Water Fluoridation

CONTENT PRIMER

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Fluoride. It's in the water. It's in your toothpaste. It's in your dentist's office and even in the foods we eat. So, what is fluoride, why is it so prevalent, and why is it important?

Fluoride (F^-) is an ion of the chemical element fluorine. While neutral elements, like fluorine, have equal numbers of electrons and protons, negatively charged ions, like fluoride, have more electrons than protons. There are many natural sources of fluoride, such as in the foods we eat and the water we drink. However, these naturally occurring sources of fluoride vary tremendously based upon what is being eaten and where the water is coming from. Some locations have naturally high levels of fluoride, while others have relatively low levels. Beyond this, there are also the sources of fluoride that we purposely introduce to ourselves, such as in toothpastes and mouthwashes to promote oral health. Fluoride plays an important role in public health. It helps prevent cavities, restores tooth decay, and generally strengthens our teeth. But how does fluoride do this? And how do we utilize it in an effective manner?

Tooth enamel is composed almost entirely of a mineral known as hydroxyapatite. The formula for hydroxyapatite is $Ca_5(PO_4)_3OH$. Hydroxyapatite is an insoluble ionic compound. In other words, it does not dissolve in water. However, solid hydroxyapatite will dissolve in acid (H^+) to form calcium ions (Ca^{2+}), phosphate ions (PO_4^{3-}) and water (H_2O) as shown in the reaction (1) below.

$$Ca_5(PO_4)_3OH(s) + H^+(aq) \rightarrow 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + H_2O(l) \qquad (1)$$

Acids that dissolve tooth enamel can come from a variety of sources. Most notably, bacteria in the mouth produce lactic acid ($HC_3H_5O_3$) from sugar via a process known as fermentation. Acids can also be introduced into the mouth by food and drink. Table 1 shows a few common acidic food additives.

Acid Name	Chemical Formula	pK_a
Acetic Acid	HCH_3CO_2	4.75
Citric Acid	$H_3C_6H_6O_7$	3.13, 4.76, 6.40
Lactic Acid	$HC_3H_5O_3$	3.86
Ascorbic Acid (Vitamin C)	$H_2C_6H_6O_6$	4.10, 11.60

Table 1. Common acidic food additives, their chemical formulas, and their pK_a values (acidic strength). Lower pK_a values correspond to stronger acidity.

So, how does fluoride help to protect tooth enamel? When hydroxyapatite is exposed to fluoride (F^-), the hydroxide ion (OH^-) in the mineral's structure can be replaced by the fluoride, forming a mineral called fluoroapatite ($Ca_5(PO_4)_3F$). The substitution of the fluoride and hydroxide anions in hydroxyapatite is represented by the reaction below (2).

$$Ca_5(PO_4)_3OH(s) + F^-(aq) \rightarrow Ca_5(PO_4)_3F(s) + OH^-(aq) \quad (2)$$

Fluoroapatite is a harder mineral, and it is less susceptible to acid attack, making it much less soluble than the naturally occurring hydroxyapatite. This means less tooth decay. The production of fluoroapatite can also help remineralize and restore parts of the enamel that have already decayed.

As mentioned in the introduction, fluoride is found in a variety of sources. The primary sources of fluoride that contribute to your dental health are from drinking water, toothpaste, and mouthwashes. Sources of fluoride in toothpaste and mouthwashes include sodium fluoride (NaF) and tin (II) fluoride (SnF_2) and sodium monofluorophosphate (Na_2PO_3F).

Source	Fluoride Source(s)	weight/volume percent (w/v%)	milligrams per gram (mg/g)	parts per million (ppm)
Toothpaste	NaF/SnF_2	0.15	1.5	1500
Daily Mouthwash	NaF	0.01	0.1	100

Table 2. Common over-the-counter sources of fluoride, the types of fluoride used, and their fluoride ion concentrations.

In Table 2, concentration is expressed in weight/volume percent (w/v%), milligrams/gram (mg/g), and parts per million (ppm). Weight per volume percentage is calculated by dividing the weight of fluoride (in grams) by a volume of 100 milliliters of total solution, then multiplying by 100 (3).

$$w/v\% = \frac{g\ fluoride}{100\ mL\ solution} \times 100 \quad (3)$$

Milligrams per gram is calculated by dividing the weight of fluoride, in mg (1 mg = 10^{-3} g), by the weight of the solvent, in g, (Equation 4).

$$mg/g = \frac{mg\ fluoride}{g\ solvent} \quad (4)$$

Concentrations expressed in parts per million are a lot like a percentage, except rather than being expressed as a fraction of 100, they are expressed as a fraction of one million. Very low concentrations are therefore expressed in ppm, and are calculated by dividing the mass of fluoride by the mass of the solution and multiplying by 1,000,000 (Equation 5).

$$ppm = \frac{mass\ fluoride}{mass\ solution} \times 1{,}000{,}000 \qquad (5)$$

Hydrofluorosilic acid (H_2SiF_6) and sodium fluorosilicate (Na_2SiF_6) used to fluoridate drinking water.

Source	Fluoride Compound	milligrams per L (mg/L)
Drinking Water	H_2SiF_6 /Na_2SiF_6	≤0.7
Groundwater	various minerals	0.1-0.7 (85% of aquifers)

Table 3. Fluoride concentrations in drinking water and groundwater.

In Table 3, concentration is expressed in milligrams per liter (mg/L). Milligrams per liter is calculated by dividing the weight of fluoride, in mg (1 mg = 10^{-3} g), by the volume of the water, in L, (Equation 6).

$$mg/g = \frac{mg\ fluoride}{g\ solvent} \qquad (6)$$

Resources

https://www.cdc.gov/fluoridation/index.html

https://cen.acs.org/materials/biomaterials/dental-enamel-does-protect-teeth/98/i41

https://www.dentalcare.com/en-us/professional-education/ce-courses/ce410/fluoride-s-mechanism-of-action

https://dailymed.nlm.nih.gov/dailymed/fda/fdaDrugXsl.cfm?setid=1f7e738f-a9d5-46bb-9a62-d01fa31756fd&type=display

https://dailymed.nlm.nih.gov/dailymed/drugInfo.cfm?setid=eeea70d7-bd29-49ae-8363-22eee6fa2f80

(reference paper cited at this website) A comprehensive assessment of fluoride in groundwater | U.S. Geological Survey (usgs.gov)