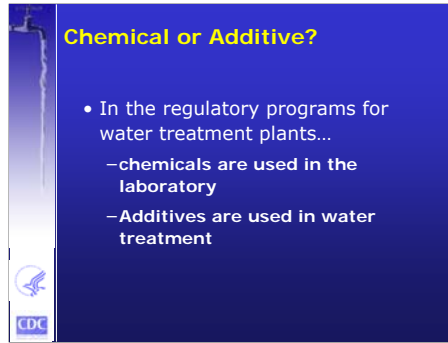


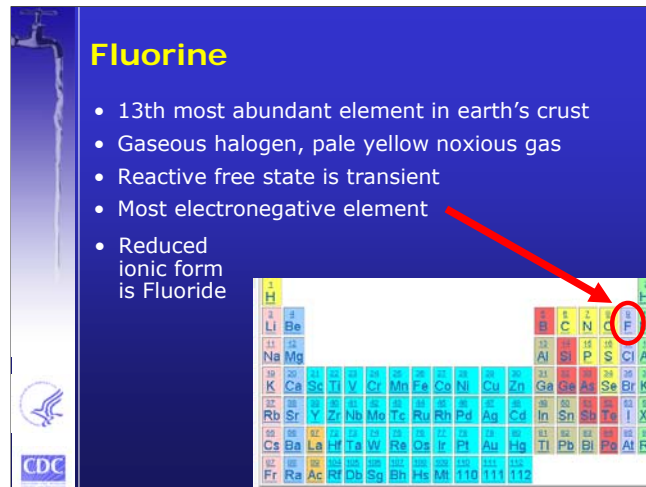


Let's talk about the additives we use for water fluoridation



You will often hear some people refer to fluoride as a “chemical”, but in the correct reference for a water treatment facility, “chemicals” are used in the laboratory, and “additives” are used in water treatment. That is the regulatory designation.

However, many people continue to refer to “additives” as “chemicals”. It would be better for state fluoridation program staff to refer to the correct “additive” designation and promote its reference as an additive to be consistent with regulatory practice.



**Fluorine**

- 13th most abundant element in earth's crust
- Gaseous halogen, pale yellow noxious gas
- Reactive free state is transient
- Most electronegative element
- Reduced ionic form is Fluoride

The slide includes a periodic table with the element Fluorine (F) circled in red. A red arrow points from the text 'Most electronegative element' to the circled Fluorine. The CDC logo is visible in the bottom left corner of the slide.

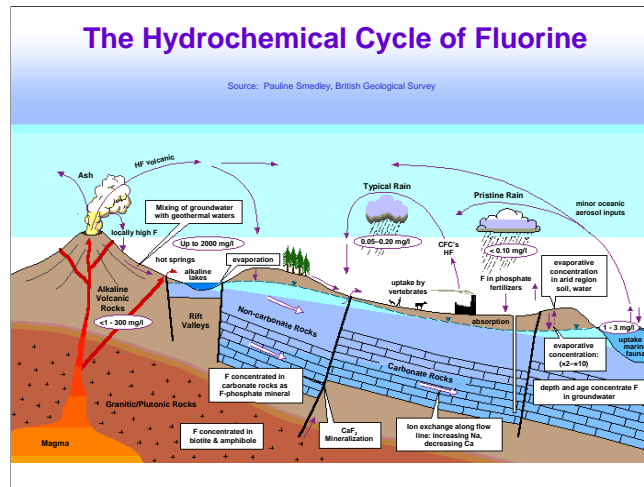
The element Fluorine in a gaseous halogen.

It is the 13<sup>th</sup> most abundant element in the earth's crust. This ranking may vary, depending upon the source of information and what their definition of what constitutes the earth's crust, meaning the top 20 miles? 30 miles? The ranking in itself is not all that important, but it is important to remember that it is present in all soils, plants, animals, and natural waters.

The reactive free state of fluorine in nature is transient for it readily combines with many elements. It is a pale yellow, noxious gas.

It is the most electronegative element, which means that many of the compounds it forms will be strongly bonded and quite stable.

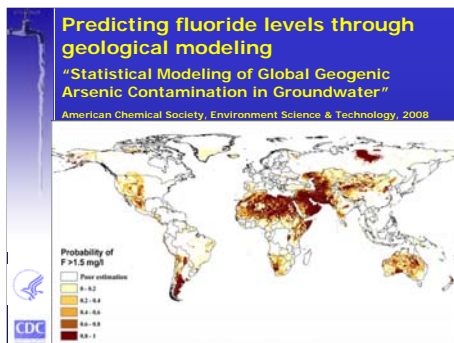
The reduced ionic form is fluoride, which is what we use for water fluoridation.



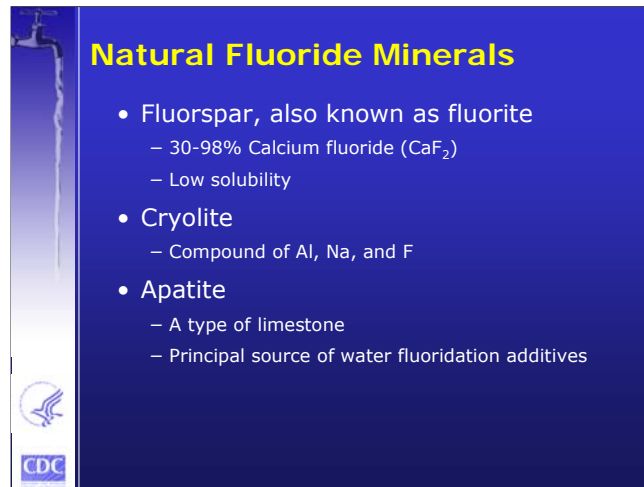
Fluoride in the atmosphere principally has a volcanic origin. Scientists have estimated that volcanic releases, are greater than other natural sources and anthropologic releases combined. Forest fires and wind driven erosion are the next most prevalent source of fluoride representing over a quarter of all fluoride sources to the atmosphere. Anthropologic releases such as coal burning and industrial releases are less than these secondary natural sources representing less than a quarter of all fluoride sources. The combined atmospheric releases result in rainwater having fluoride at approximately 0.1 mg/L.

Geological faulting extending to rocks formed deep underground, can provide a pathway for water with fluoride. As this deep water emerges, it has the potential for remineralization, in a fashion that can also be observed in teeth. Deep faults can also provide an explanation for different fluoride content of wells. If two wells are placed into the same geological formation, one well that has closer proximity to a deep fault source of fluoride will experience higher fluoride content than another well which may have a higher influence by surface water. Sometimes, it may be possible to drill another well up-gradient to obtain a lower fluoride content ground water.

In addition to natural sources, man-influenced sources of fluoride are principally released when coal is burned, along with some industrial emissions, and specialty gases. These incidental atmospheric releases will eventually degrade to hydrogen fluoride which will eventually precipitate to the earth's surface.



A recent article in Environmental Science & Technology  
**"Statistical Modeling of Global Geogenic Arsenic Contamination in Groundwater"**, by Manouchehr Amini, Karim C. Abbaspour, Michael Berg, Lenny Winkel, Stephan J. Hug, Eduard Hoehn, Hong Yang, and C. Annette Johnson, web published April 16, 2008, provides a prediction of water quality. Fluoride is often coincident with arsenic and this figure presents the estimated fluoride levels.



### Natural Fluoride Minerals

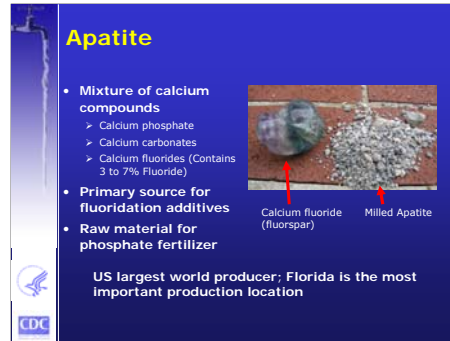
- Fluorspar, also known as fluorite
  - 30-98% Calcium fluoride ( $\text{CaF}_2$ )
  - Low solubility
- Cryolite
  - Compound of Al, Na, and F
- Apatite
  - A type of limestone
  - Principal source of water fluoridation additives

Fluoride can be found in a solid form in minerals such as:

Fluorspar, also known as fluorite, was the original source for most fluoride products, but those mines are exhausted in the US, although it is still mined in Mexico and some other countries.

Cryolite, which was heavily used for aluminum production until the mines were exhausted.

Since the early 1950's, apatite, a type of limestone, has been the principal source of water fluoridation additives.

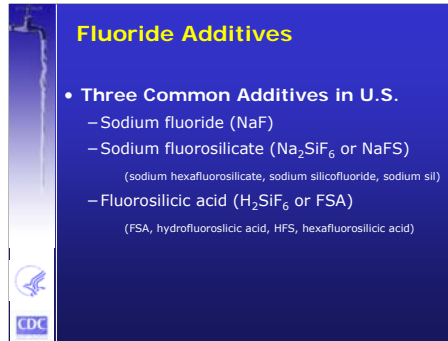


The raw material for fluoride additive production is the mineral apatite. This is a type of limestone that is a mixture of calcium compounds with relatively high phosphate and fluoride content including

calcium phosphate,  
calcium carbonates, and  
calcium fluorides.

Apatite contains 3%–7% fluoride depending on the ore deposit, and it is the primary source of fluoride for water fluoridation in the United States. Florida, North Carolina, the Gulf Coast area, and Mexico are all sources of fluoride used for water fluoridation. After the United States, China is the second largest source of apatite quarrying.

One photo shows milled apatite (a type of limestone) that is used in manufacture of phosphate fertilizers, next to a photo showing calcium fluoride, also known as fluorite or fluorspar. Calcium fluoride deposits were the historical source for fluoride products before the fertilizer industry and apatite became the principal source. Notice that the calcium fluoride crystal is transparent to opaque.



Theoretically, any compound that forms fluoride ions in a water solution can be used to adjust the fluoride concentration in drinking water.

Three compounds are commonly used in the United States:

sodium fluoride;

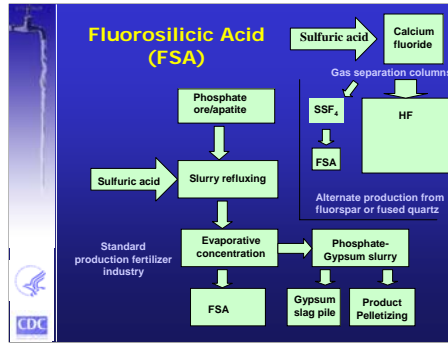
sodium fluorosilicate, also called sodium hexafluorosilicate or sodium silicofluoride (“sodium sil”); and

fluorosilicic (floor-oh-sill-liss-ick) acid, also called FSA, hydrofluorosilicic acid, HFS, and hexafluorosilicic acid

Other fluoride products have been considered in the past as possible additives but have not been used and no standards exist for their use in drinking water facilities.

Note to Instructor: this is good time to engage the audience and ask each of them which additive is used at their facility.



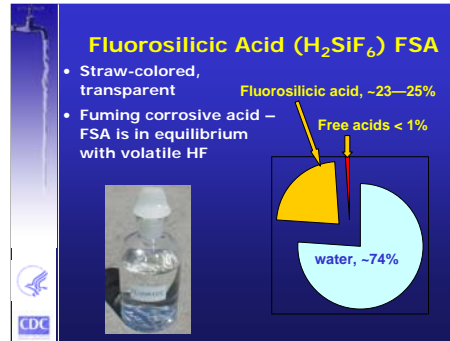


This is the basic flow chart of FSA production. Apatite, a constituent of “phosphate rock” (calcium phosphate mixed with limestone), is refluxed (mixed and heated) with sulfuric acid resulting in a phosphoric acid-gypsum slurry, the starting point for making pelletized phosphate fertilizers. Gypsum is the material that is used to manufacture drywall or “sheetrock” type wallboard. This process also releases silicon tetrafluoride and hydrogen fluoride, which are dissolved gases in the gypsum slurry. The gases are vacuum extracted and condensed into the FSA mixture used for water fluoridation.

Hydrogen fluoride and silicon tetrafluoride that otherwise would be dissolved in the gypsum slurry is recovered by evaporators and condensed. The recovered FSA is high-purity. Some sources may tell you that FSA is hazardous waste material that industry has no other way to dispose, but that is not true since it is predominately retained dissolved in the slurry with no regulatory requirement to capture.

Less than 5 percent of the water fluoridation FSA is from production of anhydrous hydrogen fluoride. Sulfuric acid addition to calcium fluoride (fluorspar), releases hydrogen fluoride along with a small quantity of silicon tetrafluoride gas. The hydrogen fluoride condenses at a higher temperature than the silicon tetrafluoride so silicon tetrafluoride remains as a gas while the hydrogen fluoride becomes an anhydrous liquid, and silicon tetrafluoride is quenched to become FSA.

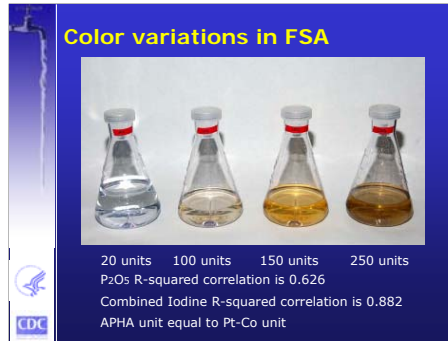
A small amount of FSA, less than 1 percent of the U.S. production, is derived from hydrogen fluoride etching of fused quartz products. The acid derived from this route is a high purity. Less than 1% of the FSA used for water fluoridation is derived from this method.



FSA is a straw-colored, transparent liquid. FSA is a fuming corrosive acid, with a pungent odor and irritating action on the skin. FSA is actually a mixture of water, FSA, and free acids, which include hydrogen fluoride. The largest fraction, approximately three-quarters of the total, is water, mixed with FSA ( $H_2SiF_6$ ), which is a dissolved solid and is the other quarter of the mixture. A trace quantity, typically less than 1%, of the mixture, is in the form of free acids. This free acid fraction includes hydrofluoric acid, also known as hydrogen fluoride (HF), along with silica tetrafluoride, phosphoric acid, sulfuric acid, hydrochloric acid, and other trace acids.

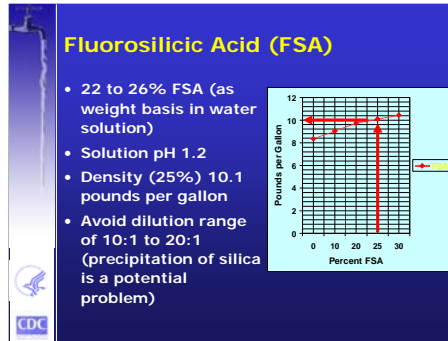
Hydrofluoric acid is volatile, which means it is a gas in solution. This is like the relationship of oxygen gas dissolved in water. The volatile hydrogen fluoride gas will leave the solution if it can reach a surface, and it is the tiny portion of volatile hydrogen fluoride that gives the characteristic odor to FSA. Hydrogen fluoride is also the portion of the mixture that produces the corrosive attack on materials and electronic devices. The rate of hydrogen fluoride formation is very slow, and this makes it possible to store the FSA in tanks for long periods.

This explanation is a simplification of the chemistry of FSA but is sufficient for the purposes of understanding the product for use in water treatment facilities.



Tests by LCI in 2007 found an increase in APHA color units (measured as Pt-Co) in FSA due to increases in the Phosphoric acid concentration and the Iodine concentration. There was a strong correlation to the increase in color with the increase in Iodine and a weaker but still significant correlation to the increase in phosphoric acid.

Use of 200 Pt-Co APHA color FSA diluted 250,000 times (to get 1 mg/L of F in finished water) would result in probable increase of total Iodine of 0.23 ppb in the finished water. NSF criteria is that the Single Product Allowable Concentration for Iodine is an increase of 0.1 mg/L and the WHO estimates that the average Iodine concentration in typical US drinking water is 4 ppb.



FSA has a solution pH of 1.2.

It is commercially available in solution concentrations ranging from 20% to 35%, with a typical solution concentration of 23%–25%.

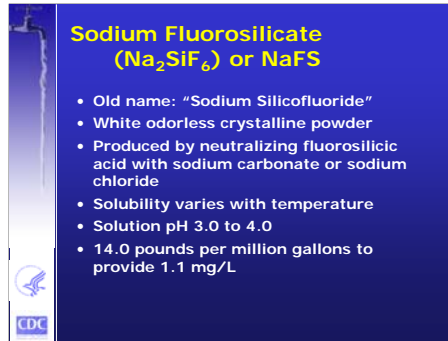
The density of a 25% acid is 10.1 pounds per gallon, which is more than the 8.34 pounds per gallon that water weighs. The chart shows how the density of the FSA increases as the concentration of the acid increases.

FSA is corrosive and care is needed when handling it.

The volatile fumes, which are hydrogen fluoride, are lighter than air. Hydrogen fluoride is less than 1% of the mixture.

If an acid has a solution concentration of 25%, what is the remaining 75%? Water. Because the acid contains a large quantity of water, shipping is a major component of its cost. Even so, it is typically still the least expensive to use for many facilities.

FSA is the most commonly used additive.



**Sodium Fluorosilicate**  
( $\text{Na}_2\text{SiF}_6$ ) or NaFS

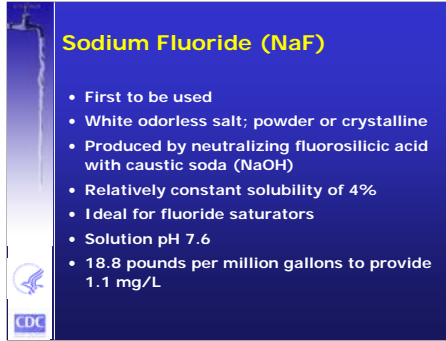
- Old name: "Sodium Silicofluoride"
- White odorless crystalline powder
- Produced by neutralizing fluorosilicic acid with sodium carbonate or sodium chloride
- Solubility varies with temperature
- Solution pH 3.0 to 4.0
- 14.0 pounds per million gallons to provide 1.1 mg/L

CDC

Sodium fluorosilicate, previously called sodium silicofluoride, is widely used for water fluoridation. It is a white, odorless, crystalline powder.

Sodium fluorosilicate is produced by neutralizing FSA with sodium carbonate or sodium chloride. During the process, sodium fluorosilicate precipitates out of solution. The acid solution is a weak hydrochloric acid (when sodium chloride is used), so heavy metals remain in the acidic stream solution and not with the precipitated sodium fluorosilicate. The heavy metals do not precipitate with the sodium fluorosilicate.

Unlike sodium fluoride, which has a constant solubility, sodium fluorosilicate has a solubility that varies with temperature; this requires a special effort to correctly dissolve the additive before feeding.



**Sodium Fluoride (NaF)**

- First to be used
- White odorless salt; powder or crystalline
- Produced by neutralizing fluorosilicic acid with caustic soda (NaOH)
- Relatively constant solubility of 4%
- Ideal for fluoride saturators
- Solution pH 7.6
- 18.8 pounds per million gallons to provide 1.1 mg/L

CDC

Sodium fluoride was the first compound used for water fluoridation, and its toxicity and physiological effects have been thoroughly studied.

Sodium fluoride is a white odorless salt, available in powder or crystalline form. It is the ideal additive for use with saturators for small systems because of its relatively constant solubility.

It is most commonly produced by neutralizing FSA with caustic soda (NaOH), but can also be produced by combining hydrogen fluoride with caustic soda. It is the most expensive of the fluoride additives because of the high cost and large amount of caustic soda required to produce it. As a result of the high cost of production, all production sources are currently located outside the United States.



There are a couple of standards you should be aware of for fluoride additives.

The AWWA specification covers the fluoride additives product quality verification as purchased. All facilities should have the AWWA standard for the additive they use for fluoridation.

The National Sanitation Foundation/American National Standards Institute (NSF/ANSI) standard covers product quality as used with respect to impurities and product integrity in distribution. A key concept is that an additive should not add more than 10% of the single product allowable concentration (SPAC), which is based on the EPA MCL of any regulated contaminant. This standard replaced the former EPA Water Additives Program in response to a request by EPA in 1984 for requirements for distribution and purity of products added during water treatment, thereby ensuring the public's protection. It was developed by a consortium of associations, including NSF International (National Sanitation Foundation), AWWA, ANSI, the Association of State Drinking Water Administrators, and the Conference of State Health and Environmental Managers. As of 2006, 45 state drinking water programs require that water treatment additives meet Standard 60. Both NSF and UL operate programs to certify products under the Standards 60.

The U.S. Food and Drug Administration (FDA) does not regulate additives to drinking water because their regulatory purview concerns only food, drugs, and cosmetic-related products. There is a 1979 Memorandum of Agreement between EPA and FDA that gives EPA all authority for drinking water regulations and FDA all authority for beverages. Commercially bottled water is considered a beverage, but potable drinking water is not considered a beverage.

Verification		STANDARD American Water Works Association Since 1881	
FSA	NaFS	NaF	
<ul style="list-style-type: none"> <li>Fluoride content</li> <li>- specific gravity</li> <li>Fluoride content</li> <li>- titration</li> <li>Free acid</li> <li>Heavy metals</li> </ul>	<ul style="list-style-type: none"> <li>Fluoride content</li> <li>-specific ion</li> <li>Moisture content</li> <li>Size (sieve)</li> <li>Insoluble matter</li> <li>Heavy metals</li> </ul>	<ul style="list-style-type: none"> <li>Fluoride content</li> <li>-specific ion</li> <li>Moisture content</li> <li>Size (sieve)</li> <li>Insoluble matter</li> <li>Heavy metals</li> <li>Saturated solution turbidity</li> </ul>	

AWWA specifications control the quality and manufacturing of the additives. Although you can and should require a supplier to provide a certified copy of all these tests on each batch delivered, facilities can in fact run the tests themselves.

If you suspect the additive delivery may not conform to the specifications, then by all means you should conduct the tests on the additive yourself and verify that the additive meets the specified criteria. For example, the percent fluoride content of FSA can vary from batch to batch; it is sold as 23% but can vary between 18% and 30%. Another example has to do with moisture; excessive moisture content of dry additive can suggest handling problems and the potential for poor solubility.

The test procedures are specified in the AWWA specification, and most water treatment laboratories should be able to conduct these tests. All facilities should have a copy of the specification on hand.

Particularly important for plant personnel is the hydrogen titration test for FSA, along with the specific electrode method for the dry additives, to verify fluoride content of the additives. With an increasing amount of imported sodium fluoride on the market, the insoluble matter and saturated solution turbidity tests are important for that product.





**NSF or USP?**


- 46 states mandate the use of NSF certified product
- Pharmaceutical grade USP only for Sodium fluoride
- Pharmaceutical grade provides less protection to consumers
  - No Arsenic criteria
  - Heavy metals as an aggregate
  - No Radiological criteria


A quick assessment of NSF versus United States Pharmacopoeia (USP). 46 states mandate the use of NSF certified product. There are three grades of sodium fluoride including AWWA/NSF, USP, and American Chemical Society (ACS) reagent grade. ACS grade is a higher quality product for the sodium fluoride is re-dissolved and then re-crystallized thereby increasing the purity.

USP provides less protection for consumers for the testing is for non-specific heavy metals, no criteria on arsenic, and no criteria on radiological exposure.


Prior to 2004, Solvay produced a “non-graded” sodium fluoride at their Illinois production facility which they sold as both AWWA/NSF and USP grades. They now sell Asian products for AWWA/NSF grade and a German produced product for USP grade. The German production facility reacts hydrogen fluoride with caustic, and this yields a lower percentage of sodium fluorosilicate to meet the fluorosilicate criteria in USP.

**What's on the horizon?**

Crystal balls are always 



- Sodium fluoride quality
- UL market share; UL-NSF cooperation
- Sodium fluorosilicate use increasing
- FSA market stabilizing at higher cost
- Solar panel and silica production





If you want to locate suppliers for various products, check the NSF International web site for certified product distributors.

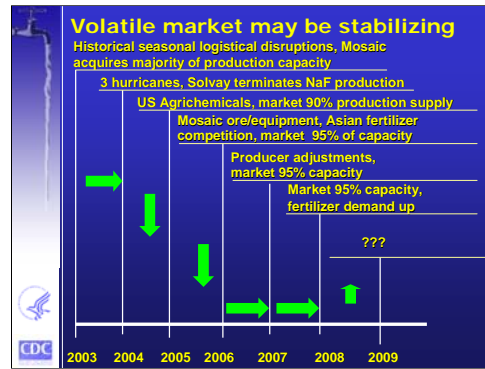


Currently, shortages of fluoride compounds occur in isolated local areas, typically related to depletion of supplies in a regional depot. Discussions with producers and suppliers indicate that there is no reason to expect any shortages at the national level.

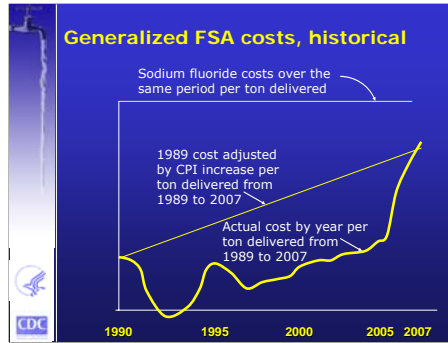
Because fluoride compounds used in water fluoridation are produced as a coproduct of the phosphate fertilizer industry, any problems in that industry could affect fluoridation. The year 2004 is an example of a rare disruption as several hurricanes required the fertilizer industry to power-down and then restart operations on several occasions. There was one month when some regional depots in the Midwest and eastern states depleted supplies before new deliveries could resume. Very few facilities were actually affected because there were sufficient on-site inventories in bulk storage tanks, and only a couple dozen facilities nationwide were affected. This type of regional depot depletion does not happen every year.

Dry additives can be imported, and currently, most sodium fluoride comes from China; there is no domestic producer.

You do need to be careful about some imports; utilities have reported that some foreign supplies have debris and purities of less than 50%. You may think you are getting a good deal, but you may use twice as much additive to get the same fluoride concentration, and you have the maintenance headaches of dealing with impurities and debris, particularly in saturators. The AWWA tests can verify the purity of the additive you are using.



What is the cause of all the supply disruptions? Well, its been downhill since Kip became the National Fluoridation Engineer.



Cost of FSA was low historically due to a declining market, but has recovered in recent years. It is back to the relative cost in the 1980's adjusted to CPI increases. \$1.00 in 1989 is worth \$1.66 in 2007. Sodium fluoride costs have been stable throughout the period due to declining market and competitive pressures from Asian sources. CPI reference <http://minneapolisfed.org/Research/data/us/calc/index.cfm>

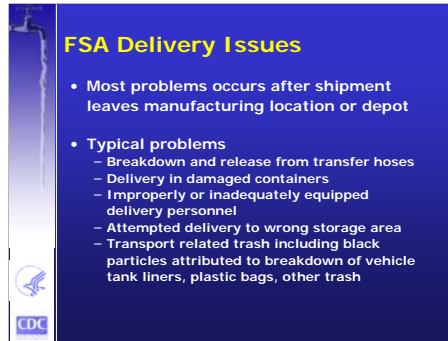
<b>HFS</b>	
<b>\$/ton del.</b>	
<b>1989</b>	<b>155</b>
<b>1990</b>	<b>125</b>
<b>1991</b>	<b>104</b>
<b>1992</b>	<b>98</b>
<b>1993</b>	<b>137</b>
<b>1994</b>	<b>152</b>
<b>1995</b>	<b>151</b>
<b>1996</b>	<b>130</b>
<b>1997</b>	<b>120</b>
<b>1998</b>	<b>117</b>
<b>1999</b>	<b>119</b>
<b>2000</b>	<b>122</b>
<b>2001</b>	<b>145</b>
<b>2002</b>	<b>140</b>
<b>2003</b>	<b>140</b>
<b>2004</b>	<b>139</b>
<b>2005</b>	<b>150</b>
<b>2006</b>	<b>224</b>
<b>2007</b>	<b>300</b>





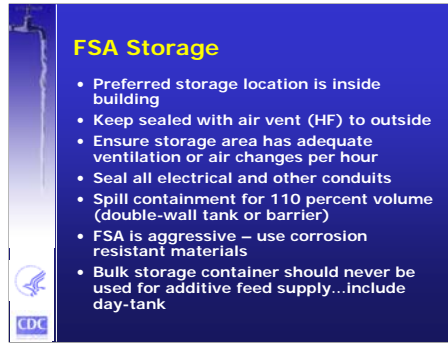
FSA can be delivered in different sized containers, including 20,000-gallon rail cars, 4,000- to 6,000-gallon truck tankers, tote tanks with 300–400 gallons, 55-gallon drums, 30-gallon carboys, and even 13-gallon carboys.





There are not a lot of problems with additive delivery, but they do occur, and you need to be prepared for them. Most problems associated with FSA delivery are related to causes that occurred after it leaves the manufacturing location or the regional distribution depot. The typical problems are

- Breakdown and release from transfer hoses, so be prepared to contain and neutralize materials discharging onto driveways and neighboring structures.
- Attempted delivery of chemicals in damaged containers of all types, so include an inspection of the containers before you allow delivery personnel to unload.
- Improperly equipped and trained delivery personnel. Verify their delivery manifest documentation and ask to see their checklist of practices before allowing them to unload to ensure that best practices are followed and that agents understand how to perform their job.
- Attempted delivery to the wrong storage location in the facility, which might endanger facilities and personnel when the vehicle must be repositioned. Also, it is not uncommon for a facility to have a truck discharge location with multiple chemical connections for different additives. Make sure your connection line is clearly marked and locked, and unlock the connection only when you are sure the agent is prepared to make the correct connection.
- Although NSF International includes provisions for certification of transport and depot deployment of delivery, on rare occasions contamination can still occur. The delivery vehicles are rubber-lined tanks and the liner can break down, resulting in black particles that can enter your system and damage equipment or block pipes or equipment. Plastic bags and other debris can also enter the delivery vehicle and result in problems. Verify that you have a strainer in the system and that the strainer is clear of debris. If you discover black particles, report it to the additive supplier promptly. Many facilities have the truck driver present a liter of additive before unloading to inspect for black particles and to conduct the AWWA tests.

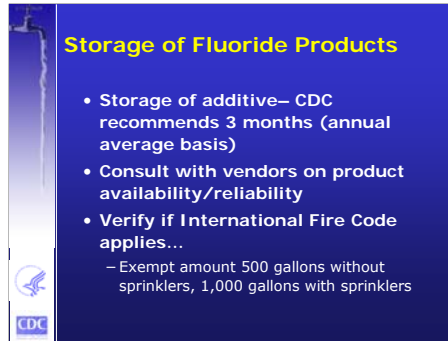


The preferred storage location is inside a building or under cover. FSA can freeze at approximately 4°F. In moderate climates, the tank can be outside if it is insulated and heat-wrapped, but this is not recommended.

Because this is liquid, it is important to have spill containment for 110% volume (double-walled tank or barrier). If concrete is used, a protective coating should be applied to minimize acid attack on the concrete in the event of a spill. Check with your coating supplier, but normally a good grade of epoxy undercoating with a top coat of high-quality urethane will be satisfactory. Be sure that you use standard operating procedures (SOPs) for filling and withdrawing from the storage tank to ensure that operators are careful and do the job right.

Keep the storage containers sealed with air vented to the outside. Terminate the vent with an inverted “U” and an insect/bird screen. FSA will produce a small quantity of hydrogen fluoride gas, which is corrosive and will etch glass, attack concrete, damage electrical circuits, and stain many things with which it comes into contact. Ensure that the containers are sealed and vented to the outside so the hydrogen fluoride gas is not released inside the storage room.

The bulk storage container, which is the large storage tank, should never be used for additive feed supply. The system should include a day tank that is used for actual feed of fluoride additive.

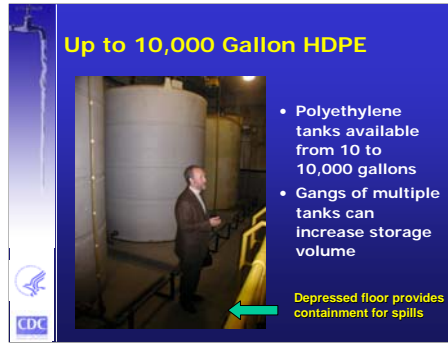


CDC recommends a storage capacity equal to 3 months of additive. With times greater than 6 months, there can be some degradation of product, particularly with the dry additives; with less 2 months capacity, you may have insufficient quantity to extend over shortages. Consult with vendors in your area for their advice about the appropriate level of storage.

Also, check to see if the International Fire Code applies in your jurisdiction. If so, then you need to include the appropriate signage, spill control for largest tank plus 20 minutes of sprinkler flow, sprinklers, leak alarm, and suitable ventilation.



Tote tanks can provide a larger volume of FSA than a 55-gallon drum. However, a tote tank should be stored on a containment pallet to hold FSA in the event of spill.

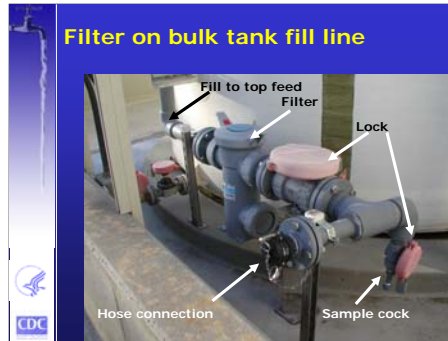


Polyethylene (HDPE) tanks are available in sizes from 10 to 10,000 gallons. Larger volumes are available by grouping several HDPE tanks together. Both cross-linked and linear types of HDPE have provided satisfactory service.

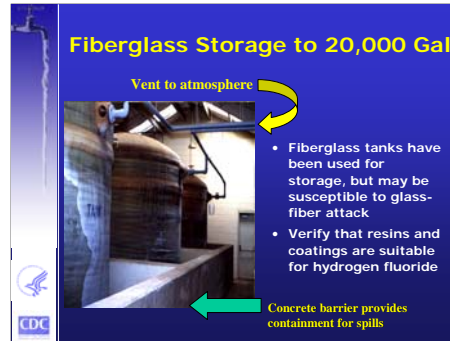
Some facilities have reported discoloration of HDPE tanks by FSA. Strong acids, can have a superficial adsorption, resulting in a chemical scorching of the surface layer. (Reference both Nalgene and PolyProcessing).

Plastic resins used for laboratory bottles and tubing products is medical grade with a minimum of antioxidants present (1 primary and no secondary antioxidant) at a relatively low level. Storage tanks may have a resin with different antioxidant character. An antioxidant effect when exposed to an oxidizing environment is "pinking", (a phenolic yellowing or gas fading). The antioxidant molecules are "activated" and can react with each other to create a color center that ranges from yellow to brown to pink. The exact color is dependent on many different factors, not the least of which is the site of attack by FSA. The stronger the hydrogen environment, the more the color will shift from yellow to pink.

This type of discoloration is cosmetic in the short term. However, as it does indicate that the antioxidant is being consumed, the ultimate long-term stability of the resin to other forms of oxidative attack (UV, O<sub>3</sub>, NO<sub>x</sub>) may be reduced, but would likely have a lifespan longer than the service life for the water treatment facility.



Since debris is the most frequently observed problem with FSA, it is advisable to have a filter on the bulk tank feed line. Here is an installation showing the hose connection (lockable) and an in-line filter so that if the delivery truck has debris, most of it will not enter the tank. Since the delivery truck uses a pressure air system to move the FSA from the truck to the tank, the feed line is blown clear at the end of the delivery, so the filter does not have FSA exposure to the operator when the filter is removed and inspected. The sample cock on the feed line allows a sampling of the delivery batch so the operator can conduct confirmatory testing such as the density (to determine concentration) and if there is debris in the load.



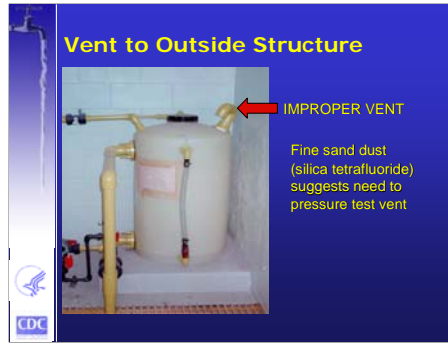
Fiberglass tanks provide the potential to store large volumes. There is mixed opinion about the suitability of these tanks. Some locations have used them successfully, but there is speculation that the glass fibers used as a reinforcement may be prone to attack by the hydrogen fluoride gas. If the gel-coat surface is intact, then the glass fibers probably have reasonable protection. Ensure that the resins and coatings used in such storage tanks are suitable for exposure to hydrogen fluoride. Periodically inspect these tanks for structural integrity. The formation of new stains can often identify leaks that are developing. Repairs are relatively inexpensive if caught early. Always use experienced contractors for such work. These tanks have some discoloration as a result of hydrogen fluoride exposure.

Always remember to have a sealed tank that is adequately vented to the outside.



A common delivery mode for FSA is a 55-gallon drum. These have been used as day tanks in some cases but normally should not be used in such a fashion. A properly sized tank made for that purpose should be used instead. This polyethylene tank shows that a tank can be easily vented with a flexible hose. The second photograph demonstrates corrosion in the vicinity of an incorrectly vented tank.





This tank is not correctly vented to the outside. Ensure that the tank is sealed and vented to the outside and that it does not release within the building. This installation will experience corrosion problems within the building.

If a tank is poorly vented, or if there is a leak in the vent piping, there are two visual signs that will indicate that the operator should take action. The first as we have discussed is evidence of corrosion, and the second is a fine white powder covering the piping and other surfaces. This white dusting is silica resulting from decay of the silica tetrafluoride gas in the FSA reacting with the atmosphere and condenses quickly. There is typically more silica tetrafluoride gas than hydrogen fluoride gas in FSA.

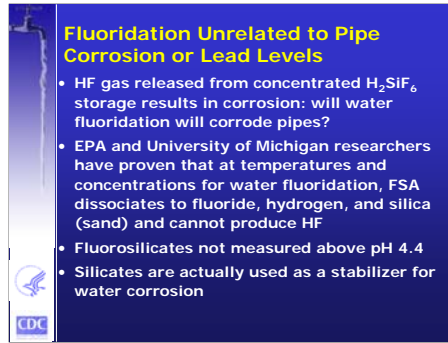
The venting system can be confirmed by air testing. Piping contractors typically have a air test system that can be used for this. The vent system can be pressurized to 2 psig and monitored for air loss. If the system loses more than 1 psig over a 2 minute period, then there is a leak and corrosion will result. The bubble method should help in identifying the leak. Do not exceed 4 psig in the test as the PE tank will not support pressures exceeding 5 psig. It is good practice to check for leaks at least once every 5 years.



FSA will damage concrete surfaces. Along with the use of corrosion-resistant pipe materials, provide surface protection to the concrete where leaks could occur.

A dual application of epoxy undercoat with urethane topcoat normally provides suitable protection for minor leaks. Alternative, a spray-on manhole rehabilitation polyurethane will also provide suitable protection to concrete.

Consult with reputable coating manufacturers for acceptable products.



**Fluoridation Unrelated to Pipe Corrosion or Lead Levels**


- HF gas released from concentrated  $H_2SiF_6$  storage results in corrosion: will water fluoridation will corrode pipes?
- EPA and University of Michigan researchers have proven that at temperatures and concentrations for water fluoridation, FSA dissociates to fluoride, hydrogen, and silica (sand) and cannot produce HF
- Fluorosilicates not measured above pH 4.4
- Silicates are actually used as a stabilizer for water corrosion

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Some operators have incorrectly speculated that, because hydrogen fluoride gas released from storage tanks results in corrosion, then by extension, water fluoridation will corrode pipes.

EPA and University of Michigan (Ann Arbor) researchers have proven that at the temperatures and concentrations used for water fluoridation, FSA achieves virtually complete dissociation when added to water to the product ions of fluoride, hydrogen, and silica (which is sand) and cannot produce corrosive hydrogen fluoride gas after it is diluted. So, once FSA is added to drinking water, hydrogen fluoride is no longer a problem.


Silicates are actually used as a water stabilizer reducing water corrosion, and sodium silicate is referred to in the water industry as “activated silica”.



## Pipe Corrosion Factors



- Galvanic series of metals
- Ionic influences on solutions
- Aquatic buffering
- pH

Pipe corrosion factors are the galvanic metals series, ionic solutions, buffering, and solution pH.



## Galvanic influences

- Oxidation-Reduction potential
- Metals are cationic and seek electrical neutrality with anionic balance: rusting steel allows a ferric metal to return to a ferrous metal state - oxidation
- Electrical potential drives electron transfer



The galvanic series measures the potential for one metal to sacrifice electrons to another metal.

**Galvanic series of metal nobility**

Increasing cationic ↑  
 ↓ Increasing anionic



- Magnesium
- Zinc
- Aluminum
- Cadmium
- Tin
- Lead
- Steel
- Copper
- Nickel
- Chromium
- Stainless
- Brass
- Titanium
- Silver
- Gold

Electrical current in soil or between cationic-anionic connectors


Electrical current in water

Pipe wall

The diagram shows a pipe wall with a positive (+) charge on the left and a negative (-) charge on the right. Two yellow curved arrows indicate the flow of electrical current: one arrow points from the positive side to the negative side above the pipe wall, and another arrow points from the negative side to the positive side below the pipe wall, representing the current in the water.



  


As the electrons are sacrificially released, an electric current is set up.




## Ionic influences

- **Solution ionic character conducts electrical current**
  - ion type minor...F is 1.3 times Cl based on electronegativity
  - ion concentration major
- **Chloride, typically 10 to 100 mg/L, is one- to two-orders of magnitude greater than fluoride. Up to 200-300 mg/L in drinking water. Sea water is 10,000 mg/L**





The movement of the electrical current that may be induced is also influenced by the ionic character of the solution. Since fluoride is a minor and practically inconsequential component of the total solution ionic character, it is a minor influence.




## Buffering

- **Ionic damping of electrical or electron transfer or potential**
  - Hardness and alkalinity (often 10 to 200 mg/L)
  - Silicate (typically 10 to 30 mg/L)
  - Phosphates





Buffering can attenuate the electron transfer or potential. Hardness, silicates and phosphates all contribute to surface stabilization.



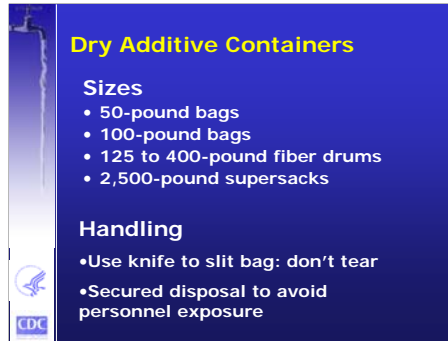


**pH**

- Range of 1 to 14
- Fluoride at 1 mg/L is overwhelmed by natural buffering of waters
- Influence of changing pH from 7.4 to 7.3?
  - less than 1% of range
- Can be a larger factor for concrete pipe, less for plastic pipe



The pH determines the ionic speciation. Since fluoride is a minor element of the water chemistry, it typically does not alter the finished water pH except in very soft waters where a minor change of less than 1 percent may be experienced.



Dry additives can be delivered in 50- and 100-pound bags, in 125- to 400-pound drums, and even in 2,500-pound supersacks.

Handling of bags requires special consideration. Use correct lifting technique to avoid personnel injury, and never tear bags open. Always use a knife to slit bag to minimize release of loose dust. After use, wrap bag inside a plastic bag for disposal and use secured placement to avoid exposure to someone else. Don't just toss bags into a dumpster. Coordinate with the trash hauler and landfill operator so their personnel do not have exposure to fluoride dust.



There are not a lot of problems with additive delivery, but they do occur. Most problems associated with dry additive delivery occur after the additive leaves the manufacturing location or the regional distribution depot.

- One problem is attempted delivery of chemicals in damaged or punctured bags, so include an inspection of bags and pallets before you allow delivery personnel to unload. Often pallets are wrapped in plastic at the manufacturing location, so if you purchase by the pallet, ensure that the shipping wrap is undamaged. Inspect for evidence of rough handling and fork lift punctures.
- Improperly equipped or untrained delivery personnel is another problem. Verify the delivery manifest documentation and ask to see a checklist of practices before you allow unloading to ensure that best practices are followed and that the agent understands how to correctly perform their job.
- Another problem is attempted delivery to the wrong storage location in the facility, which might endanger facilities when the vehicle is repositioned.
- Although NSF International includes provisions for certification of transport and depot deployment of delivery, contamination can still occur. Especially for smaller facilities, all the chemical additives used in the facility may be supplied by a single supplier and they might mix bags of different additives on a common pallet. Verify that no damage has occurred to the bags and that the additives maintain their integrity.
- Another problem can be degradation of product during transport. If the additives are exposed to weather during transport, they can hydrate (adsorb water), which can change their properties and handling characteristics. Do not accept delivery of product exposed to the elements.



**Dry Additive Storage**

- Separate room – do not mix additives, secured access
- Good ventilation
- Elevated platform – keep dry additives on pallets
- Limit stacks to 6 bags
- Protected from elements: additives cake when compressed and exposed to moisture
- Convenient to feed location



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Dry additives should be kept in a separate room with secure access that is convenient to the feed location. Avoid storing other additives, lubricants, yard-care fertilizers, etc., in the same room. Do not mix additives.

The room should have good ventilation in the event of dusting.

It is best to have an elevated platform, and keep the dry additives on pallets so they are not in contact with the floor.

Limit stacks to six bags high and protected from the elements. Additives cake when compressed and exposed to moisture. Do not overbuy as the additives will slowly adsorb moisture from the air and hydrate, resulting in “fish-eyes” that may never be successfully dissolved. Limit purchases to a maximum 6-month supply.



Supersacks are a 2,500-pound delivery package that is common in the bulk handling market, and sodium fluorosilicate is available for delivery in supersacks. They hold the equivalent of one pallet of bags. Supersacks have forklift loops for lifting and transporting. For facilities that use a lot of sodium fluorosilicate that can be designed with a large storage hopper, this can be a cost-effective means of handling the additive.

Supersacks should be stored on an elevated platform so that they are not in contact with concrete floors. They must be protected from the elements, and should not be stacked.

**Don't Let Your Fluorides Wander**

- Dispose of Empty Bags/Drums Properly
- Don't Burn the Containers
- Limit Unauthorized Access to Storage and Disposal Areas.



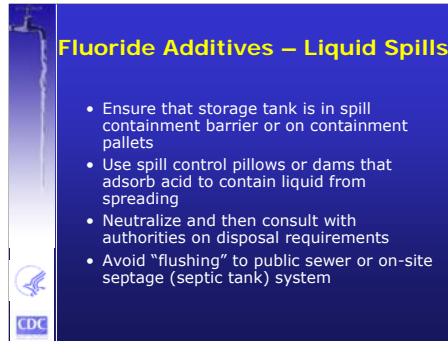
Disposal of the bags needs to be properly conducted. The bags still have a residual of fluoride product posing a hazard for other users such as haulers and disposal operators. Don't burn the containers as burning product could release hydrogen gas, and the bags should not be placed in dumpsters loose. Instead, fold into a plastic bag and secure the top. Advise the garbage hauler that they should take the appropriate precautions for their operators. And limit access to storage and disposal areas to staff trained in proper handling procedures.



What do you do if you have a spill of your fluoride products?

With your dry compounds, shovel them up and, if not contaminated, use them.

If the compounds are suspected of contamination, then they should be properly disposed of in a landfill. Follow local and state codes and regulations. Sodium fluorosilicate is a regulated hazardous substance, and you do not want to expose a landfill operator to excessive sodium fluoride even though it is not a regulated substance. Check with your state water fluoridation program specialist for advice.



Liquid spills require a little more effort. Proper preparation starts by having a containment barrier such as a corrosion-coated concrete curbing surrounding the tank sufficient to hold 110% of the contents of the tank, or drums and totes can be stored on containment pallets. Even with good containment, it is possible for a release to occur (broken pipe, etc.), so you should keep on hand spill control pillows or dams that adsorb acid to contain liquid from spreading in the event of a spill. “Spill kits” are commercially available and many utilities have them. Conduct an annual inspection of your spill kits to ensure that the contents are up to date. If there are multiple chemicals in the tank form, clearly label all spill kits as to their application.

Once contained, neutralize and then consult with authorities about disposal requirements. Avoid “flushing” to a public sewer or on-site septage (septic tank) system. Local jurisdictions have sewer use ordinances prohibiting discharge of non-domestic chemical releases and states have septic tank regulations prohibiting unauthorized use of subsurface leach systems for chemical disposal.



**Fluoride Additives – Liquid Spills**

Neutralization – Lime

$$\text{H}_2\text{SiF}_6 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaSiF}_6 + 2\text{H}_2\text{O}$$

$$\text{CaSiF}_6 + 2\text{Ca}(\text{OH})_2 \rightarrow 3\text{CaF}_2 + \text{SiO}_2 + 2\text{H}_2\text{O}$$

**Calcium fluoride and silica (sand) are considered non-hazardous and accepted at most landfills**

0.39 pound of lime is required to neutralize one pound of acid for an acid strength of 25%

CDC

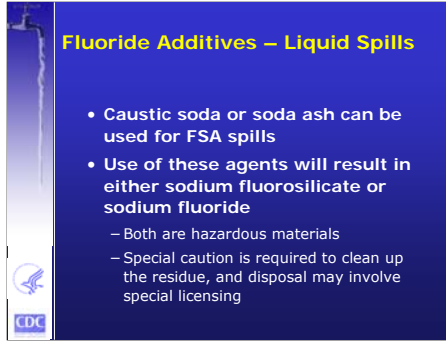
If a spill occurs, as a result of either a leaking pipe or tank or a burst hose, the first thing to do is to contain the acid. Small quantities of acid can be cleaned up with spill control pillows that absorb the acid, and lime can be used to create a dike to contain the spill.

Lime is the best choice for neutralizing acid, and lime is another additive that is available at many water treatment plants. A good practice is to have several bags of powdered lime in storage near to the delivery point so that if a spill occurs, it can be quickly deployed to prevent spreading. Replace the bags yearly so that they don't cake with excessive moisture over time.

In the reaction of acid and lime, the calcium fluorosilicate is unstable, and almost everything formed will be calcium fluoride ( $\text{CaF}_2$ ) and silica ( $\text{SiO}_2$ ).

These two products are accepted at most landfills, as they are nonhazardous chemicals. However, be sure to consult with the local landfill operator so that no employees at the landfill are exposed to excessive fluoride during placement.

For an acid strength of 25%, you need about 0.39 pound of lime to neutralize a pound of acid.



**Fluoride Additives – Liquid Spills**

- Caustic soda or soda ash can be used for FSA spills
- Use of these agents will result in either sodium fluorosilicate or sodium fluoride
  - Both are hazardous materials
  - Special caution is required to clean up the residue, and disposal may involve special licensing

If lime is not available for neutralization, then caustic soda or soda ash can be used for FSA spills. However, use of these agents will result in formation of either sodium fluorosilicate or sodium fluoride, which may be considered hazardous materials. Special caution is required to clean up these residues, and disposal may involve special licensing. Check with your state hazardous waste regulatory group and consult with the local landfill and fire chief.