

ISWS  
MP-46

INOIS

Loan Copy

Education

FIELD  
RESOURCES

# Illinois State Water Survey

CHAIRMAN

THOMAS PARK

CHEMISTRY..... H. S. GUTOWSKY

ENGINEERING..... ROBERT H. ANDERSON

FORESTRY..... STANLEY K. SHAPIRO

GEOLOGY..... LAURENCE L. SLOSS

SOUTHERN ILLINOIS UNIVERSITY..... JOHN C. GUYON

UNIVERSITY OF ILLINOIS..... WILLIAM L. EVERITT

6 ISWS  
MP-46

Amore, Francis J.  
REMOVAL OF WATER SUPPLY  
CONTAMINANTS - IRON AND  
MANGANESE: TECHNICAL  
LETTER 23

ILLINOIS 61801

AREA CODE 217  
PHONE 333-2210

WILLIAM C. ACKERMANN, CHIEF

SWS0991

Subject: Technical Letter 23

April 1977

Removal of Water Supply Contaminants -- Iron and Manganese

This is the ninth 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 secondary drinking water standards. Compliance is only recommended and not required for secondary standards.

## Contaminant

This Technical Letter is concerned with iron (Fe) and manganese (Mn) as contaminants of drinking water. In 1976 there were about 600 water supplies in Illinois which exceeded the iron standard of 0.3 milligram per liter (mg/l) and about 300 water supplies which exceeded the manganese standard of 0.05 mg/l. These two elements are covered in a single letter because of certain similarities in their chemistry and methods of removal.

## Prevalence and Uses

Both iron and manganese are essential trace elements. Iron is involved in oxygen transport by the blood and in a number of electron transport cycles in the body. Manganese is involved as a cofactor in several enzyme systems.

Both iron and manganese are widely distributed in nature with some highly concentrated localized deposits. Iron and manganese are found in groundwater primarily from leaching of geological deposits containing the metals or from contamination due to industrial usage. Iron may also occur in water as a result of corrosion of iron and steel pipes.

Iron has been of great importance since antiquity. Iron and its alloys have been used to form tools and machines which have played an important role in all facets of man's technological development. In addition to the use of iron as a metal, a variety of iron salts are widely used as pigments in inks, paints, ceramics, rubbers, etc. The salts are used as catalysts in the production of various organic compounds. Iron salts are used in the production of leather, as mordants in dyeing of fabrics, as a food and feed supplement, to impart a greenish-brown tint to optical glass, as a photographic developer, as a pesticide, as a preparation for treating anemia, etc.

Manganese is used as an alloying agent in the production of various steels, manganin, copper manganese, ferromanganese, etc. Various salts and compounds of manganese are used as driers in paints and varnishes, as a mordant in dyeing, as a feed supplement, as a trace constituent of fertilizer, as an antiknock additive, as a porcelain colorant, in alkaline batteries, and a variety of other uses.

### Health Effects

Both iron and manganese are considered necessary for good health. The drinking water standards for iron and manganese are based on esthetic rather than health considerations. There are no reported ill-health effects due to ingestion of small amounts of iron or manganese. Exposure to and inhalation of manganese dust give rise to symptoms similar to Parkinson's disease. There have been deaths of young children from ingestion of large amounts of iron pills. However, limited solubility of iron and manganese in water would prevent levels which could give rise to deleterious health effects. Concern with high levels of iron and manganese is based on objectionable taste and appearance and staining of clothes and plumbing fixtures.

### Maximum Levels

The approved maximum limit in drinking water for iron is 0.3 mg/l and for manganese 0.05 mg/l.

### Removal

A wide variety of techniques have been found to be effective in removing iron and manganese from water. Most of these techniques are based on the limited solubility of various forms of iron and manganese.

#### *A. Aeration with Sedimentation or Filtration*

The more soluble forms of iron and manganese are ferrous ( $\text{Fe}^{+2}$ ) and manganous ( $\text{Mn}^{+2}$ ) ions. Both of these are subject to air oxidation to higher oxidation states which are less soluble except at very low pH ( $\text{pH} < 4$ ). Aeration converts iron from ferrous to ferric ( $\text{Fe}^{+3}$ ) and manganese from manganous to manganese IV ( $\text{Mn}^{+4}$ ) which precipitate as ferric oxide and manganese dioxide, respectively. Sedimentation or filtration are normally carried out after aeration to remove the precipitated iron and manganese.

Aeration can be accomplished merely by agitation, by flowing over cascades, weirs, steps, troughs, etc., by flowing through trickling devices such as coke beds, limestone beds, and perforated trays, or by diffusing air into the water.

Manganese is not as easily oxidized as iron so aeration is frequently insufficient for manganese removal. High pH favors the oxidation of manganese, but even at a pH of 9 simple aeration may be insufficient.

Aeration is ineffective for removal of organically bound iron or manganese complexes with humic or fulvic acids. Chemical coagulation is necessary for the removal of organically bound iron and manganese.

#### *B. Chemical Oxidation, Sedimentation, and Filtration*

Iron and manganese are chemically oxidized by chlorine or permanganate. Normally the water is aerated before chemical oxidation to strip out dissolved gases and to add oxygen to the water. The chemical oxidation is more rapid than simple aeration and is effective in oxidizing the manganese. The amount of oxidant required will depend on the water being treated. Any constituent in the water which can be oxidized will consume oxidants. Sedimentation and filtration are usually necessary since a significant amount of the precipitate is not heavy enough to settle out immediately. Chlorine and permanganate work equally well as oxidants. Permanganate has the slight advantage in that it is less affected by pH.

Chemical oxidation has no effect on removing organically bound iron or manganese, unless the organic to which they are bound is susceptible to oxidative destruction.

#### *C. Manganese Zeolite*

Manganese zeolite is a natural greensand which is treated with permanganate. Iron and manganese are removed by oxidation, precipitation, and filtration rather than by ion exchange. The process is the same as chemical oxidation and filtration except that the oxidant is held on the greensand rather than being mixed into the water. The zeolite is regenerated by removal of metal oxides through backwashing followed by treatment with potassium permanganate. This method effectively removes both iron and manganese. However, it does not remove iron and manganese which are bound to organic molecules in the water.

#### *D. Coagulation and Sedimentation*

Chemical coagulation with sedimentation can effectively remove iron and manganese from water. General adjustment of the pH to about 9 to 10 is made to precipitate the hydrated oxides of manganese and iron. At this pH the hydrated oxides of iron II and manganese II will be precipitated as well as the oxidized forms. A chemical coagulant, such as alum, is required to produce a more compact and stable floc from the light and difficult-to-settle precipitates. The coagulant acts to neutralize charges which might

result in colloid formation and to flocculate the iron and manganese precipitates. Normally calcium oxide or hydrated lime is used to raise the pH of the water to form insoluble aluminum hydroxide which agglomerates the colloidal iron and manganese particles.

Coagulant aids such as bentonite, silica, or polyelectrolytes can be used to improve the flocculation efficiency and to provide a more compact and stable floc with more rapid settling.

#### *E. Lime Soda Softening*

Lime soda softening will remove iron and manganese even without oxidation since the hydrated oxides will precipitate at the high pH used in reducing the hardness due to calcium and magnesium. The calcium carbonate and magnesium hydroxide precipitates effectively carry down the iron and manganese. Filtration removes the residual particles from the water.

#### *F. 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 depends on the mineral content of the raw water.

Although reverse osmosis can be used to reduce the iron and manganese 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 m<sup>3</sup>/day 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.

This system is applicable only to the soluble forms of iron and manganese. The insoluble forms will clog the membranes and greatly decrease the efficiency of the system. Since it is extremely difficult to maintain the anaerobic conditions necessary to prevent some oxidation of the iron and manganese and subsequent precipitation during treatment, this system is of only limited utility for iron and manganese removal.

#### *G. 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 iron and manganese 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 depends 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.

This system is applicable only to the soluble forms of iron and manganese. The insoluble forms will clog the membranes and greatly decrease the efficiency of the system. Since it is extremely difficult to maintain the anaerobic conditions necessary to prevent some oxidation of the iron and manganese and subsequent precipitation during treatment, this system is of only limited utility for iron and manganese removal.

## *H. 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 distilled water is corrosive to the distribution system, it is necessary to increase the hardness. This can normally be accomplished by appropriate blending of the finished water and the raw water.

Some pretreatment of the feedwater may be necessary to remove suspended solids 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<sup>3</sup>/day plant (183 gpm). The operating costs for energy are also high, since there is only partial heat recovery in this process.

## I. Ion Exchange

Ion exchange involves the exchange of undesirable ions in the water with innocuous species. The process uses either natural or synthetic resins as the exchange media. Ion exchange has been used extensively for softening of water. There are two basic types of ion exchange resins, cation and anion. The cation exchange resins remove positively charged ions, and the anion exchange resins remove negatively charged ions. By using a mixed bed resin containing both anion and cation exchange resins, it is possible to get complete demineralization. This water can then be blended with raw water to provide a finished water of the desired quality and reduce the cost of treatment.

Since it is not possible to selectively remove iron and manganese from water by ion exchange, it is necessary to demineralize a water and blend finished water and raw water to obtain an acceptable iron and manganese level. For this reason, this approach is somewhat impractical for the removal of a single contaminant from a water supply unless ion exchange is already in use or planned for use to achieve other ends. The cost for an ion exchange plant depends on the percent reduction in contaminant. In general the cost will be one-half to one-fourth of the cost for a reverse osmosis plant.

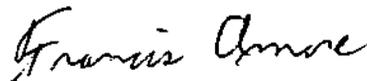
Only *soluble* iron and manganese are removed by ion exchange. Any precipitate will be removed by filtration in passing through the resin bed. This will result in clogging of the bed, greatly reducing efficiency. Since it is extremely difficult to maintain the anaerobic conditions necessary to prevent some oxidation of the iron and manganese with subsequent precipitation during treatment, ion exchange is not of practical utility for iron and manganese removal.

### 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,



Dr. Francis Amore  
Associate Professional Scientist