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February 1977

Subject: Technical Letter 18
Removal of Water Supply Contaminants -- Toxic Metals (Cd,Pb,Hg,Ag)

This is the fourth in a series of Technical Letters dealing with state of the art methods for removal of contaminants from water supplies so that the supply will be in compliance with state and federal drinking water standards.

Contaminant

This Technical Letter is concerned with the toxic metals cadmium, lead, mercury, and silver as contaminants of drinking water. In 1976 there were no supplies in use in Illinois which exceeded the state and federal drinking water standards for these toxic metals. All of these elements have been grouped together because of certain similarities relative to their chemistry, toxicity, and methods of removal.

Prevalence and Uses

The metals cadmium, lead, mercury, and silver are found in groundwater supplies due to leaching of underlying geological deposits or due to contamination from industrial discharges. Lead may be found in finished waters from lead water lines particularly for soft and acid water.

All of these metals are widespread throughout the earth's crust with some localized high level deposits. Because of their industrial importance, their ores have been mined, and man's activities have redistributed them in the environment.

Cadmium has been used extensively as a protective coating on iron and steel, and as an alloying agent with other metals. A number of its salts have been used as pigments in paints and polishes. Cadmium is used as a stabilizer in plastic and in curing certain types of rubber. Cadmium is also used in batteries. In addition to its direct use, cadmium occurs indirectly because of its presence as a contaminant in zinc for galvanized steel piping.

Lead has found widespread use since antiquity. It has been used as piping in water distribution systems, as a pigment and as a drier in paints, as a glazing compound, as a component of certain glasses, as a plate material in storage batteries, as an antiknock additive in gasoline, as a pesticide (mainly as lead arsenate), as a component of low melting alloys, and as bullets and bird shot.

Mercury is widely used in the electrical industry in batteries, energy cells, rectifiers, power tubes, lamps, and switches. It is used in industrial controls in switches, gauges, seals, and valves. Mercury is used as the fluid in diffusion pumps, barometers, manometers, and thermometers. A continuous flow mercury cathode is used for the production of chlorine and caustic soda. Mercury amalgams are used in dentistry for filling cavities. Mercury salts are used as catalysts in the production of certain polymers. Organo-mercurials are used as fungicides and bacteriocides in paints, as slimicides in the paper and pulp industry, and as contraceptive jellies, as an antiseptic, and as a diuretic in the pharmaceutical industry. Mercurials also find wide usage in a variety of industries in addition to those mentioned above.

Silver is used in the electronic industry because of its high electrical conductivity. Silver and its salts are used extensively in the photographic industry. Silver is also used in jewelry, decorative metal ware, and coins. Silver has been used as a water disinfectant. While it is not very effective, the possibility of residual silver from this practice exists.

Health Effects

Concern over these metals is based on their chronic toxicity. All of these metals are known to accumulate in the body with long-term exposure to low levels. None of these metals are considered to be necessary trace elements in man.

Although all of these elements have certain unique effects, they share a broad range of common effects. General effects are vomiting, diarrhea, abdominal pains, dizziness, headache, and numbness or tingling of the extremities. They usually cause some kidney and liver damage after long-term exposure. Central nervous system disorder is also associated with chronic exposure. Often personality changes are observed such as loss of memory, easy excitability, lack of security, and general nervousness. They are all general protoplasmic poisons which inactivate enzyme systems. Some of the unique symptoms are reported here. High levels of cadmium have been reported to cause high blood pressure. Excessive exposure to cadmium can result in decalcification of bones, making them brittle and easily broken. Lead is known to cause basophilic stippling of the red blood cells. Anemia due to interference with heme production results from excessive lead. Exposure to excessive amounts of lead can result in encephalitis, particularly in children. Excessive exposure to mercury can result in sore and tender gums, loss of teeth and hair. Chronic exposure to mercury can cause jerky movement of fingers, eyelids, tongue and lips with partial paralysis of face and limbs. Continued exposure to silver results in coloration of fingernails and gums with a permanent bluish pigmentation of skin after long exposure. There is little or no evidence that gradual ingestion of low levels of silver produces any significant physiological problems. The cosmetic effect is far more evident.

Maximum Levels

The maximum level of cadmium (Cd) is 0.01 milligram per liter (mg/1), lead (Pb) is 0.05 mg/1, mercury (Hg) is 0.002 mg/1, and silver (Ag) is 0.05 mg/1.

Removal

Cadmium, lead, mercury, and silver will exist in water as positively charged ions. They may be present as inorganic complexes with chloride or carbonate ions. They may also form complexes with organics in the water such as tannins or humic or folvic acids. Most of the salts of these metals are insoluble so that the metals may exist as particulate precipitates or colloid solids or associated with other suspended solids in the water. Mercury can also exist as an organic positively charged species. Methyl mercury is the most commonly encountered organic mercury found in water. It behaves somewhat differently from inorganic mercury, but it can usually be removed with varying efficiencies by the same techniques that are used for inorganic mercury removal.

A. Coagulation and Sedimentation

Coagulation and sedimentation have been shown to remove a variety of metals with varying degrees of efficiency. The process involves removal by formation of insoluble materials that settle to the bottom. Normally the efficiencies range from 50 to 90 percent. The efficiencies are dependent on the coagulants used, the pH, and the nature of the water. Alum coagulation may be effective for removal of these elements in the pH range of 8 to 9. Iron coagulants are generally effective over a somewhat broader pH range and tend to work even at a pH of 7. Plant costs range from $25,000 to $45,000 per 1000 cubic meters per day (m^3/day) [183 gallons per minute (gpm)] depending on whether sedimentation is used or solid contact is used. Operating costs are $25,000 to $35,000 per 1000 m^3/day (183 gpm) capacity. Coagulant aid and filtration may be necessary or beneficial in some cases. Care must be taken to prevent formation of colloidal particles which will contain the metals. Any turbidity in the finished water suggests possible carry-over of metals as colloidal particles.

B. Lime Soda Softening

Lime soda softening has been reported to be effective in removing lead, mercury, and cadmium and should work for silver as well. The process involves the precipitation of insoluble forms of the metal from solutions as oxide. Generally large excesses of lime need to be used to achieve high removal efficiencies. A pH of 11 or higher is reported to be best so subsequent pH adjustment of the water may be required. The efficiency of the process is dependent on the quality of the treated water so pilot studies are necessary.

C. Ion Exchange

Zeolite ion exchange as used for water softening is applicable to the removal of metals other than calcium and magnesium. The metals to be removed are exchanged for sodium ions from the ion exchange resin. The resin can be regenerated with brine. The efficiency of this process is influenced by the hardness of the water and the total dissolved solids. Generally, removal efficiencies of 90 percent or better are reported for most metals with maximum concentration varying from less than 0.1 to about 1 mg/1 according to the Federal Environmental Protection Agency. Careful control of regeneration is necessary so that breakthrough of the ions of interest does not occur. Cost of ion exchange is dependent on the total dissolved solids of the water as well as plant capacity.

D. Adsorption Processes

Recent work has reported that certain toxic metals can be removed from water by adsorption onto activated carbon. The adsorption process involves removal of metals by adsorption at active sites on a solid material which the water contacts. Only limited work has been carried out in this area so the efficiency and general applicability of this process is not known.

E. Reverse Osmosis

Reverse osmosis involves the removal of soluble minerals by passage of water through a semipermeable membrane. To get water to pass through the membrane it is necessary to apply pressure to the water containing the minerals to overcome the natural direction of flow which would be for pure water to diffuse into the mineral-containing water. The amount of pressure necessary is dependent on the mineral content of the raw water. Although reverse osmosis can be used to reduce the toxic metal level, its application is impractical and costly unless it is already in use for the treatment of brackish water. The most significant cost is plant construction. For a 1000 mVday plant (183 gpm), construction costs will be about $250,000 based on 1976 costs. This cost does not include costs for any interest during construction, site and site improvement, discharge facilities, storage and delivery facilities, or special treatment. Operating costs are about $18,000 for a plant of that capacity.

F. Electrodialysis

Electrodialysis involves the removal of salts by means of ion selective membranes and a d.c. current to assist transport of the ions across the membrane. There is depletion of ions on one side of the membrane if current is passed for any length of time, while there is concentration on the other side of the membrane. Any level of desalting can be achieved by increasing the residence time or increasing the current density.

For efficient operation good water pretreatment is required. This should include coagulation of colloidal particles, oxidation of iron and soluble organics, carbon filtration, and finally acidification.

Although this process can be used for the reduction of toxic metal levels, its application is impractical and costly even if other contaminants are to be removed unless the equipment is already in use or planned for use to reduce brackish water to an acceptable salt level. The cost for electrodialysis is dependent on the level of contaminant to be reduced. In general it will be more costly than reverse osmosis. The pH of the effluent may require adjustment to protect the distribution system.

G. Distillation

Distillation involves the volatilization of water to separate it from all dissolved or suspended materials which are not volatilized. Normally the water is heated under pressure to improve the thermal efficiency of the method by recovering some of the heat. This process produces water of very low dissolved solids. Since the water is corrosive to the distribution system, it is necessary to increase the salt content. This can normally be accomplished by appropriate blending of the finished water and the raw water.

Some pretreatment of the feed-water may be necessary. Most often only deaeration is necessary, but in some situations it may be necessary to remove suspended sol ids and calcium and magnesium to prevent scaling.

Distillation is a relatively expensive and impractical solution for the removal of specific contaminants from water. The process involves the removal of a large volume of water from a small amount of dissolved material. This results in an unfavorable energy requirement since it is essentially independent of the contaminant level and only dependent on the amount of water to be treated. The major cost is plant construction which will be about $1.2 million for a 1000 m^3/day plant (183 gpm). The operating costs for energy are also high, since there is only partial heat recovery in this process.

H. Miscellaneous Processes

Recently a number of new processes have been applied to the removal of these metals from waste waters. Some of these processes involve use of starch polymers as precipitants of the metals and use of modified cellulosic material as adsorbent for the metals. These processes may be applicable to treating drinking water. However, at the present time, these methods have not been evaluated as to their applicability to drinking water. Future work may determine whether or not these methods might be practical processes for water treatment.

General Comments

All of the removal techniques discussed above require pilot-scale testing for a specific application to determine their efficiency. Pilot-scale studies are also needed to determine what, if any, pretreatment is necessary to insure good operating efficiency. All of the processes which effectively demineralize the water require some adjustment of pH and/or hardness and alkalinity to prevent corrosion of the distribution system.

Technical Letters are issued as part of the Water Survey's continuing service to citizens of Illinois. Should you need further clarification, please let us know.

Very truly yours,

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