

FLUORIDATION

The Good, the Bad and the Ugly

Part 2

By C.F. 'Chubb' Michaud, CWS-VI

In Part 1 of this series we pointed out that fluoride, although beneficial as a topical dental treatment, can be detrimental to human health if taken in excess. Currently, about 60 percent of the US population consumes tap water that is 'medicated' from the 'factory' with 0.7 to 1.2 ppm of fluoride. Ninety-seven percent of western Europe's tap water¹ is fluoride-free and its residents enjoy an equal level of dental health. My conclusion is that there is no real need for fluoridating our drinking water supplies any longer; we get sufficient (if not excess) fluoride from our food intake. More recent studies confirm that dental fluorosis caused by excess fluoride in the diet is affecting over 30 percent^{2,3} of school children around the country in both fluoridated and non-fluoridated communities.

Should we reduce our fluoride intake?

We have encouraged people to cut down on their sodium intake with public announcements and the listing of sodium on food labels. We are encouraging reduction in the consumption of trans-fats by regulating its use in the public food supply. We finally put a cap on safe levels of chlorine in drinking water. Should we not be trying to limit the amount of fluoride we consume, now that we know we are overexposed?

Exercise your choice

The public may not have much choice as to whether municipally supplied drinking water contains fluorides, but they *do* have a choice as to whether or not they drink it. Fluoride-removal technology, which is well known and very effective when properly designed and operated, presents a great opportunity for water treatment professionals.

Methods of fluoride removal

There are five general methods of fluoride removal applicable to residential and municipal water supplies. These are:

1. Distillation
2. Chemical precipitation
3. Adsorption
4. Ion exchange
5. Reverse osmosis

Distillation

Distillation is the world's oldest method of water purification, having been invented by Mother Nature on Day 1. Water is heated to produce water vapor, which is captured and condensed by cooling it back to water. Vacuum/compression distillation is the modern method for this and is carried out very efficiently from an energy point of view. Unlike chlorine, which is volatile

(chloride salts are not), fluoride is left behind and moderately pure water is obtained.

Distillation can be very economical if there is waste heat available from some other process. It is not practical for large-scale municipal needs or even whole-house POE considerations. It should, however, be a consideration for seawater purification, where RO or other means are not practical. For home use, there are some very compact POU devices that merit consideration, especially if there are other contaminants that should be removed. Remember, volatile organics may carry over with the distillate, so one should incorporate pre- and post-carbon filters.

Home units that can produce a few gallons a day might cost \$300 to \$1,000 (USD) and produce water for around \$0.25/gallon. Fluoride and other contaminant reduction is better than 98 percent.

Chemical precipitation

Chemical precipitation is usually done at the municipal level, where fluorides are very high (>15 ppm). Lime (CaO) is usually the precipitant of choice, forming calcium fluoride and reducing the fluoride to about eight ppm. Good performance is also achieved with lime/calcium chloride at a pH of 10. Industrial waste, containing several thousand ppm of fluoride, has been effectively treated by chemical precipitation. Further treatment is done with adsorbants. Any type of chemical process is impractical for home needs or small commercial requirements other than waste treatment.

Adsorption

Adsorption is the process by which one element or chemical sticks to the surface of another. This is brought about by the relative attraction of the two substances and the relative concentration of the contaminant (which supplies the driving force). Granular activated carbon is a well-known adsorbant for organics. A clean carbon surface is hydrophobic, which allows for organic adsorption. GAC, however, is not a candidate for the adsorption of fluoride because there is little attraction between the two, and fluorides are very water-soluble. Instead, we have to look at chemi-adsorption.

In chemi-adsorption, a reaction actually takes place between the adsorbent and the adsorbate.⁴ This occurs only on the surface of the adsorbent and is not readily reversed. Activated alumina is a very good adsorbent for fluoride, as the fluoride ion binds to the alumina as aluminum fluoride. Thanks to the high surface area of alumina, this method of removal has good capacity, which can be as high as 1.6 percent by weight (more later).

Bone char is another adsorbent for fluoride. Bone char is,

as the name suggests, produced from charred cattle bones and the resulting product is about 85 percent tri-calcium phosphate and 15 percent activated carbon. It is the calcium compound that adsorbs the fluoride in much the same manner as bones; teeth adsorb fluoride, as mentioned in Part 1. Bone char and alumina exhibit about the same capacity for fluoride removal on a volumetric basis. In both instances, the fluoride reacts with the surface of the adsorbent and is firmly held.

Both activated alumina (AA) and bone char (BC) are granular media, which makes them particularly suitable for disposable- or exchange-tank processes. Both are regenerable with caustic and acid, which usually makes regeneration unsuitable for automatic 'in-home' systems, but an excellent choice for commercial-, industrial- and municipal-level treatment. Most municipal fluoride treatments involve a combination of chemical precipitation followed by activated alumina. Fluoride can be readily reduced from up to 10 ppm to less than 0.1 ppm using either AA or BC.

Adsorption reactions are very sensitive to retention time and flow rates, as well as pH and other interfering ions, such as bicarbonates and carbonates. Under ideal conditions, AA has a capacity of 1.6 percent by weight. With AA weighing 39 lbs./cu.ft., that calculates to 0.624 lbs. of fluoride or 283,300 mg. Converting liters to gallons tells us that one cubic foot of AA can remove one ppm of F⁻ from about 75,000 gallons (283,905 liters) of water. The question remains: *under what conditions is this capacity possible?*

There have been several laboratory studies made to define the best operating parameters of AA. Most of this work was done with a 14 x 48 US mesh size media. See Figure 1 for a list of the typical properties of the raw alumina.

Pretreatment of activated alumina

The efficiency of AA for adsorbing fluoride is generally poor on the first adsorption cycle, unless AA is first regenerated or pretreated with aluminum sulfate (alum) at a level of 10 lbs./

Figure 1. Typical properties of granular activated alumina

- Chemical properties:
 - Al₂O₃...92%
 - Na₂O...0.35%
 - SiO₂...0.03%
 - Weight loss on ignition (1,000°F) ~8%
- Mesh size: 14 x 48 US
- Bulk density: 40 lbs./cu.ft.
- Surface area: 380 m²/g
- Pore volume: 0.52 cc/g
- MSDS: NSF-61 listed

cu.ft., using a two-percent solution (about 10 lbs. in 65 gallons [283.9 liters]) and a four-hour contact time (a flow rate of 0.25 gpm/cu.ft. [0.9 L/m]). This is followed by a one-hour rinse with city water at two gpm/cu.ft. [7.57 L/m]. Figure 2 shows the effect of pretreatment on capacity for two different challenge levels of fluoride.

Non-preconditioned alumina breaks through almost immediately. While this simply means a short first run for in-place regenerated commercial and municipal systems, it is unacceptable for

residential applications that require the media to work the first time and every time.

Removal capacity of AA at various flow rates

Adsorption reactions are very slow in comparison to ion exchange and are very flow-rate dependent. The data shown in Figure 2 were at a measured flow rate of only six bed volumes per hour. That's six liters per hour per liter of media or 0.75-gpm/cu.ft. While the medium still works very efficiently (for removal) at higher flows, the capacity is reduced as shown in Figure 3.

It is readily noted in Figure 3 that both efficiency of removal and capacity of AA is greatly impacted by flow rate. In the referenced lab test, throughput capacity (total fluoride removed) was reduced by 33 percent by doubling the flow from 1.5 gpm/cu.ft. (5.67 L/m) up to 3.0 gpm/cu.ft. (11.35 L/m). This would suggest that for residential POE systems, a 1.5-cu.ft. unit could handle 4.5 gpm (17.03 L/m), while maintaining a capacity of about 75,000 gallons treating a one-ppm fluoride level.

Revisiting Figure 2, it indicates that with a lower challenge level, total capacity increases. This suggests that removing fluoride levels typically added by city water supplies (0.7 to 1.2 ppm) might increase our 1.5-cu.ft. system throughput to over 120,000 gallons (454,249.41 liters), which would be suitable for a family of four for 12 months (without the influence of interfering ions). Lab studies also show that when the system is started and stopped, capacity goes up due to the benefits of deep diffusion of fluorides into the media granule.

Figure 2. Pretreated versus non-pretreated alumina

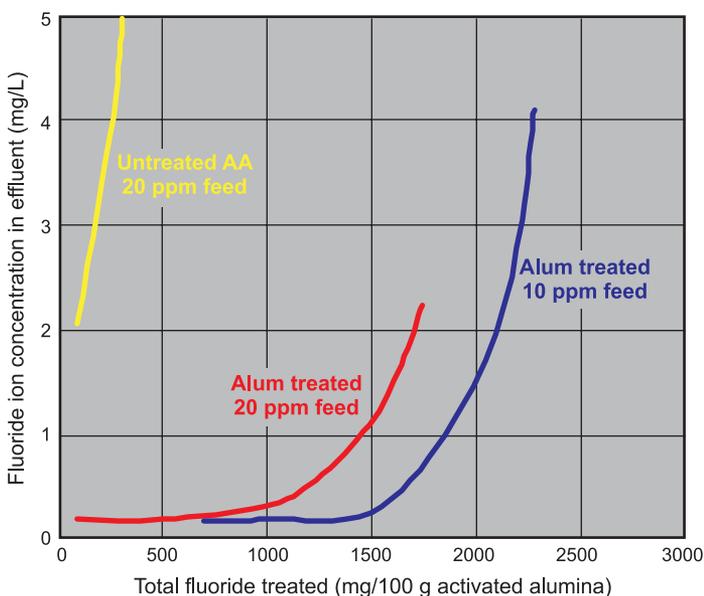


Figure 3. Removal efficiency of activated alumina versus flow rate

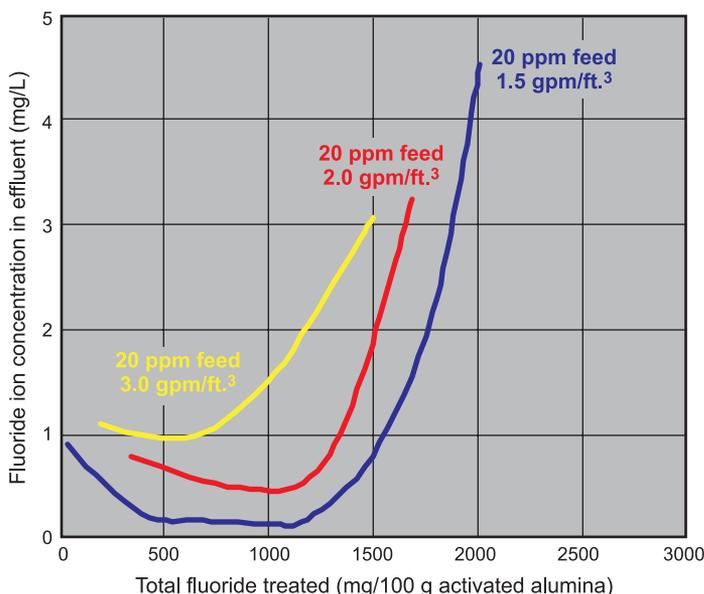


Figure 4. Impact of interfering ions on alumina capacity

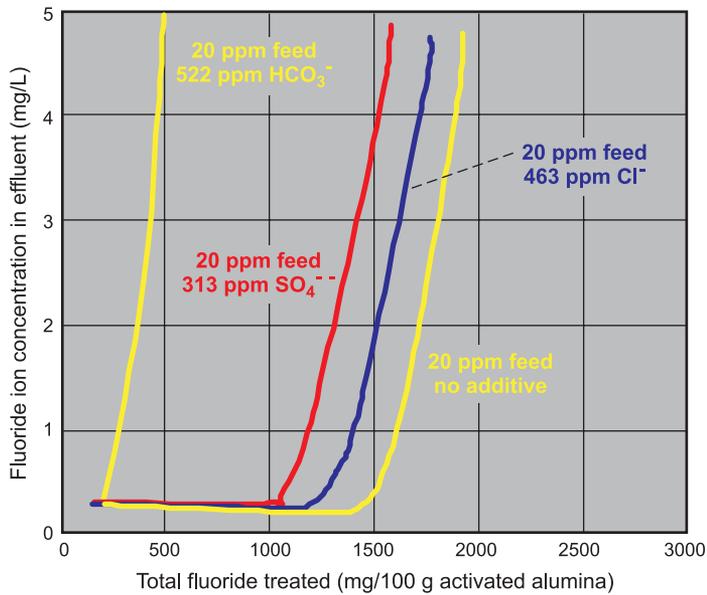
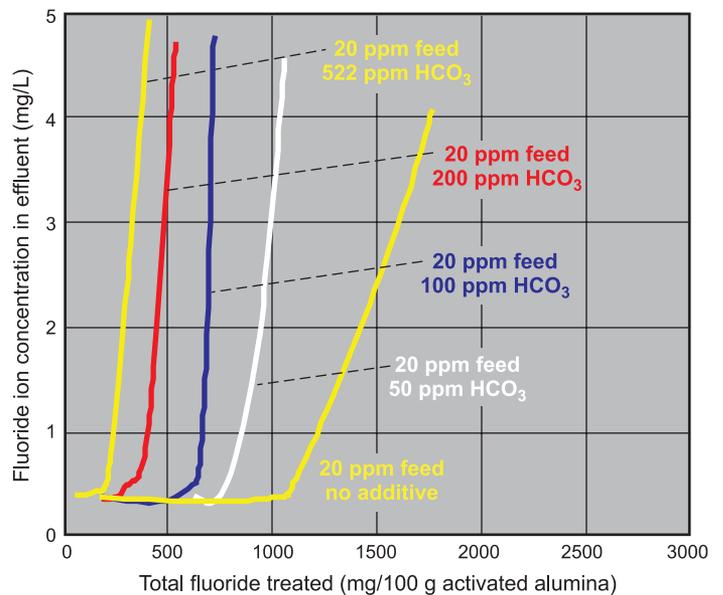


Figure 5. Effects of bicarbonate level on fluoride adsorption



By the same token, interpreting Figure 3 to an extreme by running 0.75 gpm through a 10-inch countertop filter (about 30 gpm/cu.ft.) tells us that this is not a very good application for the media. My own tests^{5,6} confirm that even the best single-housing countertop filter cartridges run at 0.5 gpm treat only about 100 gallons (378.54 liters) from a 2.2-ppm feed. Some of these systems claim to treat 20,000 gallons (75,708.23 liters) of one ppm F⁻ between changes! Obviously, these sellers have never had their cartridges tested. And some of them use raw, non-pretreated media.

Interfering ions

The data presented so far represents sodium fluoride-spiked deionized water. Typical municipal supplies (and even well water) will certainly contain a host of other ions. Figure 4 shows the effect of some of those ions on the throughput capacity of pretreated alumina at a flow rate of two gpm/cu.ft.

For these studies, DI water containing NaF was spiked with sodium chloride, sodium sulfate and sodium bicarbonate. In all cases, fluoride effluent was reduced to 0.2 ppm or less (99 percent). The effects of chloride and sulfate are very small, but bicarbonate causes a major drop in capacity. Figure 5 shows the effects of bicarbonate at various levels.

As shown in Figure 5, the presence of bicarbonate can reduce the capacity of AA by 75 to 80 percent. This, however, is extreme. Note that as little as 50 ppm of bicarbonate can reduce F⁻ removal capacity by 33 percent, and typical levels of 100 to 200 ppm will reduce it by 50 to 70 percent. But don't count AA out of this ballgame.

Ion exchange

Fluoride is a highly ionized anionic species but is predictably less selective than almost any other for anion exchange due to its lower molecular weight. If the chloride ion is given a selectivity of 1.0, the fluoride ion comes in at 0.07. Despite the low selectivity, the use of anion exchangers sized at two to four gpm/cu.ft. (7.57 to 15.14 L/m) can be highly beneficial.

In *Using Media to Remove Fluoride from Drinking Water Sources* by Frank DeSilva,⁷ the author presented a formula for rating the capacity of a Type II strong-base anion regenerated with only five lbs. (2.26 kg.) of salt/cu.ft. (He stated that you can rate the anion

at 12,000 grains/cu.ft., but you have to take *all* of the anions into account.) Convert your water analysis for bicarbonate, chloride, nitrate, sulfate and fluoride (plus others) to ppm as calcium carbonate. Add them up and divide by 17.1 to convert to grains per gallon. The use of anion resin is also a good way to reduce other contaminants, such as arsenic or nitrates, in addition to fluoride. Also, the bicarbonates are significantly reduced, as is the pH. This provides the perfect pretreatment for an AA polisher, even though the anion unit could stand alone.

New technology

Although fluoride is an anion, a special cation exchanger can be created to remove fluorides very efficiently. This involves doping the cation with aluminum to form a ligand. Using about eight lbs. (3.62 kgs.) of aluminum sulfate per cu.ft. of strong acid cation (softening resin), the cation can be made selective for fluoride. Tests with this product show very high kinetics and good capacity when tested on a 10-inch cartridge at 0.5 gpm. More work is required to determine aluminum leakage and regenerability.

A hybrid is born

In one field study of a POE system, the fluoride level was at 14.5 ppm with a pH of 9.8. Using an anion primary sized at three gpm/cu.ft., fluoride was reduced to 1.35 and pH dropped to 6.4. The AA polisher further reduced the fluoride to 0.32 and pH settled at 6.5. The anion is regenerated at five lbs./cu.ft. using NaCl. All anions in the feed water are replaced by chloride, including bicarbonate, which drops the pH. There is no need to neutralize, since the pH of the water is 6.5 but, a calcite filter could be added to raise it to near 7.0. This system has been in place for almost a year with good repeatability and a steady performance.

Reverse osmosis

RO is an excellent unit for fluoride reduction. Tests on a small undersink model operating at a line pressure of 60 psi is able to reduce city water fluoride content of 0.4 ppm to non-detectable levels without a special polishing cartridge. On high levels of F⁻, RO should reduce by at least 90 percent, and should be considered for standard backup treatment on any feed greater than five ppm.

Conclusion

Much of the choice of fluoride-removal technologies will depend upon how high the fluoride is and where the fluoride removal treatment system is located. Full chemical treatment is normally reserved for municipal and larger industrial users, whereas commercial and residential needs are best served with ion exchange, adsorbants, RO and distillation or a combination of those. Depending on the technology, knowing the pH and alkalinity of the water is very important. Keeping in mind that some people are very sensitive to fluoride, redundancy is suggested. A countertop distiller will handle drinking water needs for most families. Whole-house systems can be straight AA for levels of F⁻ up to four ppm. Above that, a regenerable anion followed by AA and a small RO system as a polisher is suggested for drinking water. Remember, if F⁻ is above the primary MCL of four ppm, the system absolutely has to work 24/7.

References

1. Featherstone, J. D. B. (2000), "The Science and Practice of Caries Prevention." *Journal of the American Dental Association*. 131: 887-889.
2. Centers for Disease Control and Prevention (2005), "Surveillance for dental caries, dental sealants, tooth retention, edentulism, and enamel fluorosis—United States, 1988-1994 and 1999-2002." *MMWR* 54:1-43.

3. National Research Council. (1993). Health Effects of Ingested Fluoride. *National Academy Press*, Washington DC.

4. Michaud, C.F. "Fluoridation: Friend or Foe?" *WC&P*, Sept 1996.

5. Technical Bulletin: *Fluoride Removal by Activated Alumina*, Systematix Co., Buena Park, CA, 2009.

6. Lab Notes: *A Study of Fluoride Removal with Cartridges*, Systematix Co., Buena Park, CA, 2009.

7. DeSilva, F., "Using Media to Remove Fluoride from Drinking Water Sources." *WC&P*, April, 2009.

About the author

◆ C.F. 'Chubb' Michaud, CWS-VI, is CEO and Technical Director of Systematix Company, which he founded in 1982. Michaud has been a member of the Water Quality Association's Board and of the Board of Governors and past Chair of the Commercial/Industrial Section. He serves on the Board of Directors of the Pacific WQA (since 2001) and Chairs its Technical Committee. A founding member of WC&P's Technical Review Committee, Michaud has authored or presented over 100 technical publications and papers. He can be reached at Systematix Inc., 6902 Aragon Circle, Buena Park CA 90620; telephone (714) 522-5453 or via email at cmichaud@systematixUSA.com.