

# Fluoride problems and Remediation process for drinking water: A Review

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**Abstract :** Fluoride is found in all natural waters at some concentration. In ground waters, however, low or high concentrations of fluoride can occur, depending on the nature of the rocks and the occurrence of fluoride-bearing minerals. High fluoride concentrations may therefore be expected in ground waters from calcium-poor aquifers and in areas where fluoride-bearing minerals are common. Fluoride has beneficial effects on teeth at low concentrations in drinking-water, but excessive exposure to fluoride in drinking-water, or in combination with exposure to fluoride from other sources, can give rise to a number of adverse effects. These range from mild dental fluorosis to crippling skeletal fluorosis as the level and period of exposure increases. Occurrence of fluoride at excessive levels in drinking-water in developing countries is a serious problem. Its detection demands analytical grade chemicals and laboratory equipment and skills. The prevention of fluorosis through management of drinking-water is a difficult task, which requires favourable conditions combining knowledge, motivation, prioritization, discipline and technical and organizational support. Defluoridation of drinking-water is technically feasible at point-of-use (at the tap), for small communities of users (e.g. wellhead application) and for large drinking-water supplies. Activated alumina and reverse osmosis are the most common technologies. Activated alumina can concurrently remove other anions, such as arsenate. Reverse osmosis achieves significant removal of virtually all dissolved contaminants. The National Environment Engineering Research Institute in Nagpur, India has evolved an economical and simple method of defluoridation, which is referred to as the Nalgonda technique. This technique has been repeatedly proven to be an economical and effective household defluoridation technique.

**Key Words:** Fluoride, fluorosis, dental fluorosis, skeletal fluorosis, defluoridation

## I. INTRODUCTION

Fluoride in drinking water is known for both beneficial and detrimental effects on health. Fluorine is a naturally occurring element that does not occur in the elemental state in nature because of its high reactivity. The world's fluoride stores in the ground are assessed to 85 million tons. Out of which 12 million tons are situated in India. The most widely recognized fluoride-bearing minerals, which constitute normal hotspot for fluoride in drinking water, are fluor spar ( $\text{CaF}_2$ ), rock phosphate, voracity & phosphorites<sup>1</sup>. It accounts for about 0.3 g/kg of the Earth's crust and exists in the form of fluorides in a number of minerals, of which fluor spar, cryolite and fluorapatite are the most common. The oxidation state of the fluoride ion is -1. Fluoride is ubiquitous in the environment, and, therefore, sources of drinking-water are likely to contain at least some small amount of fluoride. Fluoride can form compounds with other chemicals, including for example sodium fluoride or calcium fluoride. Fluoride compounds such as sodium fluoride are added to the drinking water supply for the purpose of water fluoridation. Fluoride compounds have entirely different properties than fluorine gas<sup>2</sup>. The amount of fluoride present naturally in drinking-water is highly variable, being dependent upon the individual geological environment from which the water is obtained<sup>3</sup>. The concentration of fluoride in drinking water depends mainly on the basic chemical composition of soil, the time of contact between the source of minerals and the water source, leaching of fluoride from rocks, calcium-poor aquifers, volcanic rocks, granite rocks and the amount of water withdrawn from the source over a period of time. Generally, surface water has low fluoride content while ground water possesses a huge concentration of fluoride. River water near industries/mines like bauxite, graphite, aluminum, phosphate and fertilizer does contain some fluoride. But ground water is the single biggest contributing factor for the spread of fluoride and fluorosis<sup>4</sup>. Several researchers have described about the releasing mechanism of fluoride in the groundwater. Generally, high concentration of fluoride in groundwater detected in the high evaporation and low rainfall region from arid to semi-arid part of the world. Fluoride once deposited and released into the soil and leached into groundwater, may increase fluoride concentration, until fully saturated in the water<sup>5</sup>. There are two main types of fluorosis, namely dental and skeletal fluorosis. **Dental fluorosis** is caused by continuous exposures to high concentrations of fluoride during tooth development, leading to enamel with low mineral content and increased porosity. The critical period for risk to dental fluorosis is between 1 and 4 years of age. After the age of 8 when permanent teeth have established, there is lesser risk to dental fluorosis. **Skeletal fluorosis** is developed by the disturbance of calcium metabolism in the formation of bones of the body. It results in softening and weakening of bones resulting in deformities leading to crippling. It can also aggravate calcium related disorders such as rickets in children and osteoporosis mainly in adults. For people who are exposed to high fluoride levels for decades, severe cases of crippling can occur. A daily intake of around 10-20 mg/day for adults and as low as 3-8 mg/day for children has been found to be harmful. Using these limits, the rough water safety limits of **1 mg/l of 1.5 mg/l** have been arrived at in the context of India. In 20 states of India, more than 100 districts across the country and probably more than 60 million people are consuming drinking water which has fluoride greater than 1 mg/l. Since local food can also get irrigated by the same water, food also contains fluoride in these places. This makes the total daily consumption of fluoride more than 10 mg/day which is always harmful for adults and more so for children.

## II. Effect of Fluoride on human body

Fluoride is well recognized as an element of public health concern. Fluoride is present universally in almost every water (higher concentrations are found in groundwater), earth crust, many minerals, rocks etc. It is also present in most of everyday needs, viz. toothpastes, drugs, cosmetics, chewing gums, mouthwashes etc.<sup>6, 7</sup>. Intake of more fluoride, results in multidimensional health manifestations, the most common being dental and skeletal fluorosis<sup>8, 9</sup>. Higher concentration of fluoride also causes respiratory failure, fall of blood pressure and general paralysis. Loss of weight, anorexia, anemia, wasting and cohexia are among the common findings in chronic fluoride poisoning. Continuous ingestion of nonfatal dose of fluorides causes permanent inhibition of growth. Fluoride ions inhibit a variety of enzymes often by forming complexes with magnesium ions and other metal ions.<sup>10, 11 & 12</sup>. In India, the most common cause of fluorosis is fluoride-laden drinking water which is sourced as groundwater from deep-bore wells. Over half of groundwater sources in India have fluoride above recommended levels<sup>13</sup>.

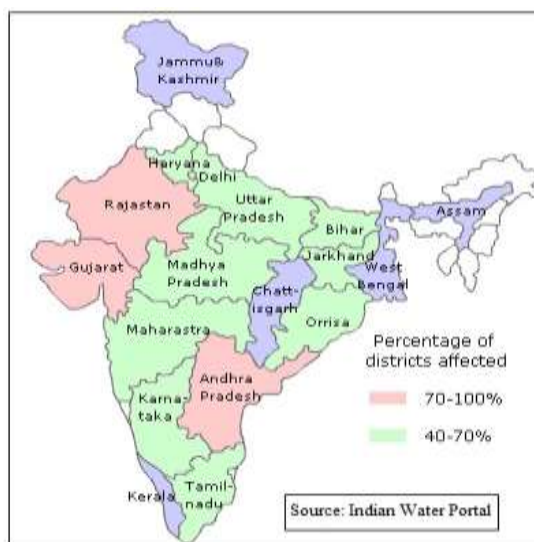


Figure-1: Percentage of State affected in India

Sl. No.	State	Affected Area (%) [Min-Max Range]	Range of Fluoride in Groundwater in mg/L [Min – Max Range]
1	Andhra Pradesh	50 – 100%	0.4 to 29
2	Gujarat	50 – 100%	0.15 to 13
3	Rajasthan	50 – 100%	0.1 to 14
4	Bihar	30 – 50%	0.2 to 8.12
5	Chhattisgarh	30 – 50%	0.9 to 8.8
6	Delhi	30 – 50%	0.2 to 32.46
7	Haryana	30 – 50%	0.23 to 48
8	Jharkhand	30 – 50%	0.5 to 14
9	Karnataka	30 – 50%	0.2 to 7.79
10	Madhya Pradesh	30 – 50%	1.5 to 11.4
11	Maharashtra	30 – 50%	0.11 to 10
12	Punjab	30 – 50%	0.4 to 42.5
13	Tamil Nadu	30 – 50%	0.1 to 7.0
14	Uttar Pradesh	30 – 50%	0.2 to 25
15	Assam	< 30%	1.6 to 23.4
16	Jammu & Kashmir	< 30%	0.5 to 4.21
17	Kerala	< 30%	0.2 to 5.40
18	Orissa	< 30%	0.6 to 9.20
19	West Bengal	< 30%	1.1 to 14.47

Table 1: Status of Fluoride and Area Affected as Percentage in the States of India and the Range of Fluoride in Groundwater as mg/L<sup>14</sup>.

## 1. Dental Fluorosis



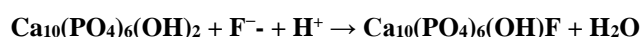
**Figure-2: Different conditions of dental fluorosis**

It (also termed mottled enamel) is an extremely common disorder, characterized by hypo mineralization of tooth enamel caused by ingestion of excessive fluoride during enamel formation<sup>15</sup>. It is caused by systemic overexposure to fluoride during the first six years of life, when the enamel of the crowns of permanent teeth is formed. The enamel contains more protein, is porous, opaque and less transparent. Clinical manifestation vary from (quantitative) narrow, white horizontally running lines, larger patches or yellow to light brown colored areas of porous enamel, to (qualitative) loss of enamel in varying degrees<sup>16</sup>. Fluoride is among the substances for which there are both lower (0.6 mg/l) and upper (1.2 mg/l) limits of concentration in drinking water, with identified health effect and benefits for human beings<sup>17</sup>. Very low doses of fluoride (<0.6 mg/l) in water promote tooth decay. However, when consumed in higher doses (>1.5 mg/l), it leads to dental fluorosis and excessively high concentration (>3.0 mg/l) of fluoride may lead to skeletal fluorosis. In general, fluoride content in water between 1.5 and 2.0 mg/l may lead to dental mottling; it appears as a range of visual changes in enamel<sup>18</sup> causing degrees of intrinsic tooth discoloration, and, in some cases, physical damage to the teeth. The severity of the condition is dependent on the dose, duration, and age of the individual during the exposure. The "very mild" (and most common) form of fluorosis, is characterized by small, opaque, "paper" white areas scattered irregularly over the tooth, covering less than 25% of the tooth surface. In the "mild" form of the disease, these mottled patches can involve up to half of the surface area of the teeth. When fluorosis is moderate, all of the surfaces of the teeth are mottled and teeth may be ground down and brown stains frequently "disfigure" the teeth (Figure 2). Severe fluorosis is characterized by brown discoloration and discrete or confluent pitting; brown stains are widespread and teeth often present a corroded-looking appearance<sup>19</sup>.

### 1.1 Mechanism of action

In the extra-cellular environment of maturing enamel, an excess of fluoride ions alters the rate at which enamel matrix proteins (amelogenin) are enzymatically broken down and the rate at which the subsequent breakdown products are removed. Fluoride may also indirectly alter the action of protease via a decrease in the availability of free calcium ions in the mineralization environment<sup>20</sup>. This results in the formation of enamel with less mineralization. This hypo mineralized enamel has altered optical properties and appears opaque and lusterless relative to normal enamel. Traditionally severe fluorosis has been described as enamel hypoplasia, however, hypoplasia does not occur as a result of fluorosis. The pits, bands, and loss of areas of enamel seen in severe fluorosis are the result of damage to the severely hypo mineralized, brittle and fragile enamel which occurs after they erupt into the mouth<sup>21</sup>.

Hydroxyapatite is converted to fluorohydroxyapatite as follows:



### 1.2 Dean's index for Dental Fluorosis

Dean's fluorosis index was first published in 1934 by H. Trendley Dean. The index underwent two changes, appearing in its final form in 1942<sup>22</sup>. An individual's fluorosis score is based on the most severe form of fluorosis found on two or more teeth<sup>23</sup>.

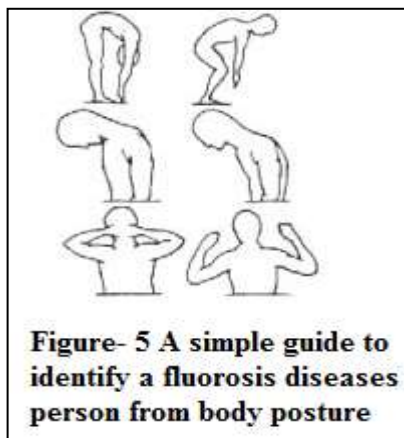
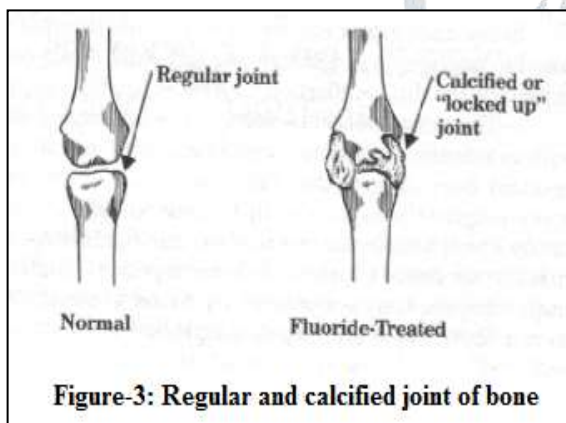
**Table 2: Dean's Dental Fluorosis index**

Sl. No.	Classification	Code	Criteria-description of Enamel
1	Normal	0	The enamel represents the usual translucent semivitriform (glass-like) type of structure. The surface is smooth, glossy and usually of pale creamy white color
2	Questionable	1	The enamel discloses slight aberrations from the translucency of normal enamel, ranging from a few white flecks to occasional white

			spots. This classification is utilised in those instances where a definite diagnosis is not warranted and a classification of 'normal' not justified
3	Very Mild	2	Small, opaque, paper white areas scattered irregularly over the tooth but not involving as much as approximately 25% of the tooth surface. Frequently included in this classification are teeth showing no more than about 1 – 2mm of white opacity at the tip of the summit of the cusps, of the bicuspid or second molars.
4	Mild	3	The white opaque areas in the enamel of the teeth are more extensive but do involve as much as 50% of the tooth.
5	Moderate	4	All enamel surfaces of the teeth are affected and surfaces subject to attrition show wear. Brown stain is frequently a disfiguring feature
6	Severe	5	All enamel surfaces are affected and hypoplasia is so marked that the general form of the tooth may be affected. The major diagnostic sign of this classification is discrete or confluent pitting. Brown stains are widespread and teeth often present a corroded-like appearance.

**2. Skeletal Fluorosis**

It is a bone disease caused by excessive accumulation of fluoride in the bones. In advanced cases, it causes pain and damage to bones and joints. Skeletal fluorosis<sup>24</sup> may occur when fluoride concentrations in drinking water exceed 4–8 mg/l. The high fluoride concentration manifests as an increase in bone density leading to thickness of long bones and calcification of ligaments (Figure-3). The symptoms include mild rheumatic/arthritis pain in the joints and muscles to severe pain in the cervical spine region along with stiffness and rigidity of the joints (Figure-4). The disease may be present in an individual at subclinical, chronic or acute levels of manifestation<sup>25</sup>. Crippling skeletal fluorosis can occur when the water supply contains more than 10 mg/l of fluoride<sup>26, 27</sup>. The severity of fluorosis depends on the concentration of fluoride in the drinking water, daily intake, continuity and duration of exposure, and climatic conditions.



UNICEF (1996)<sup>28</sup> has published a simple guide to identify a fluorosis diseased person for they cannot perform some basic exercise related to body posture. The following Figure 5 clearly explains that if a person is not able to do the three body exercises illustrated in the figure 5, then the non-skeletal manifestation of the disease confirm that person to be chronic patient of the Fluorosis.

- Left Column: Normal capacity person
- Right Column: Fluorosis diseased person
- Top – the person is unable to bend completely from the waist.
- Middle – unable to bend the neck to touch the chin on the chest and,
- Bottom – unable to bend arms to touch the back of the head.

**2.1 Mechanism of action**

The mechanism of action by which fluorine breaks down bones and causes skeletal fluorosis are: Fluorine enters the body by two paths: Ingestion or respiration. Both paths lead to corrosion of exposed tissue in high concentrations. Since the most likely form of fluorine to enter the body is hydrogen fluoride (HF) gas, this is what starts the process. Exposed tissues will be utilized by HF in neutralization reactions. This will leave F- free to pass further into the body. It reacts with the concentrated HCl in the stomach to form the weak acid, HF. This compound is then absorbed by the gastro-intestinal tract and passes into the liver via the portal vein. Since elemental F is one of the strongest oxidizers currently known, the anion F- is immune to phase 1 metabolic reaction, which is generally oxidation reactions, in the liver. These reactions are the body's first line of defense to bio transform harmful compounds into something more hydrophilic and more easily excreted. The HF is now free to pass into the blood stream and be

distributed to all tissues including bones. Bones are largely composed of Ca compounds, particularly carbonated hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ); the reaction of  $\text{Ca}^{2+}$  ions and HF forms an insoluble salt,  $\text{CaF}_2$ . This salt must be cleared by the body, which concomitantly leaches out some of the calcium that would be part of the bone matrix. This process results in increased density, but decreased strength in bones<sup>29</sup>.

### III. Remediation Process

Considering the fact that fluorosis is an irreversible condition and has no cure, prevention is the only solution for this menace. Providing water, with optimal fluoride concentration is the only way by which the generation yet to be born can be totally protected against the disease<sup>30</sup>. It can be achieved by the following methods<sup>31</sup>.

- Removal of fluoride from water (defluoridation), using suitable techniques.
- Bringing in water from a distant, safe source.
- Locating alternative sources of safe water.
- Prevention of industrial fluorosis by rigorous enforcement of procedures for minimizing industrial fluoride pollution.

#### A. Defluoridation Technique

Defluoridation was the conventional and widely tested method for supplying safe water to the fluorosis affected communities. Defluoridation is defined as, the downward adjustment of level of fluoride in drinking water to the optimal level<sup>32</sup>. Various techniques and materials were tried throughout the world for defluoridation of water. Defluoridation techniques can be broadly classified in to four categories<sup>33</sup>.

1. Adsorption technique
2. Ion-exchange technique
3. Precipitation technique
4. Other techniques, which include electro chemical defluoridation and Reverse Osmosis.

#### B. Adsorption technique of defluoridation

This technique functions on the adsorption of fluoride ions onto the surface of an active agent. Activated alumina, activated carbon and bone char were among the highly tested adsorbing agents.

#### C. Activated Alumina

Application of domestic defluoridation plant, based on activated alumina, was launched by UNICEF in rural India. IP grade aluminium hydroxide has some specifications which when not fulfilled are thrown as spoiled batch, which can be procured and used in this technique<sup>34</sup>. In 1972 discussed about a successfully functioning, activated alumina community defluoridation plant, which was commissioned in Bartlet, Texas, USA in the year 1952<sup>35</sup>. The plant could achieve a marked reduction in the prevalence and severity of dental fluorosis. The disadvantages with activated alumina are<sup>36</sup>: Adsorption of fluoride is possible only at specific pH range, needing pre-and post- pH adjustment of water. Frequent activation of Alumina is needed, which make the technique expensive. Regeneration generates concentrated fluoride solution, causing disposal problems. Adsorption efficiency of the activated alumina diminishes with increasing number of usage-regeneration cycle.

#### D. Bone char

The process of Defluoridation by bone chars as the ion exchange and adsorption between fluoride in the solution and carbonate of the apatite comprising bone char. The efficacy of the plant depends upon temperature and pH of raw water; duration for which the bone-char is in contact with raw water. The maximum amounts of fluoride adsorbed per gram of bone char surface at 25o, 35o and 45o C are about 21.1, 22.4, and 25.7  $\mu\text{mol}$  respectively. The optimum time for the adsorption to reach saturation is 9 hours and optimum pH of fluoride solution is between 7.00 and 7.50. Particle size has trivial effect on the adsorption of fluoride. If Calcium is present in the raw water, it precipitates out the fluoride. It is a highly economic technique with a defluoridation percentage of 62 to 66<sup>37</sup>. Further, the efficiency of the bone-char method of water defluoridation can be improved by pre-treating the raw water with Brushite and Calcium hydroxide<sup>38</sup>. In 1972<sup>39</sup> discussed the effectiveness of a defluoridation plant, which used bone char as the active ingredient and was functioning since 1948 in Britton, USA. It caused significant reduction of dental fluorosis in the local communities. Disadvantages of this technique are; the bone char harbors bacteria and hence unhygienic. Without a regular fluoride analysis, nothing indicates when the material is exhausted and the fluoride uptake is ceased. It is a technique sensitive procedure, since the efficiency of bone char as an adsorbent for fluoride is a function of the charring procedure which should be done cautiously. Moreover, the use of bone-char may invite cultural and religious objections<sup>40</sup>.

#### E. Brick pieces column

The basic principle of functioning of Brick piece column is the same as that of activated alumina. The soil used for brick manufacturing contains Aluminium oxide. During burning operation in the kiln, it gets activated and adsorbs excess fluoride when raw water is passed through. Replacement of filter media is required once in three months if fluoride content in raw water is 2.50 mg/l. In places where high alumina content soil is available, brickbat filter may be one of the options<sup>41</sup>.

#### F. Natural adsorbents

Many natural adsorbents from various trees were tried as defluoridation agents. Seeds of the Drumstick tree, roots of Vetiver grass and Tamarind seeds were few among them. The seeds of the drumstick tree (*Moringa oleifera*) adsorb fluoride from water. Drumstick seeds act as a coagulant. They have long been a traditional method for purification of turbid water in both India and Africa. Researchers at M. S. Swaminathan Research Foundation<sup>c</sup> (MSSRF) had shown drumstick seeds to have remarkable defluoridation efficiency, which was higher than that of activated alumina. But, these results were not reproducible. The roots of Vetiver grass (*Vetiveria zizanoides*) are another product that has traditionally been used for water purification. The roots were

effective at defluoridation and could remove as much as 70% of the fluoride from a sample. The defluoridation efficiency was higher than activated alumina, and the price was comparable. But, the quantity of grass needed is so high that, a family would need to rise acres of Vetiver grass every year in order to provide enough material for defluoridation<sup>42</sup>. Tamarind seeds were successfully tested for defluoridation by sorption. Since maximum defluoridation is achieved at an optimum pH of 7, post defluoridation pH adjustment is not required. Tamarind seeds, which are otherwise considered a kitchen- waste, can be obtained at much cheaper price<sup>43</sup>.

**G. Defluoridation by Ion-Exchange technique**

Synthetic chemicals, namely, anion and cation exchange resins have been used for fluoride removal. Some of these are Polyanion (NCL), Tul-sion A - 27, Deacedite FF (IP ), Amberllte IRA 400, Lewatit MIH - 59, and Amberlite XE – 75<sup>44,45,46</sup>. These resins have been used in chloride and hydroxy form. The fluoride exchange capacity of these resins depends upon the ratio of fluoride to total anions in water. The capacity of Amberlite XE 75 was found to be approximately 88 g/m<sup>3</sup> when fluoride to total anion ratio was 0.05. The capacity increased with increasing ratio. Polyanion removed fluoride at the rate of 862 mg/kg and 1040 mg/kg with initial fluoride concentration of 2.8 and 8.1 mg/L, respectively. Deacedite FF ( IP ) and Tulsion A - 27 could treat 2270 L and 570 L of water bringing fluoride level from 2.2 to 1.0 mg/L. Benson *et al.* (1940)<sup>47</sup> used ion exchange process in which sodium ions were removed from the solution by cationic material. The hydrogen fluoride was removed during the second stage. A 10 mg/L fluoride solution was reduced to below 1 mg/L when 2 bed pairs were used in series. Popot *et al.* (1993)<sup>48</sup> used aluminium form of the amino methyl phosphonic type ion exchange for fluoride removal. However, the presence of sulphates (100 mg/L) and bicarbonates (200 mg/L) reduced the fluoride removal capacity of the resins to 33%. The resins increased the concentration of chloride in treated water, which can cause corrosion of the water storage utensils. The treated water also had high pH. Staebler (1974)<sup>49</sup> used Amberlite IRA-400, an ion exchange resin consisting of an 8 % cross linked polystyrene matrix of trimethyl benzyl ammonium type for fluoride removal. The basic nature of the material increased the pH of the solution from 6.4 to 11.6. The chloride resins, once exhausted or saturated with fluoride, can be regenerated to their original form by passing a 4 % solution of sodium chloride followed by washing with distilled water until the elute is free from excess chloride ions. However, the regeneration process of cation and anion exchange resins required large volumes of regenerate. The waste produced is also very large. Further, the resins are very complex, contamination prone and expensive<sup>50</sup>.

**H. Defluoridation by Precipitation technique**

The two major drawbacks of Ion-exchange and adsorption techniques are: The necessary flow through system is often difficult to arrange where there is no piped water supply and gradual exhaustion of the active agent is not easily detected. In an attempt to overcome these problems the precipitation techniques have been developed. Precipitation methods are based on the addition of chemicals (coagulants and coagulant aids) and the subsequent precipitation of a sparingly soluble fluoride salt as insoluble fluorapatite. Fluoride removal is accomplished with separation of solids from liquid. Aluminium salts (eg. Alum), lime, Poly Aluminium Chloride, Poly Aluminium Hydroxy sulphate and Brushite are some of the frequently used materials in defluoridation by precipitation technique<sup>51</sup>. The best example for this technique is the famous Nalgonda technique of defluoridation.

**I. Nalgonda technique**

After extensive testing of many materials and processes including activated alumina since 1961, **National Environmental Engineering Research Institute (NEERI), Nagpur** has evolved an economical and simple method for removal of fluoride which is referred to as, **Nalgonda Technique**<sup>52</sup>. Nalgonda Technique involves addition of Aluminium salts, lime and bleaching powder followed by rapid mixing, flocculation, sedimentation, filtration and disinfection. Aluminium salt may be added as aluminium sulphate (alum) or aluminium chloride or combination of these two (Figure-6). It is responsible for removal of fluoride from water. The dose of aluminium salt increases with increase in the fluoride and alkalinity levels of the raw water. The selection of either aluminium sulphate or aluminium chloride depends on sulphate and chloride contents of the raw water to avoid them exceeding their permissible limits. Lime facilitates forming dense flocks for rapid settling of insoluble fluoride salts. The dose of lime is empirically 1/20th of that of the dose of aluminium salt. Bleaching powder is added to the raw water at the rate of 3 mg/l for disinfection. Approximate doses of alum required to obtain water with acceptable limit of fluoride (<1.0 mg/l) at various fluoride and alkalinity levels in raw water are given below (Table 2). Bulusu *et al.* stated in 1979 that Nalgonda Technique was preferable at all levels because of the low price and ease of handling<sup>53</sup>. The technique is highly versatile and has the applications like; for large communities, fill and draw technique for small communities, fill-and-Draw defluoridation plant for rural water supply, for domestic defluoridation, etc.

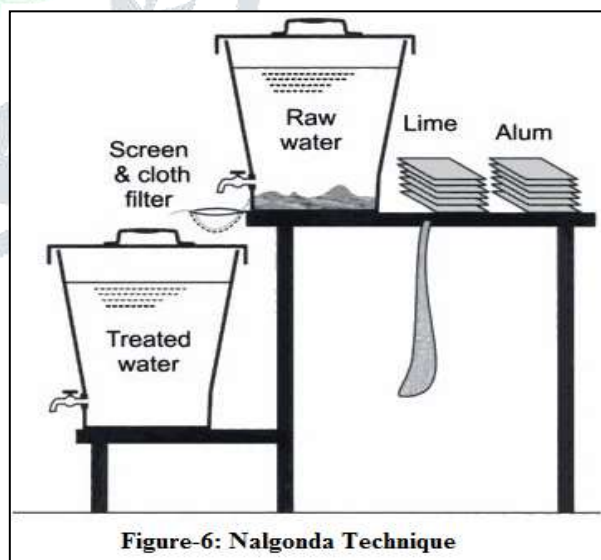


Figure-6: Nalgonda Technique

Table 3: Fluoride Removal Methods<sup>54</sup>

Methods	Domestic	Community	Domestic	Community	Domestic	Community
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	+	+	+	+	+	+
	Low Cost	Low Cost	High F removal	High F removal	Brackish Water	Brackish Water
Activated Alumina	++	++	+++	+++	+	+
Ion exchange	++	++	++	++	+	+
Reverse osmosis	+	+	+++	+++	+++	+++
Electro dialysis	+	+	+	+++	+	+++
Nalgonda process	+++	+++	+	+	+	+
Contact precipitation	++	++	++	++	+	+
Bone Charcoal	+++	+	++	++	+	+
Calcined Clay	+++	+	+	+	+	+
Water Pyramid/Solar Dew	++	++	++	++	++	++

+ = the method is unattractive or not applicable for the given situation.

++ = average suitability

+++ = the method is unattractive or not applicable for the given situation.

#### Advantages of Nalgonda technique<sup>55, 56</sup>

- Regeneration of media is not required.
- No handling of caustic acids and alkalies.
- The chemicals required are readily available and are used in conventional municipal water treatment.
- Adaptable to domestic use.
- Economical
- Can be used to treat water in large quantities for community usage.
- Applicable in batch as well as in continuous operation to suit needs.
- Simplicity of design, construction, operation and maintenance.
- Local semi-skilled workers can be readily employed.
- Highly efficient removal of fluorides from high levels to desirable levels.
- Normally, associated alkalinity ensures fluoride removal efficiency.
- Sludge generated is convertible to alum for use elsewhere.
- Little wastage of water and least disposal problems.
- Needs minimum of mechanical and electrical equipment.
- No energy, except muscle power is required for domestic equipment.
- Provides de-fluoridated water of uniform acceptable quality.
- Simultaneous removal of color, odor, turbidity, bacteria and organic contaminants.

#### Disadvantages of Nalgonda technique

- Desalination may be necessary when the total dissolved solids exceed 1500 mg/l.
- Hardness of the raw water in the range of 200 mg/l to 600 mg/l requires precipitation softening and beyond 600 mg/l becomes a cause for rejection or adoption of desalination.
- Generation of higher quantity of sludge compared to electrochemical defluoridation.
- The large amount of alum needed to remove fluoride.
- Careful pH control of treated water is required.
- High residual aluminium is reported in treated water by some authors.

#### Other techniques of defluoridation

Reverse osmosis, electrolysis and electro dialysis are physical methods that are tested for defluoridation of water. Though they are effective in removing fluoride salts from water, there are certain procedural disadvantages that limit their usage on a large scale.

### Reverse Osmosis and Electro dialysis.

In reverse osmosis, the hydraulic pressure is exerted on one side of the semi permeable membrane which forces the water across the membrane leaving the salts behind. The relative size of the pollutants left behind depends on the pressure exerted on the membrane. In electro dialysis, the membranes allow the ions to pass but not the water. The driving force is an electric current which carries the ions through the membranes. The removal of fluoride in the reverse osmosis process had been reported to vary from 45 to 90 % as the pH of the water was raised from 5.5 to 7. The membranes are very sensitive to pH and temperature. The economics of the approach also deserves evaluation under specific circumstances. The units are also subject to chemical attacks, plugging, fouling by particulate matter and concentrated and large quantity of wastes. The waste volumes are even larger than the ion exchange process. Sometimes, the pre - treatment requirements are extensive. Electro dialysis is highly energy intensive and expensive. Both processes are very complicated<sup>57</sup>.

### Defluoridation by electrolysis.

The basic principle of the process is the adsorption of fluoride with freshly precipitated aluminum hydroxide, which is generated by the anodic dissolution of aluminum or its alloys in an electro chemical cell. The process utilizes 0.3 to 0.6 kwh of electricity per 1000 liter of water containing 5 to 10 mg/l of fluoride. The anode is continuously consumed and needs to be replenished. The process generates sludge at the rate of 80-100 gm per 1000 liters<sup>58</sup>.

#### Advantages:

- Does not require addition of chemicals
- No need to pre & post-treatments
- Low volume of sludge.
- Units can be designed for any capacity.
- Units are designed for specific locations & fluoride content of water. But can be operated with varying fluoride concentrations by slightly altering the operating parameters.
- The electrochemical reactor occupies less floor space.
- Requires less electric energy (0.3 to 0.6kwh/1000 lts)

### IV. Conclusion

The occurrence of the high fluoride concentrations in ground water is a problem faced by many countries, notably India, Srilanka and China, the rift valley countries in East Africa, Turkey and parts of South Africa. Fluoride is present universally in almost every water (higher concentrations are found in groundwater), each crust, many minerals, rocks viz tooth pastes, drugs, cosmetics, chewing gums, mouth washes and so on. World Health Organization (WHO) and IS: 10500 recommend that the fluoride content in drinking water should be in the range of 1.0-1.5 ppm. There are two main types of fluorosis, namely dental and skeletal fluorosis. Dental fluorosis is caused by continuous exposures to high concentrations of fluoride during tooth development, leading to enamel with low mineral content and increased porosity. The critical period for risk to dental fluorosis is between 1 and 4 years of age. After the age of 8 when permanent teeth have established, there is lesser risk to dental fluorosis. Skeletal fluorosis is developed by the disturbance of calcium metabolism in the formation of bones of the body. It results in softening and weakening of bones resulting in deformities leading to crippling. It can also aggravate calcium related disorders such as rickets in children and osteoporosis mainly in adults. For people who are exposed to high fluoride levels for decades, severe cases of crippling can occur. The Nalgonda process, Bone charcoal and Calcined clay are low costs methods for domestic use. On a community scale, the Nalgonda process is also a low cost option. If a high fluoride removal is necessary then activated alumina, reverse osmosis and electro dialysis are preferred methods. For brackish water only reverse osmosis, electro dialysis and the Water Pyramid/Solar Dew method can be used.

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