

# How Did the Fluoride Get Into Your Toothpaste?\*

The Chemistry Behind Adding Fluoride in Dentifrices for Preventing Dental Decay

*Anil J. Elias*

**Fluoride is one of the main ingredients of modern toothpaste and has a proven record of preventing dental decay, especially among children. The history, need and development of adding fluoride based inorganic compounds in the toothpaste for preventing dental decay is presented in this article. The fine balance required for maintaining healthy teeth and at the same time preventing dental and skeletal fluorosis by controlling the amount of fluoride intake is discussed. The chemistry behind prevention of dental decay by fluoride in relation to the minerals hydroxyapatite and fluorapatite is presented. The requirement of soluble calcium in the diet and its role in removing excess fluoride when consumed is highlighted.**

## 1. Introduction

While fluorine ( $F_2$ ) is one of the most reactive elements, its anion fluoride ( $F^-$ ) is considered tamer and easier to handle. Interestingly, fluorine is not present in any of the biomolecules present in the human body. Yet human beings are dependent on this element in their daily life in many ways. It is estimated that more than 20% of the pharmaceutical drug molecules available in the market have carbon-fluorine bonds and fluoride is essential for healthy teeth maintenance. The omnipresence of fluorine in refrigerant gases, non-stick polymer coatings and inhalation anaesthetics and the requirement of fluorine gas in the purification of  $UF_6$  as nuclear fuel are other noteworthy applications of the ele-



Anil J. Elias is the Institute Chair Professor at the Department of Chemistry, Indian Institute of Technology Delhi, New Delhi. He is also the recipient of the INSA Teacher Award by the Indian National Science Academy.

### Keywords

Fluoride, toothpaste, dental caries, fluorosis, hydroxyapatite, fluorapatite, Colorado brown stain.

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ment fluorine for humanity.

To the common man the word fluoride is almost always associated with the toothpaste. An ideal toothpaste can have up to ten ingredients which include abrasives, binders, sudsers, flavours, humectants, sweeteners, preservatives, tooth whiteners, fluorides and water. Fluoride is nowadays present in almost all brands of toothpastes, especially those which advertise for prevention of tooth decay. The practice of adding fluoride to the toothpaste began in the early 1950s and continues till today. While its presence is extremely essential for preventing dental decay, excessive fluoride, if consumed can lead to a condition called fluorosis (dental and skeletal) which results in mottled teeth and bending and disfiguration of bones especially of the lower limbs. Walking this tightrope in the daily requirement of fluoride has been a challenge for communities around the world, some adding the minimum amount of fluoride in their public water supply while others taking remedial actions to neutralise the excess fluoride in their ground water. Surprisingly enough, nature has provided another element calcium, whose presence in our diet neutralizes the possibility and occurrence of fluorosis to a large extent. Let us see why and how the practice of adding fluoride in the toothpaste began and the details of the fine balance required of fluoride in our daily life.

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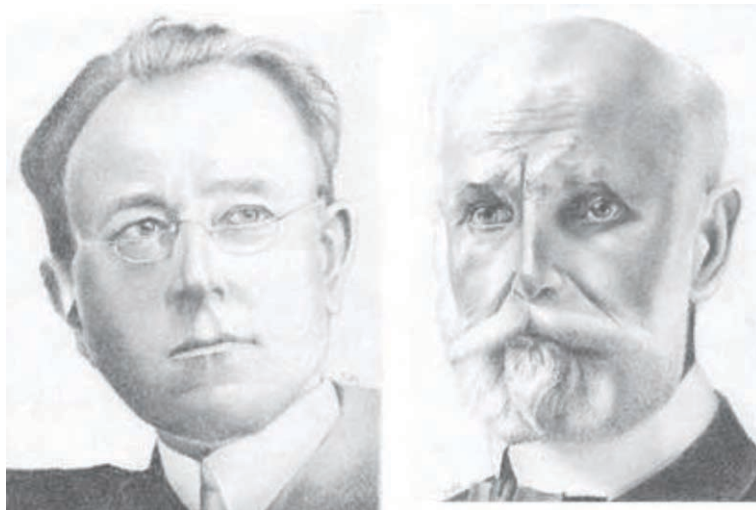
## 2. The Colorado Brown Stain

The story of the fluoride getting into your toothpaste begins in 1901 when a young dentist, Frederick McKay started his dental clinic in the town of Colorado Springs, Colorado, USA. With his observant nature he noticed that the native people of the town had teeth which were unusually brownish in color unlike the pearly white teeth sought after by many these days. In many cases, these ‘Colorado brown stains’ were so severe that the entire teeth had the color of chocolate toffee. In 1909 the inquisitive McKay invited Prof. G. V. Black who is considered as the father of modern dentistry to Colorado Springs for studying this unusual phe-

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**Figure 1.** (left) Dr. Frederick McKay and (right) Prof. G. V. Black (Pencil sketch portraits by Ms. N. Rajareethigha).

nomenon. After a study which lasted six years, they made public an interesting observation. Those people, especially children having the Colorado brown stain on their teeth surprisingly did not suffer from normal tooth decay or dental caries, prevalent very much those days. However, the origin of the Colorado brown stain remained a mystery for quite some time.

Around this time the Hall-Herault process for making pure aluminium by the electrolysis of alumina was already made into an industrial process in the United States. The Aluminium company of America was searching for natural sources of Cryolite ( $\text{Na}_3\text{AlF}_6$ ) which has been found as an excellent additive to reduce the very high temperature needed for the electrolysis of Alumina ( $\text{Al}_2\text{O}_3$ ), the ore of aluminium. Solid Cryolite was found to be present in plenty in the Pikes Peak mountain rock formation of the Colorado springs area. By 1931 researchers from the Aluminium company of America discovered that the reason for the Colorado brown stain can be linked to the relatively high concentration of fluoride present in the well water of that region which ranged from 2 to 14 mg/L. Interestingly in other regions of Colorado where concentration of fluoride was less, 1 mg/L or lower, there was no occurrence of Colorado brown stain. They figured out that when rain and snow fell on the rock formation having Cryolite, the fluoride leached out and made its way to the

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**Figure 2.** Skeletal and dental fluorosis (Photograph credits-INREM foundation and Otis Historical Archives of National Museum of Health & Medicine).



wells of Colorado Springs. During this time period, it was also observed that many communities across the world which were exposed to high concentrations of fluoride in drinking water suffered from fluorosis whose physical manifestation included mottled teeth (having opaque patches on the tooth enamel) and in severe cases bending of the bones, especially those of the lower limbs.

### 3. Fluoridation of Drinking Water

Dr H. Trendley Dean, who was a dental officer in the US public health service published a study in 1942 on the fluoride- dental caries relationship which included examining dental health of 7000 children from 21 cities of the USA. The major finding of this study was that an optimal amount of fluoride minimized the risk of severe dental or skeletal fluorosis but helped to prevent dental decay. The optimal amount was found close to 1 mg fluoride per day per adult and if the amount went beyond this limit, fluorosis was found to happen. A major outcome of this and related studies was that some of the states of the USA where dental caries was widely prevalent decided to add small calculated amounts of fluoride to their drinking water supply to prevent tooth decay. In 1945, Grand Rapids, Michigan became the first community to do so as they adjusted the fluoride content of their water supply to 1.0 ppm. After 5 years when they made a follow-up study it was found that there was significant drop in dental caries among the children who were consuming the fluoridated drinking water. This was followed by many other states fluoridating their drinking





**Figure 3.** Dr. H. Trendley Dean (Pencil sketch portrait by Ms. N. Rajareethigha).

water. Community water fluoridation thus became one of public health's greatest success stories, improving the dental health of people in the United States and a few other places around the world. The Centre for Disease Control and Prevention (CDC) of the USA named water fluoridation as one of the ten great public health achievements of the 20th century. From 1945 onwards the United States has been fluoridating drinking water; however in 2011, the U.S. lowered its recommended level of fluoride in drinking water to 0.7 mg/L.

However, fluoridation of drinking water was not universally accepted as it affects everyone using the water and some people and communities do not require extra fluoride. In many parts of Asian countries such as India and China, there is excessive fluoride in the ground water. So adding calculated amounts of fluoride to the toothpaste was found to be a better option rather than forcing everyone to consume fluoridated water.

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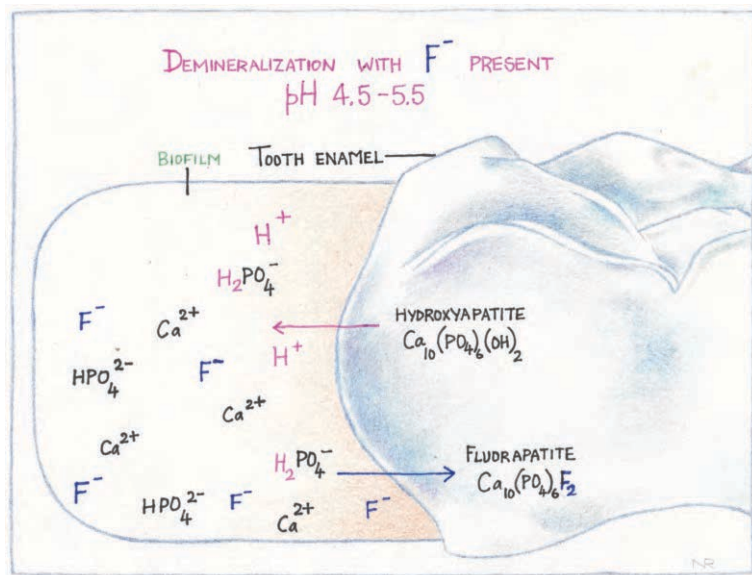


#### 4. Hydroxyapatite, Fluorapatite and the Chemistry of Fluoridation

Let us see the chemistry behind fluoride helping to prevent dental decay. Up to 70% by weight of bones of our body is a modified form of the mineral hydroxyapatite,  $(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2)$  and so is the teeth enamel and dentin, the material below the enamel. It is well known that the  $\text{OH}^-$  ion of hydroxyapatite can be replaced by  $\text{F}^-$  resulting in fluorapatite  $(\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2)$ . A key step in the dental decay i. e. initial dissolution of the teeth enamel has been identified as the reaction of the hydroxyapatite of the teeth enamel with acids such as lactic and acetic acids. These acids are generated in the mouth by the action of plaque bacteria through the fermentation of dietary carbohydrates left over in the mouth especially when we sleep. These acids react with the hydroxyapatite of the tooth enamel and convert them to soluble calcium and phosphate ions thereby resulting in the breakdown of the tooth enamel. This process is termed in the language of dentists as demineralization of the teeth. Now following a demineralization, if the ions are still present in the mouth, a re-mineralization can happen which will try to bring back the original state of the teeth. When fluoride is present in the mouth, fluorapatite, rather than hydroxyapatite, forms during the remineralization process. Fluoride ions ( $\text{F}^-$ ) replace hydroxyl groups ( $\text{OH}^-$ ) in the formation of the apatite crystal lattice. It is observed that, the presence of fluoride increases the rate of remineralization. Another property of fluorapatite is that it is inherently less soluble than hydroxyapatite, even under acidic conditions. When hydroxyapatite dissolves under acidic conditions, if fluoride is present, then fluorapatite will form during remineralization. Because fluorapatite is less soluble than hydroxyapatite, it is also more resistant to subsequent demineralization in the presence of acids. In other words when the surface of the teeth enamel has a higher percentage of fluorapatite instead of hydroxyapatite, the chances of demineralization of the enamel in the presence of acids is reduced considerably and decay is minimized or prevented.

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**Figure 4.** Schematic showing demineralization and remineralization of tooth enamel in the presence of fluoride (Hand-drawn figure by Ms. N. Rajareethigha).

## 5. Fluoride in Toothpaste

Around 1952, Harry G. Day, a biochemistry professor at the Indiana university Bloomington, along with a dentist Joseph C. Muhler and an inorganic chemist William Nebergall brought out an experimental cavity-preventing toothpaste and proceeded to run clinical trials of this paste on 1500 children and 400 adults. They added stannous fluoride ( $SnF_2$ ) to the toothpaste (fluorine concentration of 1,000 ppm) and found that it resulted in a significant reduction in dental caries in 6- to 15-year-old children who used the fluoride containing toothpaste in an unsupervised manner for a period of six months. After their work was published in a journal, the composition was taken over by the company, Procter & Gamble which made and marketed the first fluoride containing toothpaste. It launched this formula in 1955 and named it as Crest which had a combination of stannous fluoride and as abrasive calcium pyrophosphate,  $Ca_2P_2O_7$ . Crest proceeded to dominate the fluoride toothpaste market for the next ten years. The sales of this fluoride containing toothpaste was enhanced by smart advertising. 'Look mom-no cavities' was a slogan started by Procter and Gamble in these advertisements.

**Figure 5.** An example of the ‘Look, Mom—no cavities!’ advertisement of the 1950’s by Proctor and Gamble. Image credit: Art by Norman Rockwell in ‘Ladies Home Journal’, August 1958.



Another fluoride releasing agent sodium monofluorophosphate was introduced in 1967 when the company, Colgate-Palmolive provided competition for Crest. Initial attempts to introduce the easily available and inexpensive sodium fluoride as a fluoride releasing agent was not successful as it was found to react with calcium based abrasives present in tooth paste readily forming highly insoluble calcium fluoride. Sodium fluoride didn’t debut until 1982, when Proctor and Gamble came out with Advanced Formula Crest, which uses a hydrated silica abrasive that doesn’t react with sodium fluoride. The rise of gel toothpastes, which owe their translucence to silica required more of NaF. For toothpaste, the three main decay-preventing additives approved by the US Food & Drug Administration are stannous fluoride, sodium fluoride, and sodium monofluorophosphate (MFP).

So how is fluoride produced in the bulk industrially? The two main naturally available sources of fluoride are the minerals fluorapatite and fluorite. A major portion of sulfuric acid produced in the world goes for reacting with hydroxyapatite/ fluorapatite for making superphosphates for fertilizer industry. When fluorapatite is reacted with sulfuric acid, dilute hydrofluoric acid is ob-





tained as a side product from the reaction. For making anhydrous hydrofluoric acid, fluorite ( $\text{CaF}_2$ ) is reacted with conc. sulfuric acid. Neutralizing HF with NaOH results in sodium fluoride. Reaction of sodium fluoride with sodium metaphosphate results in sodium mono fluorophosphate. Reaction of stannous oxide with hydrofluoric acid gives stannous fluoride.

## 6. Excess Fluoride Removal by Soluble Calcium

Now coming back to the topic of fluorosis, the upper limit of optimum fluoride level in drinking water for a tropical country like India is 0.5 mg/L. Endemic fluorosis has been recognized as a major public health problem in 18 states of India and in certain regions of India, ground water contains fluoride up to 38 mg/L, which is extremely high compared to the maximum permissible limit. It has been reported few decades back that many districts in the state of Andhra Pradesh of India were affected by fluorosis and the fluoride levels of Nalgonda district (now part of Telengana state) ranged from 2 to 7 mg/L. Deformities of limb bones, which are notably seen in weight bearing lower limbs were observed in endemic areas of fluorosis. Quite interestingly, such deformities were found to occur only among poorly nourished people whose diet is low in milk and milk based products. In regions of north India such as the states of Haryana and Punjab where intake of dairy products containing soluble calcium is quite high, deformities are hardly observed (average amount of calcium in the daily diet of a Nalgonda villager is 300 mg while it is 900 mg in the state of Punjab). The interesting finding is that soluble calcium ions present in milk and milk products binds with fluoride in the gastro-intestinal tract and the highly insoluble calcium fluoride formed is eliminated through the feces. It is to be noted that among alkali and alkaline earth fluorides, calcium fluoride has one of the poorest solubility's in water (0.016 g/L at 20 °C). So a diet poor in calcium increases body's retention of fluoride. Fluoride increases bone metabolism and the diet's deficient in calcium intake provokes parathyroid hyperactivity. This in turn mobilizes calcium from bone to keep the serum levels, which causes weak-

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ening of bones by causing osteoporosis. Weight bearing lower limb bones suffers the maximum leading to deformities of the lower limbs. So by providing soluble calcium in milk, nature provides a simple antidote to deal with the excessive fluoride present in ground water. Over the years by providing safe fluoride free drinking water and proper nutrition, the skeletal fluorosis found in many states of India has been reduced significantly.

Unlike coffee, tea leaves are known to accumulate significant amounts of fluoride and therefore excessive tea drinkers are prone to get fluoride way beyond the minimum requirement. Here also the traditional practice of adding milk to tea helps to neutralize the soluble fluoride in tea in significant levels.

After half a century of continuously improving dental health, today it is now commonplace for children from many developed and developing countries to reach adulthood without the need for tooth removal or fillings. Studies show that there are few factors that have contributed to this significant improvement in dental health. The addition of fluoride to dental hygiene routines has played a very significant role in reducing the incidence of tooth decay. The use of fluoride toothpaste is still the primary way that utilize the anti-cavity power of fluoride. By taking remedial steps like providing fluoride free drinking water and calcium rich diet the incidences of skeletal fluorosis is being addressed in areas of excessive fluoride in ground water. Healthy teeth also require proper nutrition and nowadays a healthy diet is available for children and dairy products and dairy substitute's helps to have a balanced diet. Finally, there has been more access to preventive dental care and examinations by dentist when dental problems are identified early and measures are taken before the dental conditions become serious.

## 7. Summary

The history, development and current status of fluoride based additives in toothpaste is described. The chemistry behind the action of fluoride on the tooth enamel is discussed in relation to deminer-



alization of hydroxyapatite and remineralization to fluorapatite. The role of soluble calcium in the diet which removes excess fluoride by forming poorly soluble calcium fluoride is highlighted.

## 8. Acknowledgements

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Address for Correspondence  
Anil J. Elias  
Department of Chemistry  
IIT Delhi, Hauz Khas  
New Delhi 110 016, India.  
Email:  
elias@chemistry.iitd.ac.  
in

