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FILTRATION SYSTEMS

**THE REMOVAL OF FLUORIDE
FROM
DRINKING WATER SUPPLIES**

FOREWORD

This bulletin is offered to provide the reader with general information on the occurrence of fluorides in nature, their presence in drinking water, their regulatory background, health effects, and the various unit operations available for their removal.

Occurrence of Fluorides in Nature

Fluorides are derived from **fluorine**, a gaseous halogen element in group VIIA of the periodic table of the elements. Fluorine, atomic symbol F, CAS No. 7782-41-4, atomic number 9, atomic weight 18.998, with no known other stable isotopes, has a valence of “1”, and is the most electronegative element of all, and the most powerful oxidizing agent known.

Fluorine, a pale-yellow diatomic gas or liquid, depending on temperature, has a pungent odor, a boiling point of -188°C , a freezing point of -219°C , and a gas density of 1.695. Since fluorine reacts vigorously, frequently involving ignition, with most utilizable substances at room temperature to form fluorides, with all elements except helium, neon and argon, it is never found in its elemental state in nature, only in the form of fluorides.

Most of these compounds are complexes of calcium, fluorine and phosphorus, such as cryolite, fluorspar, and fluorapatite which are found in the U.S.A., Canada, Mexico, parts of Europe, and South Africa. Fluorine can be derived commercially by the Moissan process, the electrolysis of a mixture of hydrogen fluoride and potassium hydrogen fluoride. Uses of fluorine include the production of metallic and other fluorides, fluorocarbons, as well as the active constituents of fluoridating compounds used in drinking water and dentifrices.

Fluorides in Water Supplies

Fluoride ions normally exist in small concentrations in all water supplies. Barring unusual geological conditions, or the influence of fluoride-bearing wastes, fluoride concentrations in water supplies are normally low. Waters, generally from surface sources, with low fluoride concentrations, frequently receive fluoridation treatment to raise the fluoride level to an optimum desired for consumer protection from tooth decay. This optimum level, established by the U.S. Public Health Service (USPHS), is one-half of the (United States Environmental Protection Agency [USEPA] - established) Maximum Contaminant Level (MCL) of 4.0 milligrams per liter. Well waters generally have higher fluoride concentrations due to greater exposure of the water to fluoride-bearing minerals. There are, however, many groundwater supplies with fluoride levels low enough to also require fluoride augmentation. The vast majority of well waters contain fluoride levels close to the optimum, or within the MCL. Nevertheless, according to Letkiewics (see references), there are in excess of 2,000 water supplies in the United States in which the fluoride MCL is exceeded. Of these, nearly all have fluoride levels between the MCL and 12 mg / L. There are known water supplies with natural fluoride levels as high as 30 mg / L. In those supplies, the concentrations of other ionic species is generally also too high for the waters to be used as potable water without desalination.

Regulatory Background

Public Law 93-523, passed by the 93rd Congress in 1974, established the “Safe Drinking Water Act” (SDWA), which limits certain constituents (“contaminants”) in drinking water. The SDWA, and its 1986 amendments, initially created a unique “flexible” MCL for fluoride of 1.4 – 2.0 mg / L depending on the mean annual temperature of where the water was being served. The philosophy behind the sliding scale was that water ingestion is largely a function of ambient temperature, therefore the MCL would be lower the warmer the prevailing climate. The USEPA later abandoned this approach and established a *primary* MCL of 4 mg / L. (It will be remembered that primary MCLs are enforceable, and health-effect driven, whereas, secondary MCLs are esthetic and property-protection related). The agency then classified dental fluorosis (mottling of teeth) as a *cosmetic effect* and initiated a *secondary* MCL of 2 mg / L. Thus, as of this writing, both, a primary as well as a secondary MCL for fluoride is in effect.

Health Effects

Due to the natural affinity of fluoride ions for calcium, there is a complex interaction between ingested fluoride and skeletal components. Fluoride in drinking water between 6 – 8 mg / L has been reported to cause skeletal fluorosis (brittling of bones and stiffening of joints), while concentrations in excess of 2 mg / L have been implicated (see above) in causing dental fluorosis, especially in children during their formative years. The generally accepted (U.S. Public Health Service) “reference dose” is defined as the amount that would *not* result in any appreciable deleterious health effect over a lifetime, is 0.06 milligrams per kilogram body weight per day.

Reduction of Fluoride

In order to prevent adverse health or cosmetic effects, it is desirable to control the concentration of fluoride in drinking water supplies as close to the optimum level as possible. The optimum level of fluoride in potable water is one half of the MCL of 4 mg / L, i.e. the optimum concentration is 2 mg / L. In supplies where the fluoride exceeds the MCL, steps must be taken to reduce that level to below the MCL, preferably to the optimum level. The remainder of this bulletin addresses the removal of excess fluoride by various unit operations.

Fluoride Removal Methods

Various treatment techniques for fluoride removal have been studied. There appear to be only two (2) methods: ion exchange with activated alumina; and reverse osmosis that can *economically* reduce fluoride levels to drinking water standards. Listed below, not necessarily in order of applicability, are the available unit operations for the removal or reduction of fluoride in water.

- Activated alumina (BTGA*)
- Bone char
- Alum coagulation / flocculation
- Lime softening
- Reverse osmosis (BTGA*)
- Electrodialysis
- Ion exchange

*BTGA = “Best Technologies Generally Available”, as defined by USEPA in the 1986 amendments to the Safe Drinking Water Act.

Activated Alumina

Since the 1930's, it has been known that contact of fluoride-containing water with activated alumina would remove fluoride. Continued research into this phenomenon has led to increased knowledge about the removal of fluoride by this means, and there are a number of full-scale activated alumina fluoride removal treatment plants in operation in the United States.

Activated alumina is used much the same way as are ion exchange resins. It is thought that activated alumina removes certain species from water due to hydrolytic adsorption. Activated alumina is an amphoteric substance, with an isoelectric point of, approximately, pH 9.5. Below this pH it will remove anions, and above pH 9.5, cations. The affinity of alumina for anions seems to be inversely related to the solubility of its aluminum salt. Therefore, when treated with an acid solution, alumina behaves like an anion exchanger and fluoride is very high on the selectivity list. Activated alumina (and reverse osmosis, see below) remove arsenic *and* fluoride, among other impurities. Using activated alumina treatment, optimum removals for both contaminants may occur in a similar range of pH 5.5 to 6.0 (USEPA, 1985, USEPA, 2000). However, since arsenic V and silica are preferentially adsorbed by activated alumina media, the effectiveness of activated alumina, where arsenic and fluoride co-occur, may require some investigation.

Activated alumina is a physically and chemically stable form of highly porous aluminum oxide, (Al₂O₃). Activated alumina is produced by exposure of hydrated alumina to caustic soda and heat treatment at about 750°F. The high porosities and large surface areas make alumina an excellent adsorbent. Activated alumina is chemically inert to all but the most corrosive gases and liquids, is non-toxic, and is quite abrasion and disintegration-resistant.

The capacity of a continuous-flow activated alumina column for fluoride removal depends on three important factors:

1. **Initial Fluoride Concentration.** Studies (Choi, 1979) show that the capacity of activated alumina for fluoride removal *increases* with increased fluoride concentration.
2. **pH.** The pH of the influent water will influence the volume of water that can be treated until breakthrough occurs. An influent pH of 5.5 appears to be optimum, though the process is readily operable through a pH range of 5.0 to 8.0. At the optimum pH for fluoride removal, the alumina will also adsorb some organic molecules, as well as some metal ions, including arsenic. If both, arsenic and fluoride are present in the influent water, the alumina regeneration technique must be adjusted to accommodate this condition.
3. **Particle Size.** Commercially available activated alumina is processed in four (4) typical size ranges: 8-10, 14-28, 28-48, and 48-100 mesh, from coarsest to finest. The reaction kinetics are such that the smallest particles will provide the most rapid uptake of fluoride. Some tradeoffs have to be made because the smaller the particle size, the more readily will it be washed out of the bed during backwash. The material most frequently used is 28-48 mesh.

Reaction kinetics appear to dictate a minimum Empty Bed Contact Time (EBCT) of five (5) minutes for efficient fluoride removal. Typically, the systems are run until an on-line fluoride specific electrode senses imminent breakthrough. At that time the alumina bed must be backwashed, with 50% bed expansion, for 10-15 minutes to remove trapped suspended material, break up the packed bed, and redistribute the media.

The bed is then regenerated using sodium hydroxide (NaOH) to elute the fluoride off the alumina. Typical values for NaOH concentrations range from 0.5 to 2%, and flow rates of 0.25-3 gpm / ft³ for 1-1 ½ hours are typical. All of these operational parameters should be predetermined by bench and pilot-scale testing. It should be noted that *some* alumina (approximately 20% / year) will be dissolved to some degree by the NaOH.

Once the alumina has been eluted with NaOH, the bed must be returned to an acidic condition to allow removal of fluoride, and other anions, and to prevent prolonged high pH in the effluent. First, the caustic must be rinsed from the bed, then the bed must be rinsed with an acid solution, either sulfuric or hydrochloric. When the pH drops to the desired level, the influent acid feed is adjusted to optimum conditions.

The disposal of regenerant wastes is a problem inherent with all ion exchange processes. For fluoride removal systems located inland, typical brine disposal methods include evaporation in a lined pond or dewatering with a filter press. The resulting cake must be hauled to an appropriate dump site.

Bone Char Process

This fluoride reduction / removal method is very similar to the activated alumina process. It selectively removes fluoride (and arsenic) and, like alumina, is regenerated with dilute caustic soda (NaOH). However, the process suffers from drawbacks which generally disqualify it when compared to activated alumina. The media (when produced and available) costs about 50% more than alumina, its initial capacity for fluoride is much less than alumina, and more of its fluoride capacity is lost with each successive regeneration. Bone char is susceptible to attack by low pH water, and it irreversibly adsorbs arsenic. All these negative aspects appear to have discouraged further application and development of this removal process.

Anion Exchange

The anion exchange treatment method cannot be considered viable for the removal of fluoride from potable water supplies. Strong base anion resins do have the ability to remove fluoride, along with other anions. However, the cost of this treatment is not compatible with the financial resources of most, especially small, water suppliers. Research reports on this method have generally not been favorable.

Reverse Osmosis (RO)

A process originally designed to purify sea water, or brackish water, by the application of hydrostatic pressure to overcome osmotic pressure, and drive water molecules through a semi-permeable membrane designed to exclude other molecules. The process requires fragile and expensive stacks of cellulose-acetate or thin film composite membranes.

Fluoride ion (and arsenic V) rejection by RO membranes is pH and temperature sensitive. At low pH (~ 5.5) the fluoride rejection is close to 50%. Therefore, adequate fluoride removal can only be accomplished at relatively low raw water fluoride concentrations (~4 mg / L) unless pH is adjusted upward. At higher pH levels, calcium fluoride precipitation may cause membrane fouling problems. Recent membrane developments have shown that membranes with fluoride rejection rates of 90% at lower pH are possible, though expensive. Since the recovery of product (treated) water, as a percentage of feed water, is a function of applied pressure (up to 400 psi or more, depending on membrane type), this process tends to be energy-intensive. Reverse osmosis is capable of the removal of fluorides, but is, of course, non-selective.

Electrodialysis (ED) and Electrodialysis Reversal (EDR)

ED is an electrochemical membrane process initially developed for the purification of brackish and saline waters. Instead of hydrostatic pressure, as in the case of reverse osmosis, the process uses an applied direct current (DC) voltage to move dissolved anions and cations from alternate cells through semi-permeable membranes. This results in the purification of a portion of the feed water, and the concentration of

another. While capable of removing most contaminants, including fluoride, the process is equipment, energy and operator-intensive. The process creates a concentrate stream that requires disposal, and the process is quite wasteful of water.

EDR is an ED process which reverses the polarity of the electrodes on a controlled, predetermined time cycle, thus reversing the direction of ion movement in the membrane stack. This provides automatic flushing of scale - forming minerals from the surface of the membrane. ED and EDR systems are generally not considered economically viable for any but very small applications.

Alum Coagulation

Alum coagulation is a chemical precipitation process employing aluminum sulfate, "alum" ($\text{Al}_2[\text{SO}_4]_3 \cdot 14\text{H}_2\text{O}$), an inorganic coagulant aid, to react with fluoride and other ions in solution to form an insoluble solid. This process, though effective for many applications, is operator-intensive and expensive. Sorg reports that some researchers have found that dosages of up to 250 mg / L of alum were necessary to reduce the fluoride concentration in a water from 3.5 to 1.5 mg / L, and 350 mg / L of alum were required to reduce the fluoride level to 1 mg / L. Such dosages would add massive amounts of sulfate to the water, and result in effluent aluminum concentrations in excess of the MCL. The process is affected by many variables, such as pH, temperature, raw water chemistry and mixing procedures.

Lime Softening

Several investigators have shown that lime, or excess lime / soda, softening, a chemical precipitation process, is capable of removing fluoride from water supplies. The fluoride mechanism appears to be co-precipitation with magnesium hydroxide. Finkbeiner reported that, according to his calculations, 70 mg / L of magnesium must be removed to reduce fluoride from 4 mg / L to 1.5 mg / L, and 137 mg / L of magnesium removal are necessary to reduce fluoride from 8.0 to 1.5 mg / L. Since most waters do not contain that much magnesium, appropriate quantities of a magnesium salt must be supplied to accomplish the desired fluoride removal. The process requires large quantities of chemicals, and produces substantial volumes of sludge that require disposal.

Pilot Testing

As previously noted, neither the two (2) fluoride removal processes deemed "BTGA" by the USEPA, nor any of the other possible unit operations, are specific or selective for the removal of fluoride. Since other ions in the water may alter the process behavior, it is deemed imperative that sufficient bench and pilot testing on the water to be treated be conducted to optimize the fluoride removal parameters of the treatment processes.

Raw water quality can vary significantly, both geographically and seasonally, and since such variability will affect contaminant removal efficiency, field pilot testing of the

selected removal system(s) is strongly recommended. Raw water quality analyses should be performed, and the data evaluated, prior to pilot testing to determine all of the constituents which may affect fluoride removal.

The piloting process should include all necessary pretreatment steps (such as pH adjustment for reverse osmosis and activated alumina). The pilot process must verify fluoride removal throughout the process run cycle, and removal must be verified by a laboratory certified for such analysis. The piloting should be performed in a manner that will allow a reasonable estimation of pretreatment chemical requirement and costs for operation, labor, media replacement and / or disposal, membrane replacement, regenerant brine and / or treatment of sludge or waste water disposals.

Pilot test protocol should be reviewed by the municipal / consulting engineers and all parties should agree to the protocol before the test begins (this should include details such as which party will pay the laboratory test costs). Duplicate samples of raw and treated water should be sent to two (2) independent laboratories for verification of the laboratory test results.

The pilot test report should include field test data, charts and graphs of important data and also a summary of the field and laboratory test results. The report should also include final treatment plant design recommendations. Recommended treatment plant design should include the following; initial capital expense; and those operating expenses noted above.

Conclusion

The reduction or removal of fluoride from drinking water supplies, especially by either of the unit operations deemed "BTGA" by the USEPA is well defined. It must be remembered, however, that neither of the BTGA treatment methods is either selective or specific for fluoride reduction. Since other water quality parameters can have possible effects detrimental to fluoride removal efficiency, water purveyors are encouraged to carefully choose and pilot test processes to optimize fluoride reduction.

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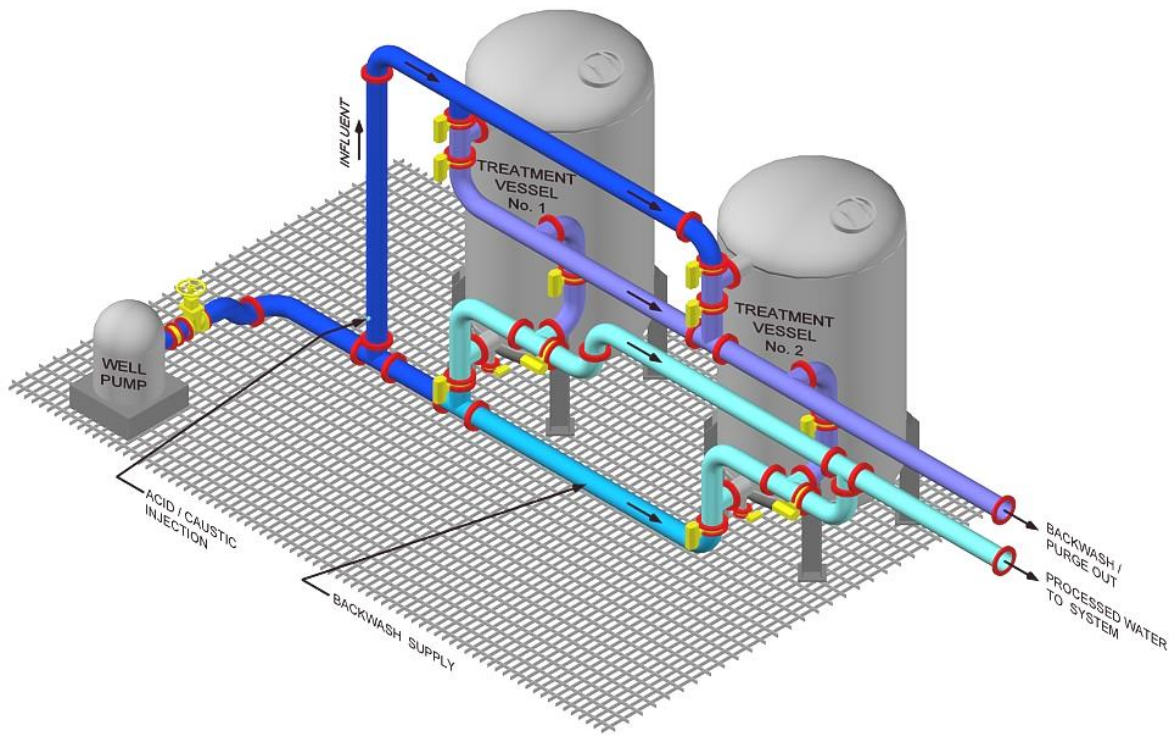
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Appendix

This bulletin was prepared for Pureflow® by Frank Baumann, P.E., Emeritus Chief of the Sanitation and Radiation Laboratories Branch of the California Department of Health Services. Opinions contained herein are those of the author, and do not necessarily reflect policy of the State of California Department of Health Services, (now California Department of Public Health).



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