

Methods of Removing Fluorides from Water*

F. J. MAIER, B.S.M.E., B.S.C.E., F.A.P.H.A.

*Sanitary Engineer, Dental Public Health Section, States Relations Division,
U. S. Public Health Service, Washington, D. C.*

INTRODUCTION

FLUORIDES in drinking water can be beneficial or detrimental depending on their concentration. Recent epidemiological studies have indicated that there is an inverse relationship between fluorides and dental caries experience.^{19, 22, 24} The promise which this relationship holds for mass control of dental decay, however, hinges on the fact that an optimal caries prophylactic effect of the fluoride is obtained within the range of 1.0 to 1.5 parts per million (p.p.m.). Greater concentrations are associated with a hypoplasia of the teeth known as mottled enamel or dental fluorosis. It is the purpose of this presentation to examine current methods for removing excessive fluorides from communal water supplies in order to prevent the occurrence of dental fluorosis. Inasmuch as present evidence suggests that the removal process should not effect a fluoride reduction below 1.0 p.p.m. in order that the beneficial effect of caries inhibition may be retained, this discussion will be concerned with the defluorination of water to the optimal limit.

Near the beginning of the 20th century mottled enamel had been noted and described.²⁵ Despite the intensive researches of several investigators, however, it was not until 1931 that its

cause was correctly determined and announced, almost simultaneously, by Churchill,¹⁴ Smith,⁴⁹ and Velu.⁵⁹ Since the discovery that fluorides were the cause of mottled enamel in the permanent teeth of children, the problem of removing excess fluorides from drinking water has been studied widely.

In 1935, Dean and Elvove^{16-18, 21} began to publish the results of their epidemiological studies relating to minimal concentrations of fluorides sufficient to produce mottling. They found that a fluoride concentration of 1.0 p.p.m. or less in a communal water supply produced no significant mottling of the teeth of children who had been using this water continuously. With higher concentrations, mottling was progressively more severe and above 6.0 p.p.m. almost all children were afflicted. In addition to mottling at this high concentration, gross calcification defects and attrition of the enamel were observed. For this reason, the dental defects caused by fluorides in drinking water are better termed dental fluorosis.

After the cause of dental fluorosis was discovered, several methods were devised for removing excessive fluorides from water. Nevertheless, at the present time (excepting some lime softening plants) only one community is known to be utilizing equipment specifically installed to reduce the fluoride content of its water supply. The lack of application of preventive measures maintains despite the undesirable disfigurement

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associated with fluorosis, the increased costs of dental care and the fact that the number of persons using water containing excessive fluorides (over 1.5 p.p.m.) exceeds 1,000,000 persons in over 500 communities.⁵⁸ This situation may be attributed to a combination of several factors, most important of which are the high capital and predicted operating costs of the removal processes and the complexity of the operating procedures.

It is impossible or impracticable in many communities to change the source of supply to one having a satisfactory fluoride concentration. Dental studies have been made in three communities, however, which previously used water high in fluorides and then changed to other sources having little or no fluorides.²³ The change resulted in no additional cases of fluorosis.^{20, 40} No community has as yet removed excessive fluorides from its water and subsequently measured the results in terms of a reduction in the incidence of fluorosis.

FLUORIDE REMOVAL METHODS

The methods utilizing the fluoride exchange properties of the apatites, such as those involving the use of the constituents of bone, the ion exchange principle, and those depending on the sorptive properties of aluminum compounds, appear to show the most promise for removing excess fluorides from water. In addition, where the fluoride concentration is not very high (less than 4.0 p.p.m.), processes involving the concurrent removal of magnesium are indicated, if hardness reduction is also contemplated.

CALCIUM PHOSPHATES

The use of bone for removing fluorides is based on the long known affinity of bone for fluorides. Probably the most plausible theory of the chemistry of this affinity may be explained on the

basis of the anion exchange properties of apatites. The carbonate radical in the apatite comprising bone, $n\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCO}_3$ is replaced by the fluorides in the water, forming an insoluble fluorapatite.⁵⁰ In the regeneration of the material with sodium hydroxide the fluorapatite probably becomes an hydroxy-apatite and the fluorides are removed in the form of soluble sodium fluoride. The hydroxy-apatite subsequently becomes available as an exchange material by the replacement of its hydroxy radical with fluoride.

One method of preparing bone for use as a fluoride removing agent⁵¹ involves boiling to remove the fat and most of the protein. It is then crushed and boiled in a solution of sodium hydroxide. The caustic is removed by thorough washing and finally is neutralized with hydrochloric acid. The material is again washed and then dried and graded for fineness. Home filters in which the prepared bone is utilized are available but there have been some objections to the taste of the treated water. Based on the expense of renewing the bone media in home filters, the cost of using this method in a municipal plant would be exorbitant (approximately \$25,000 per m.g.).* It is reported⁵⁰ that the material can be regenerated successfully by a sodium hydroxide and acid wash method, similar to that used in its preparation. Data are not available on the removal capacity of the bone after it has been subjected to numerous regenerative cycles when used with waters naturally high in fluorides and other mineral contaminants.

A similar process utilizes virgin bone black (animal charcoal) which is essentially tricalcium phosphate and carbon.¹³

* All chemical cost estimates, except where otherwise noted, are based on a fluoride ion (F^-) reduction from 6.0 p.p.m. to 1.0 p.p.m. at current (1947) chemical quotations.

In its limited use in household filter units, the material is discarded when its exchange capacity is exhausted. In a municipal installation, the cost of this procedure would be excessive (\$5,000 per m.g.). Regeneration of the material has been effected with solutions of trisodium phosphate and mono-sodium phosphate but the exchange capacity of the bed is reduced by 12 per cent after the first regeneration.

The principal chemical constituent of bone, tricalcium phosphate, can be prepared from phosphoric acid and milk of lime. The product consists essentially of tricalcium phosphate and its hydroxyapatite. Because it forms a gelatinous floc in water, fluoride removal is probably accomplished by adsorption together with the formation of a fluorapatite.^{1, 26, 28}

A porous, granular type of tricalcium phosphate has been developed for use in contact filters.³ When the fluoride removal capacity of the bed is exhausted, the material can be regenerated with a 1 per cent sodium hydroxide solution. About one pound of caustic soda is required for each cu. ft. of tricalcium phosphate.³⁰ The causticity of the bed is then neutralized by thorough washing with water and with a carbon dioxide solution.⁷ The use of carbon dioxide for this purpose, rather than hydrochloric acid as originally proposed, greatly increases the life of the bed and considerably reduces attrition losses.⁸ The rated removal capacity of tricalcium phosphate is 300 grains of fluoride per cu. ft. but this capacity decreases about 3 per cent for each 100 p.p.m. sulfates present in the water. The iron content of the water must be reduced to 0.10 p.p.m. in order to prevent clogging of the filter. A water treatment plant using this material has been operated since 1937.⁶⁰ The fluoride content of the raw water varied from 2.0 to 14.0 p.p.m. and averaged about 8.3 p.p.m. The effluent contained an average of

0.6 p.p.m. The chemical costs for the fluoride removal process at this plant totaled about \$130 per m.g. in 1944.

Tricalcium phosphate can also be formed from ortho-phosphoric acid and lime within the mixing chamber of the conventional type of treatment plant (mixing flocculation, settling and filtration).^{37, 38} The tricalcium phosphate thus formed must be removed continuously from the water and discarded. The chemical cost of this process amounts to approximately \$245 per m.g. A similar material for fluoride removal, trimagnesium phosphate, has been suggested,² but is reported to be less efficient and more expensive than tricalcium phosphate.

ADSORPTION WITH ALUMINUM COMPOUNDS

In addition to the constituents of bone for fluoride removals, a large number of other materials have been tested. These materials include aluminum sulfate, sodium aluminate, zeolites, bauxite, silica gel, sodium silicate, ferric fluoride, lime,¹¹ and various adsorbent clays and earths.⁴¹ With the exception of aluminum sulfate, all of these materials have been found to be impracticable probably because of the very low initial concentration of the fluoride ion, and in some instances because an undesirable proportion of the reagent remains in the water due to the excessive amounts of chemicals required. Aluminum sulfate and other aluminum salts have been used in combination with insoluble compounds in contact beds or as constituents of floc which is subsequently removed by settling and filtration. The fluorides might be removed by the formation of an aluminum fluoride complex or by adsorption on the floc. In addition to the fluoride removal characteristics of the aluminum compounds, they are relatively inexpensive, easy to use, and can be combined advantageously with aids to coagulation

such as clays and activated silica. The results reported on the effectiveness of aluminum hydroxide floc formed from aluminum sulphate and a source of alkalinity vary considerably. The variations can be attributed to such factors as the following: different raw waters with varying induced fluoride concentrations were used; the speed of adding the reagent and methods of mixing were different¹²; the times of contact varied; the pH was not the same; and, not all of the effluents were filtered. In general, however, 4.0 p.p.m. fluorides are removed from water when hydrous aluminum sulfate is used in concentrations of 335 p.p.m.,¹¹ 430 p.p.m.,³⁴ or 513 p.p.m.⁴⁷ According to one investigator, it required 891 p.p.m. aluminum sulfate to reduce fluorides from 6.0 to 1.0 p.p.m.⁴⁷ while according to another^{34, 35} 860 p.p.m. were required to obtain a reduction from 8.5 to 1.0 p.p.m. In order to obtain maximum fluoride reductions, optimum hydrogen ion concentration is necessary but the pH can be controlled in treatment plants by adjusting the chemical feeders.

Fluoride removal experiments in which aluminum sulfate and coagulation aids (clays and activated silica) were used together with alkalin solutions for pH control, were conducted recently in the Industrial Hygiene Laboratories at the National Institute of Health and in pilot plants at Great Falls, Md. (Potomac River raw water), and at Cincinnati, Ohio (Cincinnati City water).³⁹ Fluoride concentrations¹⁰ were determined by using the Scott modification⁴⁸ of the Sanchis procedure⁴⁶ and the Lamar adaptation³⁶ with a spectrophotometer. The results with the conventional type of plant at Great Falls (mixing, flocculation, settling, and filtration) indicated that fluorides can be reduced in two steps (6.0 to 3.5 p.p.m. and from 3.5 to 1.0 p.p.m.) using in each step 100 p.p.m. aluminum sulfate, 100 p.p.m. clay, and

about 25 p.p.m. lime. In an improvised experimental sludge-blanket type plant (precipitator) in Cincinnati approximately 25 per cent more fluorides were removed using the same chemical dosages as at Great Falls. When activated silica (Baylis Sol) was used in conjunction with alum, clay, and soda ash, a further reduction in fluorides was noted.^{4, 5, 6, 32, 33} Based on the quantities of chemicals used in the conventional pilot plant the cost is estimated to be about \$35 per m.g. The process is not as efficient with highly mineralized ground water in which excessive fluorides are naturally present. The reason for decreased efficiency under the latter conditions is not known.

Another method utilizing aluminum salts involves contact beds of insoluble material impregnated with aluminum compounds. The earliest report⁴³ suggested soaking filter beds of sand or diatomaceous earth with the precipitated hydroxide of aluminum sulfate and an alkali. The data available on the fluoride removal efficiencies of this method are not sufficient to serve as a basis for estimating costs.

A similar method involves pickling base exchange materials⁵⁴ (natural or synthetic zeolites) or naturally adsorptive materials⁵⁵ in aluminum salt solutions. Although these pickling solutions are highly concentrated, five hours of contact are required before the exchange material has been converted to an anion exchange compound. The aluminum ion is presumed to have entered into the chemical structure of the material and reversed its exchange mechanism. When the bed is exhausted, it can be regenerated with soluble aluminum salts. This method is the least efficient of those in which aluminum soaking is involved.⁴⁴

Another method involving aluminum salts and utilizing contact beds is based on the formation of insoluble compounds in the presence of excess aluminum ions. The insoluble compounds thus formed

are alleged to possess a fluoride removal capacity several times that of materials of the base exchange group. The superior performance is attributed to the much higher concentration of aluminum salts in solution and to the concomitant increase in adsorbed uncombined aluminum ions.⁵⁶ The insoluble compounds can be made from either sodium silicate, barium chloride, sodium phosphate, ferrous sulfate or titanium chloride in the presence of excess aluminum salts. The precipitates formed are washed, dried and graded. Regeneration is accomplished by washing the bed with solutions of either aluminum salts or dilute mineral acids or alkalis. No data are available on the fluoride-removing capacity of this method or of its efficiency after repeated regenerations. Until other commercial uses can be found for the insoluble materials used in this method, their cost for fluoride removal will probably be too high for use in municipal installations.

Dehydrated aluminum oxide (calcined alumina)¹⁵ or partially hydrated alumina³¹ have been suggested for use in contact beds. The calcined alumina (activated alumina) has been tried in field tests^{29, 52} and rated as fairly good with respect to fluoride removal efficiency. When the bed becomes exhausted the fluorides are removed by washing with a dilute caustic solution and neutralized with a dilute acid solution. Chemicals for regenerating the materials used in this method amount to \$275 per m.g. Because tricalcium phosphates have a better removal capacity and a lower regeneration cost than activated alumina, the latter is no longer advocated for municipal treatment plant use.

Other hydrated metallic oxides have also been suggested for removing fluorides. These include ferric oxide, chromium borate, mixed oxides of iron and manganese, bauxite and bog iron ore. All can be regenerated to varying

degrees but ferric oxide is probably the most efficient.³¹ Using caustic soda and carbon dioxide solutions for regeneration, chemicals cost approximately \$250 per m.g.

ION EXCHANGE PROCESSES

While the compounds which are subjected to aluminum solution soaking probably involve a combination of ion exchange and adsorption principles in fluoride removal, several additional products are claimed to involve predominately ion exchange processes. One of these is made from barium or ferric chloride and silicic acid with the formation of a complex metal chloride silicate. It is claimed⁵³ that the fluorides are removed from water when in contact with this material by exchange with the chloride ions. Regeneration of the materials has not been advocated and no data are available on capacities or costs. Another compound is obtained from asphaltic materials heat treated with an alkali.⁵⁷ Fluorides are presumed to be removed by anion exchange with the hydroxide. Regeneration is accomplished with an alkali but capacities and costs have not been determined.

Recently an organic resinous anion exchange material made from various diaminobenzenes or phenols and formaldehyde has been announced.⁴⁵ It is alleged that this material is somewhat selective for fluorides, removing in addition only iron, copper or other metals yielding insoluble hydroxides.⁴⁴ The material is first conditioned with a 4 per cent soda ash solution, neutralized with a dilute acid wash (500 p.p.m. hydrochloric acid) and then soaked with a 4 per cent solution of aluminum sulfate. The exchange capacity is based on 1,240 grains of fluorides per cu. ft. Chemical costs for regeneration amount to about \$90 per m.g. Further tests on this material to determine the effect of higher concentrations of radicals commonly found in ground waters and the

possibility of utilizing other regenerating chemicals are now in progress.

OTHER METHODS

The use of lime for fluoride reduction was known soon after the cause of fluorosis was discovered.¹¹ In a study of the results of lime softening plants in Ohio,⁴⁷ it was determined that fluoride reduction with lime was actually a function of the amount of magnesium removed. When waters were fluorinated with sodium fluoride and treated with magnesia, it was demonstrated that the magnesia first becomes partially hydrated, then magnesium fluoride and sodium hydroxide are formed by metathesis and finally the magnesium fluoride is attached to the magnesia, forming perhaps an oxyfluoride.⁶¹ The results of samples examined from the softening plants indicated that the quantity of fluorides removed approximately equaled the product of 7 per cent of the initial fluoride and the square root of the amount of magnesium removed. Between 45 and 65 p.p.m. magnesium must be removed to reduce the fluoride one p.p.m. Theoretically, if a residual fluoride of 1.0 p.p.m. is desired, 100 p.p.m. magnesium must be removed if the initial fluoride content is 3.3 p.p.m. A magnesium concentration of this magnitude is rare in most high fluoride waters. Consequently employment of this method would involve the addition of magnesium preferably in the form of dolomitic lime, calcined magnesite or activated magnesia.^{9, 26, 27} For average waters containing 6.0 p.p.m. fluoride and relatively high magnesium (20 p.p.m.), about eight tons of chemicals would be required per m.g. (carbon dioxide for pre- and post-carbonation, dolomitic lime and aluminum sulfate). The chemical costs would aggregate \$120 per m.g. Despite this relatively high cost and the large quantities of chemicals required (involving principally

sludge disposal problems), this method appears to be particularly applicable in the treatment of hard waters which require softening and which contain less than 4.0 p.p.m. fluorides. A refinement of this process provides a source of carbon dioxide for pre-carbonation,⁹ which is necessary to convert the magnesia to magnesium carbonate. The carbon dioxide is produced from conversion of bicarbonates by passing the water through hydrogen exchange materials.

Other chemicals and processes have been reported, many of which proved to be ineffective or impracticable. Activated carbon is quite efficient and its use is based on sound chemical principles.⁴² Almost complete fluoride removal is possible, however, only when the pH of the raw water is less than 3.0. No fluoride is removed at a pH of 8.0 or higher. Regeneration is possible with weak alkaline and acid solutions although no reports have been made as to the removal capacity of the carbon after repeated regenerations.

About one-half the fluorides originally present in water are removed using dosages of approximately 2,000 p.p.m. of either Wyoming bentonites, Fuller's earths, celite, or silica gel. To obtain this removal, however, the pH of the raw water is reduced to 2.5. In no case is any fluoride removed when the pH of the water is 8.3.⁴¹ Because of the inefficiency of these materials and their pH requirements their use is impracticable for fluoride removals.

SUMMARY AND CONCLUSIONS

More than a million persons in over 500 communities in the United States are now using public water supplies containing in excess of 1.5 p.p.m. fluorides. The disfiguring dental condition which is caused by the use of such waters for drinking purposes can be prevented in future populations of these communities by removing the excess fluo-

rides from the communal water supplies.

Most of the removal processes now available appear to be either too expensive to operate or too complicated for routine application by the average small water treatment plant operator. An urgent need is the development of a process comparable to the lime-soda ash softening process in operating costs and simplicity.

The problem of choosing the most practical method of defluorination for a particular supply is difficult, because of the almost complete absence of operational data. The choice of method for the accomplishment of a similar purpose as in other treatment processes, depends, by and large, on the rate of water consumption and on the characteristics of the raw water. For large municipal plants which treat waters requiring a reduction in hardness, it is advisable, in general, to reduce the fluorides as much as possible by the lime softening process. In some cases it would be economical to balance the costs of pre-carbonation and sludge disposal against the addition of a limited quantity of magnesium compounds. Excess fluorides remaining after this process could be removed in gravity contact filters or by an aluminum-clay floc, with subsequent separation of the floc from the water.

In small plants where softening is not desired, pressure contact filters appear to be more economical. Where the water is hard, lime softening is indicated up to a raw water fluoride content of about 4.0 p.p.m. If the fluoride exceeds this figure in hard waters, the remaining fluorides can be removed by contact filters.

The tricalcium phosphates and the resinous ion exchangers, when used in contact filters, appear to have the highest exchange capacities for fluorides. Furthermore, the chemical cost for regeneration of these materials is relatively economical.

It is evident from this examination of fluoride removal methods that our current knowledge of the chemical processes involved is very limited and that additional fundamental research in this field is needed. Further, the practical usefulness of the available methods and those now undeveloped must be tested on a pilot plant scale, and their relative worth under varying conditions must be determined. Until this information is available, endemic fluorosis will continue to be a dental hazard to a large population in many communities in this country.

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