CHAPTER 2

FLUORIDE CHEMICALS

2.1 INTRODUCTION

Fluorine, a gaseous halogen, is the thirteenth most abundant element found in earth's crust. It is a pale yellow noxious gas that is highly reactive. It is the most electronegative of all the elements. It cannot be oxidized to a positive state. Fluorine is never found in a free state in nature, but is always in combination with chemical radicals or other elements as fluoride compounds. When dissolved in water, these compounds dissociate into ions. It is the fluoride ions at the optimal levels in drinking water that are responsible for dental caries reduction. There are three basic compounds commonly used for fluoridating drinking water supplies: Sodium fluoride, sodium fluorosilicate and fluorosilicic acid.

2.2 CHEMICAL SOURCES

Fluoride can be found in a solid form in minerals such as fluorspar, cryolite, and appetite. Fluorspar is a mineral containing from 30 to 98 percent calcium fluoride (CaF_2). Fluorspar (also called fluorite) is found in most parts of the world.

Cryolite ($Na_3\ AlF_6$) is a compound of aluminium, sodium, and fluoride. It is preferred for industrial use because of its low melting point.

Apatite $[Ca_{10}\ (PO_4,\ CO_3)_6\ (F,\ Cl,\ OH_2)]$ is a deposit of a mixture of calcium compounds. (The comma in the chemical equation denotes a mixture.) These calcium compounds include primarily calcium phosphates, calcium fluorides and calcium carbonates. Also, there are usually trace amounts of sulphites as impurities. Apatite contains from 3 to 7 percent fluoride and is the main source of fluorides used in water fluoridation at the present time. It also is the raw material used for phosphate fertilizers.

Due to the dissolving power of water and the movement of water in the hydrologic cycle, fluoride is found naturally in all waters. As water moves through the earth as ground water, it contacts fluoride-containing minerals and carries fluoride ions away from them. Because all water eventually goes to the ocean, sea water also contains fluoride (approximately 1.2 ppm).

The concentration of fluoride found in fresh waters varies according to such factors as the depth at which the water is found and the quantity of fluoride-bearing minerals in the area. Generally speaking, the deeper the ground water, the greater the concentration of fluoride in the water.

2.3 FLUORIDE COMPOUNDS IN GENERAL

Theoretically, any compound that forms fluoride ions in water solution can be used for adjusting the fluoride content of a water supply. However, there are several practical considerations involved in selecting compounds. First, the compound must have sufficient solubility to permit its use in routine water plant practice. Second, the cation to which the fluoride ion is attached must not have any undesirable characteristics. Third, the material should be relatively inexpensive and readily available in grades of size and purity suitable for their intended use. Fluoride chemicals, like chlorine, caustic soda, and many other chemicals used in water treatment can constitute a safety hazard for the water plant operator unless proper handling precautions are observed. It is essential that the operator be aware of the hazards associated with each individual chemical prior to its use.

The quality of fluoride compounds used for water fluoridation in South Africa should meet the standards of the South African Bureau of Standards. The following fluoride chemicals are recommended for use in water fluoridation projects in South Africa: sodium fluoride, sodium fluorosilicate, fluorosilicic acid, sodium bifluoride and hydrogen fluoride. Imported chemicals especially should be checked for compliance with the South African standards.

2.4 SODIUM FLUORIDE

The first fluoride compound used in water fluoridation was sodium fluoride. It was selected on the basis of the above criteria and also because its toxicity and physiological effects had been so thoroughly studied. Sodium fluoride has become the reference standard used in measuring fluoride concentration. Other compounds came into use, but sodium fluoride is still widely used, because of its unique physical characteristics.

Sodium fluoride (NaF) is a white, odourless material available either as a powder of in the form of crystals of various sizes.

It is a salt that in the past was manufactured by adding sulphuric acid to fluorspar and then neutralizing the mixture with sodium carbonate.

In 1983 and 1984, the chemical industry changed the way they manufactured sodium fluoride. It is now produced by neutralizing fluorosilicic acid with caustic soda (NaOH). Its formula weight is 42.00, specific gravity 2.79, and its solubility is practically constant at 4.0 grams per 100 millilitres in water at temperatures generally encountered in water treatment practice (Table 2-1).

The relatively constant 4 percent solubility of sodium fluoride is the basis for the design of the saturator. The pH (hydrogen-ion concentration) of a sodium fluoride solution varies with the type and amount of impurities, but solutions prepared from the usual grades of sodium fluoride exhibit a nearly neutral pH (approximately 7.6). It is available in purities ranging from 97 to over 98 percent, with the impurities consisting of water, free acid or alkali, sodium fluorosilicate, sulphites and iron, plus traces of other substances.

Powdered sodium fluoride is produced in different densities, with the light grade weighing less than 1 000 kilograms per cubic meter and the heavy grade weighing about 1 400 kilograms per cubic meter. A typical sieve and analysis of powdered sodium fluoride shows 99 percent through 200 mesh and 97 percent through 325 mesh. Crystalline sodium fluoride is produced in six various ranges, usually designated roughly as coarse, fine and extra-fine, but some manufacturers can furnish many specific mesh sizes. The crystalline type is preferred when manual handling is involved, since the absence of fine powder results in a minimum of dust. Dust constitutes the most frequently encountered hazard in handling sodium fluoride. A more thorough discussion of handling precautions is presented in later sections.

Sodium fluoride has a number of industrial uses: The manufacture of vitrified enamel and glasses; as a steel degassing agent; in electroplating; in welding fluxes; in heat treating salt compounds; in sterilizing equipment in breweries and distilleries; in paste and mucilage; as a wood preservative; and in the manufacture of coated paper.

TABLE 2-1
PROPERTIES OF THE MOST COMMON FLUORIDATION CHEMICALS

	Sodium fluoride	Sodium fluosilicate	Sodium bifluoride	Hydrogen fluoride	Fluosilicic acid
Synonyms		Sodium silicofluoride, sodium hexafluorosilicate, sodium fluosicate	Sodium hydrogen fluoride Sodium acid fluoride	Hydrofluoric acid	Hydrofluosilicic acid, hexafluosilicic acid, silicofluoric acid
Chemical formula	NaF	Na_2SiF_6	$NaHF_2$	**HF**	**H_2SiF_6**
Molecular mass	42	188,05	61,998	20,006	144,08
Available fluoride in formula	45,2%	60,6%	61,29%	94,96% (as 100%	79,1% (as100%)
Appearance	White odourless hygroscopic powder or crystals	White odourless non-hygroscopic crystalline powder	White granular material with a characteristic odour	Liquefied gas, hygroscopic, strongly acidic, gas - white vapour, liquid - colourless. Extremely pungent odour	Straw-coloured, transparent, furning, corrosive liquid with sour pungent odour
Commercial purity	90-95%	Approx. 98%	98,7%	99,98	23% - 30% solution
Amount of chemical to dose 1mg fluoride/l	Aprox. 2.329 to 2.458 kg/Ml	Approx. 1.684 kg/Ml	Approx 1,63 kg/Ml	2,10-2,63kg/Ml (for 40-50%)	Approx. 4.21 to 5,497 l/Ml (for 23-30%)
Solubility (gram per 100ml)	4,00 at 0°C 4,05 at 20°C 4,10 at 25°C	0.44 at 0°C 2.45 at 100°C	3,7 at 20°C 16,4at 80°C	Not applicable	Not applicable
	Widely used in water fluoridation, mainly in small installations. Not used in large plants because of high cost and bulky saturators. Dust control necessary.	Usually cheapest fluoridation chemical, used in large installations. Dosed with dry feeder. Dust control necessary.	Corrosive and acidic solid similar to Sodium fluoride with higher fluoride content. Dust control necessary	Corrosive liquid similar to fluosilcic acid, usage depends on circumstances in the country and the availability of alternative chemicals	Inexpensive chemical, simple to dose. Suitable for both large or small installations.

pH of saturated solution	Approx. pH 7.4	Approx. pH 3,6	Approx pH 3,6	pH1 (40-50% solution)	pH 1,2 (20%-35% solution)

2.5 SODIUM FLUOROSILICATE

Fluorosilicic acid can readily be converted into various salts, and one of these, sodium fluorosilicate (Na_2SiF_6), also known as sodium silicofluoride is widely used as a chemical for water fluoridation. As with most fluorosilicates, it is generally obtained as a by-product from the manufacture of phosphate fertilizers.

Phosphate rock is ground up and treated with sulphuric acid, thus forming a gas by-product. This gas reacts with water and forms fluorosilicic acid. When neutralized with sodium carbonate, sodium fluorosilicate will precipitate out. The conversion of fluorosilicic acid (essentially a low-cost by-product, which contains too much water to permit economical shipping) to a dry material containing a high percentage of available fluoride results in a compound, which has most of the advantages of the acid, with few of its disadvantages. Once it was shown that fluorosilicates form fluoride ions in a water solution as readily as do simple fluoride compounds, and that there is no difference in the physiological effect, fluorosilicates (and fluorosilicic acid) were rapidly accepted for water fluoridation, and in many cases, have displaced the use of sodium fluoride, except in saturators.

Sodium fluorosilicate is a white, odourless crystalline powder. Its molecular weight is 188.06 and its specific gravity is 2.679.

Its solubility varies from 0.44 grams per 100 millilitres of water at 0 degrees centigrade to 2,45 grams per 100 millilitres at 100 degrees C (see Table 2-1). The pH's of solutions are definitely on the acid side, with saturated solutions usually exhibiting a pH between 3.0 and 4.0 (approximately 3.6). Sodium fluorosilicate is available in purities of 98 percent or greater, the principal impurities being water, chlorides, and silica.

Sodium fluorosilicate is sold in two commercial forms - regular and fluffy. The density of sodium fluorosilicate ranges from 1 000 to about 1 400 kilograms per cubic meter. A typical sieve analysis of the regular grade shows more than 99 percent through a 200-mesh sieve and more than 10 percent through a 325-mesh sieve.

Sodium fluorosilicate has some other industrial uses: Laundry scouring agent (neutralizing industrial caustic soaps); the manufacture of opal glass; and moth-proofing woollens. As in the case of sodium fluoride, the principal hazard associated with handling sodium fluorosilicate is dust. Precautions for dealing with this material are discussed in later sections.

2.6 SODIUM BIFLUORIDE

Sodium bifluoride ($NaHF_2$) also known as sodium hydrogen fluoride or sodium acid fluoride is a white granular material with a characteristic adour. Its moleculor weight is 61,998 and its pour density 1200kg/m^3. Its solubility varies between 3,7 grams per 100 millilitres of water at 20 degrees centigrade to 16,4 grams per 100 millilitres at 80 degrees C. The pH's of solution are acidic with saturated solutions usually exhibiting a pH between 2 and 3. Sodium bifluoride is available in purities of 98,7% with the principle impurities being sulfate, iron and lead. Preparations that contain sodium bifluoride at concentrations >1% shall be considered as corrosive and at concentrations 0,1-1% as an irritant. Sodium bifluoride decomposes on heating (>160ºC) and releases hydrogen fluoride.

Sodium bifluoride is sold in 40 X 25kg woven polypropolene bags with plastic liners on a palette, cling wrapped and labelled. In the industry it also used as a component of electrolyte for tin plating, as a laundry sour and for the bleaching of leather and other products. As in the case with other solid fluoride compounds, the principal hazard associated with handling sodium bifluoride is dust.

2.7 FLUOROSILICIC ACID

Fluorosilicic acid (H_2SiF_6), also known as hydrofluosilicic, hexafluosilicic, or silicofluoric acid is a 20 to 35 percent aqueous solution with a formula weight of 144.08.

It is a straw-coloured, transparent, fuming, corrosive liquid having a pungent odour and an irritating action on the skin. Solutions of 20 to 35 percent fluorosilicic acid exhibit a low pH (1.2), and at a concentration of 1 ppm can slightly depress the pH of poorly buffered potable waters. It must be handled with great care because it will cause a "delayed burn" on skin tissue. The specific gravity and density of fluorosilicic acid are given in Table 2-2. The average density of 23 percent acid is 1,02 kg/liter. Fluorosilicic acid (23 percent) will freeze at approximately -15.5 degrees C.

Fluorosilicic acid is manufactured by two different processes, resulting in products with differing characteristics. The largest production of the acid is a by-product of phosphate fertilizer manufacture. Phosphate rock is ground up and treated with sulphuric acid, forming a gas by-product. This gas is reacted with water, forming a weak fluorosilicic acid.

The acid is then concentrated from 23 percent to 25 percent strength. This type of acid seldom exceeds 30 percent strength. A smaller amount of acid is prepared from hydrofluoric acid (HF) and silica, resulting in a purer product at a slightly higher strength. Acid prepared from phosphate rock contains colloidal silica in varying amounts, and while this is of little consequence when the acid is used as received, dilution results in the formation of a visible precipitate of the silica. Some suppliers of fluorosilicic acid sell a "fortified" acid, which has had a small amount of hydrofluoric acid added to it to prevent the formation of the precipitate. Acid prepared from hydrofluoric acid and silica does not normally form a precipitate when diluted.

Hydrofluoric acid (HF) is an extremely corrosive material. Its presence in fluorosilicic acid, whether from intentional addition, i.e., "fortified" acid or from normal production processes demands careful handling. The HF fumes from fluorosilicic acid are lighter than air, unlike chlorine fumes, which are heavier than air. Thus, the acid fumes will rise instead of settling to the floor. (The silicon tetrafluoride [SiF_4] is a gas that is heavier than air but is not toxic.)

TABLE 2-2
SPECIFIC GRAVITY OF FLUOROSILICIC ACID

Acid* (%)	Specific Gravity (s.g.)
0 (water	1.000
10	1.0831
20	1.167
23	1.191
25	1.208
30	1.250
35	1.291

***Based on the other percentage being distilled water.**

Since fluorosilicic acid contains a high proportion of water, shipping large quantities can be quite expensive. Larger users can purchase the acid directly from the manufacturers in bulk (tank car or truck) lots, but smaller users must obtain the acid from distributors who usually pack it in drums or polyethylene carboys. Rather than attempt to adjust the acid strength to some uniform figure, producers sell the acid as it comes, and the price is adjusted to compensate for acid strength above or below the quoted figure. Note that the "23 percent basis" type of pricing applies only to bulk quantities. It is the usual practice for the supplier to furnish assay reports of the acid strength of each tank truck lot.

Attempts to dilute the acid are subject to errors in measuring both the acid and the diluting water. It is much better to use the acid undiluted as it comes from the containers in which it is shipped.
If the acid is too concentrated for the solution feeder to handle, than weaker solutions of other compounds are generally indicated - for instance, saturated solutions of sodium fluoride. CDC strongly recommends against the dilution of acid.

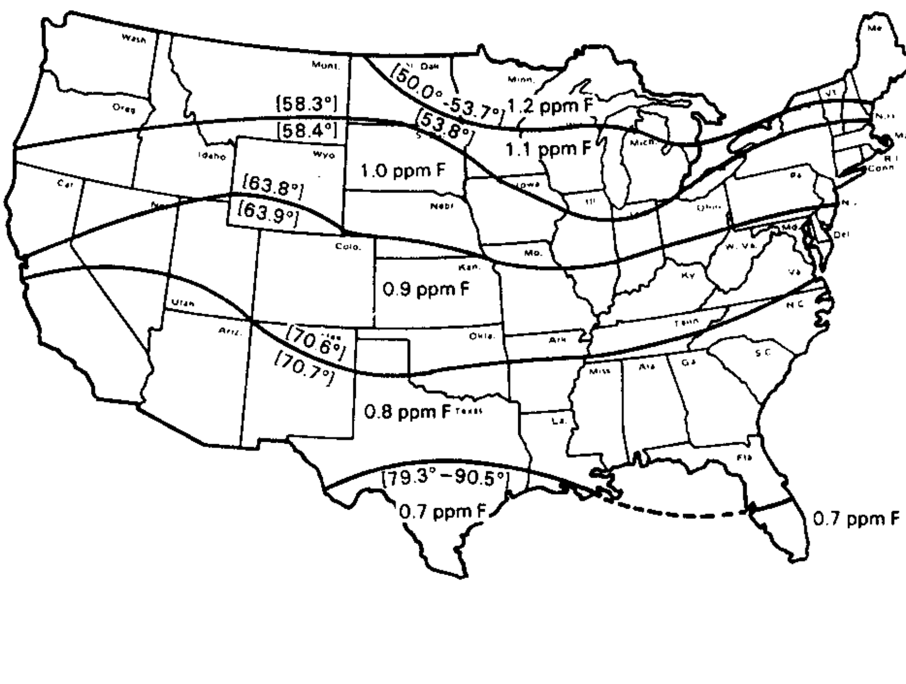
If the acid must be diluted, care should be taken to avoid the formation of a precipitate of silica, which will appear despite the quality (hardness) of the water used for dilution. Dilutions between 10:1 and 20:1 (water: acid) where insoluble silica precipitates are most likely to occur. Softening the water will not prevent this precipitation.

Like all other fluoride compounds, fluorosilicic acid has a number of industrial uses, including the sterilization of equipment in the brewery and bottling industries; electroplating; tanning of animal hides; etching of glass; refining of lead; hardening of cement; and preservation of wood. As with all other mineral acids, fluorosilicic acid should be handled with care to prevent injury to operators and damage to equipment from acid splatter or fumes. A more thorough discussion of handling precautions is presented in following sections.

2.8 HYDROGEN FLUORIDE

Hydrogen fluoride also known as hydrofluoric acid is a 99,9% liquefied gas with a molecular weight of 20.006. It is a colourless liquid with an extremely pungent odour. It has a boiling point of 19,5°C at sea level and exerts a vapour pressure of 103kPa at 20°C. The product is hygroscopic, reacts violently with water and is strongly acidic. The average density is 975Kg/m^3 at 20°C and 1100 kg/m^3 at 0°C.
In the industry the chemical is used as a catalyst in the petrol industry, a catalyst in the manufacturing of detergents, in the production of uranium hexafluoride used in the nuclear industry and in the production of fluoride chemicals.
For water fluoridation 40 – 60% hydrofluoric acid (HF) in drum and bulk tanker loads are provided. Forty per cent hydrofluoric acid is classed as a corrosive liquid, the same as for 35% fluorosilicic acid and should be handled in the same manner.

FIGURE 2-1



2.9 OTHER FLUORIDE CHEMICALS

Ammonium silicofluoride, magnesium silicofluoride, potassium fluoride and calcium fluoride (fluorspar) are being or have been used for water fluoridation. Each has particular properties that make the material desirable in a specific application, but each also has undesirable characteristics.

Ammonium silicofluoride has the peculiar advantage of supplying all or part of the ammonium ion necessary for the production of chloramine, when this form of disinfectant is preferred to chlorine in a particular situation. It has the disadvantage of hindering disinfection if there are short contact times. Also, it is more expensive than sodium fluorosilicate.

Magnesium silicofluoride and potassium fluoride have the advantage of extremely high solubility, of particular importance in such applications as school fluoridation, when infrequent refills of solution containers are desired.

In addition, potassium fluoride is quite compatible with potassium hypochlorite, so a mixture of the two solutions (in the same container) can be used for simultaneous fluoridation and chlorination. They can not be fed in dry form. Also, they are both more expensive, especially potassium fluoride, than sodium fluorosilicate.

Magnesium silicofluoride is widely used in Europe as a concrete curing compound and thus is mass produced, but it is still more expensive than sodium fluorosilicate.

Potassium fluoride is one of the main ingredients in the manufacture of nerve gas.

Calcium fluoride (fluorspar) is the least expensive of all the compounds used in water fluoridation, but is it also the most insoluble. It has been successfully fed by first dissolving it in alum solution, and then utilizing the resultant solution to supply both the alum needed for coagulation and the fluoride ion. Some attempts have been made to feed fluorspar directly in the form of ultra-fine
powder, on the premise that the powder would eventually dissolve or at least remain in suspension, until consumed. These attempts have not been very successful. Beds of fluorspar have been used in South Africa with some success.

A number of other fluoride chemicals have been suggested for use in water fluoridation, among them ammonium bifluoride. It has the advantages of solubility and cost, but its potential corrosiveness has hindered its acceptance.

2.10 DISSOCIATION OF FLUORIDE CHEMICALS

All fluoride chemicals commonly used in water fluoridation greatly dissociate to a great degree, i.e., in solution, the ions separate and become independent. (They do not tend to ionize in solution. To “ionize” means to form ions, and the fluoride compounds are already formed in ions). Water is a strong dissociating solvent.

Sodium Fluoride (NaF) has virtually 100 percent dissociation into the simple ions:

(1) NaF _ $Na^+ + F–$

Sodium Silicofluoride, Na_2SiF_6, has virtually 100 percent dissociation:

(2) Na_2SiF_6 _ $2Na^+ + SiF_6$

The SiF_6 radical also will be dissociated in several ways:

(3) $SiF_6^{=} + 2\ H_2O$ _ $4H^+ + 6F– + SiO_{2}\downarrow$

and/or

(4) $SiF_6^{=}$ _ $+ 2F– + SiF_{4}\uparrow$

and

(5) $SiF_{4}\uparrow + 3\ H_2O$ _ $4HF + H_2SiO_3$

and/or

(6) $SiF_4 + 2\ H_2O$ _ $4HF + SiO_{2}\downarrow$

and, of course

(7) HF _ H^+ + F–

When sodium silicofluoride is dissolved in water the dissociation into the sodium and silicofluoride ions takes place very rapidly (2). But, the silicofluoride ions dissociate very slowly into the silicon tetrafluoride and fluoride ions (4). The silicon tetrafluoride reacts quickly to form silicic acid (5).
Hydrofluosilicic acid ($H_2\ SiF_6$) also has virtually 100 percent dissociation very similar to Na_2SiF_6:

(8) $H_2\ SiF_6$ _ $2HF + SiF_4\uparrow$

and

(9) $SiF_4\uparrow + 2\ H_2O$ _ $4HF + SiO_2\downarrow$

and

(10) $SiF_4\uparrow + 3\ H_2O$ _ $4HF + H_2SiO_3$

and, of course

(11) HF _ H^+ + F–

Silicon tetrafluoride (SiF_4) is a gas that will easily evaporate out of water when in high concentrations. Silica (SiO_2) is very insoluble in water. Silica is the main ingredient in glass. Hydrofluoric acid (HF) is very volatile and will attack glass and electrical contacts. It will tend to evaporate in high concentrations.

Note, the symbol ↓ means to precipitate out as a solid, and the symbol ↑ means to evaporate out as a gas.