

FLUORINATION

Friend or Foe?

by C.F. "Chubb" Michau

Fluorine (F), the ninth element on the periodic chart, is a pale yellow gas which at room temperature has a very stable molecular weight of 19. Fluorine is the most powerfully oxidizing element known. No other substance can oxidize the fluoride ion (valence⁻¹) to change it to the free element. For this reason, fluorine is never found in its free state in nature.

Fluorine is the lightest weight member of the halogen family, which also includes chlorine, bromine, iodine and astatine. The word "halogen" is derived from the Greek "Hal", meaning "salt", and "Gen", meaning "to produce". Extremely reactive, all of the halogens readily produce salts. Fluorine is the most abundant halogen in the Earth's crust, measuring at 0.06 percent—nearly double that of its more familiar cousin, chlorine. Its most common form is the compound "Fluorspar", a form of calcium fluoride.

The "discover" of fluorine

Fluorine was accidentally discovered in 1771 by a chemist heating fluorspar with sulfuric acid in a glass vessel. This produced hydrofluoric acid (HF) which promptly ate the vessel. It was not until 1811 that French physicist Andre Marie Ampere described the similarities between HC1 and this still unknown mystery acid. It was Ampere who suggested the "fluorine". Fluorspar was used as a flux to improve the flow of molten metal when casting. Another French chemist, Henri Morison, isolated fluorine, as a gas, in 1886 using electrolysis of HF.

The benefits

At about this same time, scientists from the medical community completed studies showing that the enamel of sound, healthy teeth contained more fluorides than were contained in the teeth of people prone to dental decay. Further studies showed that fluorine (as fluoride ion) was absorbed by bone as well as teeth and was termed "beneficial" to the formation and health of both.

Today, fluorides are known to decrease the incidence of rickets in children by stimulating the thyroid to maintain normal metabolic rates. Minute quantities in the diet limit the acid production of bacteria in the mouth—thus reducing decay. A significant advance in oral hygiene was made when it was shown that fluoride could be applied topically as well as ingested. This led to a whole new era of tooth care products and procedures. Today, the "benefits" of fluoride are pretty much accepted worldwide. Fluoride is frequently added as the sodium salt fluoride to drinking water supplies at about the one ppm level.

Problems

There are a number of areas throughout the world that have high fluoride levels and little choice in sourcing their drinking water.

Fluorosis has been identified as stemming from excess fluoride in Algeria, Tunisia, Spain, Italy, Russia, South America and the United States.

States. Studies conducted as early as 1931 showed that some fluoride could be expected over a widespread area west of the Appalachians with the highest levels concentrated in the midwestern states. Fluorosis has also been reported in the Dakotas, Kansas, Colorado, Arkansas, Iowa, California and the Texas panhandle area.

Although fluoride contamination is most likely from natural sources, it can also be found as a result of industrial waste discharges. Of particular significance are glass manufacturers, electroplating operations, steel and aluminum production, pesticide and fertilizer use and the semiconductor industry. Fluoride levels can vary widely.

Fluoride is classified as a Class 4, or very toxic, poisonous substance. The average person can tolerate about one ounce before becoming a piece of history. Don't be too alarmed, though—the aspirin you keep in your medicine cabinet is in the same class.

Toxicity v. hazard

One should differentiate between "toxicity" and "hazard": toxicity is the ability of a substance to injure whereas hazard is the probability that exposure will produce injury. For example, walking on a slippery sidewalk is hazardous, but not toxic. Nicotine from cigarettes is toxic, but not hazardous—that is, if you don't smoke or hang around anyone who does—because the probability of encountering a lethal dose all at once is slim.

Excessive intake of fluoride may cause asymptomatic sclerosis, better known as "fluorosis", which is a densening and embrittling of bones that leads to severe joint and nerve disease. It can also cause mottling of the teeth, although this condition is primarily cosmetic and not harmful.

Further, fluorosis is a long term disease as is fluoride deficiency. Remember, fluoride is termed "beneficial", not essential. Excess levels are many times (10 ppm+) the normal levels commonly used in drinking water for the prevention of dental decay. To pose a danger, ingestion must occur over several years to decades.

Why the controversy?

So here's a substance that shows up in our food supply both intentionally and accidentally- We can live without it. A little bit is a good thing. However, a large amount is a bad thing. Kids consume enough fluoride by swallowing toothpaste to develop symptoms of fluorosis (tooth mottle) and it is classified as a toxic substance—more toxic than kerosene and bleach {Class 3}—but less toxic than amphetamines, some pesticides and drain cleaners (Class 5). So why the controversy?

We have a choice

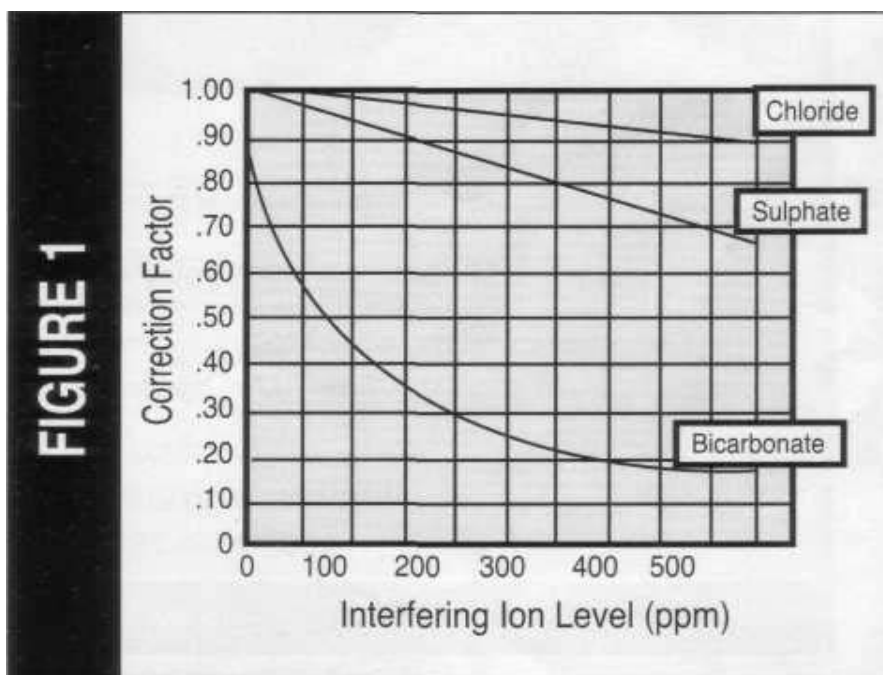
Fluoride in water, no matter what level, poses no problems for normal water uses and skin contact. However, to avoid ingestion, there are several routes one can

choose. The WQA suggests activated alumina, bone char, reverse osmosis (RO), distillation and electro dialysis as methods of removal. We can also list chloride form (salt regenerated) anion exchange as effective and, lest we forget, we can always turn to non-fluoridated bottled water.

The WQA lists four ppm as the primary MCL (maximum contaminant level) with a secondary MCL of two ppm. Most municipalities that treat for fluorides reduce the levels to one ppm or less.

Central plant treatment

The most common method of reducing fluorides from a central plant is with lime precipitation. However, depending upon the water temperature and composition, this process can leave a residual of 10 ppm or higher of P. When initial influent levels are in the 15 to 20 ppm range, prior treatment with lime will generally lower levels and reduce the loading on the subsequent treatment facility. The addition of lime produces an insoluble precipitate, CaF₂, which can be flocculated and settled out. In addition, aluminum and iron compounds used for flocculation will form



insoluble reactants with fluoride and can be dropped out in subsequent filtration steps.

Reverse osmosis

According to the United States Environmental Protection Agency (USEPA), reverse osmosis (RO) is capable of reducing fluoride by 90 to 95 percent. If you have 10 ppm or more and your goal is to eliminate F⁻ from your drinking water, you will need to treat beyond RO. Low pressure "under-the-sink" units may reject as little as 80 percent of F⁻ and would certainly require a post-polisher cartridge for complete removal.

Distillation

Distillation is an effective treatment method for the removal of fluoride. For those who wish to eliminate all dissolved mineral from their water (including fluoride) small, efficient distillers are an option.

Electrodialysis

Electrodialysis (ED) rejects fluorides at similar percentages as RO. While you have the ability of "dialing" the efficiency you wish, you will have to shoot for moderately high numbers to achieve 90 percent reduction of the F⁻. ED is less delicate than RO in that it can survive with less sophisticated pre-treatment, but is three to five times the cost of RO and has never been miniaturized below five to 10 gpm continuous feed. Regenerated installations because alumina is also regenerated with caustic and acid which presents a certain hazard for the home. However, an efficient process has been worked out for a single dose regeneration using aluminum sulfate (alum). Since alum is not considered a hazardous chemical, it is the best choice for residential installations that involve regeneration. It will require 20 bed volumes (150 gallons per cubic foot) of 2 percent alum solution being pumped through the filter bed over a 6 hour period. This technique produces slightly higher leakages than the caustic/acid and would be limited to a maximum of 10 to 12 ppm F⁻ in the feed. Again, portable exchange or disposable cartridges can be attractive.

It should be noted that both bone char and activated alumina are flow sensitive and are subject to interference from competing

ions, particularly bicarbonates (see Figure 1). As little as 50 ppm of bicarbonate can impact the capacity of activated alumina by as much as 50 percent. There is a 70 percent reduction in capacity at 200 ppm. Bone char has a similar sensitivity.

The ideal flow rate is only 1 gpm/ft³. Flow rates of 3.5 gpm/ft³ (typical residential flows) will reduce the capacity by an additional 50 percent (see Figure 2). The best bet would be to treat only the drinking water with a third faucet restricted to a flow rate of 0.5 gpm through a fractional cubic foot exchange tank.

pH also can affect the capacity. Activated alumina and bone char work best at lower pH's (below 5). Increasing from pH 7 to pH 9 can drop the capacity by 15 percent (see Figure 3).

Bone char Bone char is actually an activated

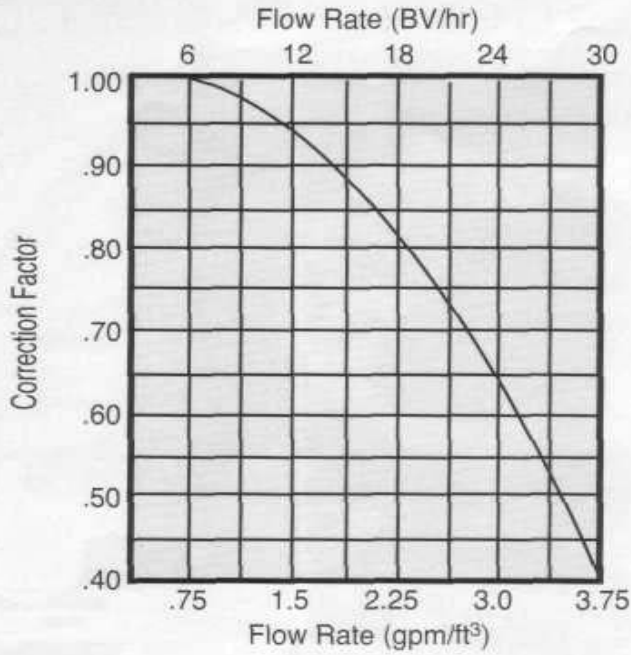
Carbon/tricalcium phosphate compound produced by charring and activating cattle bones. When regenerated with caustic and neutralized with acid, the calcium phosphate converts to the hydroxy apatite form which then reacts with fluoride to form an insoluble matrix similar to CaF₂. Effluent levels below one ppm are achievable. Capacities are on the order of one percent by weight or about 150,000 ppm of F⁻ per cubic foot. That's about 5000 gallons of eight ppm feed. Regeneration is with caustic and acid which does not lend itself to residential needs. Portable exchange or throwaway cartridges would be of use here.

Activated alumina

Activated alumina filters can reduce influent fluoride levels to less than 1 ppm and have demonstrated capacities of 1.2 to 1.4 percent fluorides by weight. The AlF⁺ bond is very strong and therefore has a very low dissociation level. Activated alumina is, therefore, very selective for F⁻. Since the bulk density of activated alumina is 46 lbs/ft³, 1 cubic foot (20,884 grams) can remove as much as 292,000 mg of P. This is equivalent to 9600 gallons of 8 ppm F⁻ contamination. A small fractional cubic foot filter could satisfy a family's annual requirements for drinking water.

The use of activated alumina does not lend itself to "in home"

FIGURE 2



Anion exchange

Anion exchange with sodium chloride regeneration presents a possible solution to the fluoride removal dilemma. The selectivity order for anion exchange places the F⁻ ion way down the list. In fact, it is the last rung on the ladder. What this means is that there is very little driving force to replace chlorides with fluorides during the service cycle. However, there is excellent regeneration kinetics to get the F⁻ back off with very low levels of salt. This gives this process a good shot at the residential market. The use of salt regenerated (sodium or potassium strong base anion exchangers for the removal of excess fluorides is not that far fetched. The mere fact that ion exchange is an equilibrium phenomenon gives us the guarantee that we can adsorb some level of capacity. But, how much?

Figure 4 shows the fluoride capacity of a Type I and Type II SBA with respect to the composition of the feed water. Since preliminary tests indicated that the presence of sulfates and carbonates had little effect on the F⁻ removal capacity, subsequent studies were limited to F⁻/Cl⁻ ratios only.

A fluoride content of 8 to 10 ppm may represent a concentration of 10-12 percent F in 80 to 100 ppm feed water. The capacity is only about 300 grains or about 500 gallons/ft³. This is with only 2 lbs of salt/ft³ and the F break is <1 ppm. With city fluoridated water assumed to be at a maximum of 2 ppm and a feed of 400 ppm, our ratio is 2/400, or .005. Nonetheless, a capacity of only 25 grains is still 200+ gallons. If we regenerate counter-currently,

FIGURE 3

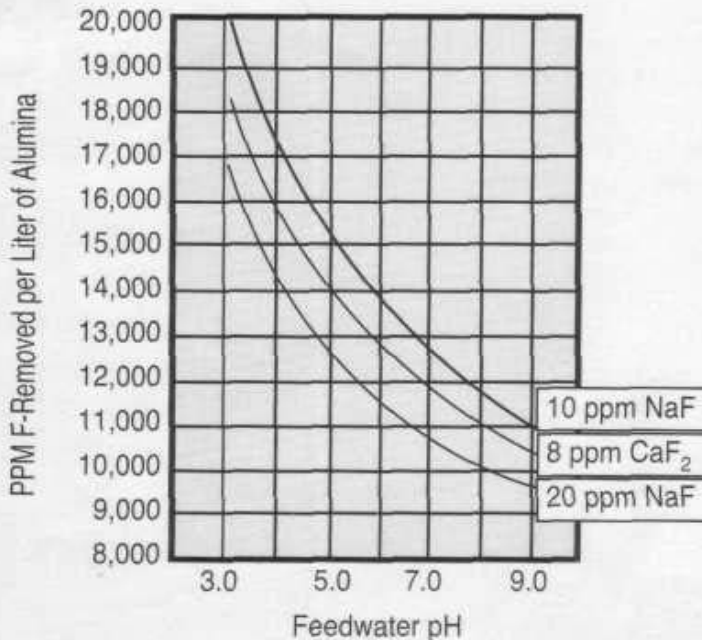
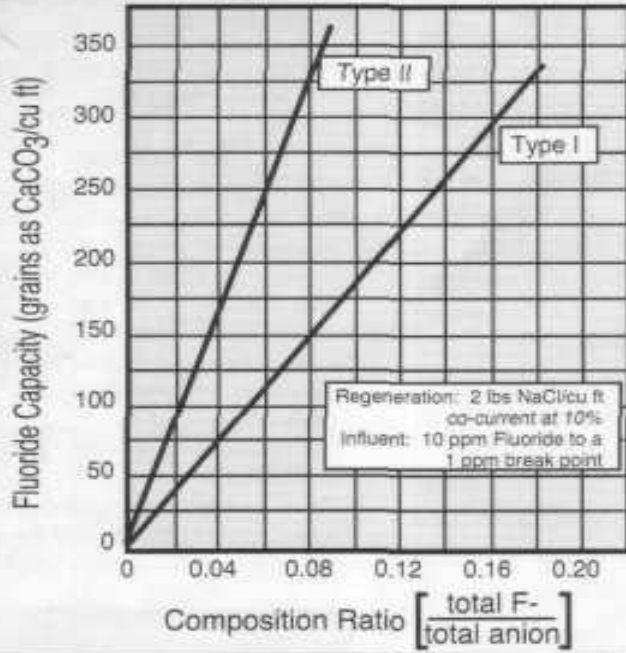


FIGURE 4



the regeneration level can be cut to 1.5 lbs/ft³ and the capacity increases by 10 percent. Use 1 cubic foot for every three people and regenerate counter-current with 1.5 lbs of salt/ft³ as a 10 percent solution drawn at 0.25 gpm/ft³.

Conclusion

Fluorides can be both a benefit and a detriment to family health. A little bit is good. A little more is not good.

Although there are several effective methods of reducing influent fluorides, there are limits in the degree of automation one can provide because of restraints on miniaturization or on the handling of regenerant chemicals and wastes.

Distillation is very simple for small volumes of water totaling one to five gad. Beyond that, distillers can get bulky. Stills also require frequent cleaning unless you have pre-softened water.

Under-the-sink RO with a polishing cartridge of activated alumina or bone char may be the most practical for

moderate volumes of water totaling five to 50 gpd.

Whole house bone char and/or activated alumina present regeneration problems that are best handled through portable exchange. Under-the-sink cartridges present an alternative depending upon water composition. Keep the flow rates below 0.5 gpm.

Whole house treatment with strong base anion with salt regeneration is effective and eliminates the handling problems of bone char and alumina. However, due to limits in capacity, regeneration would have to be every day. Anion resin cartridges may not be practical due to severe limitations on capacity.

Neither fluoride excess nor deficiency are cause for alarm over the short term. The key is to remain aware of the potential problems.

References

- Fluoride Removal by Activated Alumina, LaRoche Chemicals product bulletin, M.J. Pearson, June 1978.
- Encyclopedia Britannica, Vol 3,

"Fluoride"

● AWW A Journal, May 1996/"Regulatory Compliance Using Membrane Processes", Frederick W. Pontius.

● Ion Exchange Resins, Robert Kunin^Creger Publishing, 1972.

● Discussions with Henry Valcour, Engineer, Ionics, Inc, Watertown, MA.

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