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Heavy metals removal

Most heavy metals found in waste-treatment processes are in the inorganic form, but there are certain industries where they appear as organic compounds. Here, the technical methods that are in general use are discussed, and the optimum treatment systems for specific metals are described.

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☐ Heavy metals is the classification that is generally applied to those metals of particular concern in the treatment of industrial wastewaters: copper, silver, zinc, cadmium, mercury, lead, chromium, iron and nickel. Other metals that may be considered part of this category are tin, arsenic, selenium, molybdenum, cobalt, manganese and aluminum.

Most heavy metals found in waste-treatment processes are in the inorganic form. However, in some industries such as textiles and dyeing, heavy metals are in the organic form. Treatment technology is different for these two forms.

Inorganic heavy metals

The most common method for removal of inorganic heavy metals is chemical precipitation. Typical estimates of final concentration levels obtainable by chemical precipitation are shown in Table I [*1*].

Metals precipitate at various pH levels, depending on such factors as the metal itself, the insoluble salt that has been formed (e.g., hydroxide, carbonate, sulfide, etc.), presence of complexing agents such as ammonia, citric acid, ethylenediaminetetraacetic acid (EDTA), etc. Theoretical precipitation curves for various metals as hydroxides are shown in Fig. 1 [*2*].

It is apparent that when two or more heavy metals are found in the same waste stream, the optimum pH for precipitation may be different for each ion. The question then becomes whether it is possible and practical to precipitate one or more of the metals separately at the source at one pH, and treat the remaining stream at another pH.

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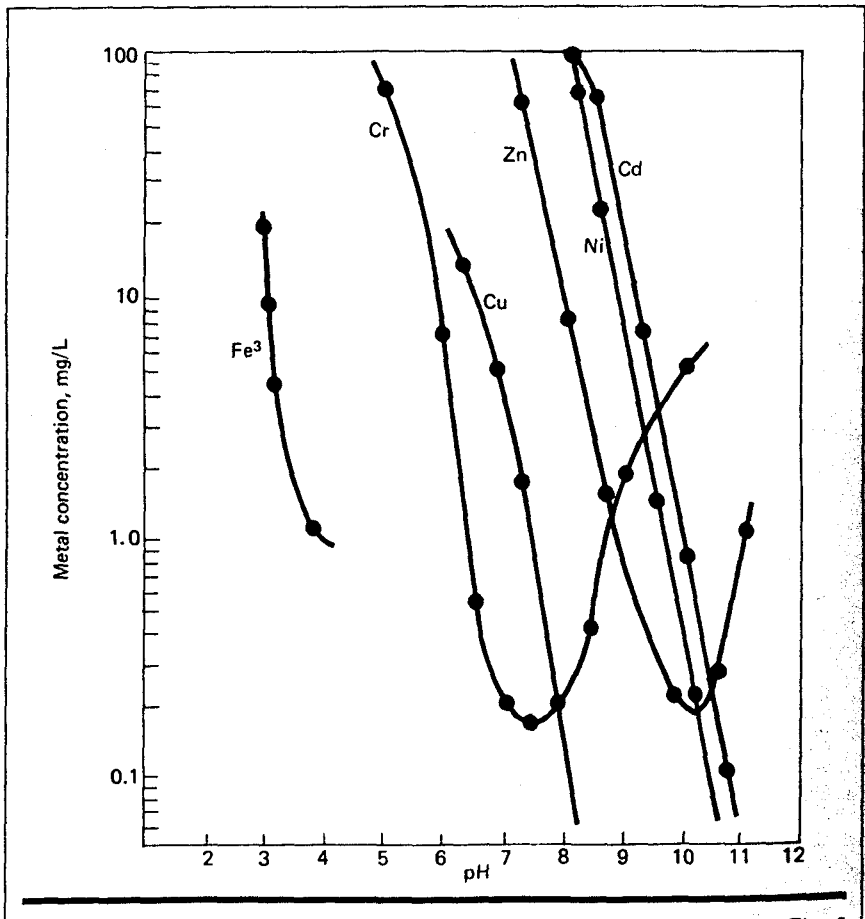
Alternatively, it must be determined if one pH can be found which will produce satisfactory—though not optimum—insolubility for each of the metal ions present in the wastewater.

The presence of complexing agents such as ammonia must also be carefully investigated. Ammonia may be controlled by careful pH adjustment, the use of sulfides,



Precipitation of heavy metals as hydroxides **Fig. 1**

Typical concentration levels obtainable through chemical precipitation **Table I**

Heavy metal	Achievable concentration, mg/L	Probable precipitating agent
Cadmium	0.3	Soda ash
Chromium^{+6}	0.05	–
Chromium, total	0.5	Caustic, lime
Copper	0.5	Caustic, lime
Iron	1.0	Caustic, lime
Nickel	0.5	Soda ash
Zinc	0.5	Caustic, lime

or removal by air stripping. Other complexing or chelating agents should also be investigated to determine their effect on the precipitation process.

In order to determine the optimum treatment process, a bench-scale testing program should be carried out using samples of the waste to be treated. Precipitation tests should use various likely chemicals to determine which produces the most acceptable effluent. The pH should be adjusted over a suitable range; use of polymers to aid in coagulation of the precipitates should also be investigated. The times required for proper mixing and sedimentation can also be determined by a bench-scale testing program.

Scale-up from bench-scale tests is usually reliable, provided that normal safety factors are applied.

Treatment methods

Chemical precipitation of heavy metals may be accomplished by either batch or continuous treatment systems. Batch treatment is usually preferred when the volumes to be treated are small, or where the waste may be variable from day to day and require modification of the treatment as characteristics change.

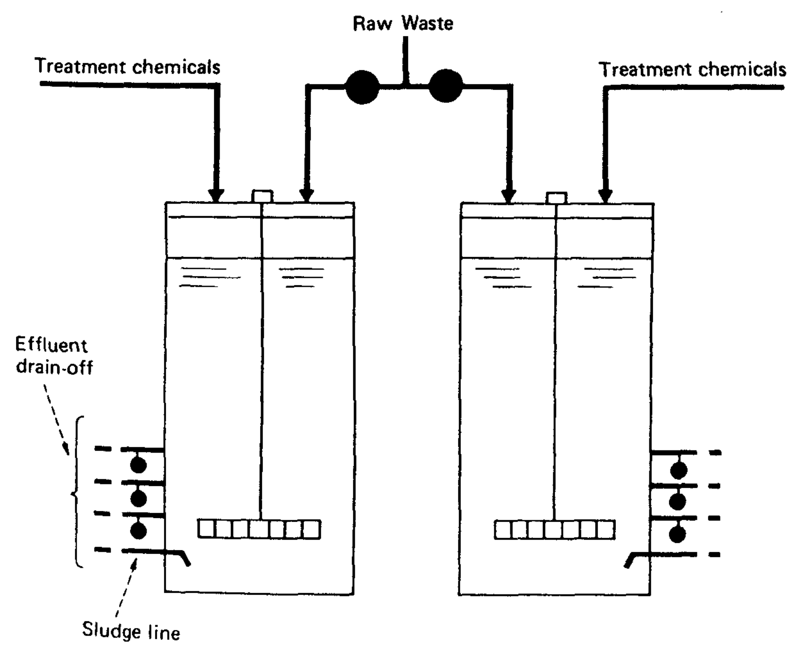
Batch treatment systems can be economically designed for flows as high as 50,000 gpd. A batch system is usually designed with two tanks, each one of sufficient volume to handle the waste generated in a specific time period—e.g., an 8-hour shift, a 24-hour day, etc. When one tank is full, a mixer is used to provide a homogeneous mixture, and a sample is taken and analyzed to determine the amount of heavy-metal contaminants present. Chemical addition based on contaminants present and pH of the waste is then calculated and the required amounts of chemicals are added. The tank contents are then mixed—using pH for controlling purposes—and, for heavy-metals removal, allowed to settle for 2 to 4 hours.

When treatment is complete, a second sample can be taken and analyzed to ensure that all contaminants have been removed. If, for any reason, contaminants are still present, treatment can be repeated or alternative treatment applied. When the operator is satisfied that the treated waste is suitable for discharge, the clear liquor is decanted. The settled sludge is drawn off periodically for disposal. The advantages of a batch treatment system are that nothing is discharged from the plant until the operator is satisfied that it meets effluent requirements. The system is also simple in its design and easy to operate (Fig. 2).

When wastewater characteristics are uniform or when volumes are large, a continuous treatment system is applicable. A usual continuous treatment system has an equalization tank of several hours to a day of detention time to even out any fluctuation in the wastewater characteristics and provide a uniform feed to the treatment system.

The first process step is the adjustment of the pH by addition of acid or alkali to the proper level for optimum precipitation. This chemical addition is controlled by a pH probe in the reaction tank, which activates the speed control of the chemical feed pump. A polymer is usually added to aid coagulation. Reaction times are in the range of 15 to 60 minutes.

The waste stream then flows to a sedimentation basin where the heavy-metal precipitate settles out of solution leaving a clear treated overflow for discharge to the receiving body of water. Detention times in the sedimentation basin usually range from 2 to 4 hours at overflow rates from 300 to 700 gal/ft^2 foot of surface area per day (Fig. 3).



Typical batch-treatment system Fig. 2

Sludge recirculation

Recirculation of precipitated sludge to be mixed with the raw waste at the time of chemical addition can have beneficial effects. The presence of the precipitated particle provides a seed for the newly formed precipitate to agglomerate.

In batch treatment systems, the settled sludge is left on the bottom of the tank. When a new batch is put in the tank, the mixer is turned on to resuspend the sludge and mix it with the tank contents.

In continuous treatment systems, the sludge can be recycled either externally around the clarifier or internally within the clarifier. With external recirculation, the sludge is pumped out of the sludge hopper in the clarifier and introduced to the raw feed in the chemical mixing tanks. With internal recirculation, the clarifier is designed with an internal mixer and baffles that provide recirculation within the clarifier.

Effluent filtration

A properly designed clarification system will remove the bulk of precipitated solids. However, the effluent may contain 5 to 20 mg/L of suspended solids including some of the heavy metal. Therefore it may be advisable to filter this effluent to ensure maximum removal of the metals.

The type of filtration system frequently used is a gravity filter with a sand bed or multimedia bed, similar to filters used for water treatment. Flowrates are 2 to 5 gpm per square foot of surface area. As the media entrap more solids, the pressure loss through the filter increases. When the loss of head is 8 to 12 ft, it is necessary to clean the filter by backwashing to ready it for reuse. Because the filter is out of use during the backwash cycle, which takes about one hour, two or more filters are usually required. Valveless gravity filters, mixed-media filters and pressure filters can be applied to this operation.

Sludge handling

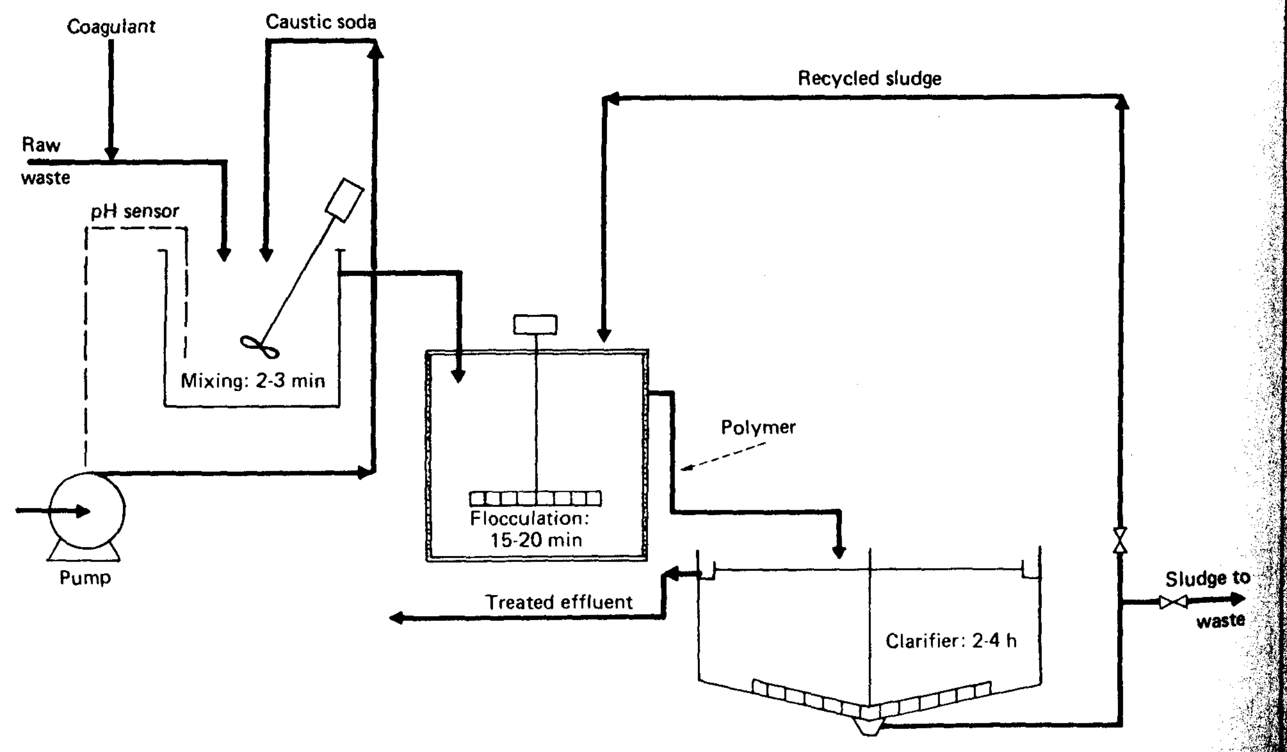
The settled sludge from a clarification basin is frequently in the range of 1 to 2% solids. Hydroxide precipitation of the metals produces sludge that is usually gelatinous in character, thereby increasing the difficulty of dewatering. Lime will produce considerably greater quantity of sludge than caustic but is ordinarily easier to dewater.

The sludge can be further dewatered in centrifuges, vacuum or plate-and-frame filters or on sludge-drying beds. Centrifuges of the solid-bowl type usually dewater the sludge a little less than vacuum filters. The units are usually compact and require minimal floor space. Centrifuges operate with varying success depending on the nature of the sludge. Field trials should be run before selecting a unit.

Rotary vacuum filters might be expected to produce a cake of 20 to 25% solids. They require a vacuum pump and a filtrate pump as well as other auxiliary equipment. They also require considerable floor space, but are quite reliable in operation.

Pressure filters of the plate-and-frame type will produce sludges a bit more concentrated than vacuum filters. These filters occupy less floor space than vacuum filters, but require more labor and operator-attention.

Sludge-drying beds can, with sufficient retention, produce a fairly dry cake. However, they require con-



Typical continuous-treatment system for heavy metals

Fig.

siderable land area, and can only be used in locations where the incursion of leachate into the aquifer will not have a detrimental effect.

Sludge disposal

One of the biggest problems facing environmental authorities today is the question of how to handle and dispose of the sludge that has been generated in heavy-metal precipitation systems. There is always a possibility that the metals will solubilize if the pH falls below the optimum range. Therefore, these sludges should not be disposed of with municipal waste because the low pH generated by decomposition of the garbage can resolubilize the precipitate.

The final sludge-disposal lagoon, or dump pit, should be located so that it will have minimal impact on surface and ground waters. Best conditions are areas where natural (clay, rock) or artificial means (plastic liner) can prevent excessive amounts of leachate from getting into the ground water. Where these conditions do not exist, it may be necessary to install a collection system at the bottom of the pond so that leachate can be collected and piped to a treatment system for re-removal of soluble metals salts.

Chemical treatments have been developed to reduce the leaching possibilities of heavy metal sludges and may be used in conjunction with a landfill program to further minimize potential leachate contamination.

Metal values from sludge

Recovery of metal values from the sludge has been studied. Digesting the sludge in an acid medium, neutralization and electrolytic recovery have been investigated [*3*]. The cost estimate for recovery of copper, nickel, and chromium in a small plant was $13.23/kg, which was quite high compared to current market prices. However, since these metal values are likely to increase as the years go by, one approach is to stockpile these metal-bearing sludges, either separately or in a regional disposal site, so that they are available for recovery in the future when the value of the metals and recovery technology make it economically attractive.

Theoretical solubilities of hydroxides and sulfides of heavy metals in pure water **Table II**

Metal	Solubility of metal ion, mg/L	
	As hydroxide	As sulfide
Cadmium (Cd^{++})	2.3×10^{-5}	6.7×10^{-10}
Chromium (Cr^{+++})	*8.4×10^{-4}	No precipitate
Cobalt (Co^{++})	*2.2×10^{-1}	1.0×10^{-8}
Copper (Cu^{++})	**2.2×10^{-2}	5.8×10^{-18}
Iron (Fe^{++})	8.9×10^{-1}	3.4×10^{-5}
Lead (Pb^{++})	**2.1	3.8×10^{-9}
Manganese (Mn^{++})	1.2	2.1×10^{-3}
Mercury (Hg^{++})	*3.9×10^{-4}	9.0×10^{-20}
Nickel (Ni^{++})	*6.9×10^{-3}	6.9×10^{-8}
Silver (Ag^{+})	13.3	7.4×10^{-12}
Tin (Sn^{++})	**1.1×10^{-4}	*3.8×10^{-8}
Zinc (Zn^{++})	1.1	2.3×10^{-7}

Sources:

"Handbook of Chemistry and Physics," 50th ed., Weast, R.C., ed., Chemical Rubber Co., Cleveland, Ohio, p. B252.

*"Handbook of Analytical Chemistry," Meites, L., ed., McGraw-Hill, New York, pp. 1-15 to 1-19, 1963.

**"Ionic Equilibrium As Applied to Qualitative Analyses," Hogness and Johnson, Holt Rinehart & Winston Co., New York, pp. 360-362, 1954.

Even at the present time, while individual plant recovery may not be economical, regional recovery systems treating metal sludges from several plants in an area may be feasible. As the cost of sludge disposal increases, recovery becomes more attractive.

Chemical usage

The chemicals most frequently used for precipitation of metals are lime, caustic and sodium carbonate. Comparative costs of these chemicals are as follows:

Precipitating chemical	Theoretical requirements, mg/L	Approximate cost, $/ton
Quicklime, CaO	0.76	25
Hydrated lime, $Ca(OH)_2$	1.00	25
Caustic, 50% NaOH	1.08	140
Soda ash, Na_2CO_3	1.42	50
Sodium sulfide, Na_2S	—	250

Because of the lower cost, lime is preferred particularly in installations which use more than one-half ton per day. Caustic is used in smaller installations where daily chemical costs will not be significant. Soda ash is used in particular cases (e.g., cadmium and nickel precipitation) where it provides a better chemical reaction.

Lime—There are several types of lime available:

Material	Theoretical requirements compared to equivalent weight $Ca(OH)_2$
Quicklime (high calcium), CaO	0.76
Quicklime (dolomitic), $CaO \cdot MgO$	0.65
Hydrated lime (high calcium), $Ca(OH)_2$	1.00

Quicklime is cheaper than hydrated lime per unit of neutralizing capacity, but it requires the use of slaking equipment (about $10,000–15,000) and requires protective clothing for workers since it can cause severe burns. Quicklime is usually used when demand is over 5 tons/day. It must be stored in air-tight bins to prevent air-slaking, lime coats, and eventual plugging of pipes. Dolomitic lime (high magnesium) reacts more slowly than high-calcium lime. Magnesium in dolomitic lime may have side effects, either good or bad, on reaction.

Hydrated lime is more expensive but does not require slaking equipment and can be fed directly to the reaction system. It is used where demand is less than 5 tons/day, and its dust is less irritating than that of quicklime. Hydrated lime tends to bulk and bridge in storage tanks, and therefore requires special agitating systems on cone bottoms. Dusting can also be a problem, and special dust collectors are required. Hydrated lime can be obtained in car lots, truck lots or 100-lb bags in completely dry form.

Caustic soda—Caustic soda, or sodium hydroxide (NaOH), is available in either liquid or dry form. Liquid caustic soda is usually preferred when smaller quantities are required because of ease of handling. It is usually obtained as 50% NaOH. Since freezing (crystallization) occurs at 53°F, indoor storage, or heating if stored outdoors, is required. Caustic is often diluted at the plant site because the freezing temperature at 20% concentration is −20°F.

Soda ash—Soda ash, or sodium carbonate (Na_2CO_3), has a theoretical equivalent weight requirement of 1.42, as compared to hydrated lime. It is not particularly corrosive by itself, and it has superior handling characteristics—little dust, good flow, and no arching in feeder. But soda ash is difficult to dissolve; it is stored in steel bins, and can be obtained in bulk by railcar or truck or in 100-lb bags.

Sometimes it provides superior precipitation, i.e. with cadmium it produces cadmium carbonate which is preferred to cadmium hydroxide for recovery purposes. Also with nickel, precipitation with carbonate gives lower final levels than precipitation with hydroxide.

Sulfides—Present technology for heavy metals removal is generally based on hydroxide precipitation, as previously described. However, when heavy metals are complexed with such agents as ammonia, cyanide, etc., hydroxide precipitation will not be sufficient to attain adequate levels. Also, with new emphasis on even-stricter effluent standards in the future, increased attention is being given to other methods of achieving even lower concentrations. Sulfide precipitation is a method of achieving these lower effluent levels.

Table II gives the theoretical solubilities of hydroxides and sulfides of various metals in pure water. In addition to having lower solubilities than hydroxides in the alkaline pH ranges, sulfides also tend to have low solubilities in the pH ranges below 7. Also, certain metal hydroxides tend to redissolve as the pH increases beyond the level of maximum insolubility [*4*].

One of the problems with the use of sulfides is that, with the use of sodium sulfide or similar compounds, excess sulfide in solution will form H_2S, which in itself is a pollution problem and requires removal. Adding exactly the right amount of sulfide is difficult to do—too little will leave some metal in solution, and too much will cause an additional pollution problem. Another problem is that metal sulfide sludges when exposed to air oxidize to the sulfate, and the metal ions can become resolubilized.

A process utilizing ferrous sulfide as the principle source of sulfide ion has been developed and appears to overcome the problem of generating H_2S from excess sulfide. The sulfide is released from the FeS only when other heavy metals with lower equilibrium constants for their sulfide form are present in solution. If the pH can be maintained at 8.5 to 9, the liberated iron will form a hydroxide and precipitate out as well.

Other removal methods

Activated carbon adsorption—Activated carbon will absorb hexavalent chromium, mercury and many meta compounds that have been complexed in the organi form as for dyes and pigments. The adsorptive capacity of any carbon depends on the pore size, size of molecule pH of the solution and the initial and final concentration. Adsorption capacity generally increases as the pH decreases and, normally, adsorption efficiency increases as the concentration increases.

In order to determine the effectiveness of activated carbon for a particular metal-bearing waste, adsorption isotherms should be developed that indicate the amount of material adsorbed at a particular concentration. These tests are usually run on several different carbons at various concentrations in order to determine which provides the most effective treatment.

Granular carbon is usually the preferred type. It is two to three times as expensive as powdered carbon, but it can be chemically regenerated and reused. Powdered carbon is less expensive but usually can only be used on a once-through basis. It is difficult to handle due to a tendency to dust, and it must be removed from the waste stream, usually by coagulation or filtration. It is important to make an economic evaluation of the two types of carbon—granular or powdered—before a final choice is made.

Ion exchange—Ion exchange is an effective means of removing heavy metals from waste streams. There are a variety of resins for specific applications with various metals. When the resins are saturated, they must be regenerated with an acid or alkaline medium to remove the metal ions from the resin bed. The regenerant solution is smaller in volume and higher in concentration than the wastewater, but these metal values must then be adequately disposed of or recovered. Ion exchange is particularly applicable for waste streams which, for one reason or another, will not respond to more conventional treatment, or where the metals can be recovered from the regenerant solution and reused.

Reverse osmosis—Reverse osmosis is a treatment system utilizing semi-permeable membranes to produce a clear permeate and a concentrate containing the metal values. The system operates at pressures up to 600 psi and has been utilized effectively in the plating industry for the recovery and reuse of nickel in plating-bath waters. Applications of reverse osmosis are still in the development stage for the recovery of other metals. The system is essentially a concentration technique and is most effective if the concentrate can be reused.

Cementation—This is a metal-replacement process that occurs when a solution containing a dissolved metallic ion comes into contact with a more active metal, such as iron. This process is particularly applicable as a means of removing copper and silver from solutions. Scrap iron or steel wool is frequently used, and the less active metal is cemented onto the iron as the iron replaces it in solution. The weaker metal—copper, silver, etc.—is recoverable as a pure metal and the iron can be precipitated as an iron hydroxide if necessary. The reaction is carried out in an acid solution.

Other active metals, such as zinc dust, can be used for the cementation of metals such as gold, cadmium, mercury and lead [5].

Removal techniques for various metals

Cadmium—This metal is generated in the waste streams from pigment works, textiles, electroplating, chemical plants, etc. The U.S. Public Health Service (USPHS) has set a limit of 10 μg/L of cadmium in drinking water. Metal finishing guidelines show an attainable limit of 0.3 mg/L of cadmium in the effluent.

Cadmium is toxic to human beings when injected or inhaled. It is toxic to fish in concentrations as low as 10 μg/L. Cadmium acts synergistically with other elements such as copper and zinc to increase toxicity [6,7].

Cadmium as hydroxide, carbonate and sulfide forms an insoluble precipitate.

Precipitation in the hydroxide form is dependent on high pH. Pourbaix has determined that theoretical solubility of cadmium hydroxide is approximately:

pH	Solubility, mg/L
8	3,000
9	30
10	0.03
11	0.003

Therefore, with lime or caustic as the precipitating agent, pH should be maintained at about 11 for maximum insolubility. Operating at such a high pH requires final treatment of the effluent discharge to lower the pH to the allowable limit of 9. Since this pH adjustment will redissolve any remaining cadmium, it is important that all precipitate be removed, preferably by filtration, before this final pH adjustment is made.

If other metals are present that precipitate at lower pH levels (8 to 9), it is often preferred to have a treatment system operating at one pH for all metals. In this case, other chemical agents must be considered.

Treatment of cadmium with sodium carbonate (soda ash) will give good levels of removal at a slightly lower pH, in the range of 9.5–10. Due to the value of cadmium, it is often desirable to send the precipitated sludge to a reprocessor for recovery of the cadmium, or to reuse it. Whether the cadmium is in the hydroxide or carbonate form may be important to the reprocessor or plant user.

Sulfide precipitation can be carried out at low pH with good removals. For example, it is reported that sulfide precipitation at a pH of 6.5 reduced a raw waste ranging from 0.5 to 1.0 mg/L of cadmium to a final effluent of 0.008 mg/L. In this particular instance, BaS was used but Na_2S, NaHS or H_2S could have been applied as well [8].

Chromium—Chromium is found in two forms in waste streams—hexavalent and trivalent. Hexavalent chromium is found in the waste streams of plating operations, aluminum anodizing, paint and dye operations, and other industries. Trivalent chromium is found in the waste streams of textile dyeing, the ceramic and glass industry and photography.

Limitations on domestic water suppliers of 50 μg/L total chromium have been recommended by the EPA [6]. The usual chromium limits for most effluents are less than 0.05 mg/L for hexavalent chromium and 0.5 mg/L for trivalent chromium.

Treatment for chromium usually consists of a two-stage process: first, the reduction of hexavalent chromium to the trivalent form and, second, precipitation of the trivalent chromium. For this reason, chrome-bearing streams are segregated and treated separately, particularly in the reduction of the hexavalent to the trivalent form. The reduced chrome-bearing stream can then be blended with other metal-bearing streams for further treatment. Waste can be treated either batch-wise or continuously. For a continuous flow-through system, equalization of the raw waste flow, by means of a holding tank with several hours detention as a first step in the treatment process, is most important.

The reduction of hexavalent chromium is accomplished at a pH of 2 to 3. The pH can be adjusted either by manual measurement or by an automatic pH control unit with the addition of sulfuric or hydrochloric acid. The level of pH controls the rate of reaction. At pH 2, the reduction reaction is almost instantaneous, while at a pH of 3, the reaction takes about 30 minutes.

After the pH is adjusted a reducing agent is added. Reducing agents most commonly used are sodium dioxide and sodium metabisulfite. The amount of reducing agent added may be controlled based on oxidation-reduction-potential (ORP) readings or by analysis of the hexavalent chromium remaining in solution. Sulfur dioxide gas is toxic, so adequate venting and safety precautions must be provided.

Typical relationship between ORP and Cr^{+6} is [9]:

ORP	Cr^{+6}
590	40 ppm
570	10 ppm
540	5 ppm
330	1 ppm
300	0

This relationship should be confirmed by field tests.

Trivalent chrome is removed by precipitation. Usually lime or caustic is added to increase the pH to between 7.5 and 8.5 for minimum solubility of chromium hydroxide. The solubility starts to increase as the pH goes below 7 on the low side and as it goes above 9 on the high side. Therefore, careful pH control in the range of 7.5 to 8.5 is important. As pointed out above, other metals in the waste stream will also precipitate in this step.

Theoretical chemical requirements per lb of Cr are:

1. For reducing with sodium metabisulfite, 3 lb. $Na_2S_2O_5$ and 1-1½ lb. H_2SO_4.
2. For reducing with sulfur dioxide, 2 lb. SO_2 plus 35 mg for each liter of water being treated.
3. For precipitation, 2.2 lb. $Ca(OH)_2$ or 2.5 lb. NaOH or 3 lb. Na_2CO_3.

Ferrous sulfate will reduce hexavalent chrome and jointly precipitate the trivalent chrome and ferric hydroxide at pH 8.5. It requires 17 parts of ferrous sulfate for each part of hexavalent chrome. This process is more expensive and produces considerably more sludge than the conventional process of pH reduction and use of SO_2. However, the overall economics are worth considering when the hexavalent chrome content is in the range of less than 10 mg/L and probably it will be the system of choice when the content is less than 5 mg/L.

Under alkaline conditions, sodium hydrosulfite can be used for the reduction of hexavalent chrome and requires 5 mg/L for each mg/L of chrome + 5 mg/L for each mg/L of dissolved oxygen present in the water. This is the most expensive method for the reduction of hexavalent chrome. It is generally used in alkaline cleaning baths with a build-up of hexavalent chrome that has been carried over from previous baths, or as an emergency treatment when hexavalent chrome is present in precipitation reactors and/or clarifiers.

Other means of removing chrome from wastewater are adsorption on activated carbon, ion exchange and biological treatment.

Chromium can be removed by activated carbon. Tests by EPA showed 98% removal of chromium by a combination of lime precipitation and activated carbon. Starting with an initial concentration of 5 mg/L, final concentration was 90 μg/L [*10*]. The activated carbon can be regenerated with sodium hydroxide if it is desired to recover the chrome. If the chrome is to be disposed of, sulfuric acid will reduce the hexavalent chrome to the trivalent state.

Ion exchange systems are used in those instances where the chrome is being recovered for reuse in the process. Chromium removals of 40 to 80% have been reported in activated sludge systems based on low initial levels of chromium. When chrome is removed in the process, it ends up in the sludge and may become a problem there [*10*].

Lead—Lead is found in waste streams from battery manufacture, printing, painting and dyeing, and other industries. Lead is a cumulative poison and concentrates primarily in the bones. It is generally felt that 0.1 mg/L can cause lead poisoning if ingested regularly [*11*]. USPHS drinking water standards recommended 50 μg/L as a maximum level [*7*].

Lead can be precipitated with lime (CaOH) or caustic (NaOH) to form lead hydroxide, $Pb(OH)_2$, with soda ash, $NaCO_3$, to form lead carbonate, $PbCO_3$, or with trisodium phosphate, Na_3PO_4, to form lead phosphate, $Pb_3(PO_4)_2$. A combination of soda ash and caustic has also been applied.

Low levels of residual lead have been obtained in bench-scale tests, but many plants are finding it difficult to attain effluent levels below 0.5 mg/L in actual waste treatment plant operations.

Bench-scale tests conducted by Nassau Smelting and Refining Co. [*12*] studied precipitation by caustic, lime and caustic soda/soda ash. It was found that both lime and caustic soda/soda ash gave good results. The optimum pH was 9.0 to 9.5. Influent lead was 5 mg/L and final lead was 0.01 to 0.04 mg/L.

Fig. 4 shows solubility levels of lead with different alkali agents. As can be seen, the soda ash/caustic soda systems produced slightly better results than the straight-lime system. Separan AP 30 was used as a coagulant aid [*12*].

A study by Westinghouse Electric Corp. compared the effectiveness of all of the above precipitation systems and their treatment costs. They found that, for their waste stream, a combination of trisodium phosphate and caustic soda (at a ratio of 1:2.5) was the mos effective precipitant system. Residual lead concentrations were below 0.02 mg/L at a pH of approximately 8.5. The total chemical cost of the treatment was $2.84/thousand gallons [*13*].

Other EPA tests using lime and activated carbon showed 99.4% removal. Starting with an initial concentration of 5.0 mg/L lead, the final concentration was 30 μg/L [*10*]. Lead removal in a biological plant is 50 to 90% and it is removed in sludge at concentrations of 830 mg/kg [*10*].

Mercury—The presence of mercury in water supplies is a major concern today. The recommended drinking water standard is 2 μg/L and quality criteria for aquatic life is 0.05 μg/L.

The standard method of removing mercury is to adjust the pH to 5 to 6 with sulfuric acid and then add sodium sulfide to an excess of 1 to 3 mg/L. This forms an insoluble mercury sulfide. After filtration on a rotary vacuum-precoat or pressure-precoat filter, the effluent contains approximately 10 to 125 μg/L (average 50 μg/L) mercury from an initial waste concentration of 0.3 to 6 mg/L. Polishing of the effluent with activated carbon or synthetic resins has been reported to further reduce the residual levels [*14*].

An effluent level of 10 to 50 μg/L of mercury may not be sufficient to meet the stringent stream standards. Therefore, it may be necessary to consider supplementary treatment systems.

A table of alternative treatment methods and levels that can be accomplished is given below [*15*]. Some of these mercury processes have not been used in full-scale commercial operation:

Technology	**Lower limit of treatment capability, μg/L**
Sulfide precipitation	10–20
Ion exchange	1–5
Alum coagulation	1–10
Iron coagulation	0.5–5
Activated carbon	
High initial Hg	20
Moderate initial Hg	2.0
Low initial Hg	0.25

Ion exchange seems to be an effective means of removing mercury down to levels of 1 to 5 mg/L. The best of all these treatment methods is reported to be a two-stage system. The pH should be on the slightly acidic side.

Use of zinc dust for reduction of mercury has been reported as effective in removing 99% of the mercury. This process is based on the reduction of the mercury to the elemental state and the formation of a stable complex with the excess of zinc. This compound is subsequently removed by conventional solids-liquid separation methods [*16*].

Silver—The principle sources of silver in wastewaters are the electroplating and photographic industries. Because of the value of silver, extensive efforts are made to recover as much of it as possible.

The allowable limit of silver in drinking water has been set by the USPHS as 50 μg/L. Fish and lower orga nisms are susceptable to silver poisoning, and concentrations of from 4 µg/L to 0.44 mg/L have proven toxic for salmon fry, eels, stickleback and lower organisms [6,7].

The two principal recovery methods are electrolytic recovery and cementation (metal replacement). In electrolytic recovery, the solution is passed through two electrodes operating on direct current. Silver deposited on the cathode is stripped off periodically for recovery.

The cementation process passes the silver-bearing liquor through a bed of iron in the form of steel wool, iron shavings, etc. The silver ion replaces the ferrous ion, with the ferrous ion going into solution and passing out with the effluent. The pH of this system must be kept between 4 and 6.5 [17].

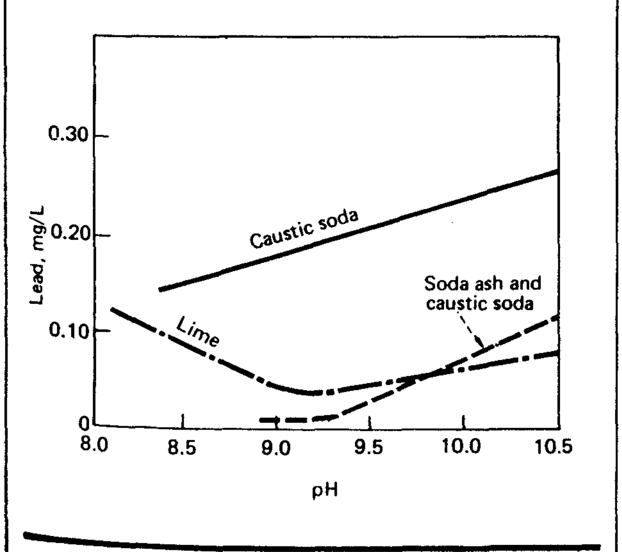
Either of these systems will reduce silver content to 50 to 100 ppm. Ion exchange has also been reported as a method of recovering silver from spent photographic solutions or plating rinse waters.

To obtain levels below 1 ppm, chemical precipitation is used. Silver can be precipitated as a chloride or a sulfide, both of which are insoluble compounds. Addition of sodium chloride, hypochlorite or chlorine will form insoluble silver chloride. In the plating industry, wastes are in the form of silver cyanide. In order to free the silver, as well as to destroy the cyanide, chlorine is added to oxidize the cyanide to cyanate and then to carbon and nitrogen. The available chlorine, furnished as chlorine gas or a hypochlorite solution, also reacts with the silver to form a silver chloride precipitate. The sequence of operations for a batch treatment system is as follows:

1. Measure cyanide with field test kit.
2. Add caustic to pH 11.
3. Add chlorine as required by the specific amount of cyanide required.
4. Mix for 15 to 30 minutes.
5. Add sulfuric acid to pH 8.
6. Add chlorine as required to maintain the residual chlorine as measured by a field test kit.
7. Mix for 15 to 30 minutes.
8. Add polyelectrolyte.
9. Settle for 4 hours and decant.

Sulfide precipitation can also be quite effective and may give lower final-effluent levels of silver. Bench-scale testing should be performed to determine whether chloride or sulfide is the preferable means of precipitation.

Sodium sulfide under acidic conditions can form hydrogen sulfide, which is very toxic. Therefore, it is important that the precipitation be carried out under alkaline conditions with the addition of amounts of caustic soda to raise the pH. Adequate ventilation should also be provided.



Lead solubility in three alkalies Fig. 4

References

1. Lanouette, K. H., and Paulson, E. G., Treatment of Heavy Metals in Wastewater, *Pollution Eng.*, Oct. 1976.
2. Feigenbaum, H. N., Removing Heavy Metals in Textile Waste, *Industrial Waste*, Mar.-Apr. 1977.
3. "Development Document for the Metal Finishing Industry," EPA Report No. 440/1-75/040-a, p. 166.
4. "Proceedings of Seminar on Metal Wastes Treatment Featuring the Sulfex Process," The Permutit Co., Paramus, N.J.
5. Dean, J. G., Bosqui, F. L., and Lanouette, K. H., Removing Heavy Metals from Wastewater, *Environmental Science & Technology*, June 1972.
6. "Quality Criteria for Water," EPA Report, preliminary draft.
7. "Water Quality Criteria," California State Water Resources Control Board, Publication 3-a, Reprint, Dec. 1971.
8. Larsen, H. P., Shou, J. K. P., and Ross, L. W., Chemical Treatment of Metal-Bearing Mine Drainage, *J. Water Pollution Control Federation*, Aug. 1973, p. 1682.
9. Russell, L. V., Treatment of CCA-, FCAP, and FR-Type Wastewaters, from "Pollution Abatement in the Wood Preserving Industry," Forest Products Utilization Laboratory, Mississippi State University, 1970.
10. Cohen, J. M., "Trace Metal Removal by Wastewater Treatment," EPA Technology Transfer, Jan. 1977.
11. "Development Documents for the Metal Finishing Industry," EPA Report No. 440/1-75/040-a, Apr. 1975, p. 76.
12. Day, R. V., Lee, E. T., and Hochuli, E. S., Bell System's Metals Recovery Plant, *Industrial Waste*, Jul.-Aug. 1974, pp. 26-29.
13. Rohrer, K. L., "Chemical Precipitants for Lead Bearing Wastewaters," Westinghouse Electric Corp.
14. Iammartino, N. R., Mercury Cleanup Routes—II, *Chem. Eng.*, Feb. 3, 1975, pp. 36-37.
15. Paterson, J. W., "Wastewater Treatment Technology," Ann Arbor Science Publishers, Oct. 1975, p. 157.
16. Rickard, M. D., and Brookman, G., "The Removal of Mercury from Industrial Wastewaters by Metal Reductions," Proceedings of the 26th Purdue Industrial Waste Conference, Purdue University, 1971, pp. 713-721.
17. "Recovering Silver from Photographic Materials," Eastman Kodak Co., Book No. 0-87985-041-8, Rochester, N.Y.

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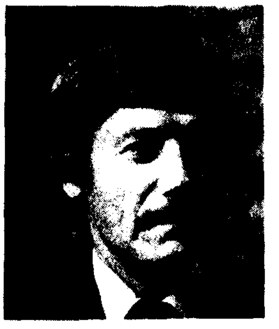

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