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Kip Duchon, retired, was the national fluoridation engineer for the US Centers for Disease Control and Prevention (www.cdc.gov), Atlanta.

Know the Basics of Water Fluoridation Additive Products

The practice of adding fluoride in drinking water treatment has spanned 75 years and improved public health. Adjusting fluoride content involves using one of three additive products. **BY KIP DUCHON**

THIS YEAR marks the 75th anniversary of water fluoridation, which entails adjusting the fluoride level in drinking water to the recommended level of 0.7 mg/L to improve oral health. According to the US Centers for Disease Control and Prevention (CDC), 72.8 percent of the US population served by public water systems (PWSs) had fluoridated water in 2016 (www.cdc.gov/oralhealth). Fluoridation's basic process is simple, effective, and safe, but water treatment plant operators need to understand the process to get the best results.

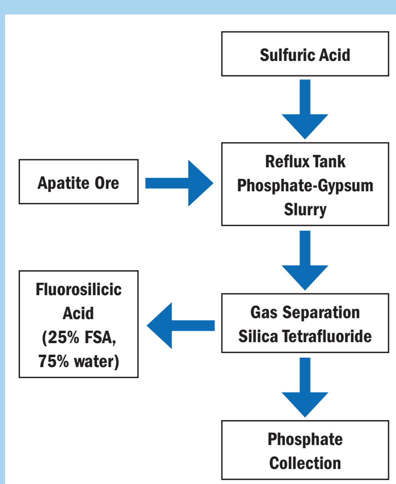
FLUORIDE ADDITIVE PRODUCTS

Fluoride is the 13th most abundant element in Earth's crust, and a small fluoride concentration is found in natural waters. According to the US Environmental Protection Agency's Safe Drinking Water Information System, approximately two-thirds of people on PWSs have a surface water source. Fluoride in surface water comes from rainwater's fluoride content, which is typically between 0.1 and 0.2 mg/L. A few groundwater sources have higher fluoride as a result of leaching from rock ores but also often have insufficient fluoride, resulting in only 3.5 percent of people served by a PWS having natural fluoride of 0.6 mg/L or greater. When water has a fluoride content of less than 0.6 mg/L, it's insufficient to improve oral health. With such low fluoride content in most source water, it's important to adjust the fluoride to the recommended 0.7 mg/L level.

Fluoride additive products are derived from two ores: apatite and fluorite. The principal source for 96 percent of water fluoridation additive products is apatite, a mineral composed of calcium phosphate with high concentrations of hydroxide, fluoride, and chloride. Apatite is the source of phosphate fertilizers. There isn't enough demand for fluoride products from apatite production to warrant capture at all phosphate fertilizer facilities, and only half of the phosphate fertilizer production facilities also capture fluoride. The other 4 percent of water fluoridation additive products is derived from fluorite, which is calcium fluoride. Fluorite is the largest source of hydrogen fluoride, an important industrial product, but it's a minor source of water fluoridation additive products.

Processing Ore to Make Fluorosilicic Acid

Nearly all water fluoridation additive products are derived from apatite ore.



Apatite is mined in open trenches and then milled to smaller pellets suitable for feeding to a reflux tank, where the pellets are mixed with sulfuric acid. The sulfuric acid is derived from processing molten sulfur, a waste product from cleaning petroleum feedstock, so phosphate production facilities use an environmentally clean process that beneficially uses the molten sulfur and generates more electrical energy than is required to operate the mining and phosphate production. Mixing apatite and sulfuric acid generates a gypsum slurry (calcium sulfate) and releases phosphate in a gaseous discharge. The phosphate is captured as the combined phosphate and vapor steam is cooled through a gas separation column, allowing the phosphate to condense from the steam. Fluoride is principally in the form of silica tetrafluoride gas, which has a slightly higher boiling temperature than the phosphate, allowing it to be condensed in a primary gas separation tank operating at a slightly higher temperature than the principal phosphate separation tank. The silica tetrafluoride gas becomes fluorosilicic acid once it condenses into an aqueous solution. Fluorosilicic acid

Water treatment facilities should always prepare standard operating procedures to govern the delivery of water additive products.

PHOTOGRAPH: KIP DUCHON

(FSA) is also known as hydrofluorosilicate (HFS), depending on shipping and different industrial uses, but AWWA standards identify it as FSA for drinking water applications. The figure on page 16 illustrates how ore is used to produce FSA.

The dry additive products, sodium fluoride and sodium fluorosilicate, are salts. Most of the dry additive product is derived from processing FSA by a partial neutralization to sodium fluorosilicate or a full neutralization to sodium fluoride. There's a small quantity of sodium fluoride in the water sector derived from hydrogen fluoride neutralization using caustic acid.

FSA USE

FSA is an aqueous acidic solution with a pH of 1.2, composed of approximately 25 percent FSA and 75 percent water. The 25 percent content level is specified by AWWA standards for two reasons: As FSA content increases (up to 40 percent), the potential for hazardous exposure increases, and as the content decreases, the logistical shipping has an increasing cost because of the water content. AWWA standards have been crafted to balance those competing considerations—a reasonable reduction in safety hazard while maintaining an economical shipping cost.

Delivery can be in 20,000-gallon rail tank cars, 6,000-gallon truck tanks, 300-gallon tote tanks, 55-gallon drums, and 13-gallon carboys. Some small to medium locations rely on "mini-bulk" delivery under a US Department of Transportation DOT-SP 12412 permit, allowing the delivery vehicle to have intermediate bulk containers so excessive storage tanks aren't required on-site but can be refilled by periodic truck servicing. Mini-bulk delivery is preferable over tote tanks, as tote tanks don't meet ASTM International's D1998 specification, which suggests a minimum tank wall thickness of 0.187 inches.

Polyethylene storage tanks are typically used for on-site storage at water production facilities because of polyethylene's excellent corrosion resistance. The fill line for the storage tank should have a locking cap and filter, as shown in the photograph on page 18. A locking cap is recommended to prevent attempted delivery to the wrong storage tank, and the filter is advised to strain debris and particulate material that can result from exfoliation of the delivery truck's rubber lining.

Water treatment facilities should always prepare standard operating procedures to govern the delivery of water additive products. These should include the following steps for FSA:

1. Review the supplier's assay of the product delivery.
2. Verify the product is FSA, using a hydrometer density test as specified in AWWA standards.
3. Unlock the delivery cap to the storage tank after verifying correct additive identity.
4. Visually inspect all connection hoses and placement of collection pails at each connection, looking for leaks that occurred during delivery.
5. Store a sample of the delivered material in a polyethylene container for 12 months in case the product needs to be verified later. The driver of the delivery should provide a copy of the product lot assay. The photograph above shows an additive delivery in progress.

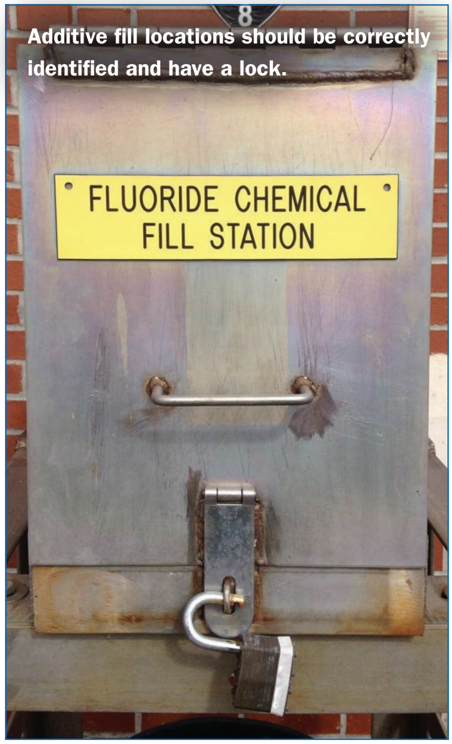
FSA is an acid, but the use of appropriate materials tolerates its corrosive nature. Polyethylene is an excellent choice for tanks and piping. FSA's most corrosive aspect is its small hydrogen fluoride content—less than 1 percent—but that small amount is highly corrosive. To minimize hydrogen fluoride corrosion, all air spaces in tanks, pump calibration columns, and other locations where an air pocket could form should be vented to the atmosphere outside of a building. If there's evidence of glass etching or other corrosion, it means there's a leak in the vent pipes that should be sealed to resolve the problem.

FSA feed systems should include a bulk storage tank, a day tank, the feed pump, and a calibration column to ensure accurate pump delivery. The bulk storage tank shouldn't be used as the feed source because there's potential for an overfeed if there's a mechanical malfunction. Instead, a day tank should be used for feeding FSA additive to prevent overfeed events. If a malfunction occurs, no more than a single day's feed would be introduced into the flow—a small quantity that wouldn't result in an overfeed event. The CDC Water Fluoridation Reporting System (WFRS) reports that the national usage of FSA for fluoridation of water represents 81 percent of the population receiving fluoridated water by FSA adjustment.

DRY SALT ADDITIVE PRODUCTS

Dry additive products are mostly derived from neutralizing FSA with caustic. The dry products are a crystalline white salt, appearing much like table salt, that can then be mixed into a brine for feeding to the flow. A key criterion is the crystalline nature be sufficiently coarse so as to minimize dusting of the salt while transferring into the feeder or saturator to minimize an operator's exposure to fine salt. Most of the product is shipped in bags but can also be ordered in supersack containers; a supersack is equivalent to one pallet of bags.

Sodium fluorosilicate, also known as sodium sil, is a partially neutralized FSA. The pH of the brine is 3 to 4. The solubility of the brine varies with temperature, and the salt takes up to several hours to reach



Additive fill locations should be correctly identified and have a lock.

saturation. Consequently, sodium fluorosilicate is never fed as a saturated solution but instead in unsaturated brines. The standard feed system is to use a dry feeder to regulate the feed of the salt into a mixer, where an unsaturated brine solution is formed and added to the flow. The feed rate of the sodium fluorosilicate is controlled by the volumetric feeder, and the unsaturated brine solution from the mixer is simply a conveyance to the water's feed point. CDC WFRS reports that national usage of sodium fluorosilicate is 13 percent of the population receiving fluoridated water by sodium fluorosilicate adjustment.

Sodium fluoride is a fully neutralized FSA. The pH of the saturated brine solution is 7.6, and the saturated brine solution has near-constant solubility of 4 percent solution at room temperature (59 to 77 °F). This yields a saturated solution of 40,000 mg/L sodium fluoride, or 18,000 mg/L as fluoride. The salt achieves this saturated brine solution within five minutes. These properties allow sodium fluoride to be used in a simple saturator tank, making it an ideal additive for small water systems. CDC WFRS reports that national usage of sodium fluoride is 7 percent of the population receiving fluoridated water by sodium fluoride adjustment.

STANDARDS AND PRODUCT CERTIFICATIONS

The AWWA Fluoride Standards Committee is responsible for the three fluoride additive standards (www.awwa.org/standards): B701, Sodium Fluoride; B702, Sodium Fluorosilicate; and B703, Fluorosilicic Acid. The committee reviews and updates the standards once every five years, and each facility adjusting fluoride in drinking water should have a current copy of the specific standard as a reference for that facility's particular additive. Available in the AWWA Store (www.awwa.org/store), these three AWWA standards specify the product quality as manufactured and purchased.

In addition to the three AWWA standards, NSF International is responsible for NSF/ANSI Standard 60, which sets criteria for water additive products to ensure purity and product integrity in distribution and use. A key aspect of Standard 60 is that a water additive product can't contain more than 10 percent of the Specific Product Allowable Contaminant for any regulated maximum contaminant level. Standard 60 provides for independent certifying entities to validate that the product meets the stipulated quality. NSF International publishes a fact sheet on fluoridation (www.nsf.org/newsroom_pdf/Fluoride_Fact_Sheet_2019.pdf) that covers the requirements of Standard 60 and how they apply to fluoridation additive products. The organization also provides a tabulation of the actual verification testing of fluoridation additive products over three periods of time, ranging from 2000 to 2017.

***Editor's Note:** This is the third of a four-article series on water fluoridation. The next article in the series will appear in the December issue and cover personnel safety and laboratory testing.*

PHOTOGRAPH: KIP DUCHON