Removal of cadmium from wastewaters

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Introduction

There has been increasing concern over the discharge of heavy metals into the environment as evidenced by actions taken by pollution regulating agencies in various industrialized nations to impose severe discharge limits for certain heavy metals. This paper describes the source and quantity of cadmium in waste waters. The effluent limitation of cadmium is presented, followed by discussions of various treatment methods including chemical precipitation and flotation, ion exchange, adsorption osmosis as well as other effluent polishing techniques applied to both industrial discharges and municipal waste waters. Finally, several methods of cadmium recovery from industrial discharges are discussed.

I. *Sources of wastewater and cadmium concentration*

According to Stubbs[50], a total of 11,444 metric tons of cadmium were processed by 5 major industrial nations (France, the Federal Republic of Germany, Japan, the United Kingdom, and the United States) in 1974; the end products were as follows: plating 3830 t (34%), pigments 2975 t (26%), stabilizers 1676 t (15%), batteries 1646 t (14%), others including alloys 1317 t (11%). Cadmium is also used to some extent in the production of television tube phosphorus, golf courses fungicides, rubber curing agents and nuclear reactor sheilds and rods, according to an Environmental Science report 1971[13]. High concentrations of cadmium in lead mine drainage have also been reported by McKee et al.[36].

Table 1. Cadmium concentrations reported for industrial and municipal wastewaters

Sources and process	Cd concentration (mg/l)	Reference
Automobile heating control manufacturing	14–22	Gard et al.[20]
Plating rinse waters		
Automatic barrel Zn and Cd	10–15	Lowe[34]
Mixed manual barrel and rack	7–12	
Plating rinse waters (large installations)	15 average 50 maximum	Pinkerton[44]
Plating rinse waters		
0.5 gph dragout	48	Nemerow[37]
2.5 gph dragout	240	
Bright dip and passivation baths	2000 5000	Lowe[34]
Lead mine acid drainage	1000	McKee et al.[36]
Municipal raw wastewater	0.008 average 0.002–0.016	Culp et al.[10]

The quality and quantity of cadmium-bearing industrial discharges depend upon the industrial source and the degree of treatment imposed. Patterson[40,43] reported cadmium concentrations in various waste waters ranging from 0 to 1000 mg/l, as summarized in table 1. Also included in table 1 is the cadmium concentration found in municipal waste water reported by Culp et al.[10].

Cadmium exists in wastewater in many forms, including soluble, insoluble, inorganic, metal organic, reduced, oxidized, free metal, precipitated, adsorbed, and complexed forms. Treatment processes for cadmium removal must be selected to remove the existing form, or cadmium must be converted to a suitable form compatible with the removal process. The following sections discuss the effluent limitations and methods available for the removal and/or recovery of cadmium from wastewaters along with the treatment efficiency and treatment cost, when such data are available.

II. *Effluent limitations*

The maximum allowable discharge concentration for cadmium was at one time set a 10 μg/l according to Federal Register 1975[14]. However, guidelines have since been developed for effluent cadmium concentrations for different categories of industrial discharges[42] as shown in table 2. These guidelines were developed from performance data obtained from various industrial wastewater treatment plants. Variations of wastewater characteristics from industrial categories or subcategories cause differences in cadmium's susceptibility to the applied treatment technology; therefore, limitation guidelines are not all alike.

Table 2. Proposed and promulgated BATEA effluent limitation guidelines – 30-day average*

Industry category	U.S. EPA development document	Cadmium (mg/l)
Inorganic chemicals	440/1-79/007	
Chlor-alkali mercury cells		0.05
Titanium dioxide-sulfate process		0.15
Titanium dioxide-chloride ilmenite process		0.10
Chrome pigments		0.19
Copper sulfate		0.05
Iron and steel	440/81-80/024b	0.10
Steam electric power	440/1-80/029b	1.00
Range: Minimum		0.05
Maximum		0.19
Median value		0.10

* Adopted from Patterson[43].

Pretreatment discharge limitations were also developed for wastewater discharged into publicly owned wastewater treatment works. The maximum allowable concentration for cadmium was 2.0 mg/l in 1976, regardless of industrial categories, according to Olson[38]. Pretreatment standards for heavy metals were later developed for different industrial categories. As an example, the cadimum pretreatment standards for the electroplating industry[15] are given below:

	Daily maximum Cd concentration	4-day average Cd concentration
Process water, flow less than 10,000 gallons/day (gpd)	1.2 mg/l	0.7 mg/l
Process water, flows equal to or greater than 10,000 gallons/day (gpd)	1.2 mg/l	0.7 mg/l

Interest in wastewater reuse is prevalent in many countries. The Orange County Water District of the state of California, USA, has conducted studies in wastewater reclamation and ground water recharge through injection wells since 1965. Public health considerations are the ultimate concern in reuse of wastewater. Stringent standards have been set on the injection water by both the California Department of Public Health and the California Regional Water Quality Control Board[3]. The cadmium concentration is not to exceed 0.01 mg/l in the injection water. This effluent limitation is consistent with the U.S. Public Health Service Drinking Water Standards.

As seen previously, the effluent limitations for cadmium varies widely from 0.01 to 1.2 mg/l depending on industrial category, where the effluent is discharged to, and whether or not the treated effluent is reused. Nevertheless, all effluent limitations can be met by the use of a treatment system employing one or more of the currently available treatment processes.

III. *Chemical precipitation*

a) Hydroxide precipitation

Metal hydroxide precipitation with coagulants is known to be effective for metal removal, including cadmium. The solubility of the metal hydroxide is determined by solubility products (K_s) and by equations relating the metal hydroxide solid species in equilibrium with soluble free metal ion or metal-hydroxide species. Solubility product constants for a number of metals have been published by Feitknecht[16]. However, because of precipitate aging, insufficient time for the soluble metal species to establish equilibrium with the precipitated metal, incomplete solids separation, or coprecipitation and adsorption effects in wastewater, solubility products provide only a general guide to metal residuals to be expected in practice. The following cadmium hydroxide solubility products constants are given by Feitknecht[17] and Bard[4].

	Aged precipitate	Fresh precipitate
$K_{s0} = -[Cd^{2+}][OH^-]^2$	$\text{Log } K_{s0} = -14.4$	-13.7
$K_{s1} = -[Cd(OH)^+][OH^-]$	$\text{Log } K_{s1} = -11.2$	-9.5
$K_{s2} = -[Cd(OH)_2^0]$	$\text{Log } K_{s2} = -6.1$	-5.3
$K_{s3} = -[Cd(OH)_3^-]/[OH^-]$	$\text{Log } K_{s3} = -5.3$	-4.6
$K_{s4} = -[Cd(OH)_4^{2-}]/[OH^-]^2$	$\text{Log } K_{s4} = -5.6$	-4.9

pH of minimum cadmium hydroxide solubility is 11.5.

Jenkins[28] reports that freshly precipitated cadmium hydroxide leaves approximately 1 mg/l of cadmium ion in solution at pH 8, but only 0.1 mg/l at pH 11. Similarly, Anderson[1] reports an effective removal of cadmium at pH 9.7. In a study of cadmium precipitation using hydrated lime for the treatment of an electric arc furnace blowdown at a steel mill, Brantner[5] reports that lime precipitation at pH 9.9 and clarification removed total cadmium from 1.66 mg/l to 1.15 mg/l while soluble cadmium was removed from 1.23 mg/l to 1.12 mg/l. Nearly all of the residual cadmium in both clarifier and filter effluents was soluble, indicating that the residual level was limited by the solubility rather than the effectiveness of solid-liquid separation.

Co-precipitation with other metal hydroxides can be more effective and affect the pH at which the minimum cadmium solubility occurs. Both Anderson[1] and Weiner[53] indicate co-precipitation with iron hydroxide at pH 8.5 resulting in near complete removal of cadmium. It was found by El-Gohary[12] that in alkaline precipitation using sodium hydroxide, co-precipitation with 100 mg/l of ferric chloride at pH 9.0 removed 97% of cadmium while co-precipitation with 100 mg/l of aluminum sulphate at pH 9.0 removed only 91.5% of cadmium. Using lime in alkaline precipitation, the same report indicates that a co-precipitation with 100 mg/l of either ferric chloride or aluminum sulphate resulted in better than 98% removal of cadmium. With coagulant aid addition (Separan NP-10) at 1-2 mg/l to lime precipitation of a plating waste, Hanson[22] reported an effluent with pH 9.0 and cadmium concentration of 0.54 mg/l. Since the effluent also contained 2 mg/l of suspended solids, it was not known how much of the residual cadmium was in the particulate form and how much in the dissolved form. The impact of solids removal on effluent concentration has been reported by Chalmers[7]. The effluent cadmium concentration was 0.7 mg/l after cyanide-chromium treatment plus neutralization and sand filtration. The effluent cadmium concentration was further reduced to 0.08 mg/l using 10-h settling followed by paper press filtration.

Cadmium precipitation is inhibited in the presence of complexing agents such as cyanide. Cyanide removal is, therefore, imperative prior to cadmium precipitation from plating baths and plating rinse waters containing cyanide. In this regard, the development of a cyanide-free cadmium plating bath with acceptable

product quality can be an answer to simplify the treatment needs.

It was recently found by Patterson[43] that carbonate alkalinity initially present in the wastewater, or induced into the wastewater as a result of treatment, could have a significant effect on alkaline precipitation of cadmium. A reduction in cadmium solubility with increasing carbonate concentration was found at treatment pH values below pH 11. Cadmium solubility was also found to be more sensitive to carbonate than to treatment pH level. For example, at pH 8.2–8.4, soluble cadmium was 1.7 mg/l at total carbonate (C_T) of 6.7 mg/l, versus 0.6 mg/l at C_T of 9.8 mg/l. At pH 7.4–7.6, soluble cadmium ranged from 62 to 2.6 mg/l as C_T varied from 3.7 to 5.7 mg/l. Carbonate, therefore, adds to a long list of interfering substances and circumstances affecting the cadmium precipitation process. The interfering characteristic may reflect site-specific or geographical factors as well as factors associated with a particular industrial category. The nature and degree of interference should be fully assessed in each specific case before any effective treatment system can be designed using the hydroxide precipitation process for cadmium removal.

b) Carbonate precipitation

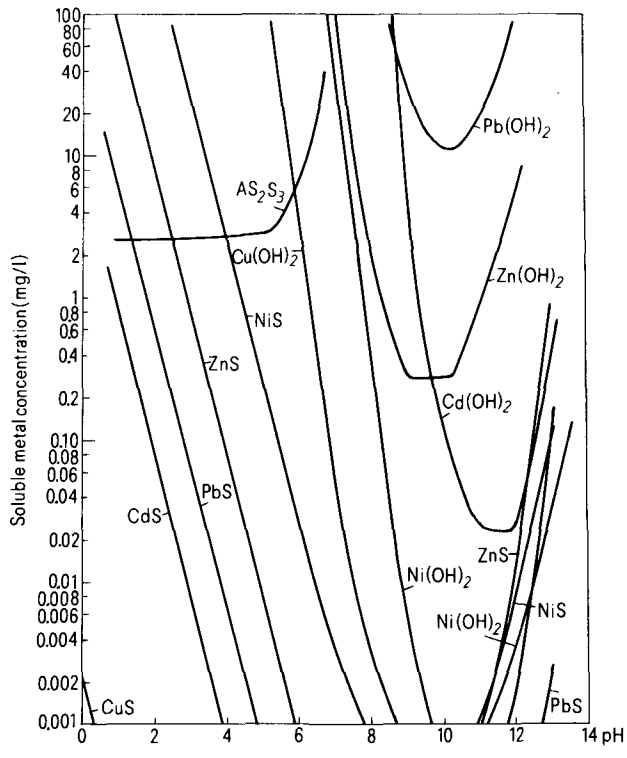
Carbonate precipitation of cadmium can be successful. A laboratory study by Patterson[41] shows that by adding sodium carbonate, treatment nearly equivalent to that for cadmium hydroxide was obtained with cadmium carbonate ($C_T = 10^{-1.33}$ mole/l, or 2800 mg/l) at pH 8.4 which yielded 1.2 mg/l cadmium compared to 0.2 mg/l for hydroxide treatment at pH 10.4 and 126 mg/l at pH 8.6. Consequently, treatment at lower pH can be achieved with the carbonate system. In addition, lower volumes of denser sludge can be obtained with relative filtration rates approximately twice that of the cadmium hydroxide sludge.

Barntner's study in 1981[5] compared pilot plant tests of carbonate precipitation with hydroxide precipitation of cadmium from an electric arc furnace blowdown. At a Na_2CO_3 dosage of 650 mg/l and a pH ranging from 8.3 to 8.7, the total cadmium concentration was reduced from 1.37 mg/l down to 0.14 mg/l in the clarified effluent. Soluble cadmium concentration was reduced from 0.79 mg/l down to 0.1 mg/l and in another test from 1.2 mg/l down to 0.04 mg/l. The clarified effluent (350 gpd/ft^2 or 14.3 m^3/day-m^2) was polished by filtering through a dual media filter (5 gpm/ft^2 or 204 l/min-m^2) which further improved the effluent quality (0.02–0.06 mg/l total cadmium) comparable to that of the hydroxide precipitation-clarification-filtration system. El-Gohary[12] reported 98% cadmium removal at pH 7.5 using 3500 mg/l of calcium carbonate. Despite the little attention given to the carbonate precipitation process, it is apparent that the process can be equally successful in cadmium removal.

c) Sulfide precipitation

There are many attractive features associated with the sulfide precipitation process in metal removal including cadmium. A high degree of metal removal can be attained over a broad pH range. Cadmium can be effectively precipitated at very low pH because of the solubility of CdS is very low at pH below 4. Figure 1 shows the calculated solubilities of metal sulfides and metal hydroxides. The high reactivity of sulfides shortens the detention time required for the process. According to Whang[54], metal sulfide sludge exhibits better thickening properties and dewaterability than metal hydroxide sludge from the hydroxide precipitation process. In addition, metal sulfide sludge is three times less subject to leaching at pH 5 as compared to hydroxide sludge and, therefore, final disposal is easier and safer. Although metal sulfide precipitates are very fine, anionic floculant can be used to facilitate liquid-solid separation.

Scrubber wastes containing high concentrations of heavy metals including cadmium from 10.5 mg/l to 15.0 mg/l were treated with a hydroxide-sulfide precipitation process reported by Schwitzgebel[48]. Lime was added to the wastes to raise the pH to 5.0–6.0. The sulfide precipitation reaction pH was varied between 7.5 and 8.5. The maximum metal separations in the water were obtained with 0.6 times of the stoichiometric quantity of sulfide required to react with Cd + Cu + Zn + Fe + Pb and at a final pH of 8.0. Both sulfide and hydroxide precipitates of metals were formed. In all cases, 98–99.6% of all heavy metals were removed with the effluent (precipitation-clarification - multi media filtration) containing only 0.05–0.08 mg/l of cadmium.



Adapted from M. Blythe et al., Characterization of Boliden sulfide-lime precipitation system. USEPA report, 600/S2-81-081, August 1981.

Full scale testing of the sulfide precipitation process was also reported by Schwitzgebel[48] at the Boliden Metall Corporation, Skelleftehamn, Sweden. The wastewater was partially neutralized to pH 2.5–3.0 with NaOH, and then Na_2S was added. The removal of all heavy metals with the exception of zinc was complete. Cadmium concentration after sulfide precipitation-polymer sedimentation-multi media filtration was reduced from 4 mg/l down to 0.01 mg/l.

The parallel testing of 3 precipitation processes to remove metals from an electric arc furnace blowdown as reported by Barntner[5] also indicates the successful application of a hydroxide-sulfide process for metal removal. Ferrous sulfide (FeS) was applied to maintain a dosage of 130 mg/l FeS and pH was maintained at 8.0–8.5 by addition of lime. The FeS dosage of 130 mg/l was selected to be 1.5 times the calculated stoichiometric requirement for precipitation of all the metals. At pH 8.2, total cadmium was reduced from 3.3 mg/l to 0.18 mg/l (clarified effluent) and to 0.06 mg/l (filtered effluent) while soluble cadmium was reduced from 0.4 mg/l to 0.02 mg/l (both classified and filtered effluents). The removal was comparable or better than the hydroxide precipitation and the carbonate precipitation processes.

d) Other chemical processes

Sodium borohydride precipitation. The use of sodium borohydride ($NaBH_4$) as a reducing agent is a cost-effective alternative to remove cadmium from wastewater. The $NaBH_4$ process is irreversible, extremely rapid, and results in nearly total removal of the dissolved metal even at low initial concentration. It also offers the potential to recycle a significant portion of the metal since the metal is chemically reduced to the elemental state, usually as a compact precipitate.

Sodium borohydride may be used as the primary treatment procedure or in conjunction with or following alkaline neutralization. The stoichiometric quantity of $NaBH_4$ required is $^1/_{12}$ the weight of cadmium reduced. In actual practice the borohydride to cadmium ratio is usually somewhat higher, since other reducible compounds may react with the borohydride. When a low initial level of dissolved cadmium (2–15 mg/l) is present in the wastewater, thorough mixing of the $NaBH_4$ is essential. Sodium borohydride is generally used as an aqueous caustic solution which is stored and handled in the same manner as 50% caustic soda.

Cook[9] reports successful cases of $NaBH_4$ application in metal removal and/or recovery. One of these cases concerns the removal of silver and cadmium complexes in a wastewater from a lithographic film coating process in Glen Cove, New York. This process water is first pretreated to remove photographic gelatin and dyes as they may interfere with the borohydride reduction and solid-liquid separation steps. After pretreatment, the process water contains 10–120 mg/l of silver and 5–60 mg/l of cadmium. The silver is present in the form of finely divided insoluble silver halides with some soluble silver species present. Ferric chloride is introduced into a 7500-gal (28.4 m^3) reactor followed by caustic soda to adjust to pH 11 prior to borohydride addition. The reactor is stored continuously. At pH 11, substantial amounts of cadmium crystallize and ferric hydroxide also occur, improving the subsequent solid-liquid separation. Sodium borohydride is then added over a 15-min period followed by mild agitation for 30 min to improve the setting characteristics of the precipitate. After 60 min of setting, the supernatent is filtered through a precoated filter. The filtrate has averaged a consistent 0.09 mg/l for both silver and cadmium in the final discharge. The alkaline-$NaBH_4$ process in this case was evaluated versus alkaline precipitation sulfide precipitation, and carbon absorption. The alkaline-$NaBH_4$ process gave the best overall result based on effluent silver and cadmium concentrations, cost and suitability of the precipitated silver for further recovery.

Hydrogen peroxide oxidation-precipitation. This process which simultaneously oxidizes cyanides and cadmium to form cadmium oxide precipitate is called Kastone process[2]. It is claimed that cadmium oxide precipitates better than cadmium hydroxide resulting in better solid-liquid separation and therefore better overall removal. This proprietary process is reported as suitable for small plating operations but more detailed information on dosage requirement and effluent cadmium concentration is lacking.

Ozonation. Metal complexes in solution disappear upon ozonation. Krause[33] conducted tests on ozonation of organically complexed heavy metals. Experimental studies indicated that the complexing ability of chelates was destroyed during ozonation of Cd-EDTA, Zn-EDTA, and Ni-EDTA. Shambaugh[51] reported that in general an ozone contact time on the order of 10 min would destroy metal-EDTA complexes. A much shorter contact time would be required to reduce uncomplexed metal solubilities when the metal has a higher oxidation state. Uncomplexed metals such as zinc and cadmium which do not possess higher oxidation states do not exhibit a solubility reduction upon ozonation. Data and information leading to a successful design of a full scale treatment plant removing cadmium by ozonation do not exist to date.

Electroflotation. The successful removal of cadmium and cyanide simultaneously has been demonstrated by Poon[45], using an electroflotation process. The specially designed reactor consists of a stainless steel screen cathode placing above a 5-cm layer of sea water, and a platinated columbium screen serving as the anode below the cathode. The plating wastewater is placed on top of the cathode. Hypochlorite and chlorine gas generated from the sea water by the anode oxidize cyanide and liberate cadmium from the cyanide-cadmium complex preceeding alkaline precipitation. Free oxygen and ozone produced at the anode also assist in destroying the cyanide-cadmium complex. Simultaneously cathodic generation of hydroxides raise the pH resulting in alkaline precipitation of cadmium which is carried up to the surface by the rising gas bubbles. With 20 mg/l of cadmium and 45 mg/l of cyanide, it takes 53 min or longer to

reduce to 0.2 mg/l cadmium and 0.5 mg/l cyanide with a power consumption of 0.23–0.40 kwh/g of cadmium removal.

A performance equation was developed for cadmium removal by electroflotation as in the following:

$R = 4.45\ P^{-0.36}\ D^{0.37}\ C^{0.66}\ S^{0.077}\ H^{-0.91}$ where R is Cd removal in g/kwh, P is power input in W, D is wastewater depth in the reactor in cm, C is initial Cd concentration, S is electrode spacing in cm, and H is initial pH of the wastewater. The equation indicates that a combination of lower power input and deeper wastewater column make more effective treatment. For operation, the residual chlorine concentration in the solution can be monitored as a ocntrol. The treatment process can be terminated 3–5 min after the residual chlorine has reached 1.0 mg/l, with both cadmium and total cyanide meeting the effluent quality standards.

The treatment system is compact and easy to operate. Operation requires no skill greater than that necessary for electroplating. A cost analysis shows a total treatment cost of US$0.76/m^3 (1982 dollar value). The cost is competitive with that of alkaline precipitation with lime followed by clarification-filtration.

IV. *Physical treatment*

a) Ion exchange

Ion exchange is capable of removing heavy metals including cadmium. The cations cadmium are exchanged for H_2 or Na. The cation exchange resins are mostly synthetic polymers containing an active ion group such as HSO_3. When all the ionized exchange sites are replaced, the resin can be regenerated by passing a concentrated solution of ions through the bed which reverses the chemical equilibrium. The ion exchange system may be put in series with more than one bed in parallel. Mixed bed systems have also been marketed for heavy metal removal where high regeneration frequency or large ion exchange volumes are required, a moving bed ion exchanger can be used which enables continuous regeneration and eliminates a large parallel system.

Na-type zeolite can be used successfully for cadmium removal. According to Onodera[39], natural zeolite of 10 mesh size was dipped in a 10-fold solution of boiling 1 N NaCl solution to obtain Na-type zeolite. Wastewater containing 10 mg/l Cd^{2+} was adjusted to pH 4.5, mixed with the Na-type zeolite 800 g/m^3 wastewater, stirred for 1 h and settled. The Cd^{2+} removal was about 90%, compared to about 30% with natural zeolite. Another resin was also found to be very effective in removing heavy metals including cadmium from an industrial wastewater containing Pb, Zn, Hg, Cd, Cu, Ni, Al, Ca, Cr^{3+}, Fe, and Ag[8]. It was reported that an industrial wastewater containing Hg 1.2, Cd 0.72, Cu 0.1, Pb 0.2, and Ca 202 mg/l respectively was treated with a thiocarbanic acid group-containing phenolic resin to remove Hg and then with an iminopropionic acid salt group-containing epoxy resin. The Hg, Cd, Cu and Pb concentrations were respectively 0.1 µg/l, and 0.05, 0.1, and 0.05 mg/l in the effluent, after 5000 l of wastewater/l resin.

Another promising exchanger material for effective removal of Cd^{2+} and other heavy metal is chromium ferrocyanide gel, reported by Srivastava[49]. The inorganic gel is prepared by adding chromium chloride gradually to potassium ferrocyanide. The produce with an exchange capacity as great as 3.65 meq/g is obtained with $Cr^{3+} = 0.071$ M, $Fe^{2+} = 0.218$ M, $H^+ = 0.01$ M and mixing ration of $Cr^{3+}/Fe^{2+} = 0.327$. The exchanger shows a great selectivity for Ag^+, Cu^{2+}, Tl^+, Zn^{2+}, Co^{2+}, Mn^{2+} and Fe^{3+}. Wastewater from an industry containing Cd^{2+}, Zn^{2+}, and Mn^{2+} equivalent to 150, 200, and 250 mg/l was allowed to pass through a column of chromium ferrocyanide gel (15 cm × 0.85 cm^2) at a flow rate of 0.8 ml/min. The effluent was found to be completely free of these ions and also did not show the presence of Cr or Fe ions even in traces. For batch operation, a stirring time of 1 h is adequate for equilibration with this exchanger material. The chromium ferrocyanide gel is stable in salt and acid solutions up to a concentration of 2 M, but is unstable in alkali solutions. However, only partial recovery of cadmium (25%) from the exchanger material is possible.

b) Adsorption

Aluminosilicate adsorption. Several commercially available aluminosilicate adsorbents are able to remove Cd^{2+} from wastewaters. The type tested by Huang[26], Zeolite A, Blazer, Mordenite, Zeolex 23, Zeo 49, Zeosyl 100, were able to adsorb Cd^{2+} successfully at pH 9. Mordenite, a crystalline solid exhibited the greatest Cd^{2+} adsorption capacity at pH 5 and performed as well as other species. All of them could achieve near 100% removal of Cd^{2+} at a dose of 3–5 g absorbent/l. It is therefore possible to remove Cd^{2+} from plating wastewaters to 0.1 mg/l. At pH 3.0, the Mordenite species exhibited decreasing Cd^{2+} adsorption. This is a feature promising for regeneration of Mordenite with strong acid.

Starch xanthate adsorption. Starch xanthate and a cationic polymer such as polyethylenimine forming a complex can precipitate heavy metal from solutions. The process is expensive because almost all cationic polymers are expensive. However making starch xanthate from corn starch made insoluble by crosslinking eliminates the need for the expensive polymer. The crosslinked corn starch is commercially available. It is combined with sodium and sulfur by reaction with carbon disulfide and lye (NaOH), yielding insoluble sodium starch xanthate. In metal solutions it acts like a resin, exchanging the sodium for the metal.

According to Wing[55], cadmium concentration is reduced from 56 mg/l to 9 µg/l with an initial pH of 3.0. The required solid starch xanthate is in the range of 0.037 to 0.0859 g/50 ml for such efficient removal. If the initial pH is greater than 5, stoichiometric quantity (one xanthate group per metal ion) of xanthate is sufficient. Since the solid starch xanthate is basic, the pH of the treated solution will increase, and

effective removal is always achieved in the pH range of acceptable discharge. The process is effective over a pH range from 3 to 11 and in the presence of up to 10% salt. Only a few minutes would be required to complete the removal. The cost of 500 g of dry insoluble starch xanthate containing 8% sulfur was US$0.20-0.22, 1975 dollars. The product has a metal binding capacity of 1.1 moles metal/g.

Carbon adsorption. Certain commercially available carbons can be very effective in removing Cd^{2+} from electroplating wastewaters. Nuchar S-A and Nuchar S-N powdered carbons are found by Huang[24] to have a Cd^{2+} adsorption capacity far superior to that of granular carbons such as Filtrasorb 400 and Darco HD 3000. Pore size is probably not a critical parameter for equilibrium absorption capacity. Instead the superiority of powdered carbons over the granular carbons is due to differences in the chemical reactivity of their surfaces. According to Huang[23], powdered activated has low pH_{zpc} (pH at zero electrophoretic mobility) values and excellent adsorption capacity for cationic metal ions while granular activated carbon, having high pH_{zpc} values, is relatively poor for metal ion adsorption.

The kinetics of adsorption in Huang's study[26] are favorable for both the fuoroborate and cyanide systems. The maximum adsorption level is reached within the first 10 min of contact of the carbon with the wastewater. This rapid rate of removal is not affected by variations in pH, ionic strength, carbon/Cd^{2+} concentration, temperature and mixing rate. The fast adsorption rate is considered a significant advantage over the chemical precipitation process which is often a slower process.

For a given carbon dose, the adsorption density increases for increasing Cd^{2+} concentration in solution. However the percent of Cd^{2+} removed decreases with higher initial adsorbate concentration. This phenomenon is typical of the carbon adsorption process. The same phenomenon is not as noticeable at pH values greater than 8 due to precipitation effects in the fluoroborate bath and cadmium cyanide complex formation in the cyanide system. At pH 7 and a carbon/Cd ration of 0.25 g/mg, as much as 85% Cd^{2+} removal is obtained in the fluoroborate system.

For both the fluoroborate and cyanide wastewaters, the adsorption density is approaching its maximum level in the neutral pH range. This constitutes an advantage over many chemical precipitation techniques requiring pH adjustment to 10-11 for maximum removal. Because of the high molar ratio of cyanide/Cd^{2+} of 10:1 in the typical cyanide system, resulting in competition between the two ions for available carbon sites, Cd^{2+} adsorption is not as rapid as in the fluoroborate system. The adsorption rate can be enhanced by either increasing the carbon dose or by reducing the initial cyanide concentration in the wastewater.

For continuous flow treatment application, Huang[25] uses a packed column in which the powdered carbon Nuchar S-A is aggregated into beads of a size of 0.6 mm in diameter using polyvinylalcohol and glutaraldehyde. The aggregated powdered carbon exhibits similar adsorption capacity as the original activated carbon (1.1337 g Cd^{2+}/g carbon); although the kinetics of adsorption is slower. The study shows a column packed with a gross mass of 41 g of aggregated carbon can be used for 4 consecutive runs, with acid regeneration following each run, and treat 173 l (or 1587 bed volume) of Cd^{2+} containing tetrafluoborate plating wastewater before losing its adsorption capacity. Chemical regeneration using strong acids such as HC1, $HC10_4$, and H_2SO_4 gives good regeneration results.

c) Foam flotation

This technique relies upon a surfactant that causes a nonsurface-active material to become surface active forming a product that is then removed by bubbling a gas through the bulk solution to form a foam. Foam flotation can be divided into 3 catagories, namely, ion flotation, precipitate flotation, and adsorbing colloid flotation.

Ion flotation is a process that involves the removal of a nonsurface-active ion (a colligend) by the addition of a surfactant (a collector) which yields an insoluble product. Kobayashi[29] reports the effects of anionic and cationic surfactants on the ion flotation of Cd^{2+}. Sodium α-sulfolaurate is determined to be most effective for the flotation of Cd^{2+} ion achieving as high as 97% removal. About 97% of Cd^{2+} ions could be floated at a pH of 11.3 when cationic surfactant is used with bentonite. Ferguson[18], however, reports that increased ionic strength, Ca^{2+}, and phosphate interference make ion flotation impractical for Cd^{2+} removal.

Precipitate flotation is the process in which the nonsurface-active material forms a precipitate with something other than the collector, which in turn makes surface active by the collector. Adsorbing colloid flotation is defined as the removal of dissolved material by adsorption on colloidal particles followed by the removal of colloid particle, dissolved material, and the collector by flotation. These 2 flotation processes, unlike the ion flotation process, do not require stoichiometric amounts of the collector since only electrical attraction exists between the collector and the precipitate but sufficient surfactant must be used to form stable foam. Kolayashi[30] also investigates the removal of Cd^{2+} ions from an aqueous solution by adsorbing particle flotation using bentonite and a cationic surfactant, hexa-decyltrimethylammonium chloride. It is found that the most suitable method is to conduct flotation in the region of the coagulation flotation of bentonite.

Huang[27] studies both precipitate flotation and absorping colloid flotation of Hg^{2+} and Cd^{2+} from aqueous systems. Sodium lauryl sulfate and hexadecyltrimethylammonium bromide (HTA) are used as collectors. $Fe(OH)_3$, $A1(OH)_3$, FeS, and CuS are used as adsorbing colloids. Floc foam flotation of both metals with CuS and HTA is very effective resulting in residual Hg^{2+} concentration as low as 5 ppb and Cd^{2+} as low as 20 ppb. Floc foam flotation of Cd^{2+} with FeS and HTA yields residual Cd^{2+} as low as 10 ppb.

V. *Cadmium recovery*

Various techniques are available to recover cadmium from wastewaters, among which evaporation is an established method and reverse osmosis is a very promising one.

a) Evaporation

Single-stage or two-stage (double effect) recovery unit can be used for cadmium recovery. The single-stage unit is more common but a two-stage unit saves steam (energy). The use of atmospheric evaporative towers for recycling reusable chemicals in the electroplating industry is reported by Kolesar[31]. Atmospheric evaporative recovery is economical for rinses bearing the dragout from processes not self destructive by nature (e.g. Zn, Cd, Cu, Ni, and Cr plating baths). Schrantz[47] reports evaporation as a technique to separate Cr, Ag, and Cd from rinse water for subsequent reuse in the plating baths. Three 2.4-m (8-ft) by 3.0-m (10-ft), by 5.6-m (15-ft) high evaporations handle 189 l/h (50 gal/h) of rinse water each and form a closed loop with the Cr, Ag, and Cd plating baths. No sludges are produced, and there is no connection to sewers. A 20-month payback period is projected for these evaporators. A single-effect, 378 l/h (100 gal/h) evaporator is installed on a 5-barrel, 3-m^3 (800 gal) bath cadmium plating line in a Connecticut plant, according to Gallo[19].

Both capital and operational costs for evaporative recovery systems are high. Chemical recovery and water reuse values must offset these costs for evaporative recovery to become economically feasible. A closed loop system design for rinse and plating is most attractive.

b) Reverse osmosis

Reverse osmosis with cadmium cyanide bath is less developed, but suitable membranes are now available to make it practical. There is also promise that reverse osmosis will be cheaper and less energy-consuming than evaporative recovery. Donnelly[11] examines reverse osmosis treatment of plating bath rinse waters, emphasizing closed loop operation with water recycle for rinsing and concentrated chemical recycle for plating baths. Three commercially available membrane configurations, i.e., tubular (cellulose acetate), spiral wound (cellulose acetate), and hollow fiber (polyamide) are tested with diluted plating bath wastewaters. Watts-type nickel, nickel sulfamate, copper sulfate, copper pyrophosphate, nickel fluoborate, zinc chloride, and copper, zinc, and cadmium cyanide are all found attractive systems for treatment by reverse osmosis. Kosrrek[32] reports Cd^{2+} removal amounts to 95–99% by reverse osmosis.

c) Other cadmium recovery systems

Other promising cadmium recovery systems include electrochemical ion exchange and adsorption. Roof[46], is successful in recovering cadmium from plating solutions by the use of an electrochemical cell with graphite anodes. Cadmium is deposited on a carbon-fiber cathode while cyanide is removed at the anode. Recovery of cadmium is either by electrowinning or dissolution into a heated cyanide strip solution. Full-time use of this system is expected to yield a high degree of cadmium recovery alone with an effluent Cd^{2+} concentration of 0.4–0.6 mg/l.

Treatment of wastewater containing cadmium by ion exchange and adsorption has been discussed previously. Ion exchange can be used as a polishing treatment or recovery process. The concentrated solution obtained upon regeneration of the ion exchange resin is, in general, more suitable for economical recovery procedures than the initial dilute cadmium waste streams. The same general rule applies to cadmium recovery from adsorbents. Wing[55] reports successful recovery of cadmium and other metals by washing the sludge with nitric acid in an insoluble starch xanthate process. Similarly strong acids such as HCl, $HClO_4$, and H_2SO_4 can be used to regenerate activated carbon for cadmium adsorption. A concentration factor of 30 can be obtained using 1M H_2SO_4 solution according to Huang[24]. A wastewater containing 10^{-4} M Cd^{2+} therefore can be concentrated to approximately 3.3×10^{-3} M. In the case of cyanide baths there may be concern that acid-stripping produces hazardous cyanide gas. However, it is known that once adsorbed, cyanide ions are oxidized to less hazardous CNO^- species on the carbon surfaces.

VI. *Cadmium removal from domestic wastewater treatment*

Although most publicly owned treatment works are using secondary or biological treatment processes not designed for heavy metal removal, some heavy metal, including cadmium can be removed by biological uptake and by sludge adsorption. Olson[38] reports the 1979 annual average removal of cadmium from a trickling filter treatment plant to be 77.5%, producing an effluent of 0.04 mg/l cadmium on the average. The range of removal for that year is 58–92%.

In a pilot plant study by Maruyama[35], 5 mg/l of Cd^{2+} as $CdCl_2$ is added to raw municipal wastewater which then undergoes chemica coagulation, settling, dual media filtration, and activated carbon adsorption treatment. Chemical coagulants are iron (ferric sulfate, 45 mg/l Fe), low lime (260 mg/l lime and 20 mg/l Fe as ferric sulfate), and high lime (600 mg/l lime). With the high lime system, the respective accumulated removals for coagulation-setting, filtration and adsorption are 97, 98 and 99.7%. Both the low lime and the ion systems are less effective but a total removal of 98–99% still can be achieved.

In an extensive literature review and technical evaluation of various treatment processes in removing heavy metals from municipal wastewater treatment plants, Culp al.[10] summarize the cadmium removal in the following two tables:

Table 3. Literature and actual plant survey data (Cd concentration in raw wastewater, average 0.008 mg/l: range 0.002–0.016 mg/l)

Treatment process	Range of removal (%)	Average removal (%)
Activated sludge	30–64	54
Trickling filtration	0–5	0
Coagulation-sedimentation (ferric addition)	61–75	68
Coagulation-sedimentation (lime)	0–95	30
Coagulation-sedimentation (alum)	68–76	72
Filtration after biological treatment		32
Filtration after physical-chemical treatment		38
Activated carbon adsorption	0–23	0
Ground injection (infil-percolation)	12–13	

Table 4. Potential of cadmium removal from wastewater (based on plant operating data and results of various test programs)

Treatment process	Average removal (%)	Average effluent concentration (mg/l)
Activated sludge	71	0.002
Trickling filter	38	0.005
Rotating biological contactor	57	0.003
2-Stage nitrification	71	0.002
2-Stage nitrification-denitrification	71	0.002
2nd effluent + filtration	71	0.002
Alum addition to aeration basin	92	0.001
$FeCl_3$ addition to primary treatment	91	0.001
Tertiary lime treatment of nitrified effluent	98	0.0002
Tertiary lime treatment followed by ion exchange	98	0.0002
Carbon adsorption of 2nd effluent	71	0.002
Carbon adsorption of 3rd lime effluent	98	0.00002
Carbon adsorption of 3rd lime, nitrified	98	0.0002
Carbon adsorption of 3rd lime, ion exchange	98	0.0002
Physical-chemical, with lime	38	0.005
Physical-chemical, with $FeCl_3$	80	0.002

It appears that secondary treatment alone or secondary treatment followed by nitrification-dentrification cannot remove cadmium from municipal wastewater by more than 71%. Physical and/or chemical method of polishing the effluent is required to reduce cadmium to a concentration safe to be discharged into the natural environment. It would be very expensive to treat large quantities of wastewater to reduce cadmium to such a low level. Applying treatment at the source without discharging into a sewer leading to a municipal treatment plant is a most cost-effective approach.

VII. *Cost of cadmium removal*

In this section, the cost comparison of cadmium treatment and cadmium recovery systems are given. Four treatment systems are compared, namely, alkaline neutralization precipitation with lime; sulfide precipitation using insoluble FeS; ion exchange with cation exchange resin; and activated carbon adsorption. The alkaline precipitation process includes coagulation-clarification-sand filtration and discharge to sewer line. Sludge is thickened and dewatered before final disposal. The sulfide precipitation process uses two-stage neutralization while FeS and polymer are added simultaneously in a third precipitation tank. Sludge filter is used to dewater CdS and $Fe(OH)_2$ solids without thickening. The total annual costs provided by Huang[24] are estimated or taken from the Centec report 1979[6] for alkaline precipitation, and from a U.S. EPA report 1980[52] for sulfide precipitation, as well as Zanitsch's[56] work for ion exchange. Cost comparisons are listed in table 5.

Assuming that sludge treatment and disposal is operable, alkaline precipitation is by far the most cost-effective treatment process. However ion exchange and carbon adsorption processes offer an opportunity to recover cadmium and water for reuse which could offset some of the costs.

A cost comparison for 2 cadmium recovery systems is given by Gurklis[21]. The evaporative recovery system uses a 2-stage 50-gallon evaporative recovery unit. The associated costs are presented in table 6. A reverse osmosis recovery unit handling the same rate of flow at 50 gal/h (187.4 l/h) is less costly resulting in a lower operating cost as shown in table 7. It should be noted also that some saving in chemical cost is also

Table 5. Cost comparisons of cadmium treatment

Treatment process	30 gpm	40	60	80	100
Alkaline precipitation	50	55	62.5	70	80
Sulfide precipitation	110	175	–	–	–
Ion exchange	60	75	110	136	160
Carbon adsorption column	–	77	95	110	125
complete mix	–	90	102	110	120
Total annual cost	$1,000				

Table 6. Costs for evaporate recovery of cadmium cyanide solution double-effect 50 gal/h unit

Investment costs	
Purchased cost	$30,000
Cost of installation and auxiliary items	10,000
Operating costs	
Interest/year (10%)	2,000
Depreciation/year (20%)	8,000
Steam at $4.00/1000 lb., 800,000 lb.	3,200
Electricity at 4¢/kwh, 42,000 kwh	1,680
Labor at $12.00/h, 240 h	2,900
Total operating costs	$17,780
Area plated/year (240 days)	480,000 ft^2 (44,600 m^2)
Recovery unit cost	$0.37/$ft^2$ ($4.0/$m^2$)

Table 7. Costs for recovery of cadmium cyanide plating solution by reverse osmosis

Investment Cost	
Operating costs	
Interest/year (10%)	1,000
Depreciation/year (20%)	4,000
Electric (50 kwh/day)	500
Maintenance (5%)	1,000
Membranes	1,500
Total operating costs	$8,000
Area plated/year	480,000 ft^2 (44,600 m^2)
Unit recovery cost	$0.17/$ft^2$ ($1.8/$m^2$)

realized in both recovery systems which would otherwise be spent in a treatment system. The saving, approximately $3,300/year is therefore a credit against the treatment system.

1 Anderson, J.S., Phillips, J.M., and Schriver, C.B., Water contamination by certain heavy metals. Paper presented at the 44th Annual Meeting, Wat. Poll. Control Fed., 1971.
2 Anonymous, New process detoxifies cyanide wastes. Envir. Sci. Technol. *5* (1971) 496-497.
3 Argo, D.G., and Culp, G.L., Heavy metals revomal in wastewater treatment processes: part I, Water and sewage works, vol. 119, No. 8, pp. 62-65.
4 Bard, A.J., Chemical Equilibrium. Harper and Row, New York 1966.
5 Brantner, K.A., and Cichon, E.J., Heavy metals removal: Comparison of alternative precipitation processes. Ind. Waste Proc., 13th Mid. Atlantic Conf., Ann Arbor Science 1981, p. 43-50.
6 Centec Co., Environmental pollution control alternatives: Economics of wastewater treatment alternative for the electroplating industry. U.S.E.P.A. Report No. 625/5-79-016; 1979.
7 Chalmers, R.K., Pretreatment of toxic wastes, Water Poll. Control, London 1970, pp. 281-291.
8 Chemical Abstract, Heavy metal removal from wastewater, Japan Patent 80 54, 084, 1980, Chemical Abstract *93* (1980), 155451.
9 Cook, M.M., and Lander, J.A., Sodium borohydride controls heavy metal discharge. Pollut Engng *13* (1981) No. 12.
10 Culp, Wesner, and Culp. Water reuses and recycling, vol. 2, Evaluation of treatment technology. US Department of Interior, Office of Water Research and Technology, OWRT/RU-79/2, 1979.
11 Donnely, R.G., Reverse osmosis treatment of electroplating wastes. Plating *61* (1974) 432.
12 El-Gohary, F. Lasheen, M.R., and Abdel-Shafy, H.I., Trace metal removal from wastewater via chemical treatment, Proc. 1st int: Conf. Management and Control of Heavy Metals in the Environment, London 1979.
13 Environmental Science and Technology report. Metals focus shifts to cadmium. *5* (1971) 754-755.
14 Federal Register, 1975, vol. 40, No. 248, December 24, p. 59570.
15 Federal Register, 1981, vol. 46, No. 18, January 28, p. 9469.
16 Feitknecht, W., and Schindler, P., Solubility constants of metal oxides, metal hydroxides and metal hydroxide salts in aqueous solution. Pure appl. Chem. *5* (1962) 130.
17 Feitknecht, W., and Schindler, P., Pure appl. Chem. *6* (1963) 130.
18 Ferguson, B.B., Hinkle, C., and Wilson, D.J., Foam separation of lead (II) and cadmium (II) from wastewater. Separation Sci. *9* (1974) 125.
19 Gallo, B.R., and Culotta, J.M., Save on plating waste system. Wat. Wastes Engng *9* (1972) A18-A19.
20 Gard, S.M., Snavely, C.A., and Lemon, D.J., Design and operation of a metal wastes treatment plant. Sew. ind. Wastes *23* (1959) 1429-1438.
21 Gurklis, J.A., and Vaeler, L.E., Cadmium plating with environmental restriction, Proc. Workshop on Alternatives for Cadmium Electroplating in Metal Finishing NTIS PB-298 841, p. 104-112, 1979.
22 Hansen, N.H., and Zabban, W., Design and operation problems of a continuous atumatic plating waste treatment plant at data processing division, IBM, Rochester, Minnesota. Proc. 14th Purdue Industrial Waste Conf. 1959, p. 227-249.
23 Huang, C.P., and Ostovic, F.B., The removal of Cd (II) from dilute aqueous solutions by activated carbon adsorption. J. envir. Engng Div., ASCE *104* (1978) 863-878.
24 Huang, C.P., and Smith, E.H., Removal of Cd (II) from plating waste by an activated carbon process, Ch. 17, Chemistry in Water Rinse, vol. 2, p. 355-399. Ed. W.J. Cooper. Ann Arbor Science 1981.
25 Huang, C.P., and Wirth, P.K., Activated carbon for the treatment of cadmium wastewater. Paper presented at the National Conf. Hazardous and Toxic Wastes Management, June, 1980, Newark, N.J.
26 Huang C.P., and Wirth, P.K., Treatability of cadmium (II) plating wastewater by aluminosilicate adsorption, p. 87-94. Ind. Waste Proc., 13th Mid. Atlantic Conf., Ann Arbor Science 1981.
27 Huang, S., and Wilson, D.J., Foam separation of mercury (II) and cadmium (II) from aqueous systems. Separation Sci. *11* (1976) 215.
28 Jenkins, S.H., Knight, D.G., and Humphreys, R.E., The solubility of heavy metal hydroxides in water, sewage and sewage sludge; I. The solubility of some metal hydroxides. Int. Air Water Pollut. *8* (1964) 537-556.
29 Kobayashi, K., Effects of anionic and cationic surfactants on the ion flotation of Cd^{2+}. Bull. chem. Soc. Japan *48* (1975) 1745.
30 Kobayashi, K., Studies of the removal of Cd^{2+} ions by adsorbing particle flotation, Bull. chem. Soc. Japan *48* (1975) 1750.
31 Kolesar, T.J., The use of atmospheric evaporative towers for recycle and waste elimination. Plating *61* (1974) 571.
32 Kosrrek, L.J., Removal of various toxic heavy metal and cyanide from water by membrane processes, Ch. 12, Chemistry in water reuse, vol. 1, pp. 261-280. Ed. W.J. Cooper, Ann Arbor Science 1981.
33 Krause, H., Research on the destruction of complexing and chelating agents in radioactive wastes by oxidation. Kernforschungszentrum, Karlsruhe, AEC Accession No. 32047, Rept. No. KFK-287.
34 Lowe, W., The origin and characteristics of toxic wastes with particular reference to the metals industries. Water Pollut. Control, London (1970) 270-280.
35 Maruyama, T., Hannah, S.A., and Cohen, J.M., Metal removal by physical and chemical treatment processes. J. Water Poll. Control Fedn *47* (1975) 962.
36 McKee, J.E., and Wolf, H.W., Water Quality Criteria, 2nd ed. California State Water Quality Control Board, Publication No. 3-A, 1963.
37 Nemerow, N.L., Theories and practices of industrial waste treatment. Addison Wesley, Reading, Mass. 1963.
38 Olson, J.L., and Eick, R.W., POTW removal credits and revised categorial pretreatment standards, 3rd Conference on Advanced Pollution Control for the Metal finishing Industry, EPA-600/2-81-028, p. 11-15. U.S. EPA Publication, 1981.
39 Onodera, Y., Removal of heavy metal ion from industrial wastewater. Agency of industrial services and technology, Japan, Kokai *549* (1977) 1734, Chem. Abstract *87* (1977) 43802 b.
40 Patterson, J.W., and Minear R.A. Wastewater treatment technology, 2nd ed. National Technical Information Service, PB 216-162, 1973.
41 Patterson, J.W., Allen, H.E., and Scala, J.J., Carbonate precipitation for heavy metals pollutants. J. Wat. Pollut. Control Fedn *49* (1977) 2397-2410.
42 Patterson, J.W., Guidance for BAT-equivalent control of selected toxic pollutants. Report to the U.S. Environmental Protection Agency, Region V, Chicago, Ill, 1981.
43 Patterson, J.W., Effect of carbonate ion opn precipitation treatment of cadmium, copper, lead and zinc. Proc. 36th industrial waste conference, pp. 579-602. Purdue University, 1981.
44 Pinkerton, H.L., Waste disposal, inorganic wastes, electroplating engineering handbook, 2nd edn. Ed. A. Kenneth Graham. Reinhold Publ. Co., New York, 1962.
45 Poon, C.P.C., Removal of copper, nickel, zinc, cadmium, and cyanide from plating wastewater by electroflotation, Proc. 1st Int. Conf. Management Control of Heavy Metals in the Environment, London, 1979.
46 Roof, E., Electrochemical reactor and associated in-plant changes at Varland metal services. Paper presented at the 3rd EPA/AES pp. 16-22. Conf. on Adv. Pollution Control for the Metal Finishing Industry, 1980.
47 Schrantz, J., Pan Am. Recycles Vis. Evaporation, Ind. Finishing *50* (1974) 30.
48 Schwitzgebel, M.B.K., Terry, J.C., Sund-Hagelberg, C., and Bhattacharyya, D., Characterization of boliden's sulfide-lime precipitation system. Project Summary, EPA-600/S2-81-081, 1981.
49 Srivastava, S.K., Studies on the use of inorganic gels in the removal of heavy metals. Water Res. *14* (1980) 113-115.

50 Stubbs, R.L., Cadmium - The metal of benign neglect. Cadmium Association, London 1975.
51 Sambaugh, R.L., and Melnyk, P.B., Removal of heavy metals via ozonation. J. Water Pollut. Control Fedn *50* (1978) 113–121.
52 U.S. EPA, Control and treatment technology for the metal finishing industry-sulfide precipitation. U.S. EPA Report No. 625/8-80-003, 1980.
53 Weiner, R.F., Acute problems in effluent treatment. Plating *54* (1967) 1354–1356.
54 Whang, J.S., Young, D., and Pressman, M., Design of soluble sulfide precipitation system for heavy metals removal. pp. 63–71. Ind. Waste Proc., 13th Mid. Atlantic Conf., Ann Arbor Science, 1981.
55 Wing, R.E., Corn starch compound recovers metals from water. Ind. Wastes Jan./Feb. 1975, 26–27.
56 Zanitsch, R.H., and Stensel, M.H., Economics of granular activated carbon water and wastewater treatment systems. Carbon Adsorption Handbook, p. 215. Ed. Cheremisinoff et al., Ann Arbor Science, 1978.

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Human health effects of exposure to cadmium

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Summary. The health effects of human exposure to cadmium are discussed with emphases on intake, absorption, body burden, and excretion; osteomalacia in Japan; hypertension; and proteinuria, emphysema, osteomalacia, and cancer in workers. Elevated blood pressure has not been observed as a result of excessive exposures to cadmium in Japan or the workplace. Renal tubular dysfunction and consequent proteinuria is generally accepted as the main effect following long-term, low-level exposure to cadmium. Studies of workers show that proteinuria may develop after the first year of exposure or many years after the last exposure. Proteinuria and deterioration of renal function may continue even after cessation of exposure. The immediate health significance of low-level proteinuria is still under debate. However, there is evidence that long-term renal tubular dysfunction may lead to abnormalities of calcium metabolism and osteomalacia. The few autopsy and cross-sectional studies of workers do not permit conclusions to be drawn regarding the relationship between cadmium exposure and emphysema. Retrospective and historical-prospective studies are needed to settle this important question. No conclusive evidence has been published regarding cadmium-induced cancer in humans. However, there is sufficient evidence to regard cadmium as a suspect renal and prostate carcinogen. Because of equivocal results and the absence of dose-response relationships, the studies reviewed should be used with caution in making regulatory decisions and low-dose risk assessments.

Introduction

The main goal of this critical review was to summarize and evaluate studies of humans which could be useful in assessing the possible health effects of cadmium exposures via air, water, or food. In particular, data were sought which would permit the extrapolation of high dose effects to low levels of exposure. As indicated in the summary, the extrapolation objective was not achieved using the human literature. Whenever there were inconsistencies between the animal and limited human health effects literatures, human data were given precedence in this review.

Intake, absorption, body burden, excretion

The main routes of cadmium intake in man are the lungs and the gastrointestinal tract. The chemical form of ambient airborne cadmium is not known. Although measurements of airborne cadmium concentrations have been made in many countries, the concentrations are not strictly comparable because of different sampling times and different analytical methods. Size distributions of particles containing cadmium are rarely determined. Hence, only rough estimates of lung deposition rates can be made[14]. On the basis of limited cadmium-containing particle size distribution data and the application of a standard lung model, about 25% of cadmium inhaled in ambient air would be deposited in the lower respiratory tract[14]. Using this deposition fraction and an assumed average daily inhalation of 20 m^3, the amount of cadmium deposited in the lower respiratory tract has been estimated: rural areas, 0.0005–0.215 µg/day; urban areas, 0.01–3.5 µg/day; industrialized areas with cadmium emissions, 0.05–25 µg/day. The highest level of 25 µg/day is probably found only in the vicinity of an operation such as a smelter[14]. The rate of absorption through the lungs is a function of the chemical form and size distribution of the inhaled particles. Various rates have been reported. One model based on human smokers predicts 50% of inhaled cadmium from tobacco smoke is absorbed[17]. One pack of 20 cigarettes can contain 30 µg of cadmium of which 2–4 µg can be inhaled[17,18,21]. In the general environment 13–19% of the cadmium inhaled is absorbed[14].

Ingestion of cadmium occurs via water and food. Tap water which is not particularly contaminated contains < 2 µg/l cadmium. This corresponds to an intake of 2–4 µg/day.