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SEPARATION OF HEAVY METALS: REMOVAL FROM INDUSTRIAL
WASTEWATERS AND CONTAMINATED SOIL*

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Abstract

This paper reviews the applicable separation technologies relating to removal of heavy metals from solution and from soils in order to present the state-of-the-art in the field. Each technology is briefly described and typical operating conditions and technology performance are presented. Technologies described include chemical precipitation (including hydroxide, carbonate, or sulfide reagents), coagulation/flocculation, ion exchange, solvent extraction, extraction with chelating agents, complexation, electrochemical operation, cementation, membrane operations, evaporation, adsorption, solidification/stabilization, and vitrification. Several case histories are described, with a focus on waste reduction techniques and remediation of lead-contaminated soils. The paper concludes with a short discussion of important research needs in the field.

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Introduction

A number of specialized processes have been developed for the removal of heavy metals from waste discharges and for the remediation of contaminated soils and groundwaters. For the removal of metals from solution, these unit operations involve chemical precipitation (hydroxide, carbonate, sulfide, or combinations thereof), coagulation/flocculation, ion exchange, solvent extraction, cementation, complexation, electrochemical operations, evaporation, filtration, and membrane processes. Several reviews are found in the technical literature that summarize the various physical/chemical treatments for heavy metal removal (Dean et al., 1972; Lanouette, 1977; Patterson and Minear, 1975; Peters et al., 1985a).

Subsurface soils and groundwaters can become contaminated with heavy metals as a result of a number of activities, including the application of industrial waste, fertilizers and pesticides; mining, smelting, and metal plating/metal finishing operations; automobile battery production; vehicle emissions; and fly-ash from combustion/incineration processes.

For soils contaminated with organic pollutants, a number of techniques can be considered for remediation of a particular site, including thermal treatment, steam and air stripping, microbial degradation, and chemical oxidation. Fewer treatment techniques exist for the remediation of metal-laden soils. Unlike organic degradation, metals cannot be degraded away; only the form or phase of the metals can be changed. Metals are the only hazardous constituents that cannot be destroyed or altered by chemical or thermal methods (Connor, 1990); they must be either be treated or converted into the most insoluble form possible to prevent their reentry into the environment. Metals can be removed either by flotation or extraction. Process parameters affecting extraction technologies for the cleanup of soils include extractant type and concentration, suspension pH, competition from hydrous oxides, electrolyte type and concentration, contact time, and soil characteristics (Elliott and Peters, 1993).

Migration of metals can also be minimized by solidifying or vitrifying the soil and fixing the metals in a nonleachable form. In solidification processes, lime, fly-ash, cement-kiln dust, calcined clays, soluble silicates, and other additives are added to bind the soil into a cement-like mass and immobilize the metallic compounds (Connor, 1990). In vitrification processes, the soil is formed into a glassy matrix by applying current across embedded electrodes. The soil is heated to about 3600°F, the temperature at which it melts, producing the solid, glass-like material that immobilizes waste constituents within the matrix. Solidification is very expensive because the waste must be thoroughly characterized to determine compatibility with the specific treatment processes. Many existing technologies result in a solid with unsatisfactory long-term stability. Solidification/stabilization also results in an increase in the waste volume. Following remediation, site reuse is limited and long-term monitoring is generally required. For these reasons, solidification/stabilization is generally limited to radioactive or highly toxic wastes (U.S. EPA, 1982).

Purpose

The purpose of this paper is to review the processes currently available for wastewaters laden with heavy metals and for remediation of contaminated soils and groundwaters. This paper could not possibly include all the research and applications of heavy metal removal from wastewaters/groundwaters and soils; rather, this paper seeks to highlight many of the significant

contributions to the field of separation science with a focus on remediation and treatment of heavy metals in the environment.

Background

This section describes each of the common technologies used to treat heavy-metal-contaminated soils and wastewaters. The first section is aimed at wastewater treatment techniques.

Chemical Precipitation

Chemical precipitation involves transforming a soluble compound into an insoluble form through the addition of chemicals, such that a supersaturated environment exists (i.e., the solubility product is exceeded). Table I lists values of solubility products of various metal hydroxide, metal carbonate, and metal sulfide species.

It should be noted that there is a fine line of distinction between chemical precipitation and solidification/stabilization (s/s) operations. In s/s operations, the contaminants become incorporated into a cement-like matrix to render the contaminants less prone to leaching. Sludges are chemically treated by mixing a binder material to improve the physical and chemical stability of the sludge. Materials such as portland cement, silicates, pozzolanic materials, and fly ash have been used as solidification/stabilization agents. The goal of s/s technologies is to minimize the leaching potential of the contaminants. Likewise, the goal of chemical precipitation operations is to make the contaminant less soluble. Solidification/stabilization techniques are used to immobilize heavy metals, but they have also been used to immobilize organic contaminants as well. In general, organics with low water solubility are immobilized fairly well in solidification/stabilization operations, while higher solubility organics are not (Connor, 1990). Chemical precipitation techniques are rarely used to precipitate organic compounds from solution, although organics can adsorb onto precipitate forms such as hydrous metal oxides.

Chemical precipitation is the most common technique used for treatment of metal-containing wastewaters (U.S. EPA, 1980; Peters et al., 1985a; Patterson, 1988; Patterson and Minear, 1975), with oxidation/reduction plus precipitation being a closely related technique (Patterson, 1988). Alternative techniques have primarily focused on opportunities for metals recovery and include selective sorption/desorption, differential precipitation, and sludge beneficiation and extraction (Patterson, 1988). Clifford et al. (1986) cite the following advantages for precipitation/coprecipitation contaminant removal processes: (1) low cost for high volume, (2) process is often improved by high ionic strength, and (3) it is a reliable process well suited to osmotic control. Limitations include the following: (1) stoichiometric chemical addition requirements; (2) high-water-content sludge must be disposed of; (3) part per billion effluent contaminant levels may require two-stage precipitation; (4) processing is not readily applied to small, intermittent flows; and (5) coprecipitation efficiency depends on initial contaminant concentration and surface area of the primary floc.

Precipitation can be broadly divided into two categories: (1) chemical precipitation and (2) coprecipitation/adsorption. Chemical precipitation is a complex phenomenon resulting from the induction of supersaturation conditions. Precipitation proceeds through three stages: (1) nucleation, (2) crystal growth, and (3) flocculation. Metal salt solubility can be predicted (at

Table I List of Solubility Products for Various Heavy Metal Compounds (adapted from Dean, 1979, and Benefield et al., 1982)

Compound	pK _{sp}	K _{sp}	Compound	pK _{sp}	K _{sp}
CdCO ₃	11.28	5.2x10 ⁻¹²	Mn(OH) ₂	12.72	1.9x10 ⁻¹³
Cd(OH) ₂ - fresh	13.6	2.5x10 ⁻¹⁴		12.70*	2.0x10 ⁻¹³
Cd(OH) ₂ - aged	13.7 *	2.0x10 ⁻¹⁴	MnS - amorphous	9.6	2.5x10 ⁻¹⁰
CdS	26.1	8.0x10 ⁻²⁷	MnS - crystalline	12.6	2.5x10 ⁻¹³
			MnS	15.15*	7.0x10 ⁻¹⁶
CoCO ₃	12.84	1.4x10 ⁻¹³	NiCO ₃	8.18	6.6x10 ⁻⁹
Co(OH) ₂ - fresh	14.8	1.6x10 ⁻¹⁵		6.85*	1.4x10 ⁻⁷
Co(OH) ₃	43.8	1.6x10 ⁻⁴⁴	Ni(OH) ₂ - fresh	14.7	2.0x10 ⁻¹⁵
α-CoS	20.4	4.0x10 ⁻²¹		15.80*	1.6x10 ⁻¹⁶
β-CoS	24.7	2.0x10 ⁻²⁵	α-NiS	18.5	3.2x10 ⁻¹⁹
Cr(OH) ₃	30.2	6.3x10 ⁻³¹	β-NiS	24.0	1.0x10 ⁻²⁴
	30.17*	6.7x10 ⁻³¹	γ-NiS	25.7	2.0x10 ⁻²⁶
CuCO ₃	9.86	1.4x10 ⁻¹⁰	NiS	20.52*	3.0x10 ⁻²¹
	9.60*	2.5x10 ⁻¹	PbCO ₃	13.13	7.4x10 ⁻¹⁴
Cu(OH) ₂	19.66	2.2x10 ⁻²⁰		12.82*	1.5x10 ⁻¹³
	18.80*	1.6x10 ⁻¹⁹	Pb(OH) ₂	14.93	1.2x10 ⁻¹⁵
CuS	35.2	6.3x10 ⁻³⁶		14.38*	4.2x10 ⁻¹⁵
	36.10*	8.0x10 ⁻³⁷	PbS	27.9	8.0x10 ⁻²⁸
FeCO ₃	10.50	3.2x10 ⁻¹¹		28.15*	7.0x10 ⁻²⁹
	10.70*	2.0x10 ⁻¹¹	Sn(OH) ₂	27.85	1.4x10 ⁻²⁸
Fe(OH) ₂	15.1	8.0x10 ⁻¹⁶	Sn(OH) ₄	56.0	1.0x10 ⁻⁵⁶
	14.74*	1.8x10 ⁻¹⁵	SnS	25.0	1.0x10 ⁻²⁵
Fe(OH) ₃	37.4	4.0x10 ⁻³⁸	SrCO ₃	9.96	1.1x10 ⁻¹⁰
	37.22*	6.0x10 ⁻³⁸	ZnCO ₃	10.84	1.4x10 ⁻¹¹
FeS	17.2	6.3x10 ⁻¹⁸		10.52*	3.0x10 ⁻¹¹
	18.39*	4.0x10 ⁻¹⁹	Zn(OH) ₂	16.92	1.2x10 ⁻¹⁷
Hg ₂ CO ₃	16.05	8.9x10 ⁻¹⁷		16.35*	4.5x10 ⁻¹⁷
Hg(OH) ₂	23.7	2.0x10 ⁻²⁴	α-ZnS	23.8	1.6x10 ⁻²⁴
Hg ₂ S	47.0	1.0x10 ⁻⁴⁷	β-ZnS	21.6	2.5x10 ⁻²²
HgS (red)	52.4	4.0x10 ⁻⁵³	ZnS	22.8*	1.6x10 ⁻²³
HgS (black)	51.8	1.6x10 ⁻⁵²			
MnCO ₃	10.74	1.8x10 ⁻¹¹			
	9.40*	4.0x10 ⁻¹⁰			

Sources: Dean, J.A. 1979. **Lange's Handbook of Chemistry**, 12th ed. 1979. J.A. Dean, Ed., McGraw-Hill Book Company, New York, NY;

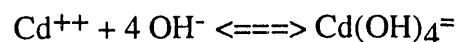
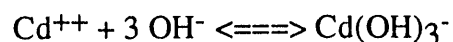
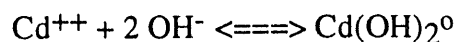
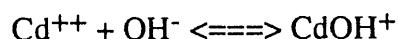
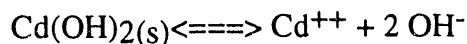
*Benefield, L.D., J.F. Judkins, Jr., and B.L. Weand. 1982. **Process Chemistry for Water and Wastewater Treatment**, Prentice Hall, Inc., Englewood Cliffs, NJ.

equilibrium) from thermodynamic calculations. These thermodynamic calculations cannot assess the kinetic rate, the influence of precipitate induction parameters, and the degree of supersaturation required to induce nucleation. It is important to note that the stability constants reported in the technical literature can vary by several orders of magnitude. As an example, Table II (adapted from Patterson, 1988) summarizes the logarithms of the stability constants for the cadmium hydroxide system reported from several reference sources. Patterson (1988) points out that the shape of the cadmium hydroxide solubility curve (as a function of pH) can vary significantly, depending on the particular stability constants chosen.

Table II Logarithm of Stability Constants Reported for Cadmium (adapted from Patterson, 1988)

Stability Constant	Reference					
	Smith and Martell (1976)	Baes and Mesmer (1976)	Sillen and Martell (1971)	Snoeyink and Jenkins (1980)	Dean (1979)	Sawyer and McCarty (1978)
K ₁	3.90	3.92	5.00	4.16	4.17	6.08
K ₂	7.70	7.65	8.90	8.40	8.33	8.70
K ₃	8.75	8.70	11.60	9.10	9.02	8.38
K ₄	8.70	8.65	—	8.80	8.62	8.42
K _{sp}	-14.65	-13.65	-13.60	-13.60	-13.60	(-13.60)

Chemical Reactions Involved:



Solubility Constant Expression:

$$K_{\text{sp}} = (\text{Cd}^{++}) (\text{OH}^-)^2$$

Stability Constant Expressions:

$$K_1 = \frac{(\text{CdOH}^+)}{(\text{Cd}^{++})(\text{OH}^-)}$$

$$K_2 = \frac{(\text{Cd}(\text{OH})_2^\circ)}{(\text{Cd}(\text{OH})^+)(\text{OH}^-)} = \frac{(\text{Cd}(\text{OH})_2^\circ)}{K_1(\text{Cd}^{++})(\text{OH}^-)^2}$$

$$K_3 = \frac{(\text{Cd}(\text{OH})_3^-)}{(\text{Cd}(\text{OH})_2^\circ)(\text{OH}^-)} = \frac{(\text{Cd}(\text{OH})_3^-)}{K_1 K_2 (\text{Cd}^{++})(\text{OH}^-)^3}$$

$$K_4 = \frac{(\text{Cd}(\text{OH})_4^{=})}{(\text{Cd}(\text{OH})_3^-)(\text{OH}^-)} = \frac{(\text{Cd}(\text{OH})_4^{=})}{K_1 K_2 K_3 (\text{Cd}^{++})(\text{OH}^-)^4}$$

The U.S. Environmental Protection Agency has estimated that there are in excess of 13,000 generators of metal plating/metal finishing wastewaters (U.S. EPA, 1980). Treatment of these wastewaters is usually accomplished through hydroxide precipitation; nearly 75% of the plating facilities employ precipitation treatment (primarily hydroxide treatment) as the treatment technique scheme for removal of heavy metals from solution (Patterson and Minear, 1975). Hydroxide precipitation is by far the most commonly used process industrially (Patterson and Minear, 1975, Dean et al., 1972; Peters et al., 1985a). Treatment of the metal plating/metal finishing wastewaters is estimated to generate approximately 11 million metric tons annually of sludge (FOO6) requiring special handling and disposal (Bricka and Cullinane, 1987). In chemical precipitation operations, the generator of the wastewater is faced with the problem of first removing the metal contamination from the wastewater and then disposing of the residual materials resulting from the wastewater treatment process.

Coprecipitation/Adsorption

When a solid phase is precipitated from solution, impurities that are normally soluble under the conditions of the precipitation may adsorb onto nuclei or crystals and be removed with the parent solid as a single phase. This phenomenon is known as coprecipitation. Coprecipitation/adsorption is a co-removal process for removal of contaminants from wastewaters.

Five major types of coprecipitation have been identified (Kolthoff, 1932; Salutsky, 1959; Christian, 1977; Patterson, 1988):

- (1) Surface adsorption - in which the impurities are not incorporated into the internal crystal structure, but rather stay adsorbed to the outer surface of the precipitate. This adsorption involves a primary adsorbed ion layer, which is held tightly, and a counter-ion layer, which is held more or less loosely. Surface properties of the forming solid phase (including electrostatic charge) serve to attract or repel secondary constituents in the surrounding aqueous matrix.

- (2) Occlusion - in which the impurities are not incorporated in the crystal lattice, but are adsorbed during the growth of the crystals and give rise to the formation of imperfections in the crystal. Adsorption phenomena during the growth of the crystals are primarily responsible for the amount of occlusion.
- (3) Isomorphic inclusion (or mixed crystal formation) - in which the impurity fits nicely into the crystal lattice of the precipitate and becomes incorporated into the lattice in place of a lattice ion of similar dimension and chemical characteristics. Thus, the impurity becomes permanently incorporated into the crystal lattice, resulting in a mixed crystal.
- (4) Mechanical entrapment - involves the physical enclosure of a small portion of the mother liquor with tiny hollows or flaws that form during the rapid growth and coalescence of the crystals. The pockets remain filled with the mother liquor and eventually become completely enclosed by the precipitate.
- (5) Postprecipitation - in which the precipitate is allowed to stand in contact with the mother liquor, and a second substance will slowly form a precipitate with the precipitating reagent. This type of precipitate contamination is closely associated with surface adsorption.

Regardless of which type of coprecipitation occurs, the initial incorporation of the impurity into the solid phase is the result of adsorption. This adsorption may be due to chemisorption, resulting from the coordination between the impurity and one or more constituent ions of the crystal lattice, or physisorption, resulting from electrostatic interactions, Van der Waal's forces, or dipole-dipole interactions. Chang (1985) and Chang and Peters (1985) have presented data for the coprecipitation/adsorption of cadmium, lead, and zinc onto CaCO_3 sludges.

Patterson (1988) noted that little effort has been made to control coprecipitation. Possible control mechanisms include pH control (which influences the surface charge of the precipitate solid and the speciation of the soluble phases), control of the oxidation state of the soluble species, choice of coprecipitant salt and dosage, and process configuration.

Applications

Chemical precipitation processes offer significant potential to remove soluble ionic species from solution, particularly materials such as heavy metals. The technique is not generally applicable for treatment of contaminated soils. It can, however, be used to treat industrial wastewaters and contaminated groundwaters (employing a pump-and-treat technique). This technique therefore has applicability for removal of soluble ionic species from aqueous solution. Chemical precipitation can also be used as a pretreatment technique to remove heavy metals from solution prior to biodegradation of hazardous organic compounds.

Precipitation Techniques for Heavy Metal Removal

There are five basic techniques that can be used to remove heavy metals from solution. These techniques include formation of metal hydroxides, metal carbonates, metal sulfides, and xanthate treatment, or combinations thereof. Each technique is described briefly below.

Hydroxide Precipitation

In the hydroxide precipitation process, heavy metals are removed by adding an alkali, such as caustic or lime, to adjust the wastewater pH to the point where the metal(s) exhibit its (their) minimum solubility. In general, the solubilities of metal hydroxides in solution decrease with increasing pH to a minimum value beyond which point (the isoelectric point) the metals become more soluble due to their amphoteric nature. Figure 1 (Peters and Ku, 1985; Ku and Peters, 1986) shows the solubility relationships for various metal hydroxide and metal sulfides. Newkirk et al. (1981) note that attempts to quantify the minimum solubilities under ideal conditions differ considerably with what is observed in actual practice due to the influences of complexing agents (and other contaminants which may be present), temperature, and ionic strength. Further, Bowers et al. (1981) note that in heterogeneous systems, coprecipitation and complexation of more than one species may be occurring.

The metals precipitate as metal hydroxides and can be removed by flocculation and sedimentation/filtration operations. The extent of precipitation depends on the solubility product

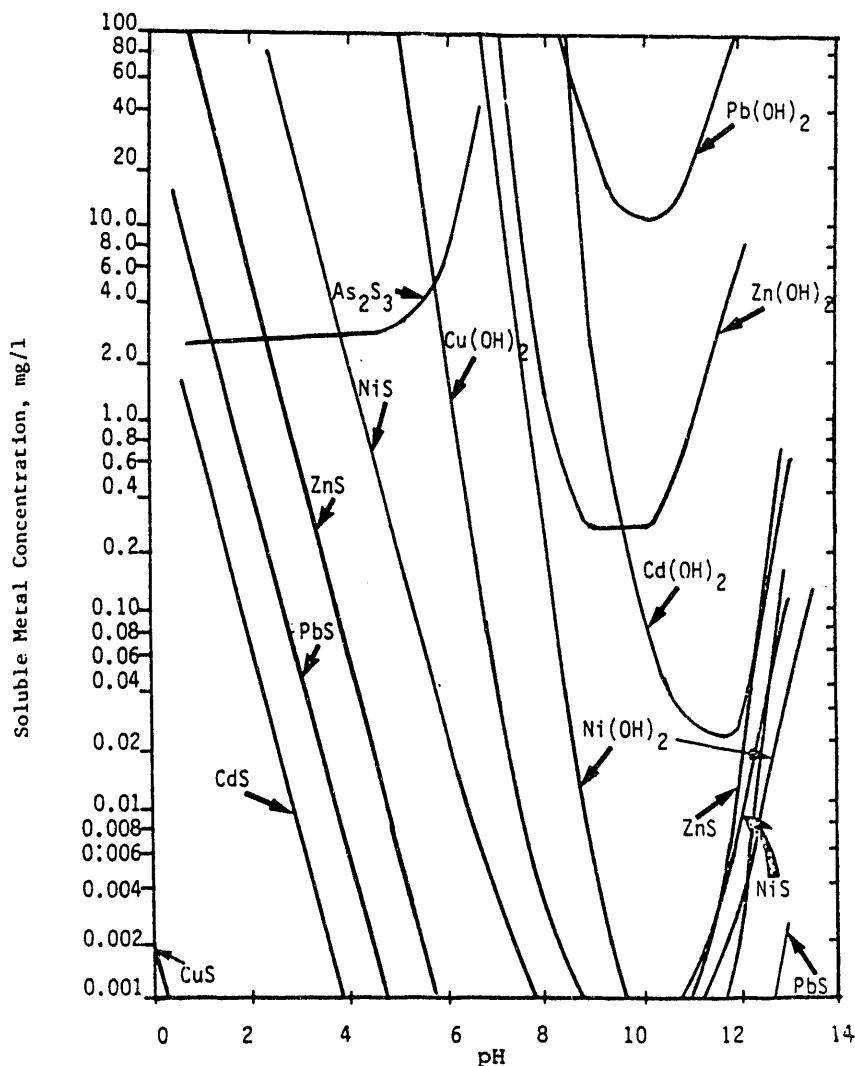


Figure 1 - Solubilities of metal sulfides and metal hydroxides as a function of pH

(K_{sp}) of the metal hydroxide and the equilibrium (stability) constants, K_i 's, of the metal hydroxyl constants, plus the stability constants for other complexing agents that may be present (EDTA, NTA, citrate, tartrate, gluconic acid, cyanide, ammonia, etc.). The effectiveness of the solid/liquid separation is heavily dependent on the physical properties (size, density, etc.) of the metal hydroxide precipitates. Widespread use of this technique is due to its relative simplicity, low cost of precipitant (lime), and ease of pH control (Peters et al., 1985a; Peters and Ku, 1987). Advantages and limitations of metal hydroxide precipitation are summarized in Table III. Clifford et al. (1986) note that a staged precipitation process can be used for mixed-metal wastes because of the variation in the pH of their minimum hydroxide solubilities.

Carbonate precipitation

Carbonate precipitation of heavy metals has been shown to be an effective treatment alternative to hydroxide precipitation. Carbonate precipitation can be accomplished using soda ash (sodium carbonate). Patterson et al. (1977) studied the feasibility of carbonate precipitation for heavy metals removal. Carbonate has several advantages over that of conventional hydroxide precipitation (Patterson et al., 1977; Clifford et al., 1986):

- Optimum carbonate precipitation treatment occurs at lower pH conditions than those for optimum hydroxide treatment.
- Metal carbonate precipitates are reported to be denser than the hydroxide precipitates, causing improved solids separation.
- Carbonate sludges have better dewatering characteristics than hydroxide sludges.

Sodium bicarbonate can also be used to precipitate heavy metals out of solution (Barber, 1978). Such treatment has the dual advantage of precipitating the metal carbonate while holding pH within a narrow range at nearly optimum conditions. Although sodium bicarbonate is not as efficient in removing metal from solution as other bases, it has the advantage of neutralizing excess acidity, which helps meet wastewater discharge standards. The sodium bicarbonate acts as a buffer to maintain alkalinity near the optimum pH level. Some metals, such as zinc, do not readily precipitate, regardless of the amount of carbonate added. However, by mixing soda ash (sodium carbonate), sodium bicarbonate, and lime (calcium hydroxide), it is possible to precipitate zinc as zinc hydroxide while using the carbonates to stabilize pH. Sodium bicarbonate treatment has the additional advantage of easy handling, simple application, ability to function in continuous flow operation, and moderate cost (Barber, 1978).

For the case of nickel and zinc, no benefit was realized by using carbonate precipitation as opposed to hydroxide precipitation; the optimum pH for metal removal corresponded to pH values predicted by the theoretical metal hydroxide solubility diagram (Patterson et al., 1977). No advantages in terms of denser sludges or better filtration characteristics were observed for the zinc carbonate and nickel carbonate systems. Beneficial results were observed using carbonate precipitation for cadmium and lead removal. Comparable residual cadmium concentrations were observed at approximately 2 pH units lower for carbonate treatment versus hydroxide treatment. The cadmium carbonate precipitates had approximately the relative filtration rate as compared with that for the cadmium hydroxide system. Treatment equivalent to that for lead hydroxide at

Table III Advantages and Limitations Associated with Metal Hydroxide and Metal Sulfide Precipitation (adapted from Peters et al., 1985a)

Type of Precipitation	Advantages	Limitations
Hydroxide	• Easy of automatic pH control • Well-proven and accepted in industry. • Relatively simplistic operation. • Low cost of precipitant (lime).	• Hydroxide precipitates tend to resolubilize if the solution pH is changed. • The removal of metals by hydroxide precipitation of mixed metal wastes may not be effective because the minimum solubilities for different metals occur at different pH conditions. • The presence of complexing agents have an adverse effect on metal removal. • Chromium (VI) is not removed by this technique. • Cyanide interferes with heavy metal removal by hydroxide precipitation. • Hydroxide sludge quantities can be substantial and are generally difficult to dewater due to the amorphous particle structure. • Little metal hydroxide precipitation occurs for $\text{pH} < 6$. • Processing is not stable for large flow and concentration variations in the influent. • Start-up and shutdown times are longer than those for packed-bed and membrane processes.
Sulfide	• Attainment of a high degree of metal removal even at low pH ($\text{pH} \sim 2-3$).	• Potential for H_2S gas evolution. • Concern for sulfide toxicity.

Table III (Cont.)

Type of Precipitation	Advantages	Limitations
Sulfide (Cont.)	• Low detention time requirements in the reactor due to the high reaction rates of sulfides. • Feasibility of selective metal removal and recovery exists. • Metal sulfide sludge exhibits better thickening and dewatering characteristics than the corresponding metal hydroxide sludge. • Metal sulfide precipitation is less influenced by the presence of complexes and chelating agents than is the corresponding metal hydroxide precipitation. • Metal sulfide sludge is reportedly three times less subject to leaching at pH 5 as compared to metal hydroxide sludge (Whang et al., 1981). • Metal sulfide sludges generally have smaller volumes and easier to dewater than the corresponding metal hydroxide sludge.	• Process is relatively complex and expensive (as compared to hydroxide precipitation).

pH 10.5 was obtained with the lead carbonate system at pH 7.5 and a total carbonate concentration of 0.08 moles/L, or at pH 10 and a total carbonate concentration of 0.002 moles/L. The lead carbonate system yielded a denser precipitate than the lead hydroxide system with improved filterability characteristics.

Additional laboratory carbonate precipitation studies have been performed by McAnally et al. (1984) and McFadden et al. (1985), in which combined chemical treatment was performed for removal of nickel from solution. These studies are described in more detail in the section on combined treatment.

Sulfide precipitation

Sulfide precipitation has been demonstrated to be an effective alternative to hydroxide precipitation (Bhattacharyya et al., 1979, 1981a,b; U.S. EPA, 1980; Kim, 1981; Kim and Amodeo, 1983; Ku, 1982, 1986; Ku and Peters, 1986, 1988; Peters et al., 1984a,b, 1985; Peters and Ku, 1984, 1985, 1987, 1988) for removal of heavy metals from industrial wastewaters. Advantages and limitations associated with this processing technique are listed in Table III. Eliminating sulfide reagent overdose prevents formation of the odor-causing H_2S . In currently operated soluble sulfide systems that do not match demand, the process tanks must be enclosed and vacuum evacuated to minimize sulfide odor problems.

Two main processes exist for sulfide precipitation of heavy metals (U.S. EPA, 1980): soluble sulfide precipitation (SSP) and insoluble sulfide precipitation (ISP), the difference being in how the sulfide ion is introduced into the wastewater. This EPA publication provides an excellent description and review of the sulfide precipitation processes. In the SSP process, sulfide is added to the wastewater in the form of a water soluble sulfide reagent such as sodium sulfide (Na_2S) or sodium hydrosulfide ($NaHS$). The addition of the solution may be made by periodic analyses of metal contents or it may be controlled by means of a feedback control loop employing ion-specific electrodes. The process can be operated either in the batch mode or the continuous mode. In the ISP process, a slightly soluble ferrous sulfide (FeS) slurry is added to the wastewater to supply the needed sulfide ions required to precipitate the heavy metals. Since most of the heavy metals are less soluble than ferrous sulfide (see Table I), they will precipitate as metal sulfides. Since the FeS has a very low solubility with a sulfide concentration of 0.02 ug/L , emission of H_2S is minimized. In practice, FeS is freshly prepared by mixing $FeSO_4$ and $NaHS$. Advantages of the ISP process include the absence of any detectable H_2S gas and reduction of Cr^{+6} to Cr^{+3} (U.S. EPA, 1980). Disadvantages of the process include considerably larger than stoichiometric reagent consumption and large quantities of sludge being generated due to the ferrous hydroxide formation (U.S. EPA, 1980). The addition of FeS is not automatically controlled in response to the metal contents. The rate of FeS addition is determined by jar tests on the wastewater before it enters the sulfide precipitation tank. The process normally requires two to four times the stoichiometric amount of FeS (U.S. EPA, 1980). The use of an excessive amount of FeS adds to the chemical cost of the process; it further results in the production of a large amount of sludge. The SulfexTM process (Scott, 1979) produces almost three times more sludge than the conventional hydroxide precipitation process (Kim, 1981).

In the SSP process, the high sulfide concentration often causes rapid precipitation of metal sulfides (high nucleation rates), resulting in small particulate fines and hydrated colloidal particles. This results in poor settling characteristics and poor filterability of the flocs. In the

presence of chelating agents, hydroxide precipitation is not possible, even at high pH. With sulfide precipitation, heavy metal removal is possible even with chelating agents present, although the metal sulfide precipitation is influenced by the presence of chelating agents (Ku and Peters, 1986, 1988; Peters and Ku, 1984, 1985, 1987, 1988; Peters et al., 1984b). In the absence of chelating agents, little metal hydroxide precipitation occurs for $\text{pH} < 6$. Metal sulfide precipitation can be conducted over a very wide pH range, typically from $\sim \text{pH } 2$ to $\text{pH } 12$ (see Figure 1). Because metal sulfides are less soluble than the corresponding metal hydroxides (see Table I), better removal efficiencies are achieved over a broad pH range. In addition, metal sulfides are less amphoteric than the corresponding metal hydroxides and are therefore less likely to resolubilize. Metal sulfide sludges usually have lower volumes and are easier to dewater than metal hydroxide sludges.

An alternative to using FeS in the ISP processing technique involves addition of calcium sulfide (CaS) (Kim, 1981; Kim and Amodeo, 1983). In this technique, the problems of delivery of the insoluble sulfide ions and the generation of large amounts of sludge can be minimized through the addition of CaS. The addition of CaS as a slurry produces easily settleable precipitates. Calcium sulfide particles act as nuclei for production of metal sulfide particles, and the dissolved calcium ion functions as a coagulant. Since calcium is mostly dissolved in the wastewater after reaction, the increase in the sludge volume is minimal. For this same reason, the CaS dosage requirement is nearly stoichiometric (in contrast to the overstoichiometric dosage requirement for FeS).

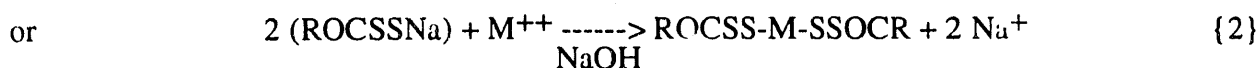
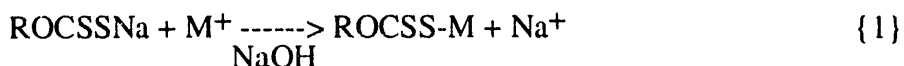
Xanthate precipitation

In xanthate treatment, metal contaminants exchange with sodium ions contained in the xanthated materials to form an insoluble complex. The xanthate acts as an ion exchange materials removing heavy metals and replacing them with sodium and magnesium. The heavy-metals-laden material can be removed from solution by sedimentation and filtration. Contrasted versus metal hydroxide precipitation, xanthate treatment offers the following advantages (Federal Remediation Technologies Roundtable, 1992):

- A higher degree of metal removal;
- Less sensitivity to fluctuations in pH (metal xanthates do not exhibit amphoteric solubilities);
- Less sensitivity to the presence of complexing agents,
- Improved sludge dewatering properties; and
- The capability of selective removal of metals.

Wing and Rayford (1977) state that the process will probably not be economical for initial metal concentrations exceeding 100 mg/L, although xanthate treatment could be used as a secondary treatment to further lower the metal concentration to below discharge limits.

This process was developed by the U.S. Department of Agriculture (Wing et al., 1975, 1978; Wing 1974; Wing and Rayford, 1976, 1977). Xanthates are sulfonated organic compounds. The xanthate-metal precipitation process can be represented as follows:



where M^+ or M^{++} are the metal ions.

Whereas hydroxide precipitation is effective over the pH range of approximately 9 to 12, xanthate precipitation is effective over a much wider pH range (~ 3 to 12), with maximum effectiveness above pH 7. Solutions with pH less than 3 rapidly decompose the xanthates (Wing, 1974). The hierarchy (Flynn et al., 1980) for selective removal of heavy metals by xanthate treatment is in the following order: $\text{Na} \ll \text{Ca-Mg-Mn} < \text{Zn} < \text{Ni} < \text{Cd} < \text{Pb-Cu-Hg}$. This technique, however, still produces significant quantities of sludge that must be handled in accordance with the Resource Conservation and Recovery Act (RCRA). Wing (1974) noted that contaminants could be introduced by treating water with starch xanthates and a cationic polymer; possible contaminants include small ionic species (Cl^- from the cationic polymer; and Na^+ , OH^- , and CS_3^- from the xanthate), small nonionic species (CS_2 and COS from the xanthate), and the polyelectrolytes themselves. The presence of sequestrants (diglycolate, NTA, polyphosphate, or citrate were used in his study) at concentration levels of 0.1 g/L did not affect removal of mercury. Starch xanthate effectively treated 10 other metals: Cd^{+2} , Cr^{+3} , Cu^{+2} , Fe^{+2} , Fe^{+3} , Pb^{+2} , Mn^{+2} , Hg^{+2} , Ni^{+2} , Ag^+ , and Zn^{+2} . The treatment can be performed using either batch or continuous precipitation. Wing and Rayford (1977) reported that the insoluble starch xanthate-metal sludge settled rapidly and dewatered to 50 to 90% solids content after filtration or centrifugation. Preliminary cost estimates (1976) to make the insoluble starch xanthate was \$0.30/lb. Using other starch-based products that can be used range in price from \$0.30 to \$0.75/lb (1976). The chemical cost of treatment for a 50-mg/L Cu-EDTA rinse with lime and polymer was estimated in 1976 to be \$0.07/1,000 gal (Wing and Rayford, 1977).

In a laboratory investigation, Bricka and Cullinane (1987) prepared several synthetic sludges containing the contaminants Cd, Cr, Hg, and Ni. The wastes were treated using hydroxide and xanthate (cellulose and starch) precipitation. The treated sludges were subjected to Extraction Procedure (EP) Toxicity tests. All the solidified sludges passed the EP Toxicity test, except for the solidified hydroxide sludge, which failed for Hg. The unsolidified cellulose xanthate sludge failed the EP Toxicity test for Ni and Cd, while the unsolidified hydroxide sludge failed the EP Toxicity test for every metal tested (Cd, Cr, Ni, and Hg) (Bricka and Cullinane, 1987). The xanthate precipitated sludges appear to be an effective method to immobilize heavy metals.

Combined precipitation treatment

In combined precipitation systems, the chemical treating agents (precipitants) from more than one of the previous chemical precipitation systems are combined (example: combining carbonate and hydroxide precipitations). It should be pointed out that, in a very broad sense, each precipitation

system (with the exception of metal hydroxide precipitation) involves a combined precipitation system because the precipitations are generally performed at a particular pH. For $\text{pH} > 6$, metal hydroxide precipitation is possible. Metals are preferentially removed from solution by sulfide precipitation. However, coprecipitation of metal sulfides and metal hydroxides is possible. The majority of investigations using combined precipitation systems involve bench-scale studies.

McAnally et al. (1984) studied the use of soluble sulfide and carbonate for their effectiveness in reducing nickel in a synthetic nickel plating wastewater. Employing jar tests, an optimum pH range for nickel removal from the synthetic wastewater was determined to be 10.0 to 11.0. Optimum nickel removal occurred at pH 11 where a residual total nickel concentration of 0.1 mg/L was obtained with a sulfide:nickel weight ratio of 2.0 and a carbonate:nickel weight ratio of 20.0. At pH 10, a similar degree of removal (0.2 mg/L residual total Ni) was obtained using a $\text{CO}_3^{2-}:\text{Ni}^{++}$ ratio of 10.0 and a $\text{S}^{2-}:\text{Ni}^{++}$ ratio of 0.5. The excellent nickel removal is probably due to a coprecipitation phenomena. To treat the synthetic nickel wastewater, the pH was adjusted by dropwise addition of 1N NaOH and an equivalent amount of 1N CaCl_2 solution to simulate lime addition. The carbonate was added in the form of NaHCO_3 . Such conditions likely led to the precipitation of calcium carbonate (CaCO_3), which has been shown to be an excellent adsorbent for Cd, Pb, and Zn (Chang and Peters, 1985; Faust and Schultz, 1983; Peters and Chang, 1984, 1985). Coprecipitation and adsorption of $\text{Ni}(\text{OH})_2$ and NiS onto the CaCO_3 surfaces may have caused the excellent Ni removals. McAnally et al. (1984) did not report the residual calcium concentrations to ascertain whether this was the case or not.

In a similar study to that of McAnally et al. (1984), McFadden et al. (1985) investigated the effect of iron as a coprecipitator of nickel, as well as carbonate addition, pH adjustment, and polymer addition. For pH adjustment along with carbonate addition, the optimum nickel removal occurred for a total carbonate concentration (C_T) of 50 mg/L at pH 11. These conditions resulted in the soluble and total nickel concentrations being <0.10 and 0.10 mg/L, respectively. All three C_T concentrations employed (50, 100, and 200 mg/L) at pH 10 and 11 achieved at least 96% and 99% removal of the total and soluble nickel, respectively. McFadden et al. (1985) suggested that the calcium may provide a nucleus for CaCO_3 formation, thereby increasing settleability, although they do not report the final residual calcium concentrations of the treated wastewater. The initial Ca^{++} concentrations were of the same level as those employed by McAnally et al. (1984). Coprecipitation of Ni onto the CaCO_3 surfaces may indeed be an explanation for the high nickel removals observed.

Nickel removal using hydroxide precipitation was the most efficient for the synthetic wastewater at pH 10-11, depending on the Fe:Ni ratio and C_T (McFadden et al., 1985). Both the soluble and total nickel at pH 10, Fe:Ni = 2, and $C_T = 0$, were reduced to <0.10 mg/L. Identical results occurred at pH 11, Fe:Ni = 2, and $C_T = 100$ mg/L as CaCO_3 . At pH 9, the best overall removal was obtained for a Fe:Ni ratio of 1.0 and $C_T = 50$ mg/L as CaCO_3 , where the total and soluble residual nickel concentrations were 0.20 and 0.10 mg/L, respectively. For the actual wastewater, the most efficient soluble nickel removal occurred at pH 10 with a Fe:Ni ratio of 0.7 and $C_T = 0$, resulting in a total and soluble nickel concentration of 0.30 and 0.25 mg/L, respectively. The use of anionic and cationic polymers did not enhance the removal of nickel appreciably. For the actual wastewater, the lowest cost to treat the wastewater was \$0.5349/1,000 gal (in 1985 dollars) for conditions of pH 10, Fe:Ni ratio of 0.7, and $C_T = 0$.

Using ferrous sulfide as a coprecipitator, heavy metals (Cu, Cd, Ni, Cr, and Zn) were shown to be significantly reduced in concentration from the influent wastewater (Schlauch and Epstein, 1977). FeS treatment was found to be superior to conventional hydroxide precipitation employing lime as the precipitant.

Chang and Peters (1985) observed that cadmium could be very effectively removed using conventional lime softening operations; the maximum contaminant level of 0.01 mg/L for Cd could be met for pH in the range of 7.3 to 11.0. Calcite was the only morphological form observed for the continuous CaCO₃ precipitation. The residual calcium concentration increased ~30-40 mg/L in the presence of cadmium, indicating an inhibitory effect on CaCO₃ precipitation. Removal of cadmium was attributed primarily to physical adsorption onto the CaCO₃ sludges.

Talbot (1984) described a process using less than stoichiometric addition of sulfide, yielding a combined hydroxide-sulfide treatment. At pH 8.0, a solution initially containing 15.0 mg/L Cd was lowered to <0.05 mg/L using the Talbot process, while hydroxide treatment provided a residual concentration of 4.8 mg/L. For a water containing 2.9 mg/L Hg, conventional hydroxide treatment resulted in no mercury removal, while the Talbot process lowered the mercury level to <0.001 mg/L at pH 8.0. The operating cost of the Talbot process is comparable with that of conventional hydroxide precipitation. A smaller quantity of sludge is generated by the Talbot process (as compared with conventional hydroxide precipitation), thereby lowering the sludge disposal costs.

The Talbot process (Talbot, 1984) basically involves the understoichiometric addition of sulfide to the wastewater. Bhattacharyya et al. (1979) likewise observed that a sulfide of 60% of the theoretical requirement provided effective removal of heavy metals (Cu, Cd, Hg, Pb, and As). Peters et al. (1985b) also observed that understoichiometric addition of sulfide, even as low as 0.5 × stoichiometric requirement, likewise provided excellent removal of zinc and cadmium and decreased the resulting sludge volume. Peters et al. (1985b) proposed the idea that metals could be selectively precipitated, removed, and recovered from a mixed-metal wastewater, by proper control of the solution pH, sulfide dosage, chelant dosage, type of chelant, and temperature, in a cascading series of reactors. For example, zinc can be selectively precipitated from at pH 6.0, stoichiometric sulfide dosage, and addition of EDTA (Peters et al., 1985b). Pugsley et al. (1970) were the first investigators to note that selective removal of a particular heavy metal could be achieved in a cascading reactor system through proper control of the dosage rates. Preliminary cost estimates showed that the sulfide treatment to be ~ \$9.27/1,000 gal of plating wastewater, which compared favorably with the ~ \$9.45/1,000 gal of plating wastewater by conventional hydroxide precipitation (Peters et al., 1985b). Considerable cost savings can also be realized through reuse, recycle, and recovery of the waste metals from the plating process.

Higgins and Slater (1984) observed that treatment of a mixture of metals is somewhat more effective than the treatment of metals individually. Sulfide treatment lowered the solubility of nickel and cadmium. Ferric hydroxide precipitates reduced the metal solubilities by incorporation of other metals into an amorphous precipitate and provided surface sites for adsorption. Addition of ferrous sulfate to an alkaline environment ($7 < \text{pH} < 10$) caused the iron to precipitate as iron hydroxide and aided in the flocculation of solids in the process. Such treatment was very effective in reducing hexavalent chromium to the trivalent form. A combination of ferrous sulfate and sodium sulfide produced a sludge that was easily removed, yet minimized the amount of sludge production.

Coagulation/Flocculation

Coagulation/flocculation is capable of removing heavy metals from solution. Coagulation refers to charge neutralization of the particles. Flocculation involves slow mixing to promote agglomeration of the destabilized particles. The U.S. EPA (1978) investigated the use of lime softening and coagulation (using ferric sulfate or alum) to remove Pb^{+2} , Cd^{+2} , Cr^{+3} , and Cr^{+6} . While lime softening achieved removals exceeding 98% in the pH range of 8.5-11.3 for cadmium, cadmium removals by ferric sulfate and alum coagulation were lower than that of lime softening and were shown to be pH-dependent; cadmium removals increased with increasing pH. Ferric sulfate coagulation of a river water containing 0.3 mg/L Cd showed removal to increase from ~20% at pH 7.2 to greater than 90% at pH > 8. Alum coagulation results also increased with increasing pH; however, above pH 8, removals depended on raw water turbidity. Both ferric sulfate and alum coagulation achieved greater than 97% removal of lead from a river water containing 0.15 mg/L Pb in the pH range of 6-10. Experiments using well waters under similar conditions had removals by ferric sulfate and alum coagulation of >97% and 80-90%, respectively. When the lead concentration was increased to 10 mg/L, ferric sulfate coagulation again achieved removals exceeding 95%, whereas alum coagulation achieved only ~80% removal. Using Cr^{+6} waters, ferric sulfate achieved the best results, removing ~35% at pH 5.5 on a river water containing 0.15 mg/L Cr^{+6} . Alum coagulation could do no better than 10% removal throughout the entire pH range, while pH has only a slight effect on removal of Cr^{+3} by alum and iron coagulation. Ferric sulfate coagulation achieved excellent Cr^{+3} removals, in excess of 98%, throughout the pH range of 6.5-9.3. Alum coagulation, although less effective, obtained removals exceeding 90% for the pH range of 6.7-8.5. Above pH 8.5, removals began to decrease; at pH 9.2, the removal had decreased to 78%. For an initial Cr^{+3} concentration of 10 mg/L, ferric sulfate and alum coagulation both achieved removals in excess of 98% in the optimum pH range.

Daniels (1975) provided an excellent review on heavy metal removal by iron salts and polyelectrolyte flocculants. Removal of certain heavy metals from wastewaters can occur simultaneously with removal of suspended solids, BOD, and total phosphorus when chemical treatment is employed. The insoluble fractions of Fe, Cr, Cu, Ni, and Zn are captured by sequential coagulation and flocculation.

For treatment of base metal mine drainage, use of an anionic polymeric flocculent provided greater clarifier operational reliability and reduced mean metal concentrations in the overflow (Huck and LeClair, 1975). Polymer addition substantially improved the sludge settling characteristics. Aulenbach et al. (1984) noted that addition of alum or sodium aluminate at dosages that effectively remove phosphorus is beneficial in the removal of Cu, Cr, and Pb from wastewaters. Chromium removal was enhanced by sodium aluminate addition, but was unaffected by alum addition. Both aluminum salts increase the removal of lead. Nilsson (1971) studied the removal of Pb^{+2} , Cu^{+2} , Cr^{+3} , Hg^{+2} , Cd^{+2} , Zn^{+2} , Ni^{+2} , Co^{+2} , and As^{+5} by aluminum sulfate and calcium hydroxide treatment. Orthophosphate had no effect on the precipitation. The concentrations of Pb, Cu, Cr, Cd, Hg, and As were reduced to low levels by both precipitants, while Ni, Zn, and Co were precipitated only for pH < 9.5. The precipitation of Cu and Pb were severely inhibited by the presence of nitrilotriacetic acid (NTA).

Ion Exchange

Ion exchange is an effective means of removing heavy metals from wastewaters. It is a reversible chemical reaction, where the removal of heavy metals is accomplished by the exchange of ions on the resin for those in wastewater. When the resin is saturated, it must be regenerated with an acid or alkaline medium to remove the metal ions from the resin bed. The regenerant brine is lower in volume and higher in concentration than the original wastewater, but these metals must then be adequately treated or recovered.

There are a variety of resins for specific applications with various metals. Synthetic organic resins are most commonly used due to their ability to be manufactured for specific applications (U.S. EPA, 1981). The use of several inorganic gels for removal of heavy metals has also been studied (Srivastava et al., 1980) due to their stability under more severe physical conditions. Liquid-ion exchange (LIE) is an effective unit operation used to purify and concentrate minerals from various solutions in the hydrometallurgy industry. There have been limited applications in industrial wastewater treatment. Removal of heavy metals such as Cd, Cr, and Zn are effectively handled by LIE. Technically, almost every metal ion can be removed or recovered by some ion exchange process, but economical concern plays a very decisive role in the commercial application of ion exchange. Ion exchange is an ideal method for removal of trace amounts of impurities from dilute wastewaters, with the high quality treated water ready for reuse.

Because ion exchange is efficient in removal of dissolved solids from normally dilute spent rinse waters, it is well suited for use in water purification and recycle. Many of the plating chemicals, acids, and bases used in metal finishing operations are ionized in solution and can be removed by ion exchange. Factors that make ion exchange effective for such applications include (U.S. EPA, 1981):

- Ion exchange can economically separate dilute concentrations of ionic species from solution.
- The process can consistently provide a high purity water over a broad range of conditions.
- The resins used for separation are durable under severe chemical environments.

Ion exchange is also used for "end-of-the-pipe" pollution control where toxic heavy metals and metal cyanide complexes are selectively removed from combined waste streams before discharge. Ion exchange has been employed as a polishing step following conventional hydroxide treatment to lower the metal concentration in the discharge; it has also been applied as a means of directly treating wastewaters to remove heavy metals and metal cyanide complexes. In comparison with conventional precipitation treatment, ion exchange treatment offers the following advantages (Gupta et al., 1985):

- Precipitation and clarification equipment require a lot of space, while ion exchange equipment is very compact.
- Metal hydroxide sludges must be transported to a landfill licensed to handle them; ion exchange avoids the generation of these sludges.

- No economical method is currently available to recover the metal values from metal finishing sludges so the metals cannot be recycled. Ion exchange allows convenient recovery of the metals.
- Ion exchange is a versatile process that accommodates metal ion concentration variations and reasonable changes in flow rate without deterioration in system performance.

Ion exchange has also been used to a limited extent to selectively remove toxic pollutants from an untreated wastewater while allowing most of the nontoxic ions to pass through. To facilitate this application, common approaches include (U.S. EPA, 1981):

- Weak acid cation exchange resin in an application of the wastewater-softening type to remove heavy metals and other divalent cations from a wastewater with sodium ions.
- Heavy-metal-selective weak acid or chelating cation exchange resin for removal only of the heavy metal ions while allowing sodium, calcium, and magnesium ions to pass through.
- A stratified resin bed containing strong and weak cation and strong base anion resins to remove heavy metals and metal cyanide complexes from solution while allowing the majority of the wastewater ionic constituents to pass through.

Each of these approaches involves pH adjustment (to ensure the pH is within the operating range of the resin) and filtration (to remove suspended solids that would otherwise foul the resin bed). The pollutants from the wastewater are concentrated in the ion exchange regenerant solutions. This regenerant brine is much lower in volume and higher in concentration than that of the original wastewater. Such processing serves as an excellent pretreatment step for subsequent physical/chemical treatment or as a polishing step. Such a case history was outlined where ion exchange treatment following hydroxide precipitation enabled HurdLock Manufacturing Company to meet the state discharge limits for Cd, Cu, Cr, Fe, Pb, Ni, and Zn. As a rule, ion exchange systems are suitable for chemical recovery applications where the rinse water feed has a low concentration of plating chemicals and where a relatively low degree of concentration is required for recycle of the concentrate. Ion exchange has been commercially demonstrated for recovery of plating chemicals from acid-copper, acid-zinc, nickel, tin, cobalt, and chromium plating baths (U.S. EPA, 1981).

Several ion exchange systems have been developed. The fixed-bed ion exchange system is a conventional widely used design that required multiple columns and a lot of operator attention. Two approaches have been used to simplify the operation of ion exchange systems: the continuous ion exchanger and the reciprocating flow ion exchanger. The continuous ion exchange system provides simultaneous ion exchange, regeneration, back wash, and rinse cycles in separate sections. However, the system's capital cost is higher than that of fixed-bed systems. The reciprocating flow ion exchanger operates on the principle that for a short period, the system goes off-stream for regeneration. Capital cost and labor are minimized in this system.

As an example of recovery of valuable metals from industrial waste streams, hexavalent chromium (Cr^{+6}) can be successfully recovered using ion exchange treatment (Weber, 1972). The waste stream is first passed through a cation exchange to remove extraneous metals

(primarily Fe, Cu, Zn, Ni, and Cr^{+3}). The hexavalent chromium passes through as CrO_4^{-2} and is removed in an anion exchanger; the effluent is a demineralized water suitable for reuse. For recovery of Cr^{+6} , the regenerated water containing NaOH and Na_2CrO_4 is released. The Na_2CrO_4 solution is then passed through another cation exchanger which exchanges sodium for hydrogen releasing chromic acid (H_2CrO_4) in the effluent for recovery.

Semmens and Martins (1980) performed studies on the removal of Pb, Ag, and Cd by clinoptilolite in the presence of competing concentrations of Ca, Mg, and Na. The observed selectivity sequence was $\text{Pb}^{+2} > \text{Ag}^+ > \text{Cd}^{+2}$. The competing cations strongly influenced the metal exchange with the zeolite. Metal removal was greatest in exchange with magnesium and decreased in the order $\text{Mg}^{+2} > \text{Na}^+ > \text{Ca}^{+2}$ for lead and cadmium and in the order $\text{Mg}^{+2} > \text{Ca}^{+2} > \text{Na}^+$ for silver. The presence of calcium in solution had a profound effect on the extent of Cd removal. Both batch and continuous flow studies were performed in their study. Lead was found to be effectively removed; large throughputs could be obtained before breakthrough occurred. Alkaline pretreatment of the zeolite improved the metal removal efficiency.

Etzel and Tseng (1985) noted that a drawback in the use of ion exchange treatment is the fact that the resin must be regenerated after exhaustion, thereby complicating operation of the system. Chemical costs are high per unit of metals removed; it also results in volumes of regenerant solution which must be treated prior to discharge. Etzel and Tseng (46) investigated a novel approach to regeneration of a heavy-metal-exhausted, cation-exchange resin using a recoverable chelating agent, whereby the regenerant solution could be reused and the metal removed by the exchanger recovered. Their studies showed EDTA, NTA, and citrate could be successfully regenerate a strong acid cation exchange resin exhausted by Cu, Zn, Ni, or a metal mixture, to its original sodium form. The optimal pH range for all the chelating agent solutions was between 8 and 9 for regeneration of the resin. Regeneration effectiveness of the chelating agents was in the order $\text{Cu} > \text{Zn} > \text{Ni}$; regeneration effectiveness of EDTA, NTA, and citrate was in the order $\text{EDTA} \sim \text{Citrate} > \text{NTA}$.

Problems typically involved with ion exchange treatment include:

- Metallic fouling (from Fe, Mn, Cu, etc.) on the ion exchange media.
- Fouling due to oil, grease, silt, clay, colloidal silica, organic materials, and microbes. The choice of a proper cleaning program can restore much of the lost efficiency (Pelosi and McCarty, 1982a,b).
- The presence of free acid reduces the efficiency of operation.
- Fairly high operational costs exist.

Liquid Ion Exchange/Liquid-Liquid Extraction

Liquid ion exchange (LIE) has recently received attention as a means to remove heavy metals from plating wastes (Knocke et al., 1978; Petersen et al., 1981). This process involves a two-phase system (made up of an organic liquid containing a dissolved, water-insoluble active

compound and the heavy metals in the aqueous phase) involving liquid-liquid extraction. The liquid extractant is typically present at a 10-40% active level in a solvent, such as kerosene. The extractant solution is run countercurrent to an aqueous feed containing one or more heavy metals, usually at a temperature slightly above ambient to improve the exchange kinetics and to facilitate phase separation. Acid-treating the organic fraction releases the metal in a concentrated water-soluble form.

Several advantages have been cited for application of LIE technology (Knocke et al., 1978; Petersen et al., 1981):

- LIE can selectively extract a desired metallic cation from a feed solution containing a significant amount of metallic impurities.
- LIE can concentrate the desired cation in final aqueous solution so that it can be treated by methods inappropriate for the initial dilute feed.
- LIE is well suited for process automation and efficient metal recovery from a mixed-metal hydroxide slurry.

One major drawback with liquid-liquid extraction is its limited ability to concentrate the metals during the extraction process; in most cases, extraction produces no more than a ten-fold increase in metal concentration.

This process has been used successfully by the copper and uranium industries (Dean et al., 1972) and offers promise in the plating and metal finishing industries. Petersen et al. (1981) studied the use of LIE in removing cadmium and nickel from both segregated and composite wastestreams. Langmuir and Freundlich isotherm equations adequately described the removal of heavy metals in their system. They estimated the cost of a typical moderate sized plating facility employing reduction and lime precipitation was \$4.71/1,000 gal. As a comparison, using anion exchange to remove chromate and liquid ion exchange for the removal of nickel and cadmium, the treatment cost was estimated to be \$2.45/1,000 gal.

Stary (1963) studied the extraction of 32 different metals using 8-hydroxyquinoline (8HQ); 8HQ exhibited selectivity in extraction. Most metal-oxinates were extremely soluble in chloroform and could be easily extracted. Chloroform was judged to be suitable for extracting large concentrations of metals. Clevenger and Novak (1983) studied seven chelating agents for their ability to remove heavy metals from electroplating wastewater. The seven chelants included (1) cupferron, (2) dithizone, (3) benzoylacetone, (4) acetylacetone, (5) thenoyltrifluoroacetone, (6) sodium diethyldithiocarbamate (NaDDC), and (7) 8-hydroxyquinoline (8HQ). All of these chelating agents showed the extraction trend $\text{Cu} > \text{Ni} > \text{Zn} > \text{Cd} > \text{Cr}$, with Cu being extracted first at low pH. Because of precipitation problems, $\text{pH} < 7$ was required, which limited the ability of several of the chelating agents. The chelants 8HQ, NaDDC, and dithizone were able to extract metals in the pH range of 1 to 6. Liquid-liquid extraction was combined with sequential extraction in order to separate all five heavy metals. Cu and Ni were easily separated from the other elements; 83% of the Ni from a simulated electroplating regenerate was recovered with <3% contamination from the other metals. The Ni was stripped from the chelate/chloroform

with 2.4M HCl. Unfortunately, the chelate could not be reused after stripping with the acid, which severely limits its use because of the high cost of the chelating agents.

Knocke et al. (1978) investigated the use of LIE for treatment of wastewater from Tinker Air Force Base containing Ni, Cd, Cu, Cr, and Ag. Preliminary extraction studies were performed utilizing metal solution containing 100 mg/L each of Cd, Cu, Cr, Ni, and Zn. Significant results of their study are summarized below:

- Thenoyltrifluoroacetone possesses high selectivity for Cu at low pH conditions.
- 8-Hydroxyquinoline was able to extract over 99% of the Ni into the organic layer; at pH 2, over 95% of the extracted Ni could be stripped off into the aqueous phase using 2.4M HCl.
- Using 0.5M 8-Hydroxyquinoline, extraction at pH 5.4 resulted in 99% of the Cd being extracted into the chloroform layer; back extraction resulted in a 79% recovery of the Cd in the aqueous phase at pH 2.
- All seven chelating compounds investigated performed poorly for selective Cr extraction.

Clevenger (1993) noted that the characteristics to be considered for selecting an extractant/complexing agent are low emulsion-forming tendencies, capability of being regenerated, low solubility in water, high selectivity, stability, and low cost.

Flotation

Foam flotation depends on the use of a surfactant that causes a nonsurface active material to become surface-active, forming a product that is removed by bubbling gas through a bulk solution to form a foam. The use of foam flotation techniques for removal of heavy metals has been well studied (Chavalitikul and Bruner, 1981; Grieves, 1975; Somasundaran, 1975; Thackston, 1980; Huang and Wilson, 1976; Ferguson et al., 1974; Robertson et al., 1976). With dilute wastewaters containing heavy metals in the parts per billion (ppb) or parts per million (ppm) range, foam flotation offers several distinct advantages:

- simplicity;
- flexibility and effectiveness of operation;
- limited space requirements due to rapid reactions;
- production of small, concentrated volumes of sludge;
- moderate costs compared with those of lime precipitation;
- low costs in terms of labor, equipment, energy, and chemicals;

- capable of application on small, intermediate, or large scales; and
- capability of reducing the contaminant concentrations well below the standards established by regulatory agencies.

To simulate a lead-bearing waste, ferric chloride was added to form a precipitate of ferric hydroxide; the lead rapidly adsorbed onto the surface of the $\text{Fe}(\text{OH})_3$ floc (Thackston, 1980). Following pH adjustment, a surfactant sodium lauryl sulfate (NaLS) was added. Positively charged $\text{Fe}(\text{OH})_3$ floc particles were attracted to the negatively charged bubbles formed by bubbling air through the solution. The rising bubbles of NaLS, along with the $\text{Fe}(\text{OH})_3$ floc and adsorbed lead, were removed as a foam, and the compounds collapsed, forming a foamate of about 2-3% of the influent volume.

Two physical models have been used to describe the attachment of floc particles to bubbles in the presence of a surfactant (Thackston et al., 1978, 1980). In the coulombic model, ionic surfactant is adsorbed to the air-water interface of the bubble, resulting in a surface charge density on the bubbles. The charge density is usually negative because of the use of the anionic surfactants. The floc is usually given a surface charge density opposite to that on the bubbles through pH adjustment or concentration of other potential determining ions. The electrical attraction between the floc particle and the bubble is reduced by the diffuse electrical double layer in the vicinity of the surface. Wilson (1977) described methods to calculate the electrical potential in solution, the potential energy of interaction between the two interfaces, and the adsorption isotherms.

In the contact angle model, surfactant ions adsorb onto the primary layer of the floc particle. They present their ionic or polar ends to the solid and their hydrophobic tails to the solution. For sufficiently high concentrations of surfactant, the solid surface is of a hydrocarbon character and is hydrophobic. The surface tensions are such that the contact angle of the air-water interface on the solid is nonzero, thereby permitting attachment of the particle to the bubble. Using statistical mechanics, the binding energies and adsorption isotherms can be calculated. Conclusions common to both models are summarized below (Thackston et al., 1978):

- (1) Increasing ionic strength decreases the flotation efficiency.
- (2) Increasing the length of the surfactant hydrocarbon tail decreases the bulk liquid concentration of surfactant required to produce flotation.
- (3) Increasing particle size increases flotation efficiency.
- (4) Increasing temperature increases the required surfactant concentration.

Plots of the ratio F of the flux of metal out of the bottom of a column to the flux of metal at the top of a column, as a function of the column parameters, show the following (Thackston et al., 1978, 1980):

- F decreases (better performance) as specific foam area increases.
- F decreases as surface velocity increases.
- F is roughly proportional to liquid velocity.
- F increases as the liquid and foam turbulence diffusion coefficients increase.
- F decreases as the mass transfer coefficient increases, approaching a finite equilibrium-controlled limiting value.
- F decreases as the adsorption isotherm rises.
- F increases slowly as the low feed concentrations increase.

Preliminary batch studies of Thackston et al. (1978, 1980) showed the optimum pH for removal of lead was approximately 6.5 and that increasing ionic strength was detrimental to the process; above 0.05M NaNO₃, the separation efficiency declined markedly. Ferric hydroxide was much more effective for adsorbing lead than was aluminum hydroxide. Sodium carbonate was a more effective neutralizing agent than was soda ash. High sulfate concentrations reduced the optimum pH level somewhat.

In continuous flow studies, Thackston et al. (1978, 1980) found the optimum Fe⁺³ concentration was about 150 mg/L and a stable foam could be produced using about 35 mg/L NaLS. The influent flow rate and hydraulic loading rate did not alter the removal efficiency until it became so great as to produce overturning the foam (occurring at a loading of about 120 m³/day-m²). Effluent lead concentrations less than 0.15 mg/L could be maintained over a wide pH range (5.0 to 6.5) and influent flow rate range. If channeling and overturning occurred, the residual Pb concentration averaged 0.5 to 1.5 mg/L. Increasing the ionic strength to 8,500 and 17,000 mg/L NaNO₃ increased the residual Pb concentration to 0.4 and 2.0 mg/L, respectively.

Experiments were performed by Mukai et al. (1979) involving coprecipitation of a metal ion (Cd, Cu, Zn, or Hg) with ferric hydroxide floc followed by flotation using sodium oleate as a collector. The test solutions all contained 1.0 mg/L of the heavy metal involved and varying amounts of Fe⁺³. For the optimum pH range of Cd removal (8 < pH < 10), the residual Cd concentration was less than 0.05 mg/L. Favorable Cu removal was maintained over a wide pH range (6 < pH < 10), while the optimum pH condition for Zn removal was between 9 and 10. The Hg removal was about 98% at pH between 8 and 9 while the residual Hg⁺² concentration in the tailing solution was 0.03 mg/L. Because Hg is hard to coprecipitate, adoption of a multistage flotation or addition of Na₂S together with Fe⁺³ in the coprecipitation stage was required to minimize the residual Hg⁺² concentration. Flotations of cuprite and chrysocolla were performed with LIX65N reagent as a function of LIE concentration, pH, conditioning time, ionic strength, and solution Cu concentration. Flotation performance was a maximum around pH 5.5 and pH 10 in general agreement with that predicted on the basis of solubility dependence with pH. Flotation performance was low for pH in the range of 6.5 to 9.0. Beltelshees et al. (1979) studied precipitate flotation as a method to remove copper from aqueous solutions containing

between 1 and 1,000 mg/L dissolved copper. Sulfide ion was added in a slight excess to precipitate CuS, producing a relatively stable suspension of submicron (~ 0.1 - 0.5 μm) colloidal CuS particles. Varying amounts of Hyamine 2389 and Amide 23 were employed in the study. Hyamine was used to serve as the collector surfactant. The primary use of Amide 23 was that of a foam stabilizer. The minimum additions of chemical necessary for good Cu removal and steady column operation were 25 mg/L Hyamine 2389 and 5 mg/L Amide 23. In 1976, the chemical costs were estimated to be \$0.376/1,000 gal treated, or \$0.45/lb of Cu removed. The CuS particles were readily removed by flotation in a bubble column. Copper removals exceeding 90% for solutions containing 10 to 1,000 mg/L dissolved Cu were achieved. At 1 and 5 mg/L of cationic surfactant, the removal efficiency was 50% and 80%, respectively. The precipitate was concentrated in a foamate fraction, the volume of which was generally less than 5% of the initial solution volume.

The comparative cost of foam flotation was been reported to be competitive with that of lime precipitation (McIntyre et al., 1983; Slapik et al., 1984); in treating a mixed-metal wastewater containing 20 mg/L each of Cu^{+2} , Zn^{+2} , and Cr^{+3} , the treatment costs were reported to be \$0.51/1,000 L for foam flotation versus \$0.60/1,000 L for lime precipitation.

Huang and Wilson (1976) used batch-type precipitate flotation and adsorbing colloid flotation techniques to separate Hg^{+2} and Cd^{+2} from aqueous systems. HgS , CdS , and $\text{Cd}(\text{OH})_2$ were removed by precipitate flotation; $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, FeS , and CuS were used as adsorbing colloids. NaLS and hexadecyltrimethylammonium bromide (HTA-Br) were used as collectors. Floc foam flotation of both Hg^{+2} and Cd^{+2} with CuS and HTA-Br was effective, resulting in residual Hg^{+2} and Cd^{+2} concentrations below 5 and 20 ppb, respectively. Floc foam flotation of Cd^{+2} with FeS and HTA-Br yielded residual Cd^{+2} concentrations as low as 10 ppb.

Robertson et al. (1976) studied the effects of pH, ionic strength, and specific ions on the adsorbing colloid flotation of Pb^{+2} and Zn^{+2} with $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ using NaLS as the collector. Pb was effectively removed with $\text{Fe}(\text{OH})_3$ and NaLS; Zn was efficiently removed with $\text{Al}(\text{OH})_3$ and NaLS. Ferguson et al. (1974) studied the effects of pH, ionic strength, collector concentration, and interfering ions on adsorbing colloid flotation. Increased ionic strength, Cd^{+2} , and phosphate interference made ion flotation impractical. Adsorbing colloid flotation gave excellent results; PbS and CdS were adsorbed to FeS which was then removed by foaming with HTA-Br. Pb^{+2} concentrations were reduced from 0.80 to 0.025 in 34 min foaming with 15 ppm Fe^{+3} added. Cd^{+2} concentrations were reduced from 1.0 to 0.08 ppm in 45 min foaming with 25 ppm Fe^{+3} added.

Rubin and Johnson (1967) studied the effects of pH on ion flotation and precipitate flotation of several metal ion-collector systems. The anionic collector, NaLS, was used to remove both soluble and insoluble Cu^{+2} and Fe^{+3} species. Stearylamine, a cationic collector, removed dissolved copper and copper hydroxide, while soluble iron was not removed and ferric hydroxide was only partially removed using this collector. A weak acid collector was less efficient than a strong acid collector for removing iron by precipitate flotation.

In a more recent study, Gopalratnam et al. (1988) studied the simultaneous removal of oil and heavy metals from industrial wastewaters using joint hydroxide precipitation and air flotation. Three different chemical collectors were studied (Nalco-7182, Jayfloc-806, and WOF-67). The flotation tests were run for 4 min. The wastewaters studied contained 25 mg/L each of Cu, Pb,

and Zn. The optimum pH and air injection rate were 9.18 and 12,150 cm³/min, respectively. Removal of heavy metals was a sensitive function of pH, flotation collector dosage, and air injection rate. The optimal collector dosage was typically in the range of 2 to 5 mg/L (depending on the particular chemical collector and heavy metal of concern). Removals of the heavy metals and oil typically exceeded 85%; oil removals as high as 96.2 were achieved. Removals of the various heavy metals compared favorably between the individual removal; and simultaneous removal (of heavy metals and oil) studies. The removal of the various heavy metals and oil appeared to be occurring through a coprecipitation/adsorption mechanism. The authors concluded that through appropriate choice of the chemical collector, its dosage, pH, and air injection rate, the selectivity for individual metal species could be affected.

Peters and Bennett (1989a) studied the combined chemical precipitation/air flotation system for their ability to simultaneously remove heavy metals and oil. In this study, they compared the performance using hydroxide precipitation with that using sulfide precipitation. The synthetic wastewater used contained 25 mg/L each of Cu, Pb, and Zn, plus 1,000 mg/L of oil. The precipitants were rapidly mixed for 2 min, followed by a flotation time of 4 min. The effects of various collectors and their dosages, as well as the type of precipitant, were examined in terms of their ability to remove heavy metals and oil. Five different chemical collectors were investigated: NaLS, Atlasep 2A2, Nalco-7182, Nalco-7734, and TFL-365. Applied collector dosages ranged from 0 to 1442 mg/L. Removals of heavy metals and oils exceeding 93.8% can be obtained using this technique. The residual concentrations were sensitive functions of pH, collector type and dosage, precipitant type, and air injection rate. The presence of oil had little, if any, effect on the removal of Cu and Pb using sulfide precipitation, while the removal of Zn decreased by about 38% due to the presence of oil. Hydroxide precipitation resulted in lower residual concentrations than sulfide precipitation using the NaLS and Atlasep 2A2 collectors, while sulfide precipitation resulted in lower residual concentrations using the Nalco-7182 and Nalco-7734 collectors. The TFL-365 collector has lower Pb and oil concentration employing hydroxide concentration and lower Zn and Cu concentration employing sulfide precipitation. Through proper choice of precipitant type and collector dosage, residual metal concentrations lower than 0.2 mg/L can be easily obtained using this combined chemical precipitation/air flotation technology (Peters and Bennett, 1989a).

Gopalratnam et al. (1992) studied the effects of various dosages of chemical collectors on the removal of heavy metals in a combined metal hydroxide precipitation/air flotation system. The residual concentrations were sensitive functions of pH, collector dosage, and air injection rate. The optimum pH of 9.18 does not necessarily represent the maximum removal of any one metal; rather that pH condition optimized the removal of the combined metals system. A single collector dosage did not maximize the removal of each metal from the industrial wastewaters used in this study (containing Cu, Pb, and Zn). A single collector dosage was not effective for all metals, although removals in excess of 80% were consistently achieved. Metal removals were slight greater using the nozzle air flotation system as compared to the induced air flotation system. The removal of heavy metals and oil appeared to occur through a coprecipitation/adsorption mechanism.

Peters and Bennett (1989b) studied the performance of the combined chemical precipitation/air flotation system employing three different air flotation systems: dissolved air flotation (DAF), induced air flotation (IAF), and nozzle air flotation (NAF). Two wastewaters, one synthetic and one industrial, were used in these performance assessments. The synthetic wastewater used Jayfloc-806 as the chemical collector, and the industrial wastewater used Jayfloc-824 as the

collector. The initial concentrations of Cu, Pb, and Ni were 25 mg/L each, while the initial Zn concentration was 5 mg/L; the initial oil concentration was 1,000 mg/L. Removal efficiencies on the synthetic wastewater exceeded 96%. The DAF system provided the best metal removal, and the NAF system provided the poorest metal removal. The removal of oil was in the order: DAF > NAF > IAF. For the industrial wastewater, removal efficiencies were lower, on the order of 75%. Zinc had the lowest residual concentrations and copper the highest in all three air flotation systems. For lower collector dosages (< 2 mg/L), use of the DAF system resulted in the lowest residual concentrations, whereas at higher dosages (about 5 mg/L), use of the IAF system resulted in the lowest residual concentrations.

Gopalratnam et al. (1988) concluded that the combined chemical precipitation/air flotation system has great potential for simultaneously removing oil and heavy metals from solution. The advantages of this processing scheme are its simplicity, relatively low operating costs, and one stage operation (in comparison with conventional processes using a two- or three-stage operation to remove the metals and oil separately).

Complexation/Sequestration

Complexation involves the formation of a complex or chelating agent. Sequestration involves the removal of a metal ion from solution by formation of a complex ion that does not have the chemical reactions of the ion that is removed; in other words, that metal ion is tied up or complexed. Complex formation alters the chemical characteristics of the metal ions and affects the metal removal mechanisms involved (Huang and Bowers, 1980). For example, the formation of metal complexes increases the solubility of metal precipitates as hydroxides, carbonates, and sulfides. The extent of complex formation is affected by solution pH and the concentration of the participating species. Mayenkar and Lagvankar (1983) observed that dissolved chelated nickel could be effectively removed by contacting the wastewater with a bed of iron filings; the type of chelating agent present affected the reaction rate. O'Neill et al. (1975) studied the removal of Cu^{+2} , Cr^{+3} , Cr^{+6} , Fe^{+3} , and Zn^{+2} by ultrafiltration by tying up the metal ions in large molecular complexes using EDTA. Although from selectivity considerations it appeared that separation of copper and zinc in the pH range of 5-6 was possible, such was not the case. Separation of metal cations by chelation and ultrafiltration also did not appear promising. Using solely complexation for recovery of metals does not hold much promise in the plating industry.

Electrochemical Operations

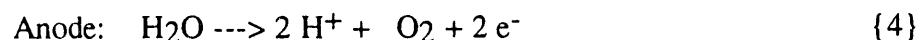
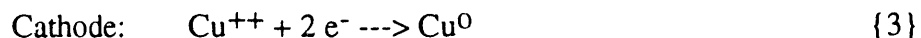
Electrolytic metal recovery is one of a number of technologies capable of removing metals from process wastewaters. The technology has been used for many years in the mining industry for electrowinning and electrorefining of ores and has been used to recover copper from pickle liquors. During the last 30 or more years, electrolytic metal recovery has been investigated for recovery of metals in dragout from plating tanks. In electrolytic recovery, a direct current is passed through an aqueous solution containing metal ions between cathode plates and insoluble anodes. The positive charged metallic ions adhere to the negatively charged cathodes, leaving a metal deposit that can be stripped off and recovered. The principles and techniques of electrochemical techniques have been described in the literature (Ahmed, 1979; Pemsler and Rappas, 1979) addressing such topics as electrode potentials; equilibrium, oxidation-reduction, and mixed potential; voltametry; electrocapillarity capacity; short-circuit current measurements;

reduction by SO₂ and CO, etc. Pemsler and Rappas (1979) point out that electrowinning is a highly energy-dependent and labor-intensive process. The capital cost of an electrowinning process is extremely high and represents a significant portion of the total cost.

A graphical representation of electrochemical equilibria (including chemical reactions such as hydrolysis and complex formation) is the Pourbaix diagram (1966). These diagrams plot the reduction potential on the hydrogen scale (E_H) versus pH, showing the domains of predominance for the various species in the system. The lines in the diagrams represent the locus of equal activity of two species in equilibrium; horizontal lines are for oxidation or reduction without hydrolysis or complex formation, while vertical lines represent hydrolysis or complex formation. Areas between lines represent field of stability for a given activity level for the chemical species considered.

Dilute rinse waters pose a special problem because cathode polarization becomes significant at low concentrations. As plating proceeds, the layer of solution adjacent to the cathode becomes depleted in metal ions, forming a polarized layer. The rate of diffusion into and across the polarized layer is lower; the layer becomes thicker and more depleted. Cathode polarization leads to a number of operational problems including a low rate of metal deposition. A number of means to reduce cathode polarization are employed, including operation at lower current density, adjusting the chemistry and solution temperature, agitating the solution, using high cathode surface areas, and reducing the diffusion layer thickness.

The theory of operation basically involves an oxidation-reduction reaction whereby electrons are supplied by an external electrical source, reducing the metal ions in the electrolyte to form elemental metal at the cathode surface. As an example, the cathodic and anodic reactions for copper are listed below:



Bennion and Newman (1972) developed an electrolytic cell using porous, fixed, flow-through electrodes as a means of removing metal ions from dilute solutions. Using this cell, the Cu concentrations were reduced from 670 mg/L to less than 1 mg/L. The controlling factor for use of the cell was its capital cost. Electrolytic recovery of Zn from a plating bath rinse stream (containing zinc cyanide solution) was accomplished using a simple batch electrochemical reactor with stainless-steel electrodes (Walters and Vitagliano, 1984). Test solutions ranged in concentration from 100 to 980 mg/L. The highest Zn removal rates were achieved using high applied currents. The single most important factor in achieving high deposition rates was agitation; mechanical mixing and nitrogen gas aeration were both effective for agitation. Zinc deposition was higher for high nitrogen gas feed rates because of the increased agitation, which reduced the concentration polarization. Agitation promotes the replenishment of Zn⁺² ions at the boundary layer as zinc deposits on the electrodes. Higher current densities provide moderately higher deposition rates than do low current densities. The NaCl dose had little effect on the deposition rates as long as sufficient NaCl was added to achieve a critical minimum conductivity level. Bishop and Breton (1983) studied the effect of cathode surface area on the recovery of copper from dilute, chelated copper rinse waters by employing an electrolytic cell consisting of a series of flow-through cathodes and anodes in an electrode cell box. The Cu

removal efficiency ranged from 80-85%. Influent pH had little effect on the chelated copper removal over the pH range of 3 to 11. Influent copper concentration and flow rate had the greatest influence on the performance of the electrolytic unit, while pH and recirculation rate had little or no effect on the overall treatment efficiency. Field data (Spearot and Peck, 1984) indicated copper could be removed to levels of less than 1 mg/L from an initial level of 100 mg/L from solutions containing EDTA, Quadrol, tartrate, pyrophosphate, ammonium persulfate etc, and peroxide sulfuric copper etc.

Electroless copper bailout treatment was evaluated in a bench-scale pilot study to recover copper at a printed circuit board manufacturing facility (Chiu et al., 1991). Optimum operating conditions (minimum quantities of sodium hydroxide and formaldehyde) were identified using the sodium borohydride system. Under these conditions, copper precipitation exceeded 99%. The clear supernatant was discharged to the industrial wastewater treatment plant and the precipitated copper was collected. On the basis of these bench-scale tests, a permanent facility was designed and constructed to treat the electroless copper bailout. The system consists of an 800-L reactor, an 800-L bailout storage tank, and a filter. The simple payback period for this system was estimated to be six months (Chiu et al., 1991).

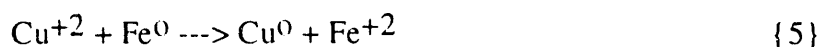
Electrochemical processes provide a means of introducing oxidant without adding extraneous chemical or ions (Poon and Lu, 1981). Ayres and Fedkiw (1983) studied the deposition of lead and copper on a reticulated vitreous carbon surface as a catalytic agent for electrodeposition of Cu^{+2} , Ni^{+2} , Pb^{+2} , and Zn^{+2} from dilute solutions (10 mg/L) using a flow-through porous electrode reactor. Lead did not catalyze the deposition of Zn^{+2} , although it did inhibit the H_2 side reaction at the highest loading level used (50 ug/cm^2). Copper showed a strong catalytic activity for Zn^{+2} and Ni^{+2} electrodeposition at loadings of 20 to 50 ug/cm^2 . The presence of 10 to 100 mg/L Cu^{+2} acted as a catalyst for CN^- electrooxidation. A current efficiency of 87% was measured as the concentration of Cu^{+2} was lowered from 95.6 to 0.05 mg/L. Ayres and Fedkiw (1983) estimated the electrical operating cost to be \$0.11/lb of copper recovered (which compared with \$0.653/lb of copper removed by hydroxide precipitation). The sludge volume of the waste generated was considerably smaller by the electrolytic recovery route than by the chemical precipitation route (0.0279 gal/lb electrochemically generated versus 4.45 gal [of 4% solids]/lb of copper removed by hydroxide precipitation).

Farkas and Mitchell (1984) developed a process for electrochemical heavy metal recovery from wastewaters. The equipment consisted of a reactor module containing the anode and cathode assemblies, two controllable power supplies, plus pumps, electrolyte tanks, etc. The cathode consisted of a bundle of thin carbon fibers connected to a feeder sheet. The surface area to volume ratio was extremely high, ~12,000 times higher than the apparent surface area to volume ratio. The large surface area enhances the mass transfer rate by several orders of magnitude. Features of the process include no generation of sludge, low operating costs, no consumable reagents required for operation, and metals are generated in a saleable form.

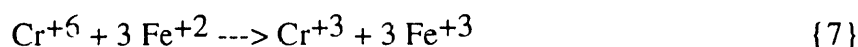
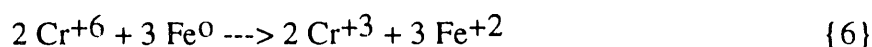
Cementation

Cementation is a metal-replacement process in which a solution containing the dissolved metallic ion(s) comes in contact with a more active metal such as iron. Cementation involves the recovery of an ionized metal from solution by spontaneous electrochemical reduction to the elemental

metallic state with subsequent oxidation of a sacrificial metal (such as iron). The reaction for copper and iron is:



The result is to replace copper with iron in solution; the copper plates onto the solid iron surface. If hexavalent chromium is present in a wastewater, it can react with either elemental or ferrous iron to yield trivalent chromium:



The cementation process can be predicted in terms of electrode potentials. Power and Ritchee (1976) concluded that if the potential difference between the sacrificial metal and the noble metal was less than 0.06 V, the reaction kinetics will be under chemical control, while diffusion of the noble metal ion to the sacrificial metal surface will control at potential differences greater than 0.36 V. Between these two limits, a mixed chemical reaction/diffusional mechanism is postulated. Gould (1993) notes that for the $\text{Fe}^0/\text{Cu}^{+2}$ system, the mechanism is controlled by diffusion of the cupric ions to the iron surface (potential difference = 0.74 V).

Advantages of the cementation process include:

- Simple control requirements. The demand for the treatment chemical is determined automatically by the rate at which the target pollutant is provided to the system. In the iron cementation of copper, the rate of iron consumption varies in proportion to the rate at which copper ion is fed to the system. This eliminates the need for close monitoring of the waste stream composition and external control of the supply rate of the treatment reagent (Gould, 1993).
- Low energy utilization.
- Recovery of valuable high purity metals, such as copper.

Gould (1993) points out that there exist many options for treatment that offer the opportunity to tailor a treatment system to a specific set of needs. Thus, while iron is very commonly used to cement copper, any more electropositive metal (such as aluminum or zinc) can be used for the same purpose. For example, zinc solution contaminated with copper might be treated by zinc cementation thereby replacing the copper with zinc.

Patterson and Jancuk (1977) studied cementation treatment of copper in wastewaters. They found copper cementation was a first-order reaction with respect to removal of copper from the wastewater. The rate of cementation was independent of the presence of oxygen. Copper cementation was independent of pH; however, above pH 3, ferric hydroxide precipitation masked and interfered with copper recovery. The copper from the continuous reactors had a

moisture content of ~38%; the dried cement product contained ~93.5% pure copper on a dry weight basis.

A more recent application of this technology involves the suspension of scrap iron in a perforated rotating drum through which the wastewater flows (Jevtitch and Bhattacharyya, 1983). Copper is cemented onto the iron and scraped off as particulate copper as it tumbles within the drum.

Membrane Operations

The use of membrane processes for water reuse, wastewater volume reduction, and by-products recovery (such as valuable metals) is gaining considerable attention in many industries. Membrane processes can be divided into three general categories: high-pressure reverse osmosis (500-1500 psi), low-pressure reverse osmosis (200-500 psi), and ultrafiltration (20-100 psi). The process consists of letting the solution flow under pressure through an appropriate porous membrane (such as cellulose acetate, polyamide, polysulfone, etc.) and withdrawing the membrane permeate product water at atmospheric pressure. For reverse osmosis (RO), the applied pressure must be considerably greater than the osmotic pressure of the rejected solutes in order to obtain adequate water flux. Ultrafiltration (UF) with neutral membranes is normally used to remove large molecular weight ($MW > 1,000$) solutes.

Belfort (1984) provided an excellent review of synthetic membrane processes and various wastewater treatment applications, and Lloyd (1985) presented an excellent review of membrane materials preparation and characterization. RO membrane flux and solute transport have been commonly described by two models: the solute diffusion model (Lonsdale, 1972) and the preferential sorption-capillary flow model (Sourirajan, 1983).

The development of synthetic thin-film composite membranes has resulted in solute removals at lower pressure over a broad pH range ($2 < \text{pH} < 12$). The new generation membranes allow simultaneous separation of metal salts and organics from aqueous systems. These low-pressure processes with composite membranes have definite advantages in terms of energy savings and capital cost. Thin-film membranes result in a high water flux (25-35 gal/ft²-day) and 95-99% removal of various chemicals (Bhattacharyya et al., 1982, 1984).

Much of the development work and commercial utilization of the RO process has occurred within the past 20 years, with particular emphasis devoted to desalination and water treatment and recovery. The power requirements typically amount to 1/4 to 1/2 hp/1,000 gal wastewater treated. This technique has shown promise for removal and recovery of metal ions from waste solutions. RO has been used to dewater mixed plating rinse streams prior to chemical precipitation/clarification to reduce the hydraulic loading to the clarifier (Cartwright, 1984). Typical operating conditions are listed below:

Feed stream total dissolved solids concentration	1,000-10,000 ppm
Toxic metals concentration	1-100 ppm
Feed rates	5-100 gpm

Cartwright (1984) estimated the existing market potential to be about $\$5-10 \times 10^6/\text{yr}$, along with a projected growth rate of 10-15%/yr. RO has also been used for electroplating solute recovery (plating salts) from rinse waters. The concentrate is returned to the plating bath and the permeate is returned to the last rinse. Over 170 baths are currently treated with RO; typical feed rates are 2-10 g/min. The existing market potential was estimated to be $\$5-10 \times 10^6/\text{yr}$, with a projected growth rate of 10%/yr (Cartwright, 1984). Continuous side-stream UF has also been used for electrodeposition paint baths for removal of water and contaminants. The concentrate is returned to the baths; permeate is used as the first rinse or is discharged.

In another membrane process, electrodialysis involves the transport of ionic species through membranes by application of a d.c. potential. The membrane contains cation or anion exchange resins, selective for only cations or anions in the waste solution. The cation exchange membrane permits the passage of cations while rejecting anions, whereas the anion exchange membrane allows anions to pass and rejects cations.

These membrane separation processes have become standard procedures for the separation of molecular solutions. In UF, the different chemical components are separated exclusively by molecular size. In RO, particle size and the chemical nature both are important for the separation of materials. For multicomponent mixtures where highly toxic or valuable materials (such as heavy metals) have to be removed from industrial wastewaters containing these ions in low concentrations in addition to a mixture of other salts, Strathman and Kock (1978) point out that RO is not well suited for this sort of separation problem. In their study, polyethylenimine showed a good selectivity for Cu^{+2} and somewhat less selectivity for Zn^{+2} , Ni^{+2} , and Ag^{+} . Quaternized polyethylenimine had a good selectivity for Pd, Pt, Hg, and Au. Polythiourea was well suited to bind Hg.

The rejection characteristics of low-pressure ultrafiltration membranes (800 mM charge capacity) has been studied for several alkaline-earth heavy metal ions and oxyanions (Bhattacharyya and Grieves, 1977). For many closed-loop processes involving water reuse, adequate rejections of up to 97% with charged UF membranes prevent the buildup of low-molecular-weight ionic solutes in the recycled water (Bhattacharyya et al., 1974, 1976, 1977). Low-flux, tight uncharged membranes (such as cellulose acetate) are commonly used to remove inorganic electrolytes. The salt rejections often exceed 98%; however, the high effective osmotic pressures and the membrane tightness often necessitate high pressure operation, which causes membrane compaction problems and a reduction in the water flux (Bhattacharyya and Grieves, 1977). They point out that selective separation of specific ionic solutes from mixed metal mixtures is not generally possible. Membrane swelling is undesirable since it could produce a loss in rejection of monovalent anions greater than that of divalent anions. Bhattacharyya and Grieves (1977) provided the following results for the chloride and sulfate salts of Cu^{+2} , Ni^{+2} , and Zn^{+2} relating to the ultrafiltrate stream concentration to the inlet stream concentration:

$$C_f = 0.093 C_i^{1.36} \quad \{8\}$$

$$R^* = 1 - 0.093 C_i^{0.36} \quad \{9\}$$

The rejection dependence on concentration for Cu^{+2} , Ni^{+2} , and Zn^{+2} sulfate salts was likewise described by:

$$C_f = 0.082 C_i^{1.21} \quad \{10\}$$

$$R^* = 1 - 0.082 C_i^{0.21} \quad \{11\}$$

Potential applications of this technology include UF of plating rinse waters, UF of toxic metal constituents from metal manufacturing wastewaters, dissolved solids reduction, and UF of photographic processing water constituents. As an example, a series of UF experiments were performed with actual rinsewaters by diluting a Watts-type bright nickel-plating solution (Bhattacharyya and Grieves, 1977). The unadjusted pH ranged from 5.2 to 6.8; the inlet Ni^{+2} concentration ranged from 35 to 940 mg/L. The rejections (at $\Delta P = 2.8 \times 10^5 \text{ N/m}^2$) of total organic carbon, conductivity, and optical density (at 400 nm) were 0.67, 0.73, and 0.90+, respectively. Bhattacharyya and Grieves (1978) also observed that cadmium sulfate rejection (88%) was somewhat greater than that of the other sulfate salts of Ca^{+2} , Ni^{+2} , and Zn^{+2} in a metal manufacturing wastewater. Using a negatively charged UF membrane, rejections of Cu^{+2} , Ni^{+2} , Zn^{+2} , and Cd^{+2} were 0.88, 0.88, 0.88, and 0.90, respectively.

Pusch and Walch (1978) point out that membrane separation processes require only about 1/10 of the energy costs of a corresponding distillation process if small to medium wastewater treatment plants are considered (plant sizes of 100 to 1,000 m^3/day). Restrictions associated with the use of membrane processing involve membrane lifetime and selectivity since strong acidic, alkaline, and/or oxidizing solutions often have to be concentrated rather neutral or pH-controlled rinse water. Conventional membranes rapidly deteriorate in such chemically active brines. Recycling is less effective if valuable materials must be isolated in the presence of large amounts of low value by-products. It becomes necessary for development of processes for separation of different salts in addition to the purification of the rinse water. These goals can be approached through several different means (Pusch and Walch, 1978):

- (1) Use of complexing agents to complex specific ions. The filtrate solution containing other contaminants could be further processed by hyperfiltration to yield a good quality rinse water to reuse.
- (2) Use of "active transport membranes" consisting of a water-immiscible liquid organic complexing agent immobilized within the pores of a microporous membrane.
- (3) Addition of chemicals (chelates, polyelectrolytes, etc.) for eventual separation of the valuable ion from the complexing agent.

Pusch and Walch (1978) noted that separation of two solutes was more effective at 40 atm than at 100 atm because of the slower increase in the contaminant rejection with increasing pressure. By adapting the properties of the membrane polymer to the properties of the solutes and by variation of the process parameters (applied pressure, solute concentration, pH, etc.), separation numbers greater than 1,000 for low molecular weight solutes can be achieved by hyperfiltration. Separation is most effective if one of the species yields a rejection greater than 99% at a high water-recovery rate.

Charged, noncellulosic UF membranes provide the advantages of good water flux at low transmembrane pressures (5×10^5 to 7×10^5 N/m²) and the selective separation of simple and complexed ions from aqueous solutions. The separation of heavy metals in the presence of complexing agents is particularly difficult with conventional processes. An extensive experimental investigation (Bhattacharyya and Cheng, 1985) was conducted with negatively charged, noncellulosic UF membranes to establish the relative rejection behaviors of complexed heavy metals under insignificant concentration polarization conditions. Three types of complexing agents were employed in their study: cyanide (CN⁻), ethylenediaminetetraacetic acid (EDTA), and oxalate (OX). The negatively charged (sulfonic acid groups) membranes used had a typical water flux of 1.3×10^{-3} cm/s at a pressure of 5.6×10^5 N/m². The rejection dependence of the heavy metals (Zn⁺², Cd⁺², Cu⁺², and Cu⁺) and free complexing agents (CN⁻, EDTA, and OX) was found to be a function of feed ratio (L/M) of complexing agent to metal, pH, ionic strength, and pressure (below 5×10^5 N/m²). For EDTA and oxalate systems, the rejections of metal were independent of initial metal concentration, whereas for the cyanide system, rejections of both metal and cyanide decreased with feed concentration. The concentration effect was further verified by the high-water-recovery experiments. At a transmembrane pressure of 5.6×10^5 N/m², metal rejections ranged between 77 and 96%. The rejection behavior was explained in terms of metal complex species distribution and the Donnan Exclusion model. The rejections of all complexed metal ions are strong functions of average species charge. Because negatively charged membranes reject divalent anions better than monovalent anions, the rejection of $ML^{2-} > ML^{-}$ was expected. The complexed metal ion charge was a function of the L/M ratio and pH. The membranes used in the study had a typical CuCl₂ rejection (R) of 34% at 1.6×10^{-4} M and 5.6×10^5 N/m². Typical rejections obtained with complexed copper species were 94%, 96%, and 80% for Cu(CN)⁻, Cu(EDTA)⁻, and Cu(OX)⁻, respectively. The rejections of free CN⁻, EDTA⁼, and OX⁼ were 30%, 85%, and 93%, respectively. For all cases, the metal rejections showed the following trend $R_{M-EDTA} > R_{M-CN} > R_{M-OX}$. High metal rejections were obtained at L/M = 1.0 and pH 4-10 with EDTA, at L/M = 4-6 and pH 9-10 with cyanide, and L/M = 10-12 and pH 6-7 with oxalate. The rejections of various species followed the order Cu(CN)⁼ > Zn(CN)₄⁼ > Cd(CN)₄⁼; Zn(EDTA)⁼ > Cd(EDTA)⁼. Removals at high water recoveries were also computed from the concentration dependence correlation and were further verified by experiments. Selective separation of metals could be obtained by adjusting the pH and complexing agent to metal feed ratio.

Cartwright (1981) described applications and potential uses of membrane processes in the plating shop. More than 100 RO systems are used to treat nickel plating rinse waters. Typical operating costs (including labor and maintenance, electrical expenditures for the high pressure pump and transfer pump, and replacement of the cartridge filter and RO membrane elements) ranged from \$0.75 to \$2.00/1,000 gal of feed water processed. The economic value of recovered nickel-plating salts usually results in a capital payback period of less than 18 months. Cartwright (1981) pointed out that few RO installations are used to treat wastewaters such as acid copper or tin-lead fluoroborate because of low evaporation rates and the low value of the plating salts.

For membrane extraction of heavy metals, metals are removed through membranes that separate these two phases (Kim, 1984). No mixing is involved and no moving parts are used, thereby eliminating many problems associated with direct mixing necessary in conventional solvent extraction processes. This new technology of the membrane extraction process employs two hollow fiber modules, one for extraction and the other for stripping. The organic solvents circulate between the two modules picking up metal ions in the extraction module. The metals are removed from the organic solvent in the stripping module. The regenerated solvent is

recycled back to the extraction module. Water droplets in the organic phase significantly deteriorate the performance of the system. The water droplets in the organic phase will carry stripping solution to the aqueous stream, thereby shifting the equilibrium relationship and causing a reduction in the removal efficiency. Because organic loss is less than that with conventional solvent extraction, it is possible to use more expensive solvent materials. Membrane extraction can be used to separate and concentrate copper, nickel, zinc, chromium, cobalt, uranium, and other heavy metals. Major advantages of this technology over other competitive processes include high selectivity for a specific metal, simplicity of operation, and high chemical and physical stabilities.

In summary, membrane processes are being used more and more within industry. To date, however, this system is primarily a concentration technique. Major limitations associated with the use of membrane processes include membrane fouling, limited life of the membranes, dissolution of the membranes by strong oxidizing agents, solvents, and other organic compounds. New generation composite membranes offer broad pH (pH 2-12) and temperature (up to 50°C) operating limits.

Evaporation/Distillation

The primary use of evaporation and distillation treatment has been for product recovery, with some limited use to treat final concentrated wastewater residues to dryness. These techniques are basically end-of-the-pipe processes. Evaporative processes are generally only economical for concentrated rinses and multistage countercurrent rinsing (Saito, 1976). This technique requires sorting of wastes by types and use of various means for exclusion and/or removal of impurities. Evaporative recovery concentrates the chemical dragout in the rinse water to bath strength, returning the concentrated solution to the process tanks. The evaporated water is condensed and returned to the rinsing system, thereby minimizing water consumption.

Patterson and Minear (1975) point out that evaporation is a well-established technology for recovering plating chemicals and water from plating waste effluents. Commercial units have been built for handling zinc, copper, chromium, and other metal plating baths. Disadvantages of the evaporation/distillation processes include:

- Relatively high capital costs.
- Relatively high operational costs (particularly for vacuum systems).
- Distillation processes are extremely energy intensive.
- The economics of distillation impose a constraint on the size range of these systems.
- These systems are complex, requiring trained personnel to operate and maintain them.

Four distillation processes are commonly used to treat spent pickle liquors (Stephenson et al., 1984). These distillation processes all have in common the use of vacuum evaporation and

addition of sulfuric acid to the spent pickle liquor at some stage in the recovery scheme. Advantages of working under vacuum include:

- The corrosive action of the mixed acid is reduced due to the lower distillation temperatures involved.
- Lower-cost materials can be used for construction.

Adsorption

Most of the applications and research efforts on activated carbon have been oriented toward organics removal (Huang, 1978). Research efforts involving removal of inorganics by activated carbon have been quite limited. Huang (1978) provides an excellent review of inorganics removal by activated carbon by considering such factors as surface properties (and their measurement) and adsorption characteristics of cationic and anionic species onto activated carbon surfaces. Important physical/chemical properties affecting inorganic electrolyte adsorption include specific surface area, pore structure, electrophoretic properties, and surface acidity.

Very little has been reported on activated carbon for removal of inorganics from wastewaters. Activated carbon was reported to be a potential adsorbent for heavy metals removal (Argaman and Weddle, 1976; Cheremisinoff and Habib, 1972). Salvaged automobile tires were shown to be capable of removing trace metals (Al, Hg, Ni, Vd, Cr, Co, Cd, Cu, Fe, Pb, Mn, Ag, and Zn) due to the various materials present in tires such as sulfur, carbon black, fillers, synthetic rubber, and antioxidants (Netzer et al., 1974; Netzer and Norman, 1974; Netzer and Wilkinson, 1974). Saito (1976) used activated carbon and sulfonated coal to remove Cu, Cd, and Fe from wastewaters; removals exceeding 98% were achieved for cupric ions treated with sulfonated coal after a one-stage extraction. For an initial copper concentration of 312 mg/L, the residual Cu concentration was reduced to 0.08 mg/L after a two-stage extraction. Significant removals were also achieved with activated carbon. The extent of heavy metal adsorption on a specific type of carbon is a function of: metal-ligand charge distribution (for example ML^{2-m} , MHL^{2-m+1} , $MOHL^{2-m-1}$); free metal and free ligand charges, the pH_{ZPC} of the carbon surface, and the polarity of the ligand molecules. The pH affects the charge distribution of the various species as well as the hydroxo group distribution at the activated carbon surface. Jevtitch and Bhattacharyya (1983) established the adsorption capacities of complexed heavy metal ions by activated carbons under equilibrium conditions. An extensive experimental investigation was conducted with activated carbons to establish the adsorption capacities of heavy metals (Cd^{+2} , Cu^{+2} , Ni^{+2} , and Zn^{+2}) in the presence of various complexing agents (EDTA, triethylene-tetramine (TRIEN), citrate, and tartrate). Adsorption equilibria were explained by species charges and carbon surface charge characteristics. In the pH range of 7.5-8.0, the active sites were positively charged. The adsorptive capacities of Cd^{+2} (and other heavy metals), free ligands, and cadmium-ligands were also a function of feed metal concentration, types of ligands present, molar ratio of ligand:metal, and pH. Complete metal-ligand species distributions were calculated using computer solutions of multiple reaction equilibria. For an equilibrium cadmium concentration of 0.1 mM (pH 7.5-8.0), the sequence in adsorption capacity for cadmium chelates was: $QCd-EDTA > QCd-citrate > QCd-TRIEN > QCd-tartrate$.

Huang et al. (1985) evaluated removal of Co^{+2} from solutions using activated carbon adsorption, with special emphasis on the effect of various organic substances on Co^{+2} removal.

Their results showed that Co^{+2} was removed by adsorption rather than by precipitation alone. Fourteen types of activated carbon were evaluated for their Co^{+2} removal capabilities. Two activated carbons, Nuchar SA and Nuchar SN, gave similar high metal removal capacities (removals approaching 100%, depending on the solution pH). The Co^{+2} removal percentage decreased with increasing surface loadings. The presence of organic acid resulted in five different cases of effects on Co^{+2} adsorption: (1) anion-induced cation adsorption, (2) complexes not adsorbable (or competitive anion adsorption), (3) complexes adsorbable (or non-competitive anion adsorption), (4) anion-induced cation adsorption and complexes not adsorbable, and (5) anion-induced cation adsorption and complexes adsorbable. Depending on the extent of complex formation and the adsorbability of the complexed Co^{+2} and of the ligand, it was possible to differentiate four different effect groups: (1) enhancement over the mid-pH range, (2) inhibition as the pH increases, (3) no effect, and (4) enhancement followed by inhibition as the pH increases. The regeneration of the exhausted activated carbon by strong acid was determined to be feasible. The adsorptive capacity of the recycled activated carbon was maintained at a 92% level after the fifth cycle.

Ku and Peters (1987) investigated the use of activated carbon as a polishing step for treatment of industrial plating wastewaters. When hydroxide precipitation was employed for removal of heavy metals, the use of activated carbon adsorption allowed significantly lower effluent metal concentrations to be achieved. The residual Zn and Cd concentrations were reduced by greater than 70% through the use of activated carbon following hydroxide precipitation. The adsorption capacity for Cd^{+2} was calculated to be between 5 and 20 mmole/gm of powdered activated carbon for pH in the range of 9 to 11, which is much lower than the 40 to 50 mmole/gm of powdered activated carbon reported by Huang and Wirth (1982). This was likely due to the interference of ammonia and cyanide on the activated carbon adsorption process (Ku and Peters, 1987). Because of the completeness and rapidity of removal of heavy metals by sulfide precipitation, little enhancement in heavy metal removal was achieved using activated carbon treatment as a polishing step. The most significant result of such a polishing step following sulfide precipitation lies in its ability to substantially reduce the sulfide concentration, thereby lessening the potential for H_2S gas evolution.

Algae has also been studied for its capability to remove heavy metals from wastewaters and for concentration of valuable metals from dilute solutions (Filip et al., 1979; Hasset et al., 1980). When algae grown in a sewage lagoon was mixed with heavy metal solutions and subsequently dewatered by an intermittent sand filter, 98% of the Cu and 100% of the Cd was removed from the solutions (Filip et al., 1979). Rapid uptake of cadmium by algae was observed in the first stage of a tertiary treatment system (Kerfoot and Jacobs, 1976). Sloan et al. (1984) studied the removal of four metals (Cd, Cu, Pb, and Zn) at different concentrations using three different algal species. Cadmium, copper, and lead could be removed in a two-stage process with the first stage being either ion exchange or passive adsorption and the second stage being removal from the solutions by passive diffusion through the cell membrane.

Swallow et al. (1980) studied the sorptive properties of hydrous ferric oxide using copper and lead as sorbates. They noted that fresh hydrous ferric oxide floc sorbed more lead than aged floc, and lead sorbed on the fresh floc was less efficiently recovered, suggesting occlusion occurred in the coprecipitation process. Variations in ionic strength and composition had no effect on the Cu^{+2} sorption isotherm. The Pb^{+2} sorption isotherm was similarly unaffected by changes in ionic strength; the presence of Cl^- dramatically decreased the fraction of Pb^{+2} sorbed at any given pH. Benjamin and Leckie (1982) studied the effects of complexation by Cl^- , $\text{SO}_4^{=}$,

and S_2O_3 on adsorption of Cd onto four different oxide surfaces. Interactions between metal ions and complexing ligands in the presence of an adsorbent surface can be divided into three groups based on the origin and strength of the interaction: (1) metal-ligand complexes may form in solution and adsorb only weakly or not at all, (2) the species may interact indirectly at the surface altering the surface electrical properties, and (3) the metal-ligand complex can adsorb strongly, enhancing the removal of metal, ligand, or both from solutions compared to the case when either one is present alone. The chloride and sulfate complexes adsorb less strongly than the uncomplexed cadmium ions. Adsorption of thiosulfate complexes is more like that of free ligand.

The effect of anions on the adsorption of heavy metals was studied by Huang et al. (1985). The role of anions in the adsorption of heavy metals was delineated by consideration of the following reaction steps: (1) anions accumulate in the double layer of a positively charged particle, (2) approach of metal ions to the soil surface is facilitated, and (3) complexes form between the heavy metal ions and the already adsorbed aqueous anionic ligands. For the soil-water environment, copper and zinc are more removable than lead and cadmium.

Various research studies have been performed to study the removal of a single heavy metal from solutions, as summarized in the following subsections.

Cadmium

Cedar wood flour cooked with alkali (17.5% NaOH) for 30 minutes to convert part of the wood to alkali cellulose was able to reduce Cd^{+2} from 8.7 to 0.4 mg/L in solution (Yamaguchi and Tatsumoto, 1974). The adsorptive characteristics of Cd^{+2} onto three activated carbons (Filtrisorb 400, Nuchar 722, and Nuchar C-190-N) were studied by Huang (1978). He investigated factors such as pH, initial cadmium concentration, dose and type of carbon, and the presence of chelating agents on cadmium adsorption. Removal efficiency increased with increasing pH for all three carbons. Since the Filtrisorb 400 and Nuchar 722 are both H-type carbons, precipitation of $CdCO_3$ occurs at high pH and is a significant removal mechanism. At the pH_{zpc} , a finite amount of Cd^{+2} adsorbed on the Nuchar 722 and significantly adsorbed on the Nuchar C-190-N. The Nuchar C-190-N, a L-type carbon which adsorbs only acidic materials, is an excellent adsorbent for cation metal removal; the Nuchar C-190-N had the greatest adsorptive capacity for Cd^{+2} adsorption of the carbons tested. Increasing the carbon to cadmium ratio 100x, a three-fold increase in removal efficiency resulted; however, the time to reach equilibrium remained unaffected. Strong chelating agents were added in an attempt to improve the cadmium removal efficiency of the Filtrisorb 400 (Filtrisorb 400 adsorbs primarily anionic species). An improvement in terms of this metal removal efficiency, from 20% without NTA, to 40% with NTA at 0.01x Cd_i , and 50% with NTA at 0.1x Cd_i , resulted in neutral pH, with comparable results observed for Cd removal performed in the presence of EDTA. Huang (1978) attributed this improvement to the formation of $CdEDTA^{-2}$ or $CdNTA^{-}$ complexes which could be electrostatically attracted by Filtrisorb 400 (whose surface charge is positive for $pH < 7$) followed by further association of Cd^{+2} ions with the adsorbed anions.

Copper

Using a synthetic seawater of high ionic strength (1.65M NaCl), Moore (1971) studied the removal of Cu^{+2} by six different activated carbons, with Barneby-Cheney PC-8592 being the

most effective adsorbent for Cu^{+2} removal. The removal efficiency was extremely poor ($< 6\%$). The activated carbons tested were all H-type carbons; at pH 4-5, the carbon surfaces are positively charged thereby repelling the predominant Cu^{+2} species (Cu^{+2} , CuCl^+ , and CuOH^+) from the carbon surface. Although pH and the total Cu^{+2} concentration were the most important factors in controlling Cu^{+2} adsorption, the magnitude of Cu^{+2} removal by activated carbon was insignificant even under optimum pH and Cu^{+2} concentration conditions. Huang (1978) investigated eight different chelating agents for their ability to improve the Cu^{+2} adsorptive capacity. Using 8-hydroxyquinoline, the most effective chelating agent used, a slight improvement in Cu^{+2} adsorption from 4 to 7% was observed. The adsorption of Cu^{+2} onto activated carbon (Aqua Nuchar A) was found to depend on the ionic strength (Nelson et al., 1974). For the concentration range of 0.001 to 0.100 M NaCl, adsorbability of Cu^{+2} was high with a distribution coefficient D of ~ 700 . For higher NaCl concentrations, D increases with increasing NaCl concentrations; D ~ 5000 near 6M NaCl. The rapid increase in Cu^{+2} adsorption with increasing NaCl concentrations was attributed to adsorption of Negatively charged CuCl_2 complexes.

Mercury

The amount of mercury removed is known to increase with decreasing pH. The effluent mercury concentration from a precipitation/filtration/adsorption process was reduced from 30-50 ppb to 3-5 ppb by lowering the pH from 7 to 2-4 (Oppold, 1971). The mercury adsorption capacity increased steadily by decreasing the pH from 9 to 2, as noted by Huang (1978). Thiem et al. (1976) noted that the removal of Hg^{+2} by activated carbon was sensitive to pH; approximately twice as much mercury was removed at pH 7 as compared to pH 9. Research by Humenick et al. (cited by Huang, 1978) using column experiments, showed that good mercury removal was attained at low pH. For a carbon column in which the influent was acidified to pH 4 and employing a contact time of 11 minutes, the effluent concentration averaged 1 ppb over a 5-day period. The column mercury removal capacity increased from 0.3 to 4.1 mg Hg removed per gram of carbon (Filtrisorb 400) by adjusting the pH from 10 to 4. By adding a precipitating chelating agent (ammonium 1-pyrrolidine dithio-carbamate), the removal capacity of Hg^{+2} by activated carbon increased significantly. Treatment of the activated carbon surface by CS_2 was also effective in increasing the Hg^{+2} adsorption capacity. During a study of the catalytic oxidation of H_2S over carbon, Sinha and Walker (1972) observed that a large amount of mercury from a mercury diffusion pump and mercury manometer was taken up by the sulfurized carbon catalyst at 140°C . In subsequent experiments, significant mercury adsorption was observed using the sulfonated activated carbon.

Chromium

Chromates can be effectively removed from wastewaters by passing chromate-laden wastewater through a column packed with platinum black catalyst-impregnated activated carbon. After treatment, wastewater initially containing 100 mg/L chromate had a residual concentrations of less than 0.1 mg/L. By mixing 200 mL $\text{K}_2\text{Cr}_2\text{O}_7$ solution with 5.0 gm of powdered coconut shell charcoal and heating in an autoclave at 200°C for 30 minutes, the concentration of chromium was reduced below 0.01 mg/L (Tagashira et al. 1975). Huang and Wu (1975) noted that removal of Cr^{+6} by calcinated charcoal was most significant at low pH and for low initial Cr^{+6} concentrations. They speculated that HCrO_4^- ions were the major species being removed.

- Landigan and Hallowell (1975) demonstrated that activated carbon could be used by small plating facilities for removal of chromium.

In a study of the adsorption of Cr^{+3} and Cr^{+6} as a function of pH, and the amount of total Cr and Cr^{+6} eluted from activated carbon at pH 4 to 6.5, Yoshida et al. (1977) observed that Cr^{+6} was readily adsorbed on activated carbon as anionic species such as HCrO_4^- and CrO_4^{2-} while Cr^{+3} was minimally adsorbed by activated carbon. In acidic solutions, Cr^{+6} was readily reduced to Cr^{+3} in the presence of activated carbon. Huang and Wu (1975) likewise studied the effect of pH on Cr^{+3} and Cr^{+6} adsorption by Filtrasorb 400 activated carbon. Cr^{+6} was twice as adsorbable as Cr^{+3} . The optimum pH for adsorptive removal was 5.5 to 6.0 and 5.0 for Cr^{+6} and Cr^{+3} , respectively. The removal of Cr^{+6} involved reduction and adsorption step occurring consecutively (Huang, 1978):

$$-d(\text{Cr}^{+6}) = 4.4 \times 10^{-3} (\text{Cr}^{+6})^{3/4} (\text{C}) (\text{H}^+)^{1/6} + 2.3 \times 10^{-3} (\text{Cr}^{+6}) (\text{C})^{1/2} (\text{H}^+)^{1/4} \quad \{12\}$$

where the first term on the right-hand side of the equation denotes the reduction rate of Cr^{+6} while the second term denotes the rate of Cr^{+6} adsorption. The concentrations are all expressed in moles/L with the exception of C (reported in gm/L). By pretreating the Cr^{+6} wastewater with Cl_2 and heating the activated carbon in 1M HNO_3 solution for 30 minutes, the residual Cr^{+3} concentration was significantly reduced in batch-mode operation.

In summary, activated carbon will adsorb hexavalent chromium, mercury, and many metals complexed in organic form. The adsorptive capacity depends on the carbon pore size, the size of the molecule, solution pH, and the initial and final concentration of the metal(s). Adsorptive capacity increases as the pH decreases and the most effective treatment results in dilute wastes. Activated carbon treatment shows promise for removing the last trace of metal (in the range of 1-2 ppm) following other treatments (such as hydroxide precipitation, electrodeposition, cementation, etc.). Activated carbon treatment has been successfully used to extract gold from cyanide solutions.

To determine the effectiveness of activated carbon for a particular metal bearing wastewater, adsorption isotherms are developed indicating the amount of material adsorbed at a particular concentration. The tests are run on several different carbons to determine which one provides the most effective treatment. Granular activated carbon (GAC) is usually preferred since it can be chemically regenerated and reused. Powdered activated carbon (PAC) is less expensive, but it can only be used on a once-through basis. PAC is difficult to handle due to a tendency to dust and it must be removed from the wastewater by coagulation and/or filtration. Activated carbon treatment has not been widely employed for removal of heavy metals (Huang, 1978).

Soil Remediation Techniques

This section is aimed at common remediation technologies for heavy metal-contaminated soils either to remove the heavy metals from the soil or to minimize the leaching potential of the soil/residue.

Solidification/Stabilization

In situ immobilization of heavy metals avoids the requirement for excavation in soils or pumping of groundwater. Metals will not migrate through the soil to the groundwater and will not hydrolyze or be desorbed from exposure to varying conditions in the soil, such as low pH or a varying oxidation-reduction potential, which tends to solubilize the metals (Czupyrna et al., 1989). The immobilized metals present no adverse environmental or health hazards in their treated state.

Migration of metals can also be minimized by solidifying and fixing the metals in a nonleachable form. In solidification processes, lime, fly-ash, cement-kiln dust, calcined clays, soluble silicates, and other additives are added to bind the soil into a cement-like mass and immobilize the metallic compounds (Connor, 1990). On-site solidification/stabilization results in an increase in the waste volume. Following remediation, site reuse is limited and long-term monitoring is generally required. For these reasons, solidification/stabilization is generally limited to radioactive or highly toxic wastes (U.S. EPA, 1982).

Gilliam et al. (1990) notes that conventional portland cement and fly-ash grouts are effective for retention of hydrolyzable metals (such as Pb, Cd, and Ni). Akhter et al. (1990) used various combinations of Type I portland cement, Type F fly-ash, blast furnace slag, lime, and silica fume to treat soils contaminated with Cd, Pb, arsenite, and chromate. In no case did fly ash improve performance when mixed with other binding agents. Slag offered superior performance compared to fly ash in any combination tested. Several mixtures, including slag, were effective in immobilizing lead (which sometimes causes problems in solidification with cement). Type I portland cement was a versatile and dependable reagent compared to the other agents used. For As and Cr, portland cement alone was superior to that of any other reagent or combination of reagents for comparable dosage levels. Inclusion of portland cement into the stabilization mixture resulted in lower concentrations than the corresponding mixture without cement (Akhter et al., 1990).

Insoluble chemicals can be introduced into the ground by spreading, filling, forced injection, suspension transport, or by placing it in a low permeable encapsulation barrier (Czupyrna et al., 1989). Spreading may suffice as a means of treating metals if the soil has a high-moisture content and the metal contaminants lie very close to the surface (which is most applicable to soils with high organic contents). Tilling is the most common method of introducing a soil treatment chemical into the ground. Routine tilling can mix dry chemicals into the soil to a depth of 1–2 ft. Using specialized equipment, chemicals can be added to depths of up to 5 ft below the surface. Fine insoluble chemicals can be transported short distances through soil voids by placing them in solutions (water or a weak solvent or acid). The suspended material is then injected in a fashion similar to chemical grouting or through nozzles in close spaced probes. Fine material can typically be transported several feet from the nozzle. In formations with high permeability and low organic content, where metals have migrated to depth greater than 10 ft or more, mixing insoluble treatment materials into the soil may be impractical. Under these circumstances, the treatment chemical can be placed into a barrier material, such as bentonite soil or asphalt emulsions used for slurry wall construction, jet grouting, or block displacement.

Once strongly adsorbing insoluble chemical additives are added and distributed throughout the soil, they will not migrate down through the soil to the groundwater. The heavy metals must be adsorbed, complexed, and/or chelated on the additive and must not hydrolyze nor be desorbed

under exposure to varying conditions in the soils (such as low pH or varying oxidation-reduction potentials, which tend to solubilize the metals). The chemical additives must be resistant to chemical and microbial degradation in the soil environment so the metals are not released from the additives over long periods of time. The chemical additives themselves must not leach any deleterious organic or inorganic substances that could contaminate the groundwater.

In situ treatment also provides a cost-effective treatment alternative to alleviate potential hazards. The costs of *in situ* immobilization consist of chemical additive costs and the soil application costs. The chemical costs to treat soil contaminated with 30 meq/kg of total metal (consisting of Cr⁺⁶ and Cd and Ni) with Valfor 200 and ferrous sulfate was estimated to be in the range of \$33,300–\$81,200/acre-ft (corresponding to \$23.9–\$33.8/ton) (Czupyrna et al., 1989). The costs of tilling dry chemicals into the soil was estimated at \$1,000/acre-ft or \$0.42/ton, based on the rental of tilling equipment and labor costs. For comparison, the costs of transporting the contaminated soil to, and disposing the contaminated soil in, a secured landfill is estimated to be in the range of \$357,000–\$595,000/acre-ft (corresponding to \$150–\$250/ton) (Czupyrna et al., 1989). This indicates that the costs of *in situ* immobilization are substantially less than the costs of transporting and disposing of the contaminated soil in a secured landfill.

In Situ Vitrification

In situ vitrification involves placing electrodes in the soil and passing an electric current between them to heat the soil to about 3,600°F (1,984°C) causing the soil matrix to melt, producing a solid, glass-like material that immobilizes waste constituents within the matrix. Since the "glass" product is formed from the waste itself, its properties are a function of that waste, unlike glassification. This glass-like material has low leachability and high structural integrity (Connor, 1990). The primary drawback to this technology is the cost, which is a function of the electrical rate and the water content of the waste or soil. Total costs range from \$100–\$250/ton for soil treatment (Connor, 1990); the normal processing rate is 4–5 tons/h.

Soil Flushing Using Chelating Agents

Pickering (1986) identified four approaches for mobilizing metals in soils: (1) changing the acidity, (2) changing the system ionic strength, (3) changing the oxidation/reduction (REDOX) potential, and (4) forming complexes. In this last technique, the addition of complexing ligands can convert solid-bound metal ions into soluble metal complexes. The effectiveness of complexing ligands in promoting the release of metals depends on the strength of the bonding to the soil surface, the stability and adsorbability of the complexes formed, and the pH of the suspension (Elliott and Peters, 1993). From an application viewpoint, the type and concentration of the complexing ligand and the system pH are the operational parameters that can be controlled.

The ability of chelating agents to form stable metal complexes makes materials such as EDTA and NTA promising extractive materials for treatment of soil polluted with heavy metals (Assink, 1986). Elliott and Peters (1993) have noted that although complexation is the major mechanism responsible for the metal solubilization, the overall release process depends on the hydrogen ion concentration and the system ionic strength. Because hydrous oxides of iron and manganese can coprecipitate and adsorb heavy metals, they are believed to play an important role in the fixation of heavy metals in polluted soils (Slavik and Pickering, 1986); their dissolution under reducing

conditions may weaken the solid heavy metal bond and thereby promote solubilization of the metal ions. Elliott and Peters (1993) noted that there are five major considerations in the selection of complexing agents for soil remediation:

- Reagents should be able to form highly stable complexes over a wide pH range at a 1:1 ligand-to-metal molar ratio.
- Biodegradability of the complexing agents and metal complexes should be low (especially if the complexing agent is to be recycled for reuse in the process).
- The metal complexes that are formed should be nonadsorbable on soil surfaces.
- The chelating agent should have a low toxicity and low potential for environmental harm.
- The reagents should be cost effective.

Elliott and Peters (1993) have noted that, although no compounds ideally satisfy all these criteria, there are several aminocarboxylic acids that form remarkably stable complexes with numerous metal ions. Examples of such complexing materials include: EDTA, NTA, and diethylenetriaminepentaacetic acid.

Extraction of heavy metals (primarily lead) has been studied by Peters and Shem (1992a,b,c) using chelating agents. They examined the use of chelating agents (EDTA and NTA) for their potential extractive capabilities. The concentrations ranged from 0.01 to 0.10M; the initial lead concentrations ranged from 500 to 10,000 mg/kg soil. The pH of the suspension in which the extractions were performed ranged from 4 to 12. Results showed that the removal of lead using NTA and water were pH-dependent, whereas the removal of lead using EDTA was pH-insensitive. Maximum removals of lead were 68.7%, 19.1%, and 7.3% using EDTA, NTA, and water, respectively (Peters and Shem, 1992c). The initial lead content (for initial lead concentrations ranging from 500 to 10,000 mg/kg) has very little effect on the metal removal efficiency for the EDTA extraction system; the applied EDTA concentration (over the range of 0.01 to 0.10M) likewise had little effect on the removal efficiency of lead from the soil (Peters and Shem, 1992c). The linear and Freundlich isotherm models provided an adequate description of the adsorption/desorption behavior (Peters and Shem, 1992b). The isotherm parameter results using the linear and Freundlich isotherm models are summarized in Tables IV and V. Over the range of the EDTA concentrations employed in their study (0.01 to 0.10 M), no significant difference in the isotherm parameters was observed as a result of the applied EDTA concentration. The presence of EDTA altered the adsorption/desorption behavior of lead on the soil, resulting in less of the metal being adsorbed. The soil having the higher silt/clay content had a greater amount of lead adsorbed onto it (as compared with the sandy soil).

Extraction of heavy metals from contaminated soils can be performed by either using *in situ* techniques or on-site extraction, following excavation (Elliott and Peters, 1993). In the case of *in situ* soil flooding, the aqueous extractive agent is allowed to percolate through the soil to promote metal mobilization. In the case of on-site extraction following excavation, the operation can be performed on a batch basis, semi-batch basis, or continuously. The contaminated soil is

Table IV Linear Adsorption/Desorption Isotherm Model for Lead onto the High Silt/Clay Content Soil (adapted from Peters and Shem, 1992b)

EDTA Concentration (moles/L)	Adsorption		Desorption	
	$\bar{k}$ (L/kg)	$q_{e,0}$ (mg/kg)	k (L/kg)	$q_{e,0}$ (mg/kg)
0.00	5570	335	—	—
0.01	5.40	107	5.90	10.5
0.05	6.28	17.4	5.96	-152
0.10	4.43	-46.7	5.38	-20.7

Table V Freundlich Adsorption/Desorption Isotherm Model for Lead onto the High Silt/Clay Content Soil (adapted from Peters and Shem, 1992b)

EDTA Concentration (moles/L)	Adsorption		Desorption	
	$1/n$	K_N	$1/n$	K_N
0.00	0.71	4760	—	—
0.01	1.05	4.69	0.92	9.44
0.05	1.10	3.30	0.95	7.05
0.10	0.93	6.29	0.94	7.58

first pretreated for size reduction and classification, and then brought into contact with the extractive agent. Finally, the soil is separated from the spent extractive agent, and the effluent is further recycled to decomplex and to precipitate the heavy metals from the solution. Alternatively, the solution can be treated using electrodeposition techniques to recover the heavy metals (Peters and Shem, 1992b).

Source Reduction/Waste Minimization

Source reduction/waste minimization is a newer concept which is gaining popularity. It seeks to minimize the quantity and/or toxicity of the wastes produced by focusing attention "up-stream" rather than treating the wastes at the end of the pipe. There have been numerous case studies information presented in the waste minimization field which are too numerous to mention and are beyond the scope of this paper. This author will address one particular case study in which he was directly involved, namely, waste minimization for a printed circuit board (PCB) facility in Taiwan (Chiu et al., 1991).

Case Study

This PCB facility was built in 1974 and produced about 15,000–20,000 m²/mo on printed circuit boards. The PCBs are manufactured by a process that applies a resist to copper foil, which is in turn bonded to the substrate. In this way, an image of the circuit is photographically formed. First, plating through-holes (PTHs) are drilled, then the board is cleaned, and the holes are coated with copper via an electroplating process. The resist image is applied and the exposed areas are further electroplated with copper, then with tin or tin/lead to assist soldering. Unwanted copper is etched away, the resist is removed, edge contacts are plated with nickel/gold, and the board is finally printed with a "solder mask" and legend. After machining, the boards are tested, packaged, and shipped for installation of the electronic components. The photographic, machining, plating, and etching industries all use water for cooling, lubricating, and chemical processing that results in wastewater. After each of the chemical stages, the board is washed with clean water to prevent cross-contamination of the chemical baths. These rinse waters are contaminated with organics, copper, lead, tin, nickel, and fluorides. The wastewater produced from chemical processing and rinsing must be treated before it is discharged into the industrial wastewater treatment plant (IWWTP). The IWWTP was built in 1989 and had a design capacity of 80 m³/h. The treatment processes involve conventional physical and chemical techniques for metals and chemical oxygen demand (COD) removal, generating 2.4 t/d of metal-containing sludge. In addition to the wastewater, waste streams generated at the facility include spent ammoniacal etchant solutions, dry film developer, resist strip, and spent solvents.

Before conducting this study, the IWWTP periodically exceeded the Taiwan pretreatment standards for copper (5.0 mg/L), COD (600 mg/L), and suspended solids (400 mg/L). In the early phases of this study (Chiu et al., 1991), audits were performed to identify opportunities for reducing hazardous wastes at the facility. The pre-site visit information collected at the facility included process flow diagrams, material inputs and outputs, production schedules, material costs, and waste disposal costs. No reliable data were available on the flow rates and compositions of most of the incoming and outgoing streams. This information was collected during the initial site visit.

Mass balance information was collected for the major sources of the copper-containing wastes. Six major production lines were identified: inner etching, external etching, black oxidation, desmearing, electroless copper, and copper plating. The results of this inventory are summarized in Table VI; the majority (93%) of the copper loading to the IWWTP was from rinse water to these six production lines. Among the lines, the external etching and electroless copper lines contributed more than 85% of the total copper loading. Attention was focused on the external etching, electroless copper, and copper plating lines.

The project team identified many feasible waste reduction options for each of the processing lines in the facility. Of the many waste reduction options identified for the various processing lines, the project team selected dragout reduction, chemical precipitation of copper in the PTH bath bailout, and sludge reduction at the IWWTP as the near-term demonstration tasks. The PCBs were immersed in various baths and allowed to drain from 3 to about 30 seconds to determine the dragout characteristics. Dragout experiments were conducted on the black oxidation, copper plating, tin/lead plating, and electroless copper production lines. During these experiments, 10 PCBs were used in each test. The weight and area of each PCB was measured before testing. The drained liquid was collected and the resulting volume was measured. The results

Table VI Summary of Major Copper-Containing Waste Sources (Chiu et al. 1991)

Source/Operation	Quantity Produced (kg/mo)		Total	Total Cu Loading (%)
	Rinse Water*	Spent Bath		
Inner etching	2.8	—	2.8	0.3
External etching	675.0	—	681.1	66.1
	3.8	—		
	2.3	—		
Black oxidation	1.4	0.3	61.7	6.0
	60.0	(Acid cleaning)		
Desmearing	—	1.1 ^a	1.6	0.2
		0.5 ^b		
Electroless copper	142.5	0.7	202.1	19.6
		(Precatalyst)		
	4.5	52.5		
		(Plating)		
Copper plating	6.0	14.4	80.4	7.8
	60.0	(Microetch)		
TOTAL	60.2	69.2	1,029.7	100.0

*Rinse water produced was estimated based on the statistical averages of flow and concentration monitored at each line.

^aOxidation.

^bReduction.

showed that drainage times of 15–20 seconds greatly decreased the quantity of dragout carried over to the rinse water tanks. The QA/QC results revealed that an increase in the drainage time did not adversely affect the quality of the manufacturing products. Table VII summarizes the dragout reduction practices implemented at 11 sources; the original design value and the modifications implemented at the facility are listed. Modification of the drainage times decreased the copper concentration in the wastewater by 36%.

The high COD wastewaters, the cleaner spent solutions, and the scrubber surface grinding wastewaters are sent to the IWWTP for physical and chemical treatment. Figure 2 shows a simplified flow diagram of the wastewater treatment plant before waste minimization practices were implemented at the facility. The first three tanks are used to equalize high COD wastewaters, cleaner spent solutions (with high Cu concentrations), and rinsing and surface grinding wastewaters. The three equalized wastewaters are combined in the following sequence: (1) the pH in the first reactor tank is maintained at pH 2–4 while FeCl₃ and H₂SO₄ are added; (2) the effluent from the first tank is sent to the second reactor tank where lime (Ca(OH)₂) is added to maintain the pH in the range of 8 to 10 under high mixing conditions; (3) the effluent from the second tank is sent to the third tank where Ca(OH)₂ or H₂SO₄ is added to maintain the pH range of 6 to 8, also under high mixing conditions; and (4) the effluent from the third tank is sent to the fourth tank where NF-100 (a polymer coagulant) is added under slow mixing

Table VII Dragout Reduction Practices Implemented at 11 Sources at the PCB Facility

Line	Source	Dragout Time (s)	
		Original Design Value	Modification Implemented
Electroless copper	Plating	0	15
	Microetching	3	15
	Activation	0	10
	Acceleration	0	10
Black oxidation	Acid cleaning	0	13
	Microetching	0	17
Copper and tin/lead plating	Acid cleaning	0	10
	Microetching	3	15
	Copper plating	3	7
	Predipping	0	10
	Tin/lead plating	3	15

conditions. The effluent from the fourth tank enters a clarifier where the supernatant is pH adjusted. The sludge from the clarifier is sent to a thickener; the supernatant is returned to the rinse and surface grinding wastewater streams, while the thickened sludge is sent to a filter press to yield sludge containing about 75% water.

Several groups of experiments were performed to optimize the performance of the IWWTP. These experiments investigated the effects associated with solution pH, influent pH, FeCl_3 coagulant dosage, and mode of chemical treating agent addition on the resulting concentrations of Cu, COD, and suspended solids. The optimum conditions determined from these experiments which were implemented at the IWWTP involve the following: pH ~ 9.5, a reduction in the FeCl_3 dosage from the design value of 200 to 100 mg/L, and addition of NaOH to bring the pH to 7, followed by addition of $\text{Ca}(\text{OH})_2$ to raise the pH to 9.5. Since implementation of these optimal conditions at the IWWTP, the plant has consistently met Taiwan pretreatment discharge standards, whereas before implementation of these conditions, the plant occasionally failed to meet the standards for Cu, COD, and suspended solids.

Implementation of the dragout reduction and rinse water reduction, plus improved operation at the IWWTP, have resulted in the reduction of sludge generation by the facility from 2.4 to 1.4 t/d (a 41.7% reduction, both of 25% solids content). The waste minimization practices have been implemented at the facility at minimal cost without noticeable deterioration in product quantity or quality.

Cb	Cobalt
Cr	Chromium
CT	Total carbonate concentration
Cu	Copper
DAF	Dissolved air flotation
EDTA	Ethylenediaminetetraacetic acid
EH	REDOX potential
F	Ratio of the flux out of the column bottom to the metal flux applied to the column (in flotation systems)
Fe	Iron
FeCl ₃	Ferric chloride
GAC	Granular activated carbon
8HQ	8-Hydroxyquinoline
H ₂ S	Hydrogen sulfide
Hg	Mercury
HTA-Br	Hexadecyltrimethylammonium bromide
IAF	Induced air flotation
IE	Ion exchange
ISP	Insoluble sulfide precipitation
IWWTP	Industrial wastewater treatment plant
k	Linear adsorption coefficient in the linear adsorption isotherm model
K _i	Stability constant
K _N	Empirical constant (corresponding to the pre-exponential frequency factor) in the Freundlich isotherm adsorption model
K _{sp}	Solubility product
1/n	Empirical constant (corresponding to the exponent) in the Freundlich isotherm adsorption model
LIE	Liquid ion exchange
M	Denotes metals
Mg	Magnesium
Mn	Manganese
Na	Sodium
Na ₂ S	Sodium sulfide
NaHS	Sodium hydrosulfide
NaCl	Sodium chloride
NaDDC	Sodium diethyldithiocarbamate
NAF	Nozzle air flotation
NaLS	Sodium lauryl sulfate
Ni	Nickel
NTA	Nitrilotriacetic acid

OX	Oxalate
PAC	Powdered activated carbon
Pb	Lead
PCB	Printed circuit board
pH	- log (H^+)
pH _{zpc}	pH of the zero point of charge
pK _{sp}	- log (K_{sp})
ppb	Parts per billion
ppm	Parts per million
QA/QC	Quality assurance/quality control
Q _{e,o}	Empirical constant in the linear adsorption isotherm model (corresponding to the amount of heavy metal adsorbed at zero concentration)
R	Rejection (in reverse osmosis applications)
RO	Reverse osmosis
SO ₂	Sulfur dioxide
SO ₄	Sulfate
SSP	Soluble sulfide precipitation
TRIEN	Triethylenetetramine
UF	Ultrafiltration
U.S. EPA	U.S. Environmental Protection Agency
Zn	Zinc

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