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Amore, Francis J.

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REMOVAL OF WATER SUPPLY  
CONTAMINANTS - FLUORIDE  
TECHNICAL LETTER 15

ILLINOIS 61801 • AREA CODE 217  
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Subject: Technical Letter 15  
Removal of Water Supply Contaminants -- Fluoride

February 1977

This is the first of a series of Technical Letters dealing with the 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 fluoride as a contaminant of drinking water supplies. In 1976 approximately 129 supplies in Illinois exceeded the new federal drinking water standards for fluoride. The majority of the supplies having high fluoride levels are found in the northwest central portion of the state in Peoria, Knox, and Fulton Counties, and in surrounding counties, and there is another concentration in the northeastern portion of the state in Cook, Du Page, and Will Counties. A large number of scattered sites throughout the state also have high fluoride levels. The levels vary from 8.0 to 1.6 milligrams per liter (mg/l) with more than 50 percent between 2.2 and 1.6 mg/l.

### Prevalence and Uses

Fluoride is found in small quantities in sea water and in most fresh waters as the fluoride ion. Fluoride is generally found in groundwater supplies due to leaching from geological deposits containing fluoride.

Fluoride has been found to be effective in reducing dental carries. For this reason it is added to drinking waters where the amount present is below the level at which it is effective. Fluoride is also added to toothpaste to aid in the prevention of cavities.

### Health Effects

Concern about elevated fluoride levels in drinking water is not based on acute toxicity effects, since the levels are extremely low relative to a lethal dose of fluoride. Rather the concern is centered on the effects of long-term exposure to low levels of fluorides.

Soluble fluorides are readily absorbed from the gastrointestinal tract. Ingestion of fluoride compounds in abnormal quantities generally results in extensive storage of fluorides in the skeleton which can impair normal body functions. Continual ingestion of fluoride from water containing 2.4 to 13.0 mg/l may result in brittle teeth, mottled enamel, and light brown or almost dark discoloration of the permanent teeth.

### Maximum Levels

The maximum allowable level of fluoride (*USEPA Interim Primary Drinking Water Regulations*) is dependent on the annual average maximum daily air temperature.

Temperature		Allowable
(°F)	(°C)	level (mg/l)
53.7 and below	12.0 and below	2.4
53.8 to 58.3	12.1 to 14.6	2.2
58.4 to 63.8	14.7 to 17.6	2.0
63.9 to 70.6	17.7 to 21.4	1.8
70.7 to 79.2	21.5 to 26.2	1.6
79.3 to 90.5	26.3 to 32.5	1.4

The temperature dependence is used to account for differences in water consumption which is related to temperature. Mean maximum temperatures in Illinois range from around 53.9°F in the northern part of the state to around 64°F in the southern part of the state.

### Removal

Both sodium and potassium fluoride are soluble. Many metals and nonmetals form complex fluoro anions. The fluoro anions differ in their behavior from simple fluorides. Fluorides in water will be present as the simple fluoride ion (F<sup>-</sup>) or as a complex fluoro anion such as hexafluoroaluminate (AlF<sub>6</sub><sup>3-</sup>) or hexafluoroferrate (FeF<sub>6</sub><sup>3-</sup>).

Any method which can effectively remove negatively charged ions from solution should be effective in reducing the fluoride level in water. Removal of fluoride or any other trace contaminant from water is generally difficult and costly. Available methods are described in the following sections.

#### A. *Adsorption Processes*

In adsorption systems fluoride is removed by adsorption onto the surface of a solid in contact with the water. The adsorption involves the interaction between fluoride and active sites on the solid. The fluoride becomes tightly bound to the surface, and thereby is removed from solution. The fluoride can subsequently be removed from the solid by appropriate washings to regenerate the adsorbent. Two adsorptive materials have been used successfully for fluoride reduction: activated alumina and bone char.

In the activated alumina process the raw water passes through a bed of activated alumina. The finished water is monitored to detect fluoride breakthrough. When this occurs the alumina must be regenerated. It has been reported recently that use of a continuous-flow fluidized bed instead of a fixed bed improves the fluoride removal efficiency. Because of the high efficiency of the process not all water needs to be treated. Finished water can be blended with raw water to obtain a product of the required fluoride level. Bicarbonate competes with fluoride for active sites. This somewhat decreases the capacity for fluoride and decreases the alkalinity of the water. For low alkalinity waters some pH adjustment of the finished water may be required.

The process using bone char is similar to that for alumina in that the raw water is passed over a bed of bone char. This procedure is somewhat more sensitive to poisoning by other extraneous elements in the water. More frequent monitoring of the finished water would be required as well as more extensive preliminary testing due to wide variability in bone char material.

Either of the adsorptive processes would be effective and represent reasonable approaches to the reduction of fluoride contaminant levels in drinking water. For a plant capacity of 1000 cubic meters per day ( $m^3/day$ ) [183 gallons per minute (gpm)], plant construction costs are estimated to be \$2100 for the activated alumina and \$1900 for the bone char process. The annual chemical costs for the 1000  $m^3/day$  plant are \$2300/mg/l of F<sup>-</sup> removal for bone char and \$2600/mg/l of F<sup>-</sup> removal for alumina. The annual operating and maintenance costs for a plant of this capacity are \$1600 for bone char and \$2200 for alumina. This amounts to about \$1.00 to \$1.30 per capita per year based on 1976 costs.

## B. *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 fluoride 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 cost will be about \$250,000 based on 1976 costs. This cost does not include any interest costs during construction, site and site improvement costs, discharge facilities, storage and delivery facilities, or any special treatment. Operating costs are about \$18,000 for a plant of that capacity.

### C. *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, oxidator of iron and soluble organics, carbon filtration, and finally acidification.

Although this process can be used for the reduction of fluoride 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.

### D. *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 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.

*E. 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.

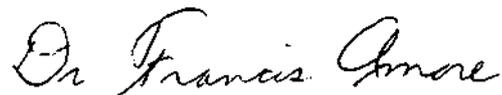
Since it is not possible to selectively remove fluoride from water, it is necessary to demineralize a water and blend finished water and raw water to obtain an acceptable fluoride level. For this reason, this approach is somewhat impractical for the removal of a single contaminant from a water supply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

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