000-50,000 mg/l
Metal plating - pickle or plating bath	600 mg/l
Chrome tanning	40 mg/l
Cooling tower blowdown water	10-60 mg/l

The U. S. Geological Survey Report [4] says that hexavalent chromium concentrations in the range of 6 to 50 µg/l were detected in 2 percent of the surface water samples, none of the samples contained in excess of 50 µg/l, upper limit set by USPHS.

Nature and Effects

The chromous ion, Cr^{++}, has a thermodynamic tendency to oxidize to the trivalent state of chromic ion, Cr^{+++}. The chromate ion CrO_4^{--} and the dichromate ion $Cr_2O_7^{-2}$ are the hexavalent states which may be reduced by heat or reducing agents to the trivalent CrO_3^{-3} state. Under aerobic conditions, Cr^{+6} in natural waters is stable and will persist for long periods. Under anaerobic conditions, Cr^{+6} will reduce to Cr^{+3} whose salts in neutral or weakly alkaline solution hydrolyze. The oxide thus formed, chromic oxide, is insoluble, deposits at the bottom and is unlikely to cause toxicity problems [8].

Chromium is not known to be either an essential or beneficial element in the body [1]. Chromium, however, is known carcinogenic agent for man, though the valence form is not clearly known [1].

The high toxicity of hexavalent chromium occurs to fish, algae, and plants, with wide variations of concentration according to the species [2]. The USPHS drinking water standards limit hexavalent chromium ion concentration to 0.05 mg/l [1].

Trivalent chromium ion is known not to have the toxicity of the hexavalent form and, moreover, is believed not to be of concern in drkinking water supplies [1].

A typical limit on hexavalent chromium to municipal sewers ranges from 3 to 5 mg/l [3].

V. COPPER

Industrial Sources

Primary sources of copper in industrial wastewaters are metal process pickling baths and plating baths. Copper concentrations in the plating bath depend on the bath type, and may range from 3,000 to 50,000 mg/l [6]. The rinse waters of the baths may contain copper concentrations of 20-120 mg/l [6].

Copper is also used in rayon manufacturing as cupro-ammonium salts and in pesticide manufacturing [6]. Copper bearing acid mine drainage also contributes significant quantities of copper to waste streams [6]. Additional potential sources are wood preserving, pulp and paper mills, fertilizer manufacturing, petroleum refining, and metal works [6].

Nature and Effects

Copper is an essential and beneficial element in human metabolism, and it is well known that a deficiency in copper results in nutritional

anemia in infants [1]. The daily requirement for adults has been estimated to be 2.0 mg [1].

Copper imparts some taste to water, but individuals vary in the acuity of their taste perception and the detectable range varies from 1 to 5 mg/1 [1]. Therefore, small amounts are generally regarded as nontoxic, but large doses may produce emesis and prolonged ingestion may result in liver damage [1].

The most acute toxicity of copper occurs to algae; 0.5 mg/1 copper as copper sulfate can be lethal to many species of algae [2]. The USPHS drinking water standards does not provide the ground for rejection, but recommends 1.0 mg/1 as the limit of copper [1].

Some municipalities established industrial effluent standards which restrict copper concentrations, ranging from 1 to 5 mg/1 [3].

VI. IRON

Industrial Sources

Potential industrial sources of dissolved iron species are mining operation, ore milling, metal processing, and chemical industries.

The most significant industrial source of iron wastewater is spent pickling solution which usually contain sulfuric acid of 5 - 20 percent concentration by weight and thus accumulate soluble iron ions until their concentration interferes with product quality, when the solution is replaced [6]. These waste pickle liquors may contain soluble iron of 70,000 - 96,800 mg/1; the rinse waters of which may contain soluble iron of 60 - 5,000 mg/1 [6].

Acid mine drainage waters are also high in soluble iron and may contain soluble iron up to 360 mg/l [6].

Nature and Effects

In water, iron exists in the ferric (Fe^{+++}) or ferrous (Fe^{++}) form, depending upon conditions of pH and dissolved oxygen concentration. At neutral pH and in the presence of oxygen, soluble ferrous iron is oxidized to ferric iron, which readily hydrolyzes to form the insoluble precipitate, ferric hydroxide, $Fe(OH)_3$. Therefore, acidic and/or anaerobic conditions are necessary in order for appreciable concentrations of soluble iron to exist. Ferrous and ferric iron may also be solubilized in the presence of cyanide, due to the formation of ferro and ferric-cyanide complexes [6]. Such species present considerable problems for both iron and cyanide treatment [6].

Iron is a highly objectionable constituent in water supplies for either domestic or industrial use. The domestic consumer complains of the brownish color which iron imparts to laundered goods and taste described as bitter and astringent. The taste of iron may be readily detected at 1.8 mg/l in spring water and at 3.4 mg/l in distilled water [1].

Iron, on the other hand, is an essential element for a body, and the daily requirement is 1 to 2 mg [1]. USPHS drinking water standards set a limit of 0.3 mg/l for iron to prevent objectionable taste or laundry staining [1].

VII. LEAD

Industrial Sources

Lead is used as an industrial raw material for storage battery manufacture, printing, gasoline, pigments, pesticides, photographic materials, and matches and explosives manufacturing [6].

The storage battery industry is the largest consumer of lead, followed by the petroleum industry in producing gasoline additives [6]. In a survey of eight battery manufacturing plants, it was reported that lead losses per battery manufactured ranged from 4.54 to 6810 mg, and that water usage ranged from 11 to 77 gallons per battery [6].

Lead is also a common constituent of plating wastes, although not so frequently encountered as copper, zinc, cadmium and chromium. Lead content of wastewater from an engine parts plating plant was reported as ranging from 2.0 to 140.0 mg/l [6].

According to the U. S. Geological Survey Report [4], about 63 percent of the surface water samples contained lead by the concentration of from 1 to 50 µg/l, but only a few samples exceeded 50 µg/l, the upper limit set by USPHS.

Nature and Effects

Salts of lead have substantial toxicity. The carbonate is toxic; arsenate is more toxic and the acetate has been reported to have killed fish in fresh water at 2.8 mg/l of lead concentrations [8]. Repeated poisoning in humans results in permanent brain damage [8]. Excessive lead dosage in blood results in anemia [8].

USPHS drinking water standards provides the ground for rejection in excess of 0.05 mg/l lead concentrations [1].

VIII. MANGANESE

Industrial Sources

Manganese and its salts are used in steel alloy, dry cell battery, glass and ceramics, paint and varnish, ink and dye, and match and fireworks [7].

Acid mine drainage may contain manganese up to 50 mg/l [6].

The highly soluble manganous chloride is used in dyeing operations, linseed oil driers and electric batteries, while the equally soluble manganous sulfate is used in porcelain glazing, varnishes and specialized fertilizers [7].

Nature and Effects

Among the many forms and compounds of manganese, only the manganous (Mn^{++}) salts and the highly oxidized permanganate anion (MnO_4^-) are appreciably soluble [6]. The latter is a strong oxidant which is reduced under normal circumstances to insoluble manganese dioxide [6].

In contrast to iron, the divalent form (Mn^{++}) is not readily oxidized to the insoluble trivalent form (Mn^{+++}), other than at elevated pH [6].

Manganese is known to be an essential nutrient, since diets deficient in manganese interfere with growth, blood, bone formation, and reproduction [1]. Daily intake of manganese from a normal diet is estimated to be about 10 mg [1].

There are two reasons for limiting the concentration of manganese in water supplies; one to prevent esthetic and economic damage, and another to avoid any possible physiologic effects from excessive intake [1]. Manganese produces a brownish color in laundered goods and impairs the taste of beverages including coffee and tea [1]. Domestic complaints arise when the level of manganese exceeds 0.15 mg/l [1].

USPHS drinking water standards recommends maximum concentration of manganese as 0.05 mg/l [1].

IX. MERCURY

Industrial Sources

The major consumptive user of mercury is the chlor-alkali industry which, without any treatment, may discharge about 0.1-0.5 lb mercury per ton of chlorine produced [6].

Other users of various mercury forms are: electrical and electronics industry, pesticides, preservative industry, dentistry, apparatus and instruments, cosmetic and pharmaceutical, power plant, etc. [6,8].

Within the chemical and petrochemical industry, mercury compounds are used as catalysts in plastics production, hydrogenation and dehydrogenation, sulfonation, oxidation, chlorination, and acidolysis [6,8].

Limited data are available regarding actual wastewater mercury levels. Effluent mercury from one chlor-alkali plant is estimated to have been 1.4-2.8 mg/l, based on 600 gpm waste discharge and 10-20 lb/day mercury loss [10]. Power generation is a large source of mercury release into the environment through combustion of fossil fuel. Coal

has been reported to contain 0.01 to 300 mg mercury per Kg coal [6]. Scrubber water may contain approximately same amount of mercury in the coal consumed.

The U. S. Geological Survey Report [4] mentions that 7 percent of the surface water samples contained dissolved mercury concentration ranging from 0.1 to 4 µg/1, but no sample in excess of USPHS limit of 5 µg/1. At a few sites, however, a combination of dissolved mercury and mercury adsorbed on suspended particles gave concentrations that exceeded 5 µg/1.

Nature and Effects

Although elemental mercury is insoluble in water, many of its salts are soluble in water. Aquatic deaths have been caused in a week to ten days by 0.05 to 0.1 mg/1, and 0.004 to 0.02 mg/1 have been reported as harmful [8]. Mercury salts are considered to be highly toxic to humans. Bacterial action called methylation usually converts mercury to methyl mercury, which has one hundred times the toxicity of inorganic salts [8]. Methylation occurs rapidly in winter and spring due to increased activity of aqueous organisms [8]. Low pH and aerobic conditions also help methylation [8]. The chloride of mercury at 10^{-4} molar concentration has been shown to inhibit respiration and aerobic or anaerobic fermentation by more than 95 percent, and to cause acute poisoning at 0.1 g level [8].

Mercury, however, is not reflected in USPHS drinking water standards.

X. NICKEL

Industrial Sources

Wastewaters containing nickel originate primarily from metal industries; particularly plating operations. In addition, silver refineries, basic steel works and foundaries, motor vehicle and aircraft industries, and printing have been known as potential sources of nickel [6].

Nickel plating bath may have nickel concentration of 75,000 mg/l, the rinse water of which may contain 156 mg/l nickel [9]. One report says nickel concentrations ranged from 0.46 to 3.4 mg/l in acid mine drainage [6].

Nature and Effects

Nickel exists in waste streams as the soluble ion. In the presence of complexing agents such as cyanide, nickel may exist in a soluble complexed form [6].

Very little information about the effects of nickel on water environment is found in the literature.

Nickel is not reflected in the USPHS drinking water standards, but some municipalities established restrictions on nickel in industrial waste discharged to sewers, ranging from 3 to 10 mg/l [3].

XI. SELENIUM

Industrial Sources

Industries using selenium include paint, pigment and dye producers, electronics, glass manufacturers, and insecticide manufacturing [6].

No information is found on the concentrations of selenium in industrial wastewaters.

Nature and Effects

Selenium is known to produce "alkali disease" in cattle, and its effects may be permanent [1]. Selenium may increase the incidence of dental caries in man [1]. USPHS set the limit for rejection as 0.01 mg/l of selenium concentration [1].

XII. SILVER

Industrial Sources

The two major sources of soluble silver wastes are the photographic and electroplating industries [7]. Less significant uses of soluble silver salts are porcelain, ink manufacturing, and antiseptic [7]. Solid silver metal is widely used in jewelry, silverware, metal alloy, etc.; but little soluble silver waste would be expected to result from use of the solid metal [7].

Silver cyanide plating baths may contain from 13,000 to 45,000 mg/l of silver [6]. This can represent appreciable silver loss by drag-out if no recovery device is adopted. For example, 75 percent of silver in the photographic industry may find its way into the fixing solution [6].

Nature and Effects

Insufficient information about the effects of silver in water environment is found in the literature. There are uncertainties in the studies made for human intake of silver [1]. USPHS drinking water standard, however, tentatively set 10 µg/l as the limit of silver.

XIII. ZINC

Industrial Sources

Industries discharging waste streams which carry significant quantities of zinc include steel works with galvanizing lines, zinc and brass metal works, plating, viscose rayon manufacturing, pulp mill, rubber process, plastic stabilizer, catalysts, cooling towers, etc. [6].

Plating solutions typically contain 41,000 mg/l of zinc, the rinse water of which may contain 85 mg/l of zinc [9]. Viscose rayon waste-waters may contain 20-120 mg/l of zinc [11].

Zinc is a fairly soluble metal, and concentrations vary widely in river waters. According to the U. S. Geological Survey Report [4], zinc was detected in the surface water samples usually in the range of 10 to 50 µg/l, but occasionally exceeded 5.0 mg/l, the recommended USPHS upper limit for drinking water.

Nature and Effects

Zinc is an essential and beneficial element in human metabolism; the activity of several body enzymes is dependent on zinc [1]. Soluble zinc salts at 30 mg/l, however, impart milky appearance to water, and at 40 mg/l, a metallic taste [1].

Inasmuch as zinc in water does not cause serious effects on health but produces undesirable esthetic effects, it is recommended but not mandatory by USPHS that concentrations of zinc be kept below 5 mg/l for drinking water standards [1]. Some municipalities set effluent limit on zinc ranging from 3 to 5 mg/l [3].

CHAPTER III

TREATMENT METHODS

I. THE DEVELOPMENT OF TREATMENT METHODS

The history of metallic ion treatment in industrial wastewaters began with metal plating industry which has occupied premier position in the field of metallic pollution. The rinse water from plating may contain any of following contaminants: hexavalent chromium, cyanide, complex cyanides of heavy metals such as cadmium, copper, zinc, silver and gold, soluble nickel salts, strong mineral acids and strong alkalis. Of these, the most troublesome are hexavalent chromium and cyanide ion for their high toxicity to aquatic life; the major job in the treatment has been the removal of these two components. For the study of metallic ion treatment, a brief review of the development of chrome plating rinse water treatment methods is presented herein.

The oldest treatment method is the batch treatment method, in which the rinse waters are collected for chemical treatment. The destruction of the toxic chemicals is accomplished by oxidation of cyanide and reduction of hexavalent chromium to trivalent form usually followed by subsequent precipitation. The water from the clarifier is discharged into a sewer and the sludge is disposed of by any convenient method. This method is still being used by many small platers which produce small volume of wastewaters.

The next developed treatment method for larger volume of plating wastewaters is the continuous flow method, which requires a tank for reduction of chromium, a mixing tank for lime addition, and a settling tank. Successful operation of this continuous method requires instrumentation and automatic control to monitor the flow and supply the proper amount of reactants [12].

Later, an "integrated system" was developed by Lancy [13] in which the reduction and precipitation process is integrated into plating process line. This method provides more effective and economical treatment of chromium wastewaters. Moreover, a significant implication of this system is that treatment process is integrated into process line.

All of the above methods are based on the idea that toxic pollutants should be destroyed and disposed of safely in contrast to the concept of recovery and reuse.

While the conventional methods are based on the "safe disposal" of metallic ions by removing them from wastewaters, a newly developed idea is based on the concept that valuable materials in the wastewaters could be recovered instead of being destroyed or disposed of. This idea is highly acceptable not only from pollutional viewpoint but also economical viewpoint, because this system provides saving of valuable materials and also reuse of wastewaters.

Being based on the recycle idea, the "closed loop" system has been developed for the recovery of metals and reuse of water. A schematic diagram of the closed loop system for the recovery of plating rinse

waters is shown in Figure 1. This closed loop system is known as the common technique for the recovery of metallic wastewaters.

This chapter mainly discusses the role of basic unit processes (chemical precipitation, ion exchange, reverse osmosis, evaporation) in metallic wastewater treatment, and explains how these processes are employed by the closed loop recovery system. In addition, the feasibility of municipal plants for metallic ion removal is discussed.

II. METAL IONS AT MUNICIPAL SEWAGE PLANTS

Since the discharge of metallic wastewaters to municipal sewers has been a widely used practice and numerous problems at the sewage plants have been reported in the literature, it is pertinent to consider the effects of the metal ions on municipal wastewater plants.

The primary object of conventional municipal sewage treatment plants has been to reduce the amount of oxygen-demanding organic materials in the water along with reduction of suspended solids and bacteria. Conventional treatment processes are classed as primary and secondary. Primary treatment usually consists of coarse screening or grinding, grit removal, and suspended material removal by settling; secondary treatment consists of some form of biological oxidation followed by further settling. Since heavy metallic ions are in the dissolved form and are biologically nondegradable, it is understandable that no effective removal of heavy metals occurs during these processes.

Though the municipal treatment process is not considered to be an effective method for the treatment of metals, there are two mechanisms

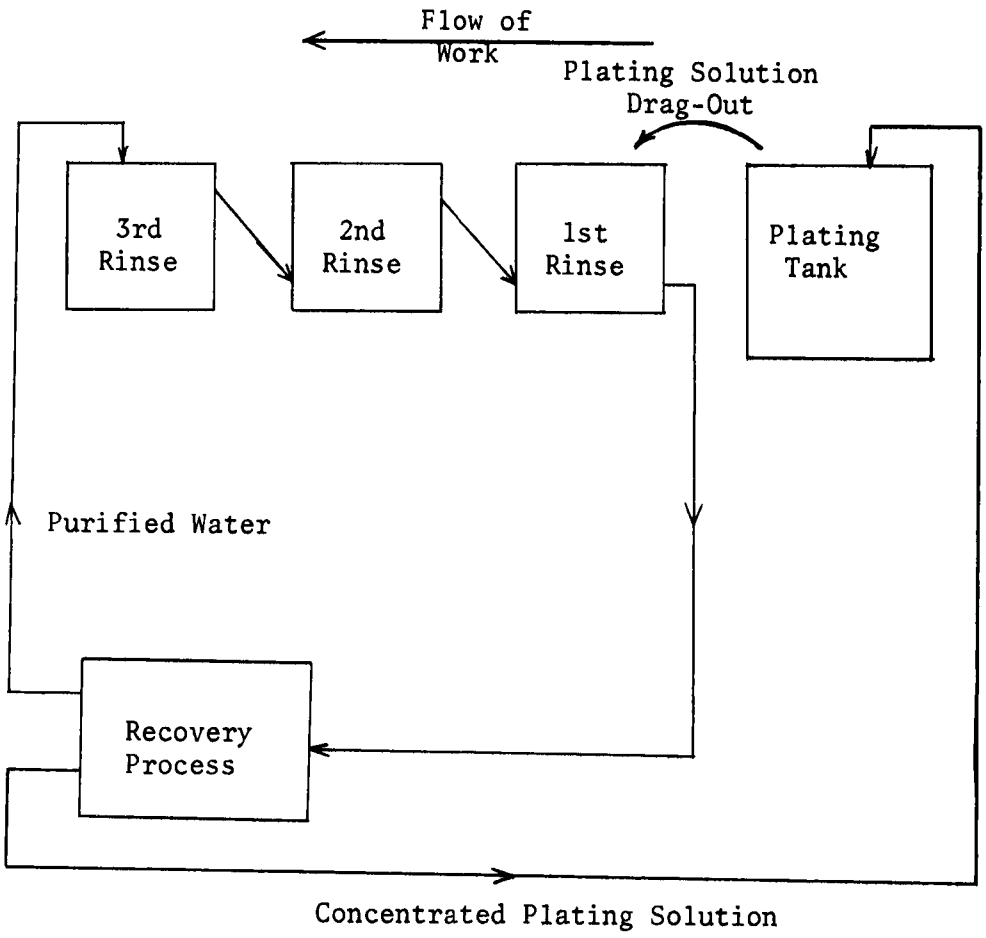


Figure 1. Closed loop recovery system for plating rinse water (14).

which apply to the removal of heavy metals to some extent; precipitation of metal hydroxides which are removed with the sludge, and sorption of soluble metals by the sludges.

The precipitation of metal hydroxides is governed by the concentration of the metal ion and pH of the solution, according to the solubility product principle. The solubility products of several cationic heavy metal oxides and hydroxides are listed in Table 5.

The precipitation of copper, chromium, nickel, and zinc by sewage has been reported by Jenkins et al. [15]. The conclusion of the study was that the percentages of the metal precipitation increased with the concentration of metals and decreased with decreasing pH. The precipitation of hexavalent chromium was dependent on the period of contact to a much greater extent than the other metals. The removal of chromate in sewage depends on the reduction of hexavalent chromium to trivalent form and subsequent precipitation of trivalent chromium [15].

Moore et al. [17] conducted pilot plant studies to determine the effects of chromium on the activated sludge process and to determine the extent of its removal. Their results indicate that concentrations of hexavalent chromium up to 0.5 mg/l were usually completely removed. For higher chromate feed concentrations, an increasing but variable amount of the chromium passed through the system.

McDermott et al. [18,19] studied the removal of copper and zinc in pilot-scale activated sludge plants. Their results showed that 95 and 74 percent of the zinc were removed at feed concentrations of 2.5 and

TABLE 5

SOLUBILITY PRODUCTS OF CATIONIC HEAVY METAL OXIDES OR HYDROXIDES [16]

Compound	Ksp
Ag_2O	2×10^{-8}
$Au(OH)_3$	8.5×10^{-45}
$BaCO_3$*	1.6×10^{-9}
$BaSO_4$*	1×10^{-10}
BiOOH	3×10^{-11}**
$Cd(OH)_2$	2×10^{-14}
$Cr(OH)_3$	1×10^{-30}
$Cu(OH)_2$	3×10^{-19}
$Fe(OH)_2$	1.8×10^{-15}
$Fe(OH)_3$	6×10^{-38}
HgO	3×10^{-26}
Mn(OH)	2×10^{-13}
$Pb_2O(OH)_2$	1.6×10^{-15}
Sn O	1×10^{-61}
$Ti(OH)_3$	1×10^{-40}**
Zn	4.5×10^{-17}

*Barium compounds that will preferentially form the hydroxide in most waters.

**Estimated value, not verified.

2.0 ppm respectively; 50 and 79 percent of copper were removed over a range of feed concentrations of 0.4 and 25 ppm.

Barth et al. [20,21] conducted pilot-scale studies on the effect of heavy metals on biological treatment processes and reported that the aeration phase of biological treatment can tolerate in the influent sewage, chromium, copper, nickel, and zinc, up to a total heavy metal concentration of 10 mg/l, either singly or in combination, without about a 5 percent reduction in overall plant efficiency. Tarvin [22] working in municipal plants reported similar conclusions. Dawson and Jenkins [23] from laboratory investigations, also indicate the similar concentration range.

There, however, have been numerous instances where the efficiency of secondary treatment plants have been grossly or completely impaired by slugs of concentrated wastes because of the toxicities of heavy metals to the microorganisms in the process. Table 6 lists some of the important common heavy metals and shows their reported effects on primary and secondary treatment plants.

Sludge digestion is another process in which the metals may cause problems. The metals concentrate in the settled sludge from primary and secondary treatment, and become concentrated even more in the sludge digestion tanks as the volume of sludge is reduced. Instances have been reported where sludge digestion processes were completely halted due to the accumulation of metals in the digestion tanks [18]. It was estimated that when the total concentration of chromium, copper, nickel, zinc and

TABLE 6

EFFECTS OF HEAVY METALS ON SEWAGE TREATMENT PLANT [3]

	Partially Precipitated With or Adsorbed by Sludge	Tolerable Concentration at Steady Flow, ppm	Concentration with Appreciable Effect at Steady Flow, ppm	Affects Oxidizing Ability of Sludge
Hexavalent Chromium				
Primary	x			
Trickling filter		1-4	10	
Activated sludge	x	2-8	5-10	x
Trivalent Chromium				
Primary	x			
Trickling filter	x			
Activated sludge	x			
Copper				
Primary	x			
Trickling filter	x		1-3	
Activated sludge	x	1	4	x
Zinc				
Primary	x			
Trickling filter	x		1-3	
Activated sludge	x		5-10	x
Cadmium				
Primary	x			
Trickling filter	x			
Activated sludge	x			x
Nickel				
Primary	x			
Trickling filter	x			
Activated sludge	x		1-3	

cadmium exceeds 400 ppm in digesters, failure can occur [24]. Such concentrations could be produced by raw sewage containing 1.5 to 3.0 ppm of these metals.

III. CHEMICAL PRECIPITATION

Theoretical Background

This treatment technique takes the advantage of the low solubility of metal hydroxides. Increase of hydroxide ion concentration forces metal ions to precipitate in accordance with the solubility product for the reaction. The basic reaction is:

$$\text{Metal ion} + \text{Hydroxide ion} \rightleftarrows \text{Metal hydroxide}.$$

The equation can be mathematically written as

$$\frac{[\text{Metal ion conc.}] \times [\text{Hydroxide ion conc.}]}{[\text{Metal Hydroxide conc.}]} = \text{constant}.$$

When the hydroxide ion concentration in the solution increases, some of the metal ions combine with the hydroxyl ions to form metal hydroxide and satisfy the equilibrium condition. Initially a small increase in the hydroxyl ion concentration would result in the formation of significant amounts of metal hydroxide, but slowly the components of the equilibrium system would reach such concentration that only a very large increase of hydroxide ion concentration would bring about significant amount of metal hydroxide formation. The reason for the reduction in the rate of metal hydroxide formation can be seen by examining the solubility constant relationship.

Precipitation of metal ions to hydroxides is applicable to cation metal ions which form insoluble metallic hydroxides. Some of metal cation species such as barium are not precipitated out by the significant increase of hydroxide ion concentration due to the high solubility products of their hydroxides. Barium, however, can be effectively precipitated out by the increase of sulfate ion concentration due to the low solubility product of barium sulfate. Generally, the effectiveness of precipitation will depend on the solubility product of resultant compounds.

Therefore, the precipitants should be selected by examining the metal ion species and the solubility product of resultant compound. Most common precipitants include hydroxide, carbonate, sulfate, sulfide, chloride, etc.

Some metallic ions have significant difference in solubility product according to the ionic valence. Metallic ions, which do not precipitate out at certain valence, may be converted to other valence at which they precipitate easily. The conversion of ferrous iron into ferric state is a good example.

Metals in solution usually exist as cations, but many metals are frequently present as metallic anions (Table 16 in the Appendix). Such metallic anions frequently found in wastewaters include arsenate (AsO_4^{---}), chromate (CrO_4^{--}), dichromate ($Cr_2O_7^{--}$), ferrocyanide ($Fe(CN)_6^{----}$), ferricyanide ($Fe(CN)_6^{---}$), permanganate (MnO_4^{-}), etc. For the precipitation of these metals, the metals should be converted into cations by suitable treatment; otherwise the

precipitants should be cations which effect, with the metallic anions, the formation of insoluble compounds. One of the practical examples is the precipitation of chromate by barium salts to form insoluble barium chromate as follows:

$$BaCl_2 + Na_2CrO_4 \rightarrow BaCrO_4 + 2\ NaCl\ .$$

In conclusion, the effectiveness of precipitation of metallic ions basically depends on the solubility product of the resultant precipitates.

Applications

Chemical precipitation has been one of the oldest and widely used techniques in the treatment of metallic ions from wastewaters. Many of the metallic ions can be removed from solution by chemical precipitation followed by sedimentation or filtration. Some information concerned with metallic ion removal at municipal sewage treatment plant was discussed in the foregoing section in relation to the precipitation of metal hydroxides.

Though the chemical precipitation is distinguished from chemical coagulation in that the metal ion itself enters into chemical reaction with the reagent instead of being mechanically adsorbed or entrained on the floc, these two phenomena may occur simultaneously in many cases of wastewaters. It, then, is possible to reduce some of the metal concentrations below that predicted by the solubility products due to the adsorption of metal ions by the chemical floc [16].

Table 7 summarizes the effectiveness of chemical precipitation for various metal ions in various wastewaters under the conditions studied.

The treatment costs of chemical precipitation depends on the characteristics and volume of the wastewaters, degree of treatment, and local conditions including sludge handling problems. Also, according to the characteristics of the wastewaters, there may be necessary additional treatment processes such as cyanide destruction, conversion of ionic forms as previously discussed. The prices of chemicals used will largely affect the operation costs.

A simple precipitation using lime, without other additional treatment processes, is, however, similar to the conventional tertiary treatment sequence of coagulation, settling, and sand filtration. Figure 2 provides approximate cost data for this sequence of operations.

Another study suggests that simple precipitation treatment costs are approximately $0.25/1000 gal without filtration and $0.45/1000 gal with filtration [26].

All of these cost estimations seem to apply to the wastewaters containing arsenic, cadmium, copper, lead, nickel, zinc, etc., which are readily precipitated by lime addition.

As mentioned previously, the trend in the treatment of industrial wastewaters requires the economical recovery of waste materials by closed-loop systems. Most precipitation processes, however, do not provide economical recovery. Even if technically possible, it requires another chemicals to precipitant, making the process too expensive.

TABLE 7

EFFECTIVENESS OF CHEMICAL PRECIPITATION ON METAL IONS IN WASTEWATERS [6]

Metal	Type of Waste	Precipitant or Coagulant	Final pH	Initial Concentration of Metal, mg/l	Final Concentration of Metal, mg/l	Percent Removal
Arsenic	--	Lime	--	0.2	0.03	85
	--	Ferric Sulfide	--	0.8	0.05	94
	--	Ferric Sulfate	--	25.0	<5.0	>80
	--	Ferric Chloride	--	3.0	0.05	98
Barium	--	Sodium Sulfate	--	--	0.5	--
	--	Sodium Sulfate	--	--	0.03-0.27	--
Cadmium	Machine Shop	Lime	--	--	0.54	--
	Municipal	--	10	--	0.1	--
Copper	Metal Proc.	Lime	--	204-385	0.5	--
	Brass Mill	Lime	--	10-20	1.0-2.0	--
	Wood Preserv.	Lime	--	0.25-1.1	0.1-0.35	--
	Brass Mill	Hydrazine + NaOH	--	75-124	0.25-0.85	--
Iron	Acid Mine Drainage	Limestone Slurry	--	145	5	96.2
	Acid Mine Dr.	Lime	--	157	1.6	99.0
	Acid Mine Dr.	Soda Ash	--	126	2.3	98.2
Lead	Plating	Lime	--	210-140	"trace"	--
	Municipal	Lime	--	0.31	0.1	--
	Battery Plant	Lime, 30 hrs.	6.8	--	0.48	--
	Battery Plant	Caustic Soda, 1 hour	5.5	--	1.6	--
	Battery Plant	Caustic Soda, 24 hours	7.0	--	0.04	--
	Battery Plant	Ammonia	7.8	--	23.9	--

TABLE 7 (continued)

Metal	Type of Waste	Precipitant or Coagulant	Final pH	Initial Concentration of Metal, mg/l	Final Concentration of Metal, mg/l	Percent Removal
Manganese	Acid Mine Drainage	Calcium Carbonate plus Lime	--	--	0.5	--
	--	Potassium Permanganate	--	1.0	0.05	--
Mercury	--	Sodium Sulfide plus Lime	--	--	0.1	--
	--	Lime and Sodium Alginate	10	18.0	0.0	--
Nickel	Plating	Ferric Chloride + Sand Filter	--	21	0.09-1.9	--
	Plating	--	--	46	0.8	--
	--	--	--	39	0.4	--
	--	Lime	9.9	100	1.5	--
Selenium	Municipal	Lime	--	--	--	16.2
Silver	--	Chlorine, 30 min.	--	--	--	90-99
	Plating	Chlorine	--	150	1.0	--
Zinc	Plating	Alkaline	--	55-120	$\leq$1.0	--
	Brass Wire Mill	Alkaline	--	36-374	0.08-1.60	--
	Viscose Rayon	Alkaline	--	20-120	0.88-1.5	--

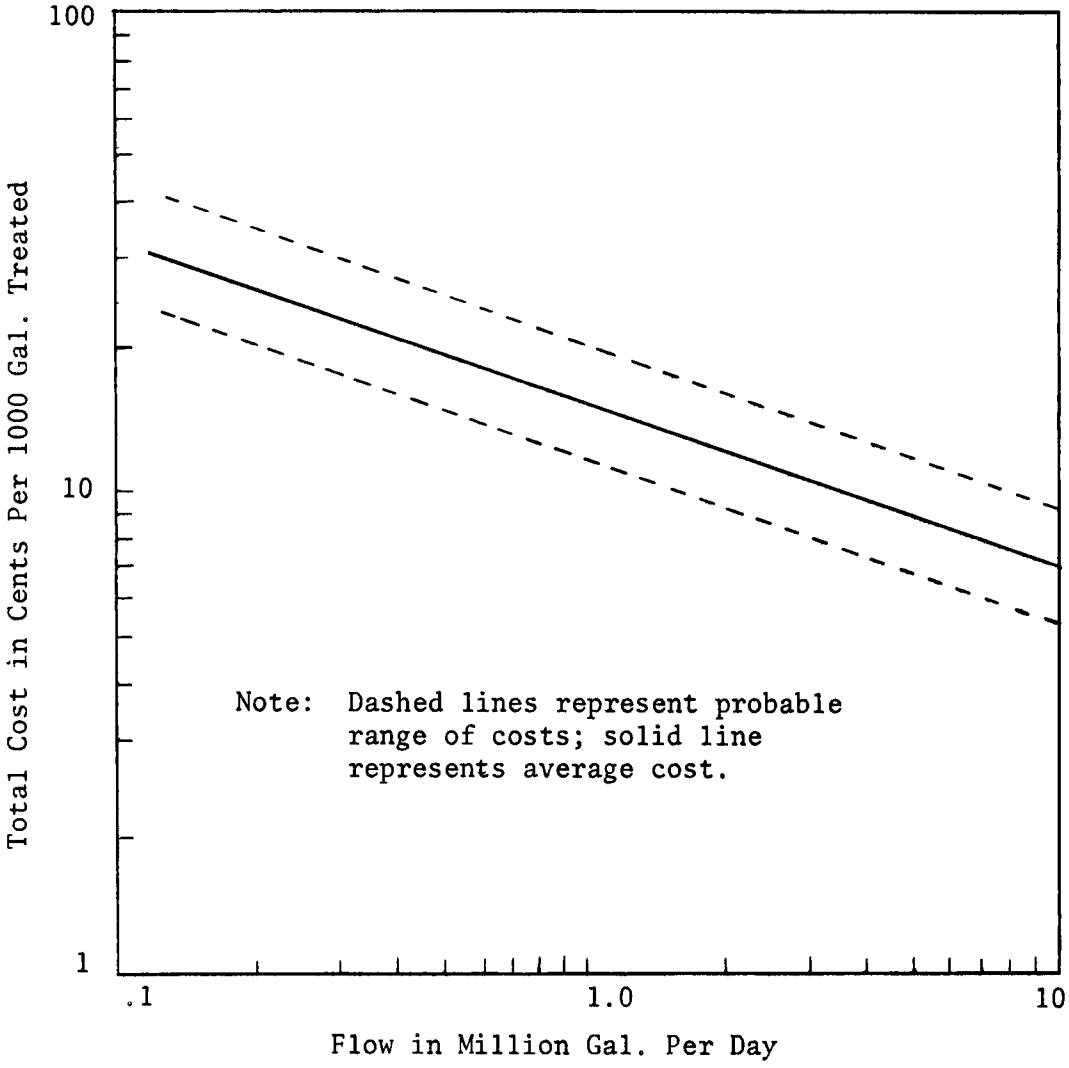


Figure 2. Costs of chemical precipitation using lime (25).

Note: Total cost of treatment by coagulation, sedimentation, and rapid sand filtration. Cost includes capital investment for 30 years at 4%, labor, power, chemicals, maintenance and repair, and heating of buildings.

Therefore, prospective applications of this chemical process are limited to a few cases. A striking example of this case is the zinc recovery method from rayon plant wastewaters.

The conventional technique for removing zinc from the spinning acid waste stream has been direct lime precipitation to a pH of about 10, with no zinc recovery. The resultant sludge has been of low zinc assay, contaminated with other compounds, and with very poor settling characteristics. The sludge presents a disposal problem and recovery of zinc suitable for recycle has not previously been possible [27].

An effective method recently developed for the recovery of zinc in viscose rayon plants was demonstrated by the U. S. Environmental Protection Agency industrial demonstration grant with American Enka Company [27]. The key to this zinc recovery process is a two-stage precipitation taking place under careful pH control, using sodium hydroxide, in contact with a circulating slurry of zinc hydroxide crystals. All of the zinc precipitates in the second step, most of impurities in the first.

The typical effectiveness of the Enka zinc recovery system is the reduction of zinc from 12.5 and 95 mg/l to 0.13 and 1.0 mg/l respectively [27].

The economics of recovery is a very strong function of the amount of zinc used in the preparation of the yarn and the ratio of acid to zinc in the spinning bath. In manufacturing industrial yarns and tire cords, it is common to use 4.5-7.5 pounds of zinc per 100 pounds of

yarn. This high concentration of zinc makes recovery extremely attractive. Textile yarns use less zinc; it offers less of a return [27].

Economical evaluation of the zinc recovery systems in comparison with conventional method is presented in Table 8 for textile yarn plant and in Table 9 for industrial yearn plant. These two cases are presented as extremes, with many plants falling between the two values. The costs associated with sludge handling and storage in conventional method are not included [27].

IV. ION EXCHANGE

Theoretical Background

Many natural materials and, more importantly, certain synthetic materials have the ability to exchange ions from aqueous solution for ions in the material itself. Cation exchange resins can, for example, replace cations in solution with hydrogen ions or sodium ions contained in the resins. Similarly, anion exchange resins can either replace anion in solution with hydroxyl ion or absorb the acids produced from the cation exchange treatment. A combination of these cation and anion exchange treatments can result in the demineralization of water.

In the practice of ion exchange, an important engineering parameter is the "exchange capacity" of resins, which is defined as the number of ion equivalents available for replacement in a specific amount of the resin.

Since the exchange capacity of ion exchange materials is limited, they eventually become exhausted and must be regenerated. Normally,

TABLE 8

ECONOMICAL EVALUATION OF ENKA ZINC RECOVERY SYSTEM FOR TEXTILE YARN PROCESS [27]

50 mm/lbs/yr of Textile Yarn	(Acid/Zn SO4 = 5.5) $\frac{\text{lbs/Zn}}{\text{100 lbs yarn}} = 1.5$	Conventional Lime Neutralization Precipitation	Two Stage Precipitation With Zinc Recycle
Total Investment (including engineering)		$425,000	$625,000
Operating Costs (all costs in $/yr)			
I. Wages		5,000	10,000
II. Electric Power @ 8 mils		7,000	9,300
III. Maintenance (3% on Invest/yr)		12,800	18,800
IV. Laboratory		All on-site, included in wages	
V. General Plant Overhead		8,000	10,000
VI. Raw Materials			
Lime ($20/ton)		72,900	64,800
NaOH ($40/ton)			20,800
Polyelectrolyte			5,500
Total Materials		$ 72,900	$ 91,100
Total Operating Cost		105,700	139,200
Fixed Charges			
Depreciation @ 15 yrs		28,300	41,600
Taxes, Insurance		2,000	3,000
Total Fixed Charges		$ 30,300	$ 44,600
Zinc Credit (@ 15.5/lb)		0	[116,000]
Net Yearly Cost Total		$136,000	$ 67,800
NET YEARLY ADVANTAGE (RECYCLE OVER CONVENTIONAL NEUTRALIZATION)		68,200	
Pretax Return on Differential Investment		$\frac{\$ 68,000}{\$200,000} = 34.1\%$	

TABLE 9

ECONOMICAL EVALUATION OF ENKA ZINC RECOVERY SYSTEM
FOR INDUSTRIAL YARN PROCESS [27]

50 mm lbs/yr of Industrial Yarn	(Acid/Zn SO4 = 2.0) lbs Zn / 100 lbs yarn = 6.0	Conventional Lime Neutralization Precipitation	Two Stage Precipitation With Zinc Recycle
Total Investment (including engineering)		$425,000	$625,000
Operating Costs (all costs in $/yr)			
I. Wages 1/2, 1 man @ $10,000/yr		5,000	10,000
II. Electric Power @ 8 mils		7,000	9,300
III. Maintenance (3% on Invest/yr)		12,800	18,800
IV. Laboratory		All on-site, included in wages	
V. General Plant Overhead		8,000	10,000
VI. Raw Materials			
Lime ($20/ton)		123,500	94,000
NaOH ($40/ton)			76,000
Polyelectrolyte			5,500
Total Materials		123,500	175,500
Total Operating Cost		156,300	223,600
Fixed Charges			
Depreciation @ 15 yrs		28,300	41,600
Taxes, Insurance		2,000	3,000
Total Fixed Charges		30,300	44,600
Zinc Credit (@ 15.5/lb)		0	[465,000]
Net Yearly Cost Total		$186,000	[197,000] Credit
NET YEARLY ADVANTAGE (RECYCLE OVER CONVENTIONAL NEUTRALIZATION)		383,600	
Pretax Return on Differential Investment		383,600 / 200,000 = 192%	
Pretax Return on Total Zn Pollution Control Facility		197,000 / $625,000 = 31.5%	

the cation resin is regenerated with an acid; the anion resin with a base.

Resins, therefore, may be considered as insoluble acids and bases, and it is possible to titrate the resins with standard acid or base solutions. In such a titration, the resin remains insoluble, but reaches and maintains an equilibrium with the titrant. This implies all resins may be described in the form of a stoichiometric equation in relation to the concentration of hydrogen or hydroxide ion and the concentration of anion or cation to be replaced.

Therefore, pH of a solution will directly affect the exchange capacity of resins. An increase of pH will increase the cation exchange capacity and will decrease the anion exchange capacity of each resin respectively, to reach a given breakthrough point.

For an example of this relationship, the capacity of Permutit Q [30] to remove zinc at various levels of sulfuric acid concentration is shown in Table 10.

Historical Background and Development

Ion exchange is one of natural phenomena; certain types of natural materials such as greensand, glauconite, and humic acid have the property. Some ancient people must have realized the ion exchange phenomenon, since Aristotle reported that salt could be partially removed from sea water through filtration in certain sand.

Modern advances were made by Thomson and Way [28]. Thomson, in his research with soil fertilizers, concluded that soluble ammonia salts

TABLE 10

CAPACITY OF PERMUTIT Q FOR ZINC AT VARIOUS LEVELS OF SULFURIC ACID CONCENTRATIONS [30]

% H_2SO_4	Total Capacity meq/l	Capacity meq/l to 10% Breakthrough	Zinc Leakage ppm
0.05		1430	2
0.1		1320	3
0.5		1040	20
1.0		830	15
1.5	643		100
3.0	308		155
5.0	115		254

could not be easily leached from soils. Way studied this phenomenon in detail and concluded that cation exchange in soils was restricted to the clay portion and that it is related to silicate compounds present in the soil.

In 1910, Grans [28] discovered the application of aluminosilicates to water softening, and his investigation determined that this material has a higher exchange capacity than did natural materials.

Until 1934, only one major application of technique was employed, that of water softening by the base-exchange or zeolite process. Hard waters were passed through beds of greensand, a natural aluminosilicate mineral, or through a synthetic material zeolite, of similar chemical structure. These minerals are permeable to water, and their structure permits the free movement of cations through the gel. Calcium and magnesium ions are retained in the zeolite, and equivalent quantities of sodium ions are released to the water. Brine is used as regenerant.

The early cation-exchange resins were rather inefficient, and in 1934 four separate announcements were made by organizations in Britain, Holland and Germany, of inventions of sulphonated coal, a cation-exchange material of higher capacity and stability than the synthetic materials [29]. During the next 10 years, the new technology of demineralizing of water was largely based on the combination of sulphonated coal and polyamine anion-exchange resins.

In 1935 Adam and Holmes [29] published their invention of the first synthetic cation and anion-exchange resins. The former were phenol-formaldehyde condensation products similar in structure to bakelite,

while the corresponding amine-formaldehyde condensates were used as anion-exchangers. As a result it was possible for the first time to remove both types of ions from solution, producing the equivalent of distilled water.

During World War II, polystyrene sulphonic cation-exchangers and polystyrene quaternary ammonium anion-exchange resins were invented in the U.S.A. The polystyrene resins, which are now manufactured throughout the world, have dominated the industry, and have become the most widely used ion-exchangers. Many other polymers, such as polyvinyl chloride, and polypyridine, have been developed into technically successful ion exchange resins, but only polyacrylates have had any real industrial import, and this to a much smaller extent than the polystyrene resins.

Applications

Ion exchange has been a well-known method for softening or demineralizing water. Similar applications have been developed in the treatment of wastewaters. Ion exchange can apply to the treatment or recovery of many of metallic ions from industrial or other wastewaters.

The effectiveness of ion exchange depends on the resins, operation period between resin regenerations, and the overall characteristics of wastewaters such as ion species to be removed, its concentration, pH, etc. Some of the effectiveness found in the literature are summarized in Table 11.

TABLE 11

EFFECTIVENESS OF ION EXCHANGE ON METALS IN WASTEWATERS [6]

Metal	Type of Waste	Resin	Initial Concentration of Metal, mg/l	Final Concentration of Metal, mg/l	Percent Removal
Barium	--	--	--	--	99
Cadmium	Municipal	Cation + Anion	"trace"	--	99.9
Chromium, hexavalent	Metal finishing	--	--	0.05 as chromate	--
	Boiler, Blowdown	--	8-10.7	0.0-0.9	--
Copper	--	--	1.02	< 0.03	--
	Plating	Amberlite IR120	45.0	"undetectable"	--
Lead	--	--	0.055	0.0015	--
	TEL Manufacturing	Cation	126.7-144.8	0.02-0.53	--
Mercury	Chlor-alkali	--	--	< 0.005	--
	--	--	--	> 0.005	--
Nickel	Plating	--	870	"complete removal"	
Silver	Municipal	Cation	"trace"	--	85.8
	Municipal	Cation + Anion	"trace"	--	91.7

The initial costs of an ion exchange unit depend upon the required resin volume. Flow rate will be limiting factor for dilute solutions, while the resin exchange capacity will dictate the volume for concentrated solutions. From several studies, a report estimates capital investments as $400 to $1200 per 1000 gpd and operation costs as 31¢ to 81¢ per 1000 gallon, without recovery of metals [6]. When metal recovery is feasible, ion exchange economics is greatly improved.

Prior to discussing the economical advantage of recovery systems, it is pertinent to study how ion exchange is employed in the recovery of metallic ions from wastewaters. As a specific case, the chromate recovery from plating wastewater is discussed herein.

The rinse water from chromium plating has the same components as the plating bath at much diluted concentrations and is usually contaminated with unnecessary metallic cations such as Fe, Cr^{+++}, Al^{+++}. Therefore, the function of recovery system is the removal of the contaminants and the concentration of diluted solution to the level of bath solution.

For the recovery of the chromium rinse water, a completely closed loop system suggested by Paulson [30], in Permutit company, is shown in Figure 3. In the figure, the rinse water is passed through the cation exchanger, Permutit Q, to remove cationic contaminants resulting in pure chromic acid solution. The concentration of rinse water is performed by the anion exchanger, Permutit S, which removes chromate and produces purified water for reuse. The anion exchanger is regenerated with NaOH, and regenerant effluent, the mixture of Na_2CrO_4 and

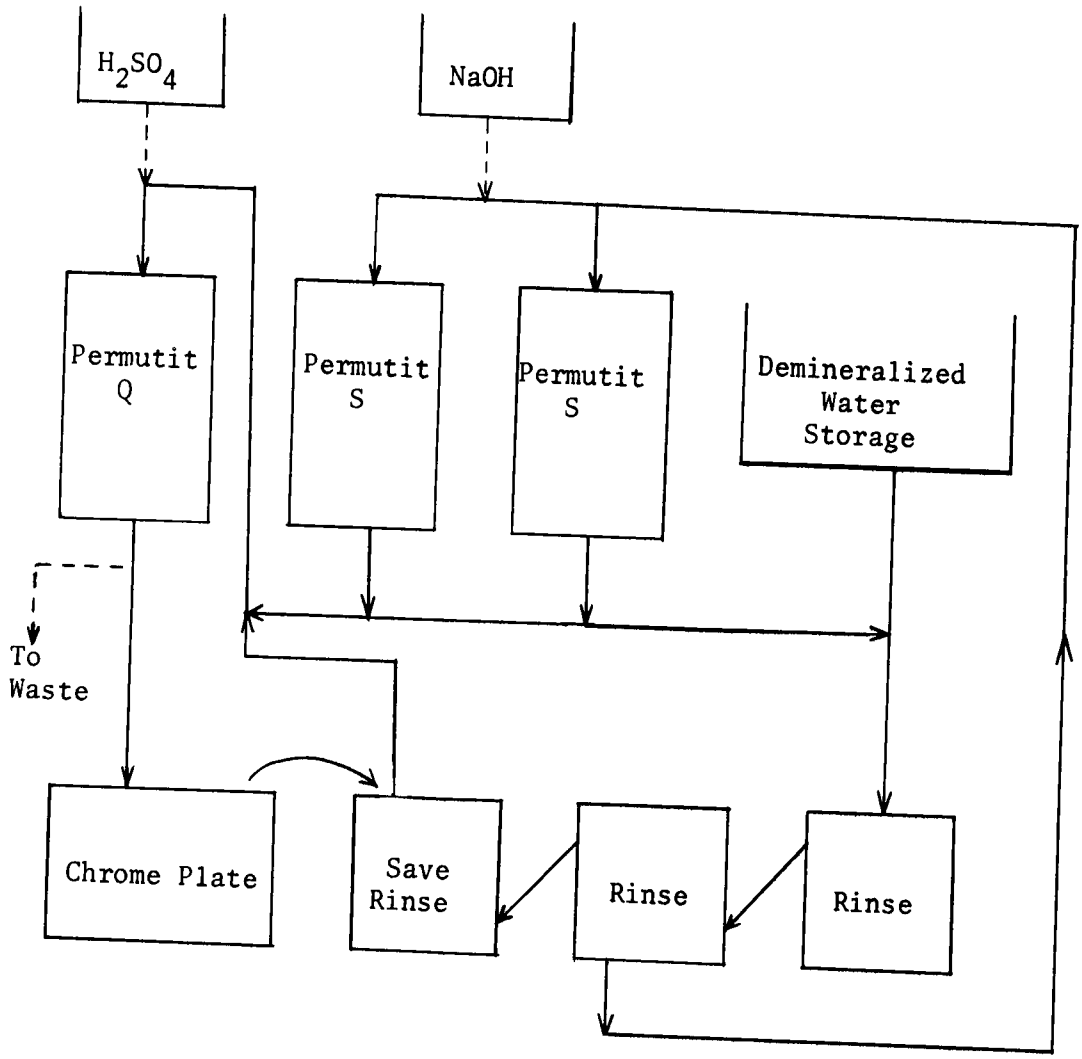


Figure 3. Chromate recovery system by ion exchange (30).

NaOH, is passed through the cation exchanger, Permutit Q, for the removal of sodium, resulting in the concentrated solution of H_2CrO_4 for reuse.

An operation costs estimation of this system is summarized in Table 12, comparing with the conventional chemical precipitation system.

The recovery method discussed for chromium rinse water is considered applicable to many other plating wastewaters in similar ways. Table 13 shows some recoverable chemicals from plating wastes by ion exchange.

V. REVERSE OSMOSIS

Theoretical Background

Osmosis is a thermodynamic tendency of a solvent to flow through a semipermeable membrane that allows free passage of solvent but not solute from a dilute solution to a concentrated one. This osmotic flow can be stopped by applying a pressure against the flow. The pressure, needed to stop the flow, is equivalent to the osmotic pressure which can be calculated by the Van't Hoff equation as follows:

$$\pi = \frac{n}{\nu} RT$$

where: π = Osmotic pressure, atm

$\frac{n}{\nu}$ = Ionic concentration, $\frac{\text{Moles}}{\text{liter}}$

T = Temperature, °K

R = Proportionality factor, 0.083 $\frac{\text{atm. liter}}{\text{moles °K}}$.

TABLE 12

COSTS COMPARISON OF ION EXCHANGE RECOVERY SYSTEM WITH CHEMICAL PRECIPITATION FOR CHROMIUM RINSE WATER [31]

Operation costs: based on 50 lb chromic acid in 10,000 gal water	
Ion Exchange Method	
1. Cation resin, based on 250 cycles	$1.20
2. Anion resin, based on 100 cycles	7.50
3. Sulfuric acid regenerant, 100 lb	2.50
4. Caustic soda regenerant, 40 lb	2.00
5. Water for regeneration, 2,000 gal	0.20
6. Total chemical costs	$13.40
7. Reclaimed chromic acid, 50 lb	15.00
8. Reclaimed rinse waters, 10,000 gal	1.00
9. Total credits	$16.00
10. Net savings of this method	2.60
11. Net savings of this method	7.10[1]
Chromic Acid Disposal	
1. Chromic acid, 50 lb	$15.00
2. Sodium bisulfite, 100 lb	6.78
3. Sodium hydroxide, 50 lb	2.75
4. Water, 10,000 gal	1.00
5. Total chemical	$25.53
6. Ion exchange method credit	2.60
7. Disposal method deficit	25.53
8. Net savings ion exchange vs disposal	$28.13
9. Net savings ion exchange vs disposal	32.63[1]

[1] Based on an anion life of 250 cycles.

TABLE 13

RECOVERY OF CHEMICALS FROM PLATING WASTES
BY ION EXCHANGE [38]

Waste	Chemical Recovery	Exchange Type	Regenerant
Brass-pickling liquor	Copper, zinc, chromium metals precipitated with soda ash and recovered by chemical means	Strongly acidic cation, hydrogen, or sodium	H_2SO_4 (66°Be)
Anodizing, chromating, chrome-plating and copper stripping wastes	Chromates for recycle	Strongly basic anion	Caustic
Cyanide leach liquors	Gold	Strongly acidic cation	H_2SO_4
Mine waters	Zinc	Strongly acidic cation	H_2SO_4
Cooling tower effluents	Chromates	Strongly basic anion; hydroxide form	Caustic
Plating wastes	Cyanides and copper	Strongly basic anion; strongly acid cation	Caustic-HCl
Copper, silver, and zinc cyanide plating wastes	Metal and cyanides	Strongly basic anion; strongly acid cation	Caustic-HCl

When excessive pressure is exerted on the concentrated solution, pure solvent moves into the diluted solution, since the membrane is a barrier to the solute.

This phenomenon in which solvent (e.g., water) is transferred by an outside force from a solution of high solute concentration to a solution of low solute concentration is called "reverse osmosis", derived from the fact of opposite flow direction to natural flow.

Therefore, the osmotic pressure is only the minimum force required to bring about reverse-osmosis. In current work, the operating pressures of reverse-osmosis systems are many times the osmotic pressure.

Historical Background and Development

The osmotic phenomenon was first noted in 1748 by Abbé Nollet, who found that water would diffuse through a pig bladder into alcohol spontaneously [34]. Further experiments during the next 100 years were hampered by the unreliability of animal membranes until 1864, when Traube prepared a selective membrane of copper ferrocyanide. This was used by Pfeffer in his experiments with sucrose and other solutions that linked osmotic pressure with temperature and solute concentrations [34]. Later, J. H. von't Hoff developed a mathematical relationship for osmotic pressure as shown in the foregoing page.

Interest in the osmotic process waned after the turn of the twentieth century because reliable membranes were not available. In the 1950's, amid predictions of water scarcity, the U. S. Dept. of Interior established its Office of Saline Water to evaluate water

purification methods. Reverse osmosis was attractive because of its simplicity and, theoretically, low energy requirements. All that was needed was a strong, corrosion-resistant, reliable, cheap, selective membrane [34].

Many natural materials have semipermeable characteristics. Besides animal and plant membranes, collodion, cellophanes, porous glass frits, finely cracked glass, and inorganic precipitates such as copper ferrocyanide and zinc and uranyl phosphates have been used historically. All, however, have the common faults of leaks, short-lived selectivity and poor reproducibility [34].

In 1958, C. E. Reid and J. E. Breton demonstrated that secondary cellulose acetate had the desired selectivity [34]. The type of membrane that is presently being used in most reverse osmosis equipment is a specially prepared cellulose acetate. The method of preparation gives a dense layer, less than one micron thick, on one side of the otherwise rather porous membrane. This dense layer is believed to be responsible for rejecting most of the impurities in the water. One type of membrane configuration is shown in Figure 4.

The application of various membranes for reverse osmosis to treat metal finishing wastewaters was studied by Rozelle [36]. The tests were conducted on seventeen different membranes for the separation of heavy metal ions (nickel, iron, copper, zinc), acids, bases, and cyanides from water. Experimental results showed that reverse osmosis is feasible and effective in treating these effluents both for pollution control and for recovery of metal ion and water for possible recycle. Simulated

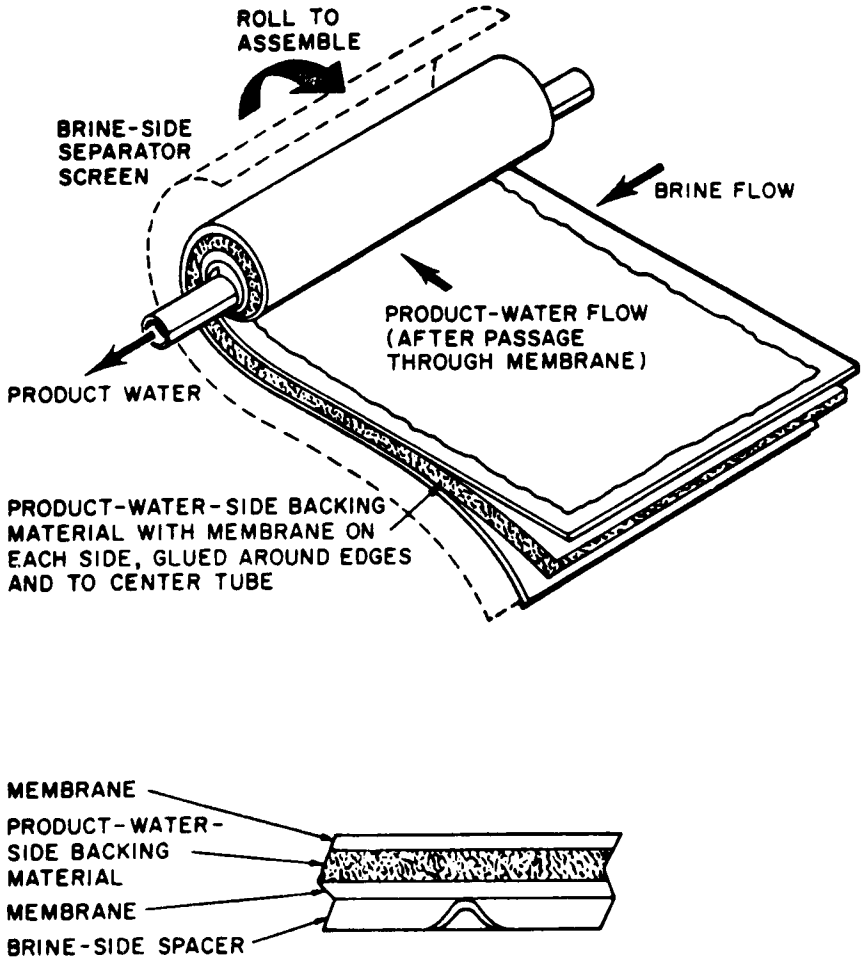


Figure 4. One type of membrane configuration in reverse osmosis (36).

acidic nickel, iron, zinc, and copper plating bath rinses were effectively treated up to 99.9 percent by ultrathin membranes of three polymers: cellulose acetate, cellulose methyl sulfonate O-propyl sulfonic acid, and β-glucan acetate dimethylaminoethyl ether. Simulated chromic acid rinses were effectively treated by ultrathin cellulose methyl sulfonate O-propyl sulfonic acid. The sulfonated polyphenylene oxide was the only membrane to withstand hydrolysis for over 170 hours by a highly alkaline (pH 11.4) copper cyanide solution.

Sleigh et al [37] studied the applicability of reverse osmosis to the demineralization of acid mine drainages, both high-ferrous and high-ferric types and to reclaim the maximum percentage of such feed-water in purified form suitable for domestic or industrial purposes, or as stream discharge. General conclusions of the study were that reverse osmosis is a promising process to treat acid mine drainages to produce potable water. Salt rejection efficiency was higher than 97 percent.

Applications

Reverse-osmosis systems for water treatment are now commercially available for any moderate need ranging from a 2.5 gpd unit for home drinking supply to a 800,000 gpd plant for industrial use. While most current applications are for teating brackish water for water supply, the scope of application is rapidly being extended to wastewater treatment, for the simplicity, the high efficiency, and the low treatment cost.

A typical application suggested by DuPont [14] for plating rinse water recovery is schematically shown in Figure 5.

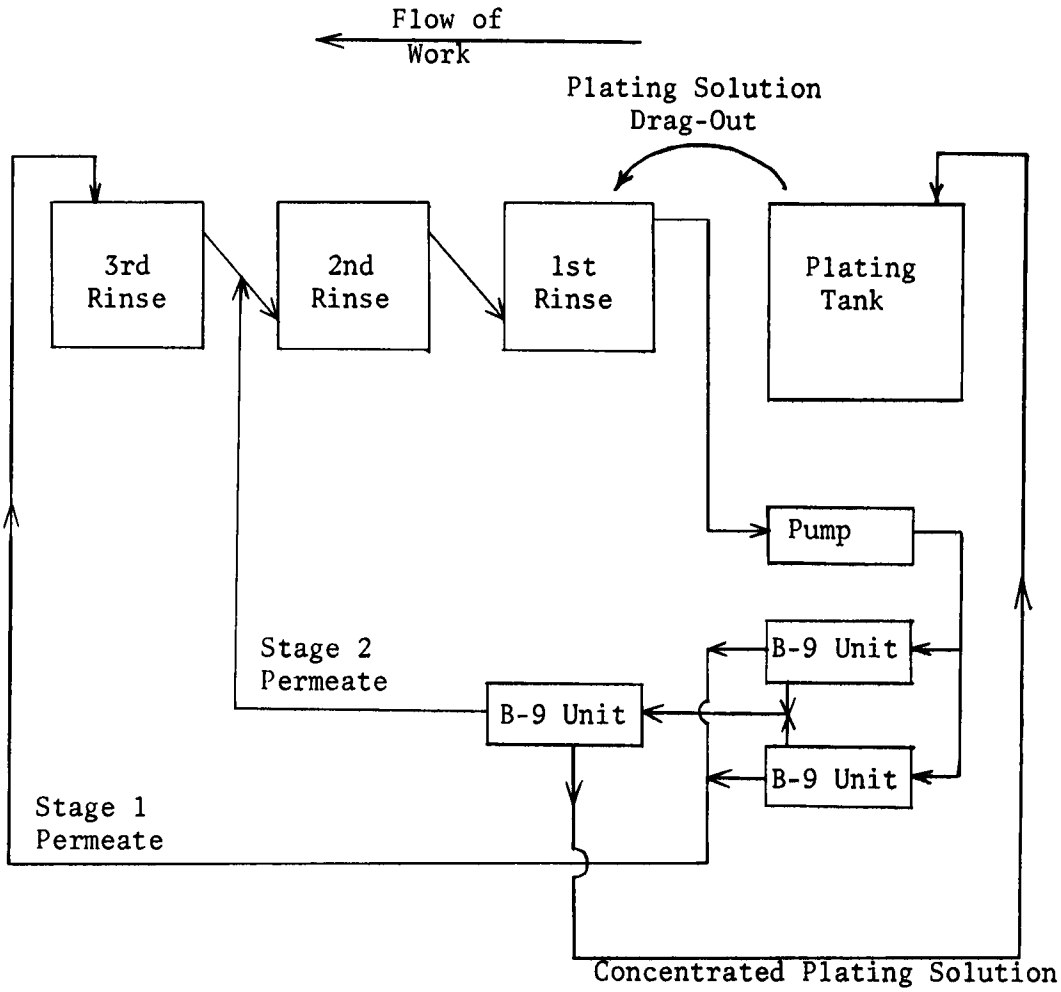


Figure 5. Electroplating waste recovery by reverse osmosis (14).

The reverse osmosis unit concentrates the rinse water and releases a dilute product water. The product water is reused as rinse water, while the concentrated fraction is returned to plating bath.

At present, any semipermeable membrane does not provide absolute rejection of metal ions. The rejection efficiency depends on the concentration of feed and on the ratio of permeate flow (diluted fraction) to the feed flow. Test data of DuPont "Permasep" on nickel solution is shown in Table 14.

There is a limitation of the extent of concentration by a single stage; however, further concentration can be achieved by multistage processes according to test data.

An economical evaluation of nickel waste treatment systems by chemical precipitation, evaporation, ion exchange, and reverse osmosis is presented by DuPont as shown in Table 15.

VI. EVAPORATION

General Description of Method

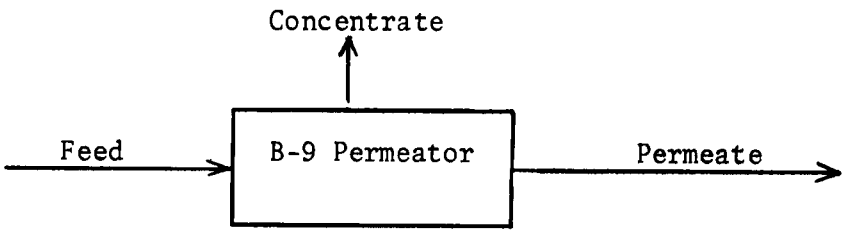
Evaporation as a technique for separating nonvolatile solids from volatile liquids has been practiced for centuries. Ancient people employed solar evaporation for the production of salt, but modern evaporators usually employ steam-heated tubes in a variety of design configurations. Since the principal operational cost of an evaporator is the cost of energy, attention has been focused on ways for reducing this cost by reusing the energy in the vapor. The multiple-effect

TABLE 14

DUPONT "PERMASEP" B-9 PERMEATORS NICKEL FIELD TEST DATA [14]

Stream Concentrations [1], ppm Ni				
Feed	Permeate	Concentrate	Conversion [2]	Nickel Rejection [3]
1,305	38	4,200	66%	97%
2,450	143	10,200	78%	94%
4,200	254	15,049	70%	94%
9,550	670	20,800	60%	93%
16,800	1,500	34,400	50%	91%

[1]



[2] $$\% \text{ Conversion} = \frac{\text{Permeate Flow Rate} \times 100}{\text{Feed Flow Rate}} .$$

[3] $$\% \text{ Nickel Rejection} = 100 - \frac{\text{Permeate Concentration} \times 100}{\text{Feed Concentration}} .$$

TABLE 15

RELATIVE ECONOMICS OF NICKEL WASTE TREATMENT SYSTEMS [14]

(4 gpm)	Chemical Destruction	Evaporation	Ion Exchange	"Permasep" RO
Equipment Cost (FOB), $	16,500	20,700	10,000	14,300
Estimated Direct Operating Costs, $/yr				
Steam	-	6,450	-	-
Power	200	200	200	200
Treatment Chemicals	7,400	-	100	-
Maintenance	500	600	500	400
Operating Labor	2,200	1,600	2,200	1,600
Amortized Permeator Replacement (1 yr)	-	-	-	3,300
Total Operating Costs, $/yr	10,300	8,850	3,000	5,500
Estimated Total Savings, $/yr				
Nickel Sulfate Recovered, lbs/yr	0	18,000	18,000	18,000
Nickel Sulfate Cost @ $.45/lb	0	8,100	8,100	8,100
Brighteners (50% Recovered)	0	4,550	-	4,550
Total, $/yr	0	12,650	8,100	12,650
Estimated Net Savings (or Cost) $/yr	(10,300)	3,800	5,100	7,150
Capital Payback Period, years	0	5.45	1.95	2.0

evaporator and the vapor recompression evaporator are commonly used to achieve this heat economy.

In multiple-effect evaporators, the temperature difference for heat transfer through tube walls is obtained by vaporizing the liquid in successive effects, each at a lower pressure or boiling temperature. This allows the steam produced in one effect to be used as the heating medium for the next. The result is that for each pound of steam originally supplied to the first effect, there is produced a number of pounds of product water approximately equal to the number of effects.

In the vapor compression evaporator, the vapor is mechanically compressed to a higher pressure and temperature for reuse in the same effect to evaporate more water. Although no heat energy is required after start-up, mechanical energy is necessary to compress the water vapor. Cheap electric power and expensive steam and cooling water strongly favor this process.

Applications

A commercially available plating waste recovery system utilizing vacuum evaporation is schematically shown in Figure 6, provided by Pfaudler Company [40]. Plating work moves from the plating bath to a series of counterflow rinse tanks. Overflow from the first (most concentrated) rinse tank collects in a holding tank from which it is drawn by vacuum into the main body of a separator. A recirculating pump then transfers it into a reboiler where some of the water is evaporated. The mixture of water vapor and rinse water reenters the separator where the

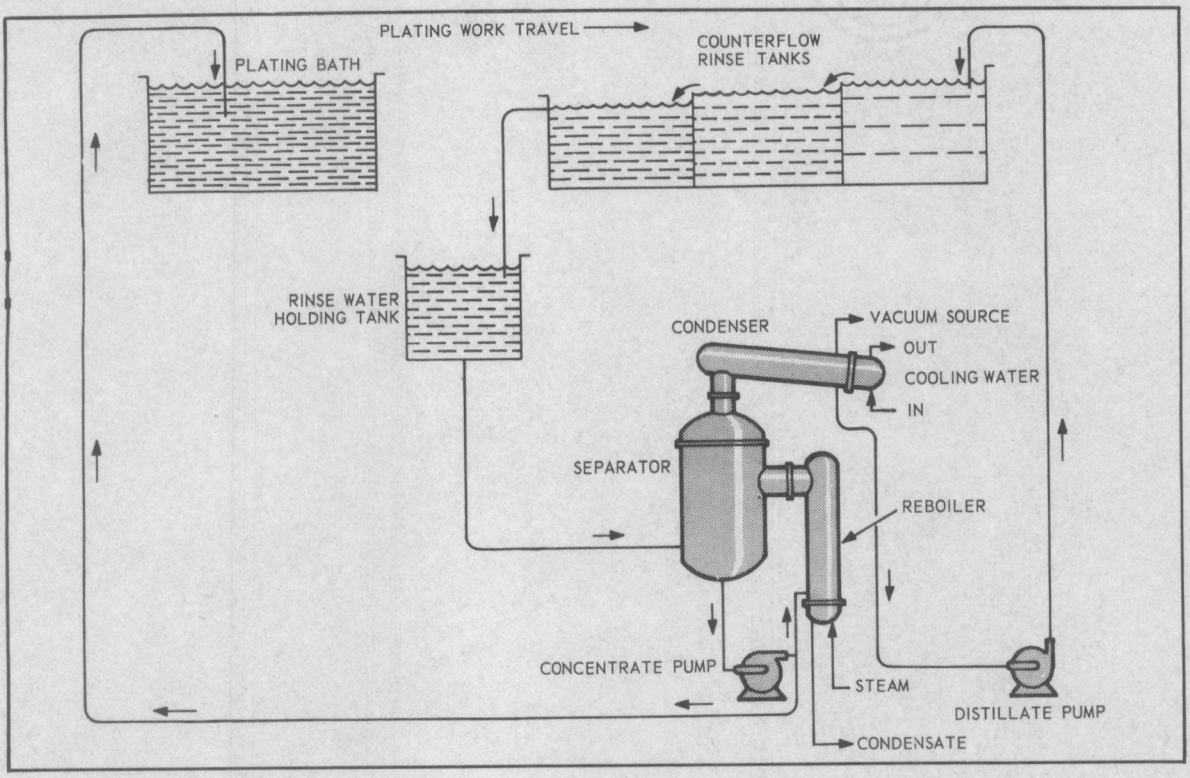


Figure 6. Plating waste recovery system by evaporation (40).

liquid falls to the bottom and is returned to the reboiler. The water vapor moves upward and passes into a condenser where cooling water condenses it into distilled water. It is then pumped to the final rinse tank for recycling as clean rinse water. The solution remaining in the separator becomes more concentrated with each pass through the reboiler. When the desired strength is reached, the recirculating pump transfers it to the plating bath for makeup.

Evaporation can be used on almost all metallic wastewaters to concentrate them to the level for reuse, except those wastes containing deteriorative components at high temperature. Effectiveness is almost 100 percent.

Culotta and Swanton [41] describe that a plating plant, by evaporative recovery, reduced process water from 3000 gal/hr to 50 gal/hr, and resulted in process chemical savings of $18,000/yr, plus equal savings in treatment chemicals. Capital and operating costs associated with such a closed loop system were reported to be approximately same as for chemical destruction [41]. Their analysis is based on labor costs of $5/man-hr and costs of $0.45/gal for zinc cyanide plating solution containing 120,000 mg/l of zinc.

CHAPTER IV

DISCUSSION

Discharge of industrial wastewaters into municipal sewers has been a widely used practice in the past. Today one of the major problems facing state agencies regulating water pollution is the establishment of codes governing the discharge of toxic materials into municipal sewerage systems for the toxic effects on the microorganisms at treatment plants. When a municipal sewage plant employing only primary treatment receives sufficient quantity of water to dilute the toxic metals, this practice may still be useful in certain cases. However, when the sewage plant employs secondary (biological) treatment, this practice requires careful study to determine the concentration level of each toxic constituent which can be permitted in sewage plant influent without upsetting the biological process. It then would be the responsibility of industry to remove any excess beyond this allowable concentration. In many cases, however, this "allowable concentration" in the limited range will not allow industries to discharge substantial amount of heavy metallic wastes, but will virtually force treatment before discharging the wastewaters to sewers or streams.

Most economical recovery processes require as little volume of waste stream as possible without being contaminated with foreign components. This means that each waste stream from different processes in a plant may require an individual treatment system rather than treatment

of combined waste streams. Also, the individual system can take advantage of other systems by their integration into each other. This factor makes the problem highly complicated.

All the unit processes, discussed in this paper, have their advantages and disadvantages; they have limitations in applications. Some of their shortcomings are inherent; others are improvable through development.

Basically, reverse osmosis, evaporation, and possibly ion exchange have the same function: concentration of a solution and releasing dilute water in the form for reuse. Limitations of the applicability of these processes depend on the concentration level to be obtained, pH of the solution, heat stability of recoverable materials, etc.

Generally, the concentration of a solution to certain level can be most economically achieved by reverse osmosis, and further concentration to higher level, if necessary, can be accomplished by evaporation.

Ion exchange has good advantages for its flexibility such as the selective removal of anion or cation which is an essential process in certain cases. Ion exchange is generally considered economical for recovery of low concentration of ions. For the recovery of high ionic concentrations, higher regenerant consumption makes the process uneconomical.

Chemical precipitation requires expensive chemicals and usually does not economically recover the metals, subsequently creating the sludge disposal problem. Its applications will be limited to certain cases which overcome the above shortcomings or to small plants where other processes are not practical.

CHAPTER V

CONCLUSION

The closed loop system for the treatment and recovery of metallic wastewaters is considered to be the best method from economical and pollutional points of view for the following reasons:

1. It provides the recovery of valuable materials and subsequent reduction of material consumption.
2. Wastewater is recycled for reuse and subsequent reduction of water consumption and sewer charge is attained.
3. No expense for treatment chemicals as required by chemical precipitation is necessary.
4. No sludge problem.
5. Space saving can be achieved.
6. Reliable, continuous, automatic operation is applicable.

Therefore, it is emphasized that the closed loop system should be a basic scheme in the design of metallic wastewater treatment systems today.

The future trend of treatment systems seems to be integration of the treatment into the plant production line. In this sense, the situation can be described as the elimination of wastewater rather than treatment.

The optimum treatment and recovery system can be established by combining the various unit processes in such a way to take the advantages of each process.

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APPENDIX

TABLE 16

LIST OF SOME METALLIC POLLUTANTS IN WATER [5]

Arsenic		
	arsenous	As^{+++}
	arsenic	As^{+++++}
	arsenide	As^{---}
	metaarsenite	AsO_2^-
	arsenite	AsO_3
	metaarsenate	AsO_3^-
	arsenate	AsO_4^{---}
	cacodylate	$As(CH_3)_2^{++}$
	methylarsenate	$HAsCH_3^-$
	phenylarsenate	$C_6H_5AsO_3H^-$
	arsine	H_3As
	trimethylarsine	$As(CH_3)_3$
	tetramethyldiarsyl	$As_2(CH_3)_4$
Cadmium		
	cadmium ion	Cd^{++}
Chromium		
	chromous	Cr^{++}
	chromic	Cr^{+++}
	chromate	CrO_4^{--}
	peroxychromate	CrO_8^{---}
	dichromate	$Cr_2O_7^{--}$
Copper		
	cuprous	Cu^+
	cupric	Cu^{++}
Iron		
	ferrous	Fe^{++}
	ferric	Fe^{+++}
	ferricyanide	$Fe(CN)_6^{---}$
	ferrocyanide	$Fe(CN)_6^{----}$
Lead		
	plumbic	Pb^{++}
	plumbate	PbO_4^{----}
Manganese		
	manganous	Mn^{++}
	manganic	Mn^{+++}
	permanganate	MnO_4^-
	manganate	MnO_4^{--}
Mercury		
	mercurous	Hg^+
	mercuric	Hg^{++}
	ammonomercuric	$Hg(NH_2)^+$
	organomercuric	RHg^+
	diorganomercury	HgR_2
Nickel		
	nickelous	Ni^{++}
	hexaminenickel	$Ni(NH_3)_6^{--}$
Silver		
	argentous	Ag^+
	argentic	Ag^{++}
Zinc		
	zinc ion	Zn^{++}

TABLE 17

1961 WHO EUROPEAN STANDARD FOR DRINKING WATER

Agent	Permissible Limit (mg/l)	Excessive Limit (mg/l)
Arsenic		0.2
Cadmium		0.05
Chromium^{+6}		0.05
Copper	1.0	1.5
Cyanide		0.01
Fluoride	1.5	
Iron	0.1	
Lead	0.1	
Manganese	0.1	0.5
Nitrate	50.0	
Selenium		0.05
Sulfate	250.0	
Zinc		5.0

VITA

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