

Chapter 1

Introduction

1. Introduction

This thesis describes a systematic study of fluoride removal from contaminated water using limestone and phosphoric acid (PA). The study includes fluoride removal from water using PA-limestone combination in different ways and a field trial of a PA-limestone method *viz.*, PA-crushed limestone treatment (PACLT) in domestic and small community level at some fluoride affected villages in Assam.

Drinking water crisis is now a global problem in the urban as well as rural areas of many countries. Millions of people die each year from largely preventable diseases caused by a lack of access to clean water and proper sanitation. The shortage of safe drinking water is one of the greatest challenges before mankind in the twenty first century. A huge amount of water pollutants like organic, inorganic, bacteriological, etc., enter the aquifers from different sources adding to the drinking water crisis. Increasing population along with global rise in industrialization is adding to environmental problems in massive dimensions. Fluoride (F^-) is an inorganic pollutant which contaminates groundwater as well as surface water. It originates from some natural and anthropogenic sources. Fluoride is creating worldwide menace as a long term consumption of drinking water containing excess fluoride can cause health problems called fluorosis¹.

1.1 Fluoride, the element

Fluorine (F) is a halogen element with atomic number 9 and atomic weight 18.998 amu. It exists as a diatomic gas in its elemental state (F_2) having melting point $-219.67\text{ }^\circ\text{C}$, boiling point $-188.11\text{ }^\circ\text{C}$ and density 1.696 g/L (at $0\text{ }^\circ\text{C}$ and 101.32 kPa). As fluorine is the most electronegative element, its elemental state (F_2) has a strong oxidising power. Thus, fluorine naturally exists mostly as fluoride ion (F^-).

1.2 Fluoride contamination in groundwater

Groundwater is contaminated with fluoride by both natural geological activities and industrial activities.

1.2.1 Natural geological sources

Fluoride contamination in groundwater is mostly due to geological sources, *viz.*, weathering of fluoride containing rocks or minerals and volcanic eruption². The volcanic lava contains fluoride which comes into contact with aquifer by dissolution process that occurs at high temperature of lava. During volcanic explosion, aerial discharge of fluoride from volcanic ash takes place and it comes to the surface during rainfall. In addition, volcanic ashes are easily soluble and hence, it can easily come into contact with groundwater. Beside these, fluoride is also released into groundwater by slow dissolution of rock minerals³. Several minerals such as, fluorite, biotites, topaz and their host rocks, *viz.*, granite, basalt and shale containing fluoride can come into contact with groundwater².

These minerals are found primarily in different types of rocks, *viz.*, igneous, sedimentary and metamorphic, which contain different levels of fluoride. Igneous and volcanic rocks have 100 mg/L to >1000 mg/L, sedimentary rocks have 200 mg/L to 1000 mg/L and metamorphic rocks have 100 mg/L to >5000 mg/L of fluoride concentration⁴. In many parts of the world, e.g., India, Sri Lanka, Ghana, South Africa etc., high-level of fluoride are underlined by crystalline igneous and metamorphic rocks and also occurs in volcanic areas⁵. Groundwater contamination of fluoride also depends on geochemical behaviour of fluorine in magma⁵. Since fluorine has a higher affinity for silicate melts than solid phases, it is progressively enriched in magmas and hydrothermal solutions through time due to the magmatic differentiation. As a result, hydrothermal vein deposits and rock that crystallize from highly evolved magmas often contains fluorite, fluorapatite and fluoride containing micas or amphiboles. Cryolite, villiaumite and topaz occur depending on the percentages of silica and calcium present in magma. The alkaline volcanoes, typical of a continental rift (East Africa), hot spot, continental margin (Andes) or island arc (Japan) and basaltic lava flows of Deccan Volcanic Province (Maharashtra, India) hold high amount of fluoride which mix with the aquifer of environs⁶. The weathering of the minerals in these fluoride bearing rocks like topaz ($\text{Al}_2(\text{SiO}_4)\text{F}_2$), fluorite (CaF_2), fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), micas and amphiboles (where F^- substitutes for OH^- within the mineral structures), cryolite (Na_3AlF_6), villiaumite (NaF), etc.³, contributes to fluoride contamination in groundwater.

Groundwater with high F^- concentration is HCO_3^- dominated. The speciation of fluoride is pH dependent⁷. The solubility of F^- in soil is very low in the pH range of 5.0-6.5. At higher pH (above 7.0), ion-exchange between OH^- and F^- takes place which increases the concentration level of F^- in groundwater. Ion-exchange takes place due to the same ionic size of F^- and OH^- . Fluoride is an essential micronutrient for both human and animal depending on its concentration levels in drinking water.

It has been found that high level concentration of fluoride is mostly found in arid regions. This is due to the fact that groundwater flow is slow which increases the contact times between groundwater and rocks for a long period. The concentration level of fluoride in water also increases during evaporation if it is in equilibrium with calcite and also when alkalinity is greater than hardness. Thus, evaporative salts which get deposited in arid region turn to get dissolved and this increases the fluoride sources. Fluoride level is less prominent in humid region as heavy rainfall dilutes the concentration level of fluoride^{4, 8}.

The concentration level of fluoride in groundwater largely depends on the contact time with aquifer minerals. The fluoride concentration increases with increase in the residence time of groundwater in aquifer minerals. Groundwater with high F^- concentration is generally associated with deep aquifer systems and a slow groundwater movement. The fluoride concentration is usually low in shallow aquifers which contain infiltrated rainwater. However, shallow aquifer near active volcanic areas contains high concentration of fluoride due to hydrothermal alteration. In such cases, the solubility of fluoride compounds increases with increasing temperature. In addition, fluoride may come in contact with water through the dissolution of hydrofluoric acid (HF) gas available in volcanic lava^{4, 9}.

1.2.2 Industrial sources

Besides the natural geological sources, fluoride contamination of groundwater also occurs from various industrial sources. The most common industries which discharge fluoride are the aluminium industry, glass and ceramic factories, coal-burning power plants, electroplating, semiconductor, phosphate fertilizer plant, brick and iron works¹⁰. High-fluoride may also be contributed from livestock including cattle, buffaloes, sheep, goats and camels living in the surrounding areas of such industries¹¹. HF is mostly used in

petroleum refineries and waste disposal from these industries leaves fluoride in groundwater.

1.3 Global scenario of fluoride contamination

Prevalence of excess fluoride related health problems, *viz.*, dental fluorosis, skeletal fluorosis and several neurological disorders due to long term consumption of such water, is a serious worldwide problem¹². Fluoride is considered as a worldwide chronic pollutant with serious health effects depending upon its concentration level present in the source¹²⁻¹⁴. Thousands of fluoride contaminated sites have been reported around the world^{13, 15}. Natural occurrences of fluoride in groundwater have been found in many parts of India¹⁵, United States¹⁶, China^{17, 18}, Tanzania^{19, 20}, Kenya²¹, South Africa²², Ethiopia²³, Turkey²⁴, Israel²⁵, Indonesia²⁵, Brazil²⁵, Finland²⁵, Ghana²⁵, Argentina²⁶, Mexico²⁷, Canada²³, Germany²⁸, Pakistan²⁹, etc.

The groundwater of India and neighbouring Sri Lanka has been reported to have fluoride concentration above 20 mg/L and 5 mg/L, respectively^{30, 31}. Fluoride concentrations of 1.06-4.07 mg/L were reported in Illinois and 0.3-4.3 mg/L in Texas of US²⁵. In the hot springs and geysers in Yellowstone National Park fluoride concentrations of 25-50 mg/L have been reported²⁵. In deep aquifers of Western US and in Southern California Lakeland, 5-15 mg/L and 3.6-5.3 mg/L of fluoride, respectively, have been reported²⁵. China has been affected by fluorosis and highest recorded level of fluoride in groundwater is 21.5 mg/L in the low-lying land of Zhuiger Basin in the Kuitun area of China³⁰. In Japan, school children from Ikeno district were affected by fluorosis where the fluoride level of the supplied water was found to be 7.8 mg/L³². Tanzania, is one of the most severely fluoride affected countries in the world where 8.0-12.7 mg/L of fluoride is reported in the groundwater²⁵. In Kenya, a country of East Africa 1-8 mg/L fluoride in groundwater has been reported²⁵. Fluoride levels of 0.05-13.0 mg/L are reported in South Africa²⁵. In Ethiopian Rift Valley, fluoride concentrations in the range of 1.5 to 177 mg/L are reported²⁵. In Indonesia and Israel, fluoride concentration level in drinking water is found in the range between 0.1-4.2 mg/L, whereas, Turkey has high fluoride levels in groundwater with a maximum of 13.7 mg/L²⁵. Reported fluoride concentration range in Brazil is 0.1-2.3 mg/L²⁵. In Finland, fluoride level of groundwater is above 3 mg/L²⁵. In Ghana, fluoride concentration in the upper regions ranges from 0.11-4.6 mg/L²⁵. Fluoride concentrations in the range of 0.9-

18.2 mg/L have been reported in the southeast subhumid pampa regions of Argentina²⁵. About 6% of the population of Mexico are affected by fluoride in groundwater²⁵. Maximum fluoride concentrations are reported as 7.8 mg/L and 8 mg/L in Hermosillo in Sonora State and in Abasolo in Guanajuato State, respectively²⁵. In Canada, fluoride concentration in groundwater has been reported to be as high as 4.3 mg/L from natural sources²⁵. Reported fluoride concentration in the Muenster region of Germany, is 8.8 mg/L²⁵. In the spring and stream sources of Naranji and the surrounding area in Pakistan, the reported fluoride concentration is 8-13.52 mg/L²⁵.

1.3.1 Fluoride contamination in India

The endemic fluorosis in human is now seen widespread in many states of India. The fluorosis disease in this country was first reported from Prakasam district of Andhra Pradesh in 1937³³. In 1937, fluorosis was reported only in 4 states of India, followed by 13 states in 1986, 15 in 1992, 17 in 2002 and now it is 20, indicating that endemic fluorosis has emerged as one of the most alarming public health problem of the country. Tens of millions of people are at risk from drinking fluoride contaminated water in India^{12, 14}. Fluoride affected states in India have been shown in Figure 1.1^{12, 14}.

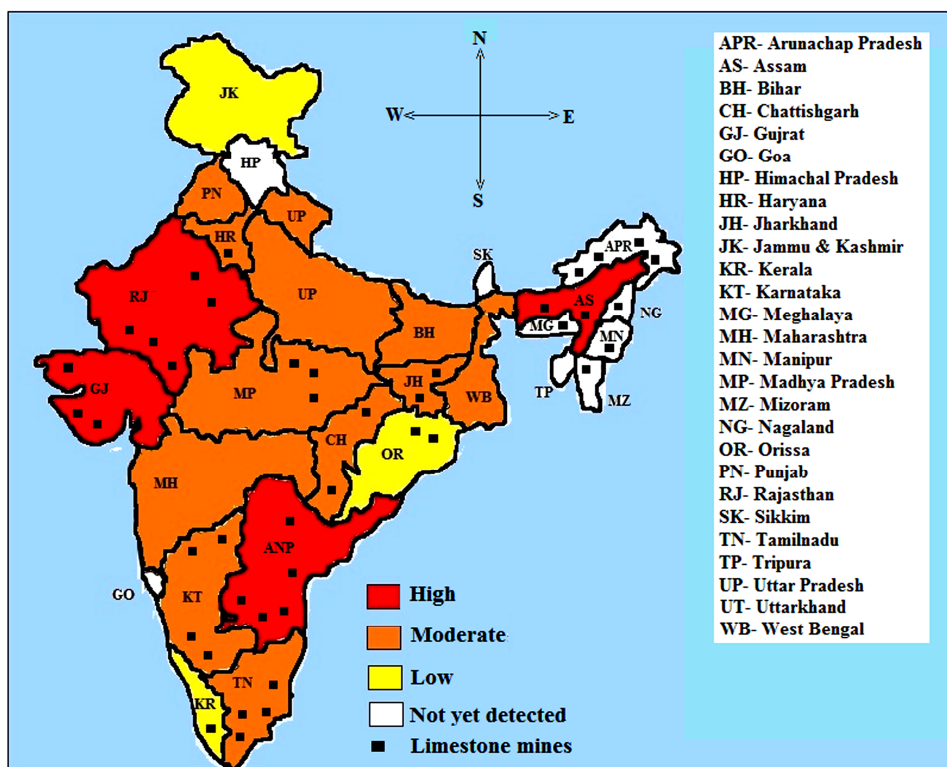


Figure 1.1. Fluoride affected areas and limestone mines in India.

Madhavan and Subramanian correlated the occurrence of fluoride in groundwater of different places in India to lithology and attributed the occurrence of fluoride mainly to granite, granite gneisses, amphibolites, quartzites, basalt and quaternary sediments and alluvium types of rocks³⁴. It has been estimated that nearly 25 million people are already fluoride affected while over 60 million more, including 7 million children in 20 states of the country are susceptible to endemic fluorosis⁶. Out of 569 districts of India, 205 districts are fluoride contaminated⁶. The fluoride affected states are: Andhra Pradesh, Assam, Bihar, Chattishgarh, Delhi, Gujarat, Haryana, Jammu and Kashmir, Jharkhand, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Orissa, Punjab, Rajasthan, Tamil Nadu, Uttar Pradesh, Uttaranchal and West Bengal^{35, 36}. According to Central Ground Water Board (CGWB), Government of India, almost all districts of Rajasthan, 15 districts of Andhra Pradesh, 27 districts in Orissa and Gujarat, 18 districts of Uttar Pradesh, 13 districts of Punjab, 12 districts each of Karnataka and Haryana and 10 districts each of Madhya Pradesh and Maharashtra are exposed to endemic fluorosis⁶. The extent of fluoride contamination in groundwater varies from 1.0 to 48 mg/L. In some districts of Rajasthan, such as Jhunjhun, Nagaur and Barmer, the fluoride content in drinking water was found up to 44 mg/L. Andhra Pradesh, one of the most fluoride affected state, has a maximum concentration of 7.83 mg/L³⁷. The endemic fluorosis was found in many poor villages with maximum concentration level of 23.5 mg/L¹⁴. In the capital of India, Delhi, many districts is fluoride contaminated with maximum fluoride concentration of 32.5 mg/L³⁷.

1.3.2 Fluoride contamination in Assam

Assam, a North-Eastern state of India, is comprised of the Brahmaputra Valley and the Barak river valleys along with the Karbi Anglong and the North Cachar Hills with an area of 78,438 km². The endemic fluorosis was reported in the districts of Karbi Anglong and Nagoan, and Guwahati, the capital city of Assam (Figure 1.2)^{14, 38-42}.

Excessive fluoride presence in the groundwater of around 1,200 km² area of the total 10,382 km² area in Karbi Anglong district has been the cause for fluorosis among most of the people. According to a survey in the Bagpani area of Karbi Anglong district, 646 people (31.3%) among 2063 people from 8 villages have been identified with dental fluorosis and 36 (1.74%) with skeletal fluorosis⁴². In Karbi Anglong district, the highest concentration of fluoride is reported to be 16.3 mg/L³⁹. However, the author has observed

fluoride concentration in Dengaon and Bagpani area of Karbi Anglong in the range of 5-20 mg/L. The other fluoride affected areas in Karbi Anglong are Dokmaka, Lungnit, Samdingbey, Thoisitumung, Garampani, Ratiagaon, Parakhowa, etc.³⁹ In these areas, reported fluoride concentrations range is 1.2-9.5 mg/L³⁹. In addition to these some areas of Nagaon district, *viz.*, Tapat Juri, Akashi Ganga, Haldiati, Nilbagan, Kaki, etc. are fluoride affected with fluoride concentrations of above 1.5 mg/L³⁹. It has also been reported that various areas of Guwahati city are contaminated with fluoride up to 6.88 mg/L¹⁴. It can be noted here that the fluoride concentration in groundwater is found to be lower in the areas of recent alluvial Brahmaputra basin. The reported value of fluoride concentration of the Brahmaputra river is less than 0.2 mg/L¹⁴. In these fluoride affected areas, most of the inhabitants are from poor economical background. The people there are vulnerable to fluorosis because of lack of good nutrition, which can prevent fluorosis to some extent.

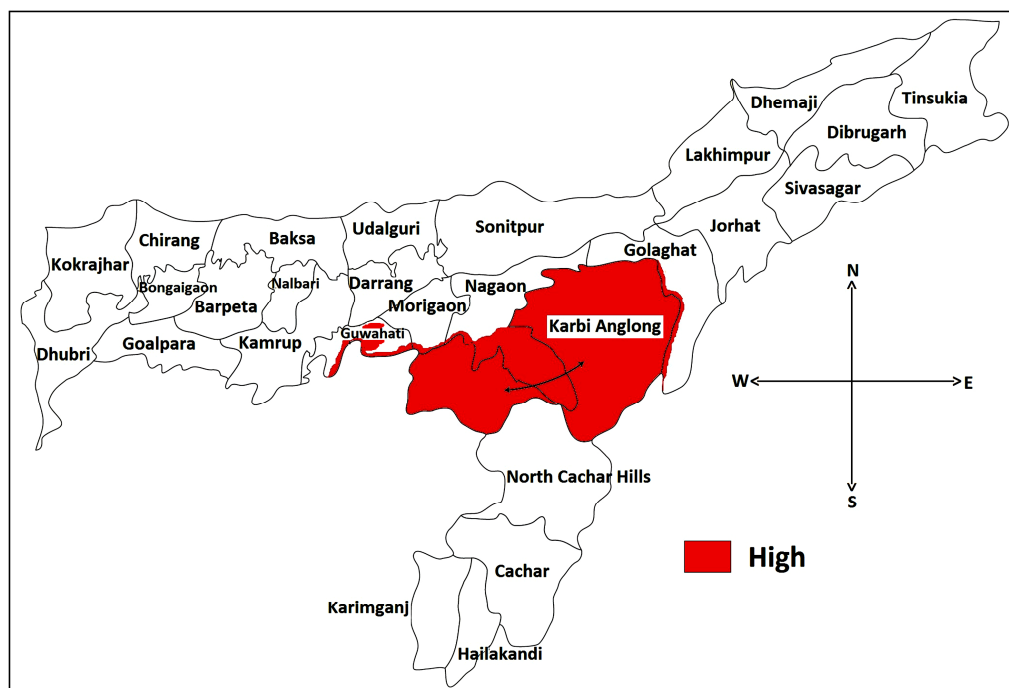


Figure 1.2. Fluoride affected areas of Assam, a north-eastern state of India.

Presence of low or high concentration of fluoride in groundwater depends on the geological conditions of an area. It has been reported that alluvial soil spreads all over the plains of North-India. In Assam, a north-eastern state of India, high level fluoride concentrations have been found in plains of Karbi Anglong district, in parts of Nagaon districts and in Guwahati city, the capital city of Assam^{14, 39}. These areas with high level of fluoride contaminated groundwater have ancient red alluvial soil with Precambrian

metamorphic rock complex basement surrounded by Precambrian hills^{39, 43}. The other parts of Assam, which are not affected by excess fluoride of groundwater, have a geological set up different from the fluoride-affected areas and consist of recent alluvial soil^{39, 43}.

Karbi Anglong receives an average annual rainfall of about 2416 mm which probably is enough to replenish its aquifers as the areas are sparsely populated and there is no major withdrawal of groundwater by industry⁴⁴. Though such rainfall is expected to reduce fluoride level, the presence of high-concentration of fluoride in Karbi Anglong may be attributed to the geological reasons which are stronger than the dilution effect due to the rainfall. For mitigation of the fluoride problem in Karbi Anglong, piped water supply from alternate river sources to the parsed villages is difficult. Rainwater harvesting may be a good option for the uses of water for purposes other than drinking as drinking rainwater is reported to cause certain health problems⁴⁵. Therefore, decentralized fluoride removal from the groundwater may be a practical approach for mitigation of the fluoride problem in Karbi Anglong and other similar areas.

1.4 Drinking water criteria for fluoride

The most probable route of fluoride exposure in humans and animals is ingestion of fluoride contaminated drinking water. Presence of fluoride in drinking water causes several diseases to human health depending on its concentration levels⁴⁶. A small concentration of fluoride is beneficial for tooth enamel especially for children below 8 years⁴⁷. However, long term exposure of fluoride containing drinking water causes dental and skeletal fluorosis, respectively¹². Therefore, it is very important to document the levels of fluoride and for establishing regulatory standards and guidelines⁴⁸.

The World Health Organization (WHO) guideline value for fluoride in drinking water is 1.5 mg/L⁴⁹. According to the Bureau of Indian Standards (BIS), the permissible upper limit of fluoride in drinking water should not exceed 1.0 mg/L⁵⁰. Many countries, like Canada, also prefer the WHO guideline value. However, in China, the drinking water standard for fluoride is 1.0 mg/L⁵¹. The United State Environmental Protection Agency (US-EPA) has set the primary standard at 4 mg/L, although the secondary standard guideline value for fluoride is 2 mg/L in US-EPA⁵². In Tanzania, the national standard value for fluoride is 8 mg/L, reflecting the difficulties to obtain safe drinking water scarcity⁵³.

1.5 Fluoride toxicity and its health effects

Fluoride in drinking water creates an intense effect on teeth and bones. The main mineral constituent of teeth enamel and bones is hydroxyapatite. Fluoride replaces hydroxide ions and form fluorapatite, which is harder. Up to a small concentration level, it is essential for strengthening tooth enamel and preventing from tooth decay¹². However, chronic ingestion of fluoride at higher doses results large amount of hydroxyapatite converting into fluorapatite which makes the teeth and bone denser, harder and more brittle and make a disease called dental fluorosis¹³. When the fluoride concentration exceeds 3.0 mg/L, dental fluorosis leads to the conversion into skeletal fluorosis³¹.

1.5.1 Dental fluorosis

Generally dental fluorosis is seen by ingestion of water having a fluoride concentration above 1.0-3.0 mg/L^{12, 54, 55}. Dental fluorosis is a condition in which excess fluoride is incorporated in developing tooth enamel⁵⁶. Fluorosis generally occurs during the critical period of tooth development and it depends on the total amount of fluoride consumed from all sources^{57, 58}. Fluoride can convert the developed enamel into more porous state⁵⁹. The extension of the porosity depends on the concentration level of fluoride in the tissue fluids during the development of tooth enamel^{59, 60}. The structural arrangement of the crystals appears normal, but the width of the intercrystalline spaces is increased which increases the degree of porosity of the enamel^{58, 59, 61}. When fluorosis occurs, the enamel losses its shine and it seems as white spots, or white opaque lines or striations, or a white parchment like appearance on the tooth surface¹⁵. In its severe form, yellowish brown to black stains have been observed. Normally, the occurrence of dental fluorosis depends on the total amount of fluoride exposure from birth to 8 years of age⁴⁷. The symptoms of dental fluorosis may not be visible in case of fully grown teeth. However, it does not necessarily mean that he or she crosses over to the safety zone and fluoride is unable to affect.

1.5.2 Skeletal fluorosis

Skeletal fluorosis may occur when the concentration level of fluoride in drinking water exceeds 3.0 mg/L^{15, 54, 55}. Whereas, dental fluorosis is an easily recognisable entity, skeletal fluorosis evades detection in earlier stage. The symptoms of skeletal fluorosis are usually similar to spondylitis or arthritis. In earlier stages, the most common symptoms

are deformation of limb bones, pain in neck and back, back stiffness, burning like sensation, muscle weakness, joint pains and paraesthesia of the limb, abnormal calcium deposited in bones and ligaments. Normally, skeletal fluorosis can be seen in the age of 30-50 years in endemic areas⁶². It is believed that it takes about 4-5 years of exposure to develop skeletal fluorosis. However, within 6 months of exposure of high fluoride concentration, it may develop skeletal fluorosis^{63, 64}. The final stage of skeletal fluorosis is osteoporosis and the victim gets crippled¹⁵.

1.5.3 Other effects

Besides dental and skeletal fluorosis, several other problems may occur due to high fluoride exposure. Some researchers indicated that chronic exposure to fluoride is further associated with decreased birth rates, increased rates of kidney stones, impaired thyroid function and lower intelligence in children, Alzheimer syndrome, thyroid disorder, neurological damage^{30, 66}. The excess concentrations of fluoride may interfere with DNA synthesis, carbohydrates, lipids, proteins, vitamin and mineral metabolism^{67, 68}. Fluoride consumption initially reacts locally on the intestinal mucosa and can later form hydrofluoric acid in the stomach, which leads to gastro-intestinal irritation or corrosive effects⁶⁸. Fluoride ingestion also interferes with a number of enzymes disrupting oxidative phosphorylation, glycolysis, coagulation and neurotransmission⁶⁸. It has been well recognized that individuals with kidney disease have a heightened susceptibility to the cumulative toxic effects of fluoride⁶⁹. In addition, high fluoride exposure for short terms affects the kidney function in both animals and humans⁶⁹. Several research groups indicated that high fluoride exposure is also responsible for bladder cancer⁶⁹.

1.6 Mitigation of fluoride menace

Fluoride contamination of groundwater is a big threat to human life as well as for plant and other animal life. To overcome the problem of fluoride contamination in drinking water, there is an urgent need to find out possible remediation. There are three options to mitigate fluoride menace which can be explained as follows.

1.6.1 Alternate water sources

Use of alternate fluoride-free water sources are the best solution to get rid of fluoride contamination. This includes surface water (ponds, lakes) and rainwater. Usually, the

surface water does not contain as high fluoride as groundwater as it does not come in contact with fluoride containing aquifer minerals. However, in poor communities, groundwater is the only available option because use of surface water becomes costly due to its requirement of purification and disinfection. Transportation of uncontaminated water from one place to fluoride affected areas is another problem. Rainwater is usually a much cleaner water source but its uneven distribution and limited storage capacity in communities or households has made it less attractive. In addition, rainwater doesn't contain the required minerals for nutrition which makes it unsuitable for drinking purpose. Fluoride concentration level of groundwater keeps changing with time both vertically and horizontally. This implies that every well has to be tested individually with regular monitoring, which may not be possible in remote areas. Thus, the option of using alternate water sources has its own limitations.

1.6.2 Better nutrition

Nutrition diet in a proper way plays a crucial role to reduce toxicity of fluoride, as a deficient diet can increase the susceptibility to adverse effects of fluoride in drinking water⁷⁰. In US, the maximum permissible limit for fluoride in drinking water is 4.0 mg/L as prescribed by US-EPA⁵². Here, the people have good nutrition facility. Some developing countries have set the permissible limit of fluoride in drinking water lower than 1.5 mg/L and set the permissible limit as 1.0 mg/L^{50, 71}. The possibility of dental fluorosis can be reduced by adequate supply of calcium in diet⁷². Some fruits or vegetable which contain Vitamin C, anti-oxidant rich diet along with protein and iron have ability to fight against the risk⁷³. Some researchers indicated that diet with high calories and magnesium is especially beneficial to children in affected areas which can prevent deformities and crippling⁷⁴. Researcher has shown that magnesium helps in eliminating fluoride from body by competing with calcium⁷⁴. To some extent, fluorosis can be reduced by proper nutrition diet, practically it sounds non-feasible. However, people from remote fluoride affected areas are usually poor and they do not have sufficient nutrition.

1.6.3 Defluoridation of water

Due to high toxicity of fluoride to human, there is an urgent need to develop an efficient, low-cost and eco-friendly method for fluoride removal from contaminated water to make

it safe for human consumption. Extensive research has been done to discover various extensive methods for fluoride removal from drinking water to acceptable levels. The treatment technology, depending on the pollutant load, may be either physicochemical or biological. Several conventional and advanced treatment methods have been proposed to remove fluoride from drinking water.

1.7 Existing fluoride removal techniques

The most common methods of fluoride removal are based on: a) Coagulation / co-precipitation, b) Membrane process, c) Ion-exchange and d) Adsorption¹⁵. Adsorption and precipitation followed by coagulation and flocculation and hybrid processes of both is widely practiced as fluoride remediation technique. Some existing fluoride removal techniques are precipitation, reverse osmosis, nanofiltration, electrodialysis, ion-exchange and adsorption^{3, 13, 15}. Among the precipitation methods, the IISc technique⁷⁵ and Nalgonda technique⁷⁶ are commonly used in India. Now a days, adsorption has been recognised as one of the most popular defluoridation technique in terms of cost and simplicity of operation. However, each of the existing defluoridation methods suffers from some shortcomings. The advantages and limitations of some existing fluoride removal techniques have been summarised in the table (Table 1.1). A detailed discussion of fluoride removal using different existing methods has been presented in the next section.

1.7.1 Coagulation/precipitation

Lime and alum are used as coagulants for fluoride removal. In the first step, lime is added to fluoride contaminated water which leads to precipitation of fluoride as insoluble CaF_2 and the pH of the treated water gets raised up to 11-12. In the second, step, alum is added which react with some of the alkalinity and insoluble $\text{Al}(\text{OH})_2$ is produced. Nalgonda technique is one of the popular techniques widely used for defluoridation of water in some developing countries like India, Kenya, Senegal and Tanzania⁷⁶. The method involves the addition of calculated amount of alum, lime, and bleaching powder to fluoride contaminated water, followed by rapid mixing. In this case, addition of alum and lime lead to the formation of insoluble aluminium hydroxide flocs, sediment to the bottom and co-precipitate fluoride, while bleaching powder ensures disinfection during the process.

Table 1.1. Advantages and disadvantages of some common techniques used for defluoridation of water.

Method	Advantages	Limitations
1) Precipitation and coagulation (Nalgonda Technique)	Most widely used and effective F ⁻ removal technique, medium cost	Toxic chemicals left in treated water (AlF complexes, SO ₄) Large volumes of waste sludge; disposal problem, requirement of acid neutralization
2) IISc method	Removed fluoride to below 1.5 mg/L, chemical used are non-toxic, practically useful	Needs pH adjustment by addition of NaHSO ₄ , Increases TDS
3) Nanofiltration	Highly efficient, no chemicals required, does not influence water taste or color	High cost, high water rejection, brine disposal problem
4) Reverse Osmosis	Excellent fluoride removal technique, all other pollutants also removed at the same time, no chemicals required, long lasting membrane	Removes all ions, wastage of water, clogging, scaling and fouling problems
5) Electrodialysis	Efficient method, No chemicals required, No waste production	High capital cost. High operational (energy) cost, problem of regeneration of resin.
6) Ion Exchange	Effectively removed fluoride up to 90-95%, taste and color of water does not change, little energy required, regenerable,	Efficiency decreases in presence of co-existing anions, high cost of resin, the treated water has a low pH with high level of chloride
7) Adsorption on various materials	Most widely used, effective even at low F ⁻ concentration, simplicity and flexibility of design, ease of operation, no waste production	Effective, mostly at pH < 7, effectiveness decreases after regeneration, disposal of large quantity of sludge

The process has been claimed as most effective technique and can be used “fill and draw type” defluoridation unit for rural areas also⁷⁶. However, some researchers have reported some limitations^{15, 77, 78} of this technique, e.g. high residual concentrations of

aluminium and sulphate in the treated water than the maximum permissible limit set by WHO standard⁴⁹.

1.7.2 Membrane process

Membrane provides selective barrier that allows to pass out particles having size smaller than the membrane pores. There is a driving force, i.e., a potential difference between the two sides of the membrane which is capable of moving the constituents across the membrane. Membrane processes are often classified by the type of driving force, including pressure, concentration, electrical potential, and temperature. Reverse osmosis (RO), nanofiltration (NF), dialysis and electro-dialysis (ED) are the membrane techniques used in fluoride removal.

High-pressure processes (i.e., NF and RO) require a relatively small pore size and they primarily remove constituents through chemical diffusion. An advantage of high-pressure processes is that they tend to remove a broader range of constituents. However, the drawback to broader removal is the increase in energy required for high-pressure processes. Electrical potential-driven membrane processes, e.g., Dialysis and electro-dialysis (ED) are also used for fluoride removal⁷⁹⁻⁸¹. Electro-dialysis uses an electric potential to mobilize the ions and membranes used are cation or anion selective, which basically means that either positive ions or negative ions will flow through depending on ionic charge.

1.7.2.1 Reverse osmosis

Reverse osmosis (RO) is a well-studied and established technology for various kind of water purification. It is applied in desalination of brackish water and sea water. It is a pressure-driven membrane process that uses a pressure gradient (between the water to be treated and permeate side) to remove molecules and ions from solutions when it is on one side of a selective membrane. The solute is retained on the pressurized side of the membrane and the pure solvent is allowed to pass to the other side. Both anisotropic and composite membranes are used and generally consist of a thin polymer layer combined with a porous support, which provides mechanical stability to the membrane. RO can effectively remove nearly all inorganic contaminants from water. In past few years, many researchers have worked on fluoride removal technology by RO and it can efficiently remove fluoride from source water⁸²⁻⁸⁷. RO is however not suitable for selective removal

of contaminants from water with low total dissolved substance (TDS). RO is energy intensive and also produces large volume of reject water.

1.7.2.2 Nanofiltration

Nanofiltration (NF) membranes have slightly larger pore size than those used for reverse osmosis and are capable of removing some divalent cations and also monovalent anions. NF usually can remove divalent ions (e.g., Ca, Mg), but not monovalent salts (e.g., Na, Cl). Many researchers reported that NF has the capability to remove monovalent anions such as fluoride, chloride and nitrate⁸⁸. Lhassani et al.⁸⁹ studied the selective demineralization of water by nanofiltration especially with respect to its application to the defluoridation of brackish water. Drioli et al.⁹⁰ have comprehensively reviewed the use of nanofiltration membranes in water and wastewater treatment. Tahaikt et al.⁹¹ carried out fluoride removal operations on underground water using a nanofiltration pilot plant with two modules. The influence of various experimental parameters such as initial fluoride content, pressure and volume reduction factor was studied. Further the authors compared the performance of three commercial membranes in fluoride removal by nanofiltration using commercial modules in pilot scale⁹². Malaisamy et al.⁹³ modified a commercially available NF membrane by layer-by-layer assembly of alternating poly-electrolyte thin films in order to promote removal and selectivity. Many configurations were tested: simple pass, double pass with one type of membranes and combination of two types of membranes and supplied batch configuration. The water parameters were followed as a function of the running conditions (time, pressure, fluoride content, etc.) in order to follow the behaviour of the membranes tested. The only main advantages of nanofiltration over reverse osmosis is that, the required pressures for NF are lower than those for RO making energy requirement is lower.

1.7.2.3 Dialysis and Electrodialysis

Dialysis separates solutes by transport of the solutes through a membrane rather than using a membrane to retain the solutes while water passes through it as in reverse osmosis and nanofiltration. The membrane pores are much less restrictive than those for nanofiltration, and the solute can be driven through by either the Donnan effect or an applied electric field. Hichour et al.⁸⁰ studied the Donnan dialysis process in a counter current flow system in which the anion-exchange membrane was loaded with sodium

chloride and the feed with 0.001 M NaF together with other sodium salts. Fluoride migrated into the receiver while other ions migrated into the feed. This technique was later used to defluoridate solutions made to simulate high fluoride African groundwater (>30 mg/L fluoride) and whatever other ions were present the fluoride in the feed could be brought below 1.5 mg/L⁹⁴. Later, combining dialysis with adsorption, the group added aluminium oxide and zirconium oxide to the receiver to force the Donnan equilibrium in the direction of fluoride flow out of the feed. In this way it was possible to maintain a flow of feed while leaving the receiving solution in place or renewing only in batches. The cation composition remained unchanged, whereas anions, except chloride, were partially eliminated and substituted by chloride ions, giving a fluoride concentration of 1.5 mg/L⁹⁵. Elazhar et al.⁹⁶ evaluated the performance of nano-filtration and electro-dialysis through pilot plant study and concluded that both technologies confirm the performance in fluoride reduction which is in compliance with the comments made from Tahaikt et al.⁹¹. About 70-75% reduction can be achieved through electro-dialysis at neutral pH⁹². The removal of fluoride from diluted solution with Neosepta AHA anion-exchange membrane has been studied by Donnan dialysis⁹⁷. The effects of concentration, pH and accompanying anion on feed phase and receiving phase composition were investigated. The results obtained for AHA membrane were compared with Neosepta AFN and polysulfone SB-6407 membranes. The transport efficiencies of the membranes were found to be in the order AFN >AHA>SB-6407.

Electro-dialysis is the removal of ionic components from aqueous solutions through ion exchange membranes under the driving force of an electric field. Annouar et al. compared defluoridation using natural chitosan as an absorbent, in comparison with electro-dialysis, and found both approaches to bring the fluoride level to within WHO guidelines⁹⁸. In a further project for defluoridation of Moroccan groundwater, the group improved the efficiency of the process by linking electro-dialysis in tandem with chitosan adsorption. The group also worked for several years on the defluoridation and general purification of brackish groundwater in Morocco and showed that electro-dialysis can defluoridate water with 3000 mg/L total dissolved salts and 3 mg/L fluoride⁹⁹. Recently Kabay's group studied the optimization of fluoride removal by electro-dialysis, evaluating the separation performance in terms of mass transfer and energy consumption. The separation performance increased when the initial concentration of fluoride in the feed solution and the applied potential were increased. However, they did not find a

change in performance with change in feed flow rate and they found that separation of fluoride was influenced by chloride but not by sulphate ions¹⁰⁰. Lahnid et al. (2008) have recently made an economic evaluation of fluoride removal by electro-dialysis¹⁰¹.

Although membrane process has proved in removing fluoride from the water stream to acceptable levels, the construction, operation and maintenance are complex with advanced control equipment which renders the process costly.

1.7.3 Ion-exchange

Many researchers highlighted the efficiency of fluoride removal by ion-exchange with other techniques^{102, 103}. Ion-exchange is a physical/chemical process by which ion on the solid phase is exchanged for an ion in the feed water. The solid phase is a synthetic resin which can preferentially adsorb the particular contaminant of concern. In this process feed water containing contaminants is continuously passed through a bed of ion exchange resin beads in a downflow or upflow mode until the resin is exhausted i.e. all sites of the resin beads have been filled by contaminant ions. At this point, the bed is regenerated by rinsing the ion-exchange column with a proper regenerant. Fluoride can be removed from water supplies with a strongly basic anion-exchange resin, e.g., chloride-fluoride resin, containing quarternary ammonium functional groups. The fluoride ions replace the chloride ions of the resin. This process continues until all the sites on the resin are occupied. The resin is then backwashed with water that is supersaturated with dissolved sodium chloride salt. New chloride ions then replace the fluoride ions leading to recharge of the resin and starting the process again. The driving force for the replacement of chloride ions from the resin is the stronger electronegativity of the fluoride ions. Meenakshi and Viswanathan¹⁰⁴ reported that the selectivity for fluoride ions is better in cation-exchange resins compared to anion exchange resins. However, the selectivity and defluoridation capacity of fluoride is dependent on the type of resin used. Viswanathan and Meenakshi (2008)¹⁰⁵ used Indion FR 10, an ion-exchanger and it was chemically altered with Ce^{3+} , Fe^{3+} , La^{3+} and Zr^{4+} to understand their selectivity for fluoride removal. The defluoridation capacity of all modified resins was found around 0.5 mg/g which was explained by electrostatic adsorption and complexation. Further, they have modified Indion FR 10 by loading Na^+ and Al^{3+} ions in H^+ type of resin¹⁰⁶. Chubar et al.¹⁰⁷ (2005) reported a new ion exchanger from double hydrous oxide ($Fe_2O_3 \cdot Al_2O_3 \cdot xH_2O$) by a sol-gel method and used for simultaneous adsorption of F^- , Cl^- , Br^- and BrO_3^- . The

maximum fluoride adsorption capacity was 88 mg/g in the pH range of 3-10. Solangi et al.¹⁰⁸ modified anionic resin Amberlite XAD-4™ and used for fluoride extraction. They observed that modified resin efficiently removed fluoride at pH 9 in the presence of other anions *viz.*, Br⁻, NO₂⁻, NO₃⁻, HCO₃⁻ and SO₄²⁻. Later, the authors modified Amberlite XAD-4™ resin by adding thiourea binding sites into the aromatic rings which showed high efficiency for fluoride removal up to 95% within the pH range of 4-10¹⁰⁹. They found that the resin could be regenerated several times and used for further fluoride removal process. However, the resins are costly and regeneration of resins creates large volume of fluoride loaded waste which again is a problem.

1.7.4 Adsorption

Among various methods used for defluoridation of water, the adsorption process is widely used and offers satisfactory results and seems to be a more attractive method for fluoride removal in terms of cost, simplicity of design and operation, environmentally benign and efficient^{13, 110, 111}. The common mechanism by which fluoride ions are adsorbed on the solid particles (adsorbent) follows three steps, *viz.*, (i) fluoride adsorption onto external particle surface, (ii) mass transfer of fluoride ion to the external surface of the adsorbent and (iii) intraparticle diffusion of fluoride ions from exterior surface along with possible ion exchange between fluoride ion with elements on the pore surface inside particles¹¹². Some common adsorbents which have been used in fluoride removal technique are elaborated below.

1.7.4.1 Activated alumina

Activated alumina has been considered as the most popular adsorbent for fluoride removal. Farrah et al.¹¹³ studied the interaction of fluoride ion with amorphous Al(OH)₃, gibbsite or alumina (Al₂O₃), with initial fluoride concentration of 2.0-20.0 mg/L at the pH range of 3-8. The results showed that at pH < 6 and total F⁻:Al ratios > 2.5, most of the amorphous Al(OH)₃ gel gets dissolved through the formation of AlF complexes. At lower F:Al ratios, some solid persisted in the pH 4-7 region and strongly sorbed F⁻ from solution. Authors observed maximum uptake of F⁻, up to 170 mg/g, in the pH range of 5.5-6.5. At lower pH, fluoride uptake decreases due to the preferential formation of AlF_x soluble species; whereas at higher pH, OH⁻ displaced F⁻ from the solid and the amount of F⁻ sorbed or converted to complexes declined rapidly towards zero between pH 6 and 8.

Ku and Chiou¹¹⁴ reported fluoride removal efficiency in presence of activated alumina and maximum fluoride removal was found to be in the pH range of 5-7. The authors claimed that when equilibrium solution pH was greater than 7.0, the adsorption of fluoride on alumina reduced which was attributed to the electrostatic repulsion of fluoride ions to the negatively charged adsorbent. Several other researchers also reported fluoride removal efficiency using alumina¹¹⁵⁻¹¹⁹.

1.7.4.2 Modified alumina

Researchers have modified alumina surface to increase the fluoride adsorption capacity of alumina. Shimelis et al.¹²⁰ have studied the fluoride adsorption on untreated hydrated alumina (UHA) and thermally treated hydrated alumina (THA) and compare their adsorption capacities. The fluoride removal efficiency increased with increasing adsorbent dosage. Fluoride adsorption efficiencies showed an increase with rise in the thermal treatment temperature up to 200 °C, but further increase in temperature resulting a lower removal efficiency. High defluoridation efficiency was achieved using both UHA and THA within a pH range of 4.0-9.0. The adsorption data fitted well to the Freundlich isotherm model with a minimum capacity of 23.7 mg F⁻/g and 7.0 mg F⁻/g for THA and UHA, respectively. The results of continuous packed bed column experiments using THA indicated that 4.5 g of THA could treat 6 L of water containing 20 mg/L fluoride before breakthrough.

Wasay et al.¹¹⁶ reported La(III)- and Y(III)- impregnated alumina for fluoride removal. The removal efficiency on various ions and metal elements were performed and was found to be in the order: fluoride > phosphate > arsenate > selenite. The fluoride adsorption capacity of alumina impregnated with lanthanum hydroxide was found as (\approx 6.65 mg/g) which is higher than unmodified alumina (\approx 3.23–3.61 mg/g). The mechanism revealed that there is an ion exchange between fluoride and hydroxide group on surface of adsorbent. The adsorbent effectively removed fluoride from initial 133 mg/L to 0.057 mg/L in the pH range 5.7-8.0. The fluoride loaded adsorbent could be reused by the treatment with aqueous solution of NaOH and HCl. Tripathy et al.¹¹⁷ modified the alumina surface by impregnating with alum and used the modified adsorbent for fluoride removal. The adsorption of fluoride increased with increase in pH and obtained a maximum of 92.6% at pH 6.5, and then decreased with further increase in pH. Fluoride removal decreased in the acidic range due to the formation of weak

hydrofluoric acid or combined effect of both chemical and electrostatic interaction between the oxide surface and fluoride ion. At pH above 6.5, fluoride removal decreased sharply due to stronger competition between fluoride and hydroxide ions on the adsorbent surface. From Langmuir isotherm, the calculated maximum monolayer adsorption capacity was found to be 40.68 mg/g at pH 6.5. From Energy-dispersive X-ray spectroscopy analysis, it was confirmed for the adsorption of fluoride on modified adsorbent. Maliyekkal et al.¹¹⁸ prepared manganese-oxide-coated alumina (MOCA) by modified alumina with manganese oxide and used MOCA for fluoride removal from water in batch and continuous-flow mode experiments. Adsorption of fluoride on to MOCA was found to be much faster and increased with time and attained equilibrium at 3 h. The decrease in adsorption after 3 h was attributed to the surface treatment of activated alumina (AAI). The maximum monolayer adsorption capacity of MOCA for fluoride was about 2.65 times higher than that of AAI (2.851 mg/g). The fluoride sorption capacity at breakthrough point for both the adsorbents (MOCA and AAI) was greatly influenced by bed depth. Recently, Cheng et al.¹¹⁹ reported La³⁺ modified activated alumina for fluoride removal with a defluoridation capacity of 6.70 mg/g.

1.7.4.3 Iron-based sorbents for defluoridation of water

Iron-based materials have also been extensively used for defluoridation of water as iron has an affinity towards fluoride. Schwertmannite, an iron-oxyhydroxysulfate mineral was used for fluoride removal from contaminated wastewater¹²¹. The maximum monolayer adsorption capacity of schwertmannite for fluoride was 50.2-55.3 mg/g at different temperatures. The used schwertmannite adsorbent was regenerable and showed about 78% ability to remove fluoride. Streat et al.¹²² used granular ferric hydroxide (GFH) for fluoride removal in batch and mini-column scale. They found that fluoride removal decreased with increase in pH and showed about 1.8 mmol/g fluoride adsorption capacities. Kumar et al.¹²³ also studied the defluoridation of water using GFH, which is similar in structure to akaganeite. At pH 6.0-7.0, GFH has an adsorption capacity of about 7.0 mg/g for fluoride. The adsorption of fluoride onto GFH was attributed to the interaction of fluoride with singly coordinated FeOH surface groups and the mechanism of fluoride adsorption was described as an ion-exchange between fluoride and hydroxyl group. A novel synthesis of nanosized goethite was introduced by Mohapatra et al.¹²⁴. The results showed that the adsorption of fluoride takes place on heterogeneous surface

of adsorbent with an adsorption capacity of 59 mg F⁻/g. Liu et al. have also performed fluoride removal using synthetic siderite which showed about 1.775 mg/g fluoride adsorption capacity in the batch experiments¹²⁵.

1.7.4.4 Carbon based sorbents for defluoridation of water

Few carbon based sorbents have also been reported for fluoride removal by some researchers. Bhargava and Killedar¹²⁶ conducted fluoride adsorption onto fishbone charcoal in a moving media adsorption system. The ratio of attained equilibrium sorbate concentration to the initial sorbate concentration was found to be a function of the sorbent–sorbate mass input rate ratio. Kaseva explained the fluoride adsorption behaviour of regenerated bone char media from water in Tanzania¹²⁷. Results indicated that the highest fluoride removal and adsorption capacity were 70.64% and 0.75 mg/g, respectively. Janardhana et al.¹²⁸ reported a continuous down flow adsorption mode using zirconium impregnated activated charcoals for fluoride removal. The fluoride adsorption capacity of impregnated activated charcoals was found to be higher about 3-5 times compared to that of fresh activated charcoal. Gupta et al.¹²⁹ developed a micronanohierarchical web consisting of activated carbon fibers and carbon nanofibers (CNF), impregnated with Al for fluoride removal from wastewater. It was observed that pre-treatment of the feed water was not required while using the Al-CNF for treating the wastewater with pH 5.0–8.0. In addition, several carbon based materials, such as graphite¹³⁰, carbon nanotubes¹³¹⁻¹³³, are also been used for defluoridation of water.

1.7.4.4.1 Carbon nanotubes

Carbon nanotubes have defluoridation capacity along with its several other applications in versatile field. Li et al.¹³² reported aligned carbon nanotubes prepared by the decomposition of xylene. After exploring its application in fluoride removal they observed that the material can efficiently remove fluoride from initial 15 mg/L with a defluoridation capacity of 4.5 mg/g at pH 7. The defluoridation capacity increases with increasing acidity due to the increasing positive charge on the surface of the adsorbent. The adsorption of fluoride by activated carbon, γ -Al₂O₃, a typical soil and carbon nanotubes has been studied under identical conditions and found that the order of adsorption is: carbon nanotubes > soil > γ -Al₂O₃ > activated carbon.

1.7.4.4.2 Alumina-impregnated carbon nanotubes

An alumina-impregnated carbon nanotube (AICN) shows a good fluoride removal. It was prepared by pyrolysis of a propylene-hydrogen mixture with Ni particles as a catalyst and the recovered product was ball-milled followed by stirring with a calculated amount of aluminium nitrate solution^{131, 133}. After that the product was heated to 500 °C under N₂ condition for 2 hours. A sponge-like alumina supported on carbon nanotubes was found, which was grounded and sieved to appropriate particle size. 0.2 g of AICN was added to 100 L fluoride containing solution and was shaken for 12 hours. It was observed that the adsorption capacity of the AICN was found to be 13.5 times higher than that of AIC-300 carbon, four times higher than that of γ -Al₂O₃ and also higher than that of IRA-410 polymeric resin.

1.7.4.5 Natural materials as sorbents for defluoridation of water

Several naturally occurring materials available abundantly and free of charge have been used for fluoride removal from contaminated water. The efficiency of three different coal based sorbents, lignite (LN), fine coke (FC), and bituminous coal (BC) were evaluated for fluoride sorption from water¹³⁴. FC and BC showed higher fluoride removal at acidic pH. In case of LN, pH range 6-12 was more favourable for fluoride uptake from water. All three sorbents showed about 77.0%-85.0% fluoride removal efficiency with fluoride adsorption capacities 6.9-7.44 mg/g. Low grade coal found in Assam¹³⁵, fly ash^{136, 137} were also examined by many researchers. Defluoridation of water was also conducted by several clays, e.g., fired clay chips¹³⁸, South African clays¹³⁹, Kaolinite clay¹⁴⁰, bentonite clay^{141, 142}, algerian clay¹⁴³ etc.

1.7.4.6 Bauxite, magnesite and gypsum

Sujana and Anand studied the feasibility of utilizing bauxite for fluoride removal from water¹⁴⁴. The Langmuir adsorption capacity was found to be 5.16 mg/g and presence of competing anions like sulphate, nitrate and phosphate had shown adverse effect, whereas carbonate ions mildly affected on fluoride adsorption on bauxite. The efficiency of thermally activated titanium rich bauxite for fluoride removal from drinking water was investigated by Das et al.¹⁴⁵. The thermal activation of bauxite was performed at moderate temperatures (300-450 °C) and activated bauxite was used for fluoride adsorption¹⁴⁶. The fluoride sorption was highly pH dependent and reached to a maximum

at pH 5.5-6.5 and thereafter decreased. The maximum monolayer adsorption capacity for fluoride was found to be 3.7-4.13 mg/g. Thole et al.¹⁴⁷ investigated the defluoridation kinetics of calcined bauxite, magnesite and gypsum in batch and continuous flow column experiments. They reported that the maximum fluoride adsorption capacities for bauxite, gypsum and magnesite were 5.6, 3.4 and 1.7 mg/g, respectively.

1.7.4.7 Laterite

Laterite ore, rich in iron and aluminium has been used for defluoridation of water. Research has been done to remove fluoride from contaminated water using laterite in batch and column experiment^{148, 149}. Further, raw laterite has been modified by acid followed by base treatment and its efficiency for removal of fluoride was investigated¹⁵⁰. The treated material obtained using 6.0 N HCl for acid treatment (time duration: 3 h) was found to be an effective adsorbent for fluoride and maximum fluoride removal was found at an initial pH of 5.0. Sujana et al.¹⁵¹ reported the defluoridation efficiency of low and high iron containing lateritic ores. The fluoride removal experiment was conducted under various operational parameters such as time, temperature, pH, initial fluoride concentration and adsorbent dose.

1.7.4.8 Zeolite

Zeolites have also been used for fluoride removal from aqueous solutions. The fluoride sorption capacities of zeolite F-9 containing surface-active sites created by exchanging Na⁺-bound zeolite with Al³⁺ or La³⁺ was reported by Onyango et al.¹⁵² It was found that this adsorbent had a high affinity for fluoride removal and adsorption of fluoride took place through an ion-exchange mechanism. They further extended their work by evaluating the surface-tailored zeolite performance with respect to drinking water defluoridation¹⁵³. Metal (Al³⁺, La³⁺ and ZrO²⁺) loaded clinoptilolite type natural zeolites have also been employed for defluoridation of water¹⁵⁴. Recently, Cai et al.¹⁵⁵ investigated the impact of metal ions such as, Cd²⁺, Ba²⁺ and Mn²⁺ on fluoride sorption by natural zeolite.

1.7.4.9 Pumice stone

Pumice, an extrusive volcanic rock has also been widely used as an adsorbent for fluoride in water treatment¹⁵⁶⁻¹⁵⁸. Asgari et al. reported that surfactant-modified pumice showed

efficient results for fluoride removal from drinking water¹⁵⁸. They functionalized pumice by the cationic surfactant, hexadecyltrimethyl ammonium. This modified pumice removed fluoride up to 96% from initial 10 mg/L after 30 min of mixing time. The maximum adsorption capacity of surfactant-modified pumice was found to be about 41 mg/g.

1.7.4.10 Layered double hydroxides (LDHs)

Layered double hydroxides (LDHs) are an interesting group of clay minerals which can be used for fluoride removal from water^{159, 160}. Lv and Duan's group investigated fluoride removal from aqueous solution by calcined Mg/Al with varying Mg:Al ratios (2:1, 3:1, 4:1) and observed that fluoride adsorption increased with increasing calcination temperature from 200 to 800 °C and maximum defluoridation capacity was 80 mg/g when calcined at 500 °C¹⁶¹. Das et al.¹⁶² reported fluoride removal from aqueous solution by thermally activated Zn/Al LDHs. The ratio of Zn:Al was taken as 2:1 followed by coprecipitation at constant pH, with portions of the LDHs calcined at 450 °C over 8 h. The sorption of fluoride increased with increasing contact time and up to 85.5% fluoride removal was achieved at 4 h. Jiménez-Núñez et al.¹⁶³ compared the fluoride removal efficiency of calcined Mg/Al, Ni/Al and Co/Al LDHs. They observed that the thermally activated Mg/Al LDH had maximum sorption capacity of 0.46 mg/g compared to Ni/Al LDH (0.45 mg/g) and Co/Al LDH (0.39 mg/g) under equilibrium conditions. To minimize energy requirement of calcinations, Mandal and Mayadevi¹⁵⁹ studied fluoride adsorption by prepared Zn-Al LDH which showed good fluoride removal.

1.7.4.11 Biosorbents for defluoridation of water

Biosorption is a promising technique for water treatment utilizing abundantly available biomaterials. Many researchers have studied fluoride removal using various biosorbents¹⁶⁴⁻¹⁷⁴. Among them, chitin and chitosan-derivatives biosorbents have gained wide attention for fluoride removal due to their low cost and has a significant adsorption potential for fluoride removal from water. The applicability of chitin, chitosan and 20%-lanthanum incorporated chitosan (20% La-chitosan) toward fluoride removal from contaminated water was evaluated by Kamble et al.¹⁶⁴. They reported that maximum fluoride removal capacity was observed in 20% La-chitosan at pH 6.7. Yao et al.¹⁶⁵ modified chitosan with neodymium and after exploring its application in fluoride

removal they observed that optimum fluoride adsorption occur at pH 7 with a maximum fluoride adsorption capacity of 11.411–22.380 mg/g at different temperatures. Besides chitosan, some other biosorbents such as algal and fungal biomass have also been used for defluoridation of water¹⁷⁵⁻¹⁷⁹.

1.7.4.12 Building materials as sorbents for defluoridation of water

Few researchers also tested the potential of building materials towards fluoride removal. Yadav et al.¹⁸⁰ tested the efficiency of brick powder (BP) for the defluoridation of groundwater and found maximum adsorption of fluoride as 51.0–56.8% in pH range 6.0–8.0. Other building materials, such as gas concrete¹⁸¹, light weight concrete¹⁸² have also been used for fluoride removal. Research has been done to investigate fluoride removal efficiency from contaminated water by hydrated cement¹⁸³ and alumina cement granules¹⁸⁴.

1.7.4.13 Hydroxyapatite

Hydroxyapatite $\{(Ca_5(PO_4)_3OH)\}$ (HAP) is a naturally occurring mineral found in both bone and skeletal hard tissues. In recent years, many researchers worked on fluoride removal by HAP due to its high affinity for fluoride. Fan et al. reported the order of fluoride adsorption capacities of various low-cost materials as: HAP > Fluorspar > Quartz (activated using ferric ions) > Calcite > Quartz¹¹². Fluoride removal efficiency using hydroxyapatite, prepared in a highly porous form using a modified chemical wet method, was studied by Hammari et al.¹⁸⁵. Porous (p-HAP) and crystalline calcium hydroxyapatite (c-HAP) were prepared and evaluated to understand their efficiency for fluoride removal. The fluoridation rate of the p-HAP was 89% using 19 g/L fluoride solution compared with 30% for c-HAP. The high specific surface area of p-HAP (235 m²/g) compared with c-HAP sample (47 m²/g) was found to favour the removal of fluoride ions from aqueous solution. Fluoride adsorption on porous hydroxyapatites (p-HAP) modified its structural and conduction properties and favoured the stable formation of fluoridated apatites. A synthetic hydroxyapatite, Bio-gel HAP has also been studied in order to remove excess fluoride from water¹⁸⁶. Nie et al. prepared aluminium modified HAP (Al-HAP) which showed defluoridation capacity of about 32.57 mg/g¹⁸⁷. Defluoridation behaviour of HAP modified with cationic surfactant, e.g., cetyltrimethyl ammonium bromide (CTAB), hexadecylpyridinium chloride and dodecyltrimethyl ammonium bromide was observed

by Prabhu and Meenakshi¹⁸⁸. The maximum defluoridation capacity onto modified forms of HAP powder with CTAB was 9.369 mg/g.

1.7.4.14 Nano-hydroxyapatite

Nano-hydroxyapatite (n-HAP) is an efficient adsorbent as it shows a very good fluoride adsorption capacity. Gao et al.¹⁸⁹ investigated fluoride removal by synthetic nano-hydroxyapatite (n-HAP), biogenic apatite (bone meal; B), treated biogenic apatite (bone meal prepared by H₂O₂ oxidation, BH₂O₂) and geogenic apatite (rock phosphate) and compared their efficiency for fluoride removal. The extent of fluoride removal was greatly increased to 90.94% (2.27 mg/g) with 0.1 g/25 mL of n-HAP, 86.45% (2.18 mg/g) of B, and 88.01% (2.20 mg/g) of BH₂O₂. The results revealed that n-HAP showed the best adsorption capacities for fluoride removal as compared to the other apatites used in this study. Later, Gao et al.¹⁹⁰ synthesized n-HAPs with different particle sizes and compared their defluoridation ability with bulk HAPs which were obtained by conventional solid-state reaction. Enhanced performances were obtained with smaller particle sized HAPs compared to bulk HAP. Sundaram et al.¹⁹¹ synthesized n-HAP by precipitation method and employed the sorbent for fluoride removal. The authors concluded that fluoride removal decreased with increasing pH and the maximum defluoridation capacity was reported as 1845 mg F⁻/kg at pH 3 and only 570 mg F⁻/kg was removed at pH 11. Poinern et al.¹⁹² synthesized nano-structured HAP from a combined ultrasonic and microwave technique and was examined for defluoridation of water. They found that synthesized nano-structured HAP efficiently removed fluoride with a maximum monolayer adsorption capacity of 5.5 mg/g at 298 K. Wang, W. et al.¹⁹³ reported the defluoridation behaviour of n-HAP, synthesized from a sol-gel method, in absence and in presence of oxalic acid, citric acid and malic acid. It was found that the defluoridation capacity of nHAP increased in presence of acids in the order: oxalic acid > citric acid > malic acid. Recently, study was done on fluoride removal by a biocomposite synthesized by incorporation of nano-hydroxyapatite in gelatin polymatrix (n-HAP@Gel)¹⁹⁴. The results demonstrated that, n-HAP@Gel biocomposite possess an enhanced defluoridation capacity of 4.157 mg F⁻/g.

As HAP and n-HAP have been recognized as good adsorbents for fluoride removal, several techniques have been reported to synthesise them, *viz.*, coprecipitation

method¹⁹⁵, sol-gel procedures¹⁹⁶, hydrothermal preparation¹⁹⁷ and microwave synthesis routes¹⁹⁸.

1.7.4.14.1 Chemical precipitation method

Among the various processing methods, chemical precipitation is the simplest route for the synthesis of nanosized HAP. Several researchers used chemical precipitation to prepare different shapes of HAP¹⁹⁹. The precipitation reaction is usually conducted at pH values higher than 4.2 and temperatures ranging from room temperature to temperatures close to the boiling point of water²⁰⁰. In chemical precipitation, various calcium and phosphate containing reagents, e.g. calcium hydroxide or calcium nitrate act as the Ca²⁺ source and orthophosphoric acid or diammonium hydrogen phosphate as the PO₄³⁻ source has been used for synthesis of HAP. Liu et al.²⁰¹ synthesized HAP nanorods of 50-80 nm in diameter and 0.5-1.2 μm in length (determined by TEM) using surfactants of CTAB and polyethylene glycol 400 (PEG 400). Zhang and Zhu²⁰² controlled the morphology of fluoride-substituted HAP nanoparticles by adding Tween-80.

1.7.4.14.2 Sol-gel method

The sol-gel method is a well-known method for the wet synthesis of HAP. This method is used for production of solid materials from small molecules. A sol is a stable dispersion of colloidal particles or polymers in a solvent and a gel is porous, three-dimensional, continuous solid network surrounding a continuous liquid phase. Several researchers reported sol-gel method for synthesis of various structure of HAP^{203, 204}. Hsieh et al.²⁰⁵ prepared nanocrystalline HAP using 2-methoxy ethanol solution of Ca(NO₃)₂ and PO(OEt)₃ at 80-90 °C for 16 h and then gelation under reduced pressure or slow evaporation in the oil bath, followed by calcination at 600 °C and subsequent washing the resultant powder in distilled water. Recently, nonalkoxide sol-gel processing for synthesis of HAP has been developed without adjusting pH^{206, 207}. Major disadvantages of this method are *viz.*, generation of secondary phase such as CaO and the high cost of starting materials, especially alkoxide-based precursors.

1.7.4.14.3 Microwave assisted route

Recently, many researchers synthesized HAP through microwave-assisted methods, in which microwave irradiation is used to activate the reaction. Microwave processing of

HAP particles was employed for sintering of HAP ceramics to produce a dense material with improved physical and mechanical properties²⁰⁸. This technique is mostly interesting due to a less energy-consuming and more reproducible manner. In actual practice, microwave treatment results in rapid and uniform heating of entire bulk of the substance to the temperature of treatment without any significant thermal stress or temperature gradient²⁰⁹. This can increase the reaction kinetics and effectively reduce duration of the process²¹⁰. As a result of fast homogenous nucleation, microwave synthesis of HAP nanoparticles is usually accomplished in less than 30 min. It is believed that microwave irradiation may also lead to a powder having some improved characteristics, including smaller size, higher purity, and narrower size distribution. Moreover, several attempts have also been made to combine the microwave irradiation with solid-state²¹¹, hydrolysis²¹², sonochemical¹⁹², solution combustion²¹³ methods and under refluxing system¹⁹⁸.

1.7.4.14.4 Hydrothermal method

Hydrothermal method is one of the most common methods for preparation of HAP. The method is generally identified by the reaction of chemicals in an aqueous solution and allowed to conduct at a high temperature typically above the boiling point of water inside an autoclave or pressure vessel²¹⁴. Several researchers reported rod-like HAP synthesized in acidic^{215, 216} or in approximately neutral conditions²¹⁷, and in alkaline conditions²¹⁸. Sadat-Shojai et al. reported that dropwise addition of $(\text{NH}_4)_2\text{HPO}_4$ solution to a $\text{Ca}(\text{NO}_3)_2$ solution, followed by hydrothermal treatment at 200 °C for 60 h lead to the formation of highly crystalline HAP nanorods²¹⁹. Recently, different structures of HAP were introduced by hydrothermal conditions, such as, plate-shaped structure²²⁰, needle like structure²²¹, spherical²²², etc. The main disadvantage of hydrothermal method is the low capability to control the morphology and size distribution of nanoparticles.

1.7.4.14.5 The mechanism of fluoride removal by HAP

The fluoride removal by HAP was suggested to take place through precipitation of HAP as fluorapatite (FAP), recrystallization of HAP to FAP and surface adsorption or ion-exchange between F^- ions and OH^- ions of HAP depending on the method employed²²³. The mechanism of fluoride removal by Ca^{2+} and PO_4^{3-} ions and subsequent contact with bone char was suggested to be the formation of FAP along with the formation of CaF_2 to

some extent²²⁴. Lin et al. reported that both precipitation and adsorption took place in fluoride removal by HAP²²⁵. They confirmed the mechanism from an adsorption measurement, electrokinetic and electron spectroscopy for chemical analysis study of HAP before and after treatment. He found that FAP was formed at the surface of HAP through adsorption followed by an ion-exchange process at low fluoride concentrations. On the other hand, CaF₂ formed on HAP through a surface precipitation process at higher concentrations of fluoride. A series of experiments was carried out by Duff to investigate the interactions of fluoride, chloride and bromide with different orthophosphate compounds²²⁶⁻²³⁸. He suggested that when fluoride solution comes into contact with HAP, at first fluoride got adsorbed on the surface of HAP and then the adsorbed fluoride exchanged with OH group present on the surface of HAP and slowly it started to be exchanged with inner OH groups of HAP. It was found that the incorporation of fluoride into HAP occurs as a result of fluoride-hydroxyl exchange reactions²²⁶. This ion exchange mechanism of fluoride removal by HAP has also been reported by Fan and his co-workers¹¹². Gasser, et al.²³⁹ observed similar behaviour in a study of fluoride removal by HAP at a neutral pH. At low initial F⁻ concentration, adsorption of H₂PO₄⁻ and H⁺ ions along with F⁻ was observed. On the other hand, CaF₂ was deposited on the surface of HAP at high F⁻ concentrations. On further increasing the concentration of F⁻, the solutions remained supersaturated with respect to CaF₂ and only F⁻ ions were adsorbed.

Gasser, et al suggested that fluoride was found to form interfacial CaF₂ at higher concentrations, which decreased the autoinhibition of HAP²⁴⁰. A Langmuir adsorption isotherm analysis also showed that dissolution of HAP hinders due to the adsorption of fluoride on HAP. The adsorption of fluoride by HAP increased with increase in temperature²⁴¹. However, at low supersaturation level, crystal growth of FAP over HAP was found to be a complicated process. In this case, ion-exchange between F⁻ ions and surface OH⁻ ions of HAP took place. Fan et al. suggested that both pseudo-first order and second-order ion-exchange mechanisms described the fluoride removal by HAP well, whereas, fluoride removal by other materials was through a pseudo-second order surface adsorption¹¹². It has been found that porous HAP has a better F⁻ retention property than crystalline HAP due to its high surface area¹⁸⁵. The F⁻ ion helps in increasing growth rates by increasing the driving forces for precipitation of biogenic apatite²⁴². The removal of fluoride from phosphogypsum was found to take place through formation of FAP along with a principal by-product in the production of PA along with calcium hydrogen

phosphate dehydrate²⁴³. Badillo-Almaraz et al. reported that the HAP has a capacity as high as 100 mmol F⁻ per 100 g of HAP at pH 7.0-7.5¹⁸⁶. Ca-deficient HAP, a by-product of phosphate wastewater treatment, had also been used to remove F⁻ ions in presence of coexisting Ca²⁺, Mg²⁺, and Cl⁻ ions. The fluoride adsorption kinetic followed pseudo-second-order and the adsorption of fluoride takes place through ion-exchange²⁴⁴. The method was applicable for the treatment of high F⁻ concentration solution giving a removal efficiency of 85%. Jiménez-Reyes et al. suggested that adsorption of F⁻ on HAP followed Freundlich isotherm with chemisorptions²⁴⁵.

1.7.4.15 Other calcium-based sorbents for defluoridation of water

Several researches have also been carried out using different calcium salts for removal of fluoride. It was found that calcium has a good affinity for fluoride ion. Fan et al. studied the defluoridation efficiency using limestone (calcite) of size range from 215 to 250 μm with initial fluoride concentration 2.5×10^{-5} to 6.34×10^{-2} mg/L. The kinetics of the process followed second-order with maximum adsorption capacity 0.39 mg/g¹¹². Reardon et al. reported that limestone (CaCO₃) in presence of CO₂ can reduce fluoride from initial 10 mg/L to below 2 mg/L due to the precipitation of CaF₂ by Ca²⁺ ions generated in situ through the dissolution of limestone²⁴⁶. Turner et al. investigated that fluoride removal efficiency increased by limestone in presence of mineral acids and showed that both precipitation as well as adsorption of fluoride on limestone surfaces contributes to the fluoride removal²⁴⁷.

Jain and Jayaram²⁴⁸ used aluminium hydroxide impregnated limestone (AILS) for fluoride removal from contaminated drinking water. The results showed that AILS can efficiently removed fluoride with maximum sorption capacities 84.03 mg/g. FTIR studies revealed that adsorption of fluoride on AILS was physisorption. An adsorbent prepared by calcinations of PA treated limestone powder has been reported recently to be effective in fluoride removal^{249, 250}. Murutu et al. performed batch and breakthrough analysis using calcined PA-treated limestone^{249, 250}. The batch experiments showed that fluoride can be efficiently removed giving a maximum fluoride adsorption capacity of lime as 22.22 mg/g. The continuous-flow performance of PA-treated lime showed that breakthrough curves saturated earlier with increase in flow rate and initial F⁻ concentration. They suggested that phosphate ions of PA can combine with the calcium ions to form calcium phosphates or HAP which has a high sorption capacity of fluoride. It is interesting to note

that both precipitation by Ca^{2+} ions and adsorption by HAP are known to be selective towards fluoride over other ions commonly present in groundwater.

Sivasankar et al.²⁵¹ reported a fluoride removal method using tamarind fruits shell which contains high content of natural calcium compounds. They modified the material with ammonium carbonate solution and the modified adsorbent showed about 22.33 mg/g fluoride adsorption capacity. The fluoride adsorption mechanism was explained by an ion-exchange mechanism. Kanno and his co-workers provided a novel method of synthesizing nano to micrometer sized HAP on the surfaces of granular limestone to improve the sorption efficiency of HAP²⁵². This HAP-coated-fine limestone material can efficiently remove fluoride from contaminated water to its acceptable range set by WHO⁵⁰. Now a days, brushite with chemical formula $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, has also been used for defluoridation of water²⁵³. Mourabet et al.²⁵³ studied the fluoride adsorption potential of brushite using batch experiments. They found that Freundlich, Langmuir and Temkin isotherm models are well fitted to describe the fluoride adsorption behaviour with a monolayer adsorption capacity of 6.59 mg/g.

Works have been carried out based on both adsorption and precipitation using limestone in presence of different acids. Murutu et al. reported a fluoride removal study using phosphoric acid treated lime in batch and continuous flow mode^{249, 250}. Here, lime was obtained from calcined limestone and the modified limestone was used for fluoride removal in presence of PA. The batch experiments showed that fluoride can be efficiently removed giving a maximum fluoride adsorption capacity of lime as 22.22 mg/g. The continuous flow performance of PA-treated lime showed that breakthrough curves saturated earlier with increase in flow rate and initial F^- concentration.

Marble, a crystalline metamorphic limestone, which mainly consists of calcium compounds like calcite, dolomite and silicon oxides²⁵⁴, has also been used for fluoride removal. Husain and Jha investigated fluoride removal capacity of marble slurry from aqueous solution²⁵⁴. The fluoride removal efficiency was 51-58% with an adsorbent dose of 15 g in the pH range of 6.0-8.0 for a minimum contact time of 2 h. Recently, Mehta et al. have reported calcined marble waste powder as a novel adsorbent for fluoride removal. The adsorbent showed about 1.20 mg/g fluoride adsorption capacity at pH 7²⁵⁵. The kinetics of fluoride adsorption reactions followed pseudo-second-order and Freundlich isotherm fitted well to the experimental data. Gandhi et al. have used chalk powder for defluoridation of water and reported about 83% fluoride removal at pH 5²⁵⁶.

Dolomite is an inexpensive and widely available geomaterial with a chemical composition of $\text{CaMg}(\text{CO}_3)_2$ which has been reported to show a good fluoride removal properties from aqueous media²⁵⁷. The fluoride adsorption by dolomite follows first-order kinetic and follows Langmuir isotherm²⁵⁷. Recently, Sasaki et al. investigated fluoride sorption behaviour on modified dolomite partially calcined in the range of 873-1373 K²⁵⁸. They reported that the temperature of calcination had a significant effect on surface chemical compositions of dolomite and hence on sorption density of fluoride. When the equilibrium fluoride concentration was >9.5 mg/L, sorption density was found to be maximum for the sample calcined at 1173 K. This indicated that sorption density was controlled by the precipitation of fluoride as CaF_2 and co-precipitation with $\text{Ca}(\text{OH})_2$ due to excess liberation of Ca^{2+} from CaO . At low concentrations of fluoride (<9.5 mg/L), the sorption density was not controlled by precipitations and maximum fluoride sorption density was observed for the sample calcined at 973 K²⁵⁸. Chaudhary and Prasad modified dolomite powder (150 μm) by thermal activation in the temperature ranges 200-800 °C and used for defluoridation of water in batch experiments²⁵⁹. They reported the maximum fluoride removal capacity as 243.25 mg/g with and $[\text{F}^-]_0$ of 500 mg/L at a fixed sorbent dose of 2 g/L. Recently, Toshiyuki et al. reported hydroxylated calcined dolomite (HCD) for fluoride removal by co-precipitation with HAP and precipitation as FAP²⁶⁰. They studied the influence of Mg^{2+} on fluoride removal in presence of $\text{Ca}(\text{OH})_2$ and HCD independently and found fluoride removal to increase with increase in Mg^{2+} concentration. Islam and Patel observed about 80.6% fluoride removal efficiency of quick lime activated by heating in muffle furnace with a maximum monolayer sorption capacity of 16.67 mg/g and attributed the fluoride removal to chemisorptions and precipitation²⁶¹.

1.8 Limestone for fluoride removal

Now a day, defluoridation of water by limestone has been widely studied. Limestone, a low-cost fluoride adsorbing sedimentary rock, is readily available in almost all fluoride affected areas in the world including India (Figure 1.1). It has been reported that limestone can adsorb fluoride to some extent¹¹². Therefore, there are scopes for developing an efficient fluoride removal method using the low-cost calcium mineral, limestone. It was reported that defluoridation of water by limestone enhanced in presence of acids, *viz.*, HNO_3 and H_2SO_4 through precipitation of fluorite (CaF_2) by Ca^{2+} ions, formed by dissolution of limestone and through adsorption of fluoride on the limestone

surfaces²⁴⁷. Calcium phosphates, *viz.*, hydroxyapatite (HAP) and nano-hydroxyapatite (n-HAP) have been reported to have high sorption capacity for fluoride^{192, 245}. However, phosphate minerals are not readily available in some countries like India. Thus, limestone can be used for fluoride removal from water due to its efficiency, cost effectiveness and user friendliness.

1.9 Limestone defluoridation and its mechanism

Fluoride removal from water by limestone has been studied by many researchers due to an affinity of limestone towards fluoride. The mechanism of fluoride removal by limestone was first proposed by Grayson²⁶². He suggested that the precipitation of CaF₂ took place through the reaction between CaCO₃ and HF. Later, many researchers worked on this statement^{263, 264}. The CaF₂ formed in this reaction possessed molecular volume of 33% smaller than that of CaCO₃ in calcite. This led to the replacement reaction which left 33% additional porosity in fluorite and facilitated the diffusion of F⁻ ions into and of CO₃²⁻ ions out of the particles²⁶⁵. The involved reactions were described as follows:



$$K_{\text{sp}} = [\text{F}^-]^2[\text{Ca}^{2+}] = 3.5 \times 10^{-11} \quad (1.3)$$

where, K_{sp} is the solubility product of fluorite. In 1979, Simonsson studied the fluoride removal by crushed limestone bed²⁶⁶. The conversion of fluorite from limestone did not affect the original size and shape of limestone particles. Initially, the rate of the reaction was independent of F⁻ ion concentration but at higher concentration of F⁻, the probability of formation of CO₂ increased hindering the diffusion process of F⁻ through newly formed CaF₂ layer and the reaction with the untreated limestone. The rate of the reaction was inhibited by some cations present in the wastewater.

The rate of the reaction between calcite and NH₄F was studied²⁶³. It has been found that the rate was depending on the concentration of F⁻ ion and surface area of calcite. Duff reported a similar study by reacting calcite with 1.0, 0.1, and 0.01 M solutions of NaF at 25 °C and found that rate of the reaction of calcite with NaF was too rapid to measure²²⁹. A mixture of crystalline CaCO₃ with NH₄F, KF and NaF when heated for several hours above 80 °C formed fluorite which was found to be a pseudomorph of calcite crystals as evidenced by X-ray diffraction and electron

microscopic techniques²⁶⁴. The course of the reaction involved penetration of F^- into the body of the grains of $CaCO_3$ forming polycrystalline CaF_2 . These studies showed the rate of the reaction between F^- and $CaCO_3$ to be very slow and established CaF_2 as the product of the reaction, significantly contributing to the development of F^- removal processes.

It has been reported that the conversion of calcite to fluorite tend to increase with increase in temperature²⁶⁶. Some researchers used calcite for reducing F^- from industrial wastewater containing HF and a mixture of HF and NH_4F , however these works were aimed at getting low F^- water to satisfy wastewater discharge criteria and not to get potable water^{267, 268}. Surprisingly, it was found difficult to remove F^- from lower initial concentration (<50 mg/L) than from higher initial concentration of F^- . This could be explained by the fact that it was difficult to achieve supersaturation of F^- and Ca^{2+} for precipitation at lower initial concentration of F^- (<50 mg/L). It was reported that fluoride could be removed from wastewater containing NH_4F only to the level of 10-20 mg/L by using a series of three limestone columns^{269, 270}. There was a correlation between effluent F^- and Ca^{2+} concentrations for defluoridation of water in fixed bed column. The effluent F^- concentration could be achieved to below 10 mg/L by adjusting the initial $[H^+]/[F^-]$ ratio in the wastewater²⁷¹ as the extent of dissolution of Ca^{2+} from calcite is pH dependant.

Limestone filtration alone cannot reduce fluoride from contaminated water to below 4 mg/L as reported by Reardon and Wang²⁴⁶. However, fluoride removal was achieved to below 2 mg/L from initial F^- concentration of 10-25 mg/L by passing CO_2 through the water before filtering through a series of two columns. The pH of the treated water was found to be 4.97 due to the formation of carbonic acid [H_2CO_3], which created dissolution of limestone to produce Ca^{2+} . The equilibrating equations were represented as follows:



The free Ca^{2+} formed in this way reacted with F^- to precipitate CaF_2 . The effluent water came out from the first column having pH = 6.53 and $Ca^{2+} = 8.07$ mg/L which was

adjusted to $\text{pH} = 8.42$ and $\text{Ca}^{2+} = 0.58 \text{ mg/L}$ after treatment of the water through a second column. The main advantage of this method is that no chemical is required except CO_2 gas and the process does not need column regeneration²⁴⁶.

The excess F^- from the semiconductor industry wastewater was removed by using fluidised bed reactor through a precipitation method using CaCl_2 , $\text{Ca}(\text{OH})_2$, etc.²⁷²⁻²⁷⁴. After this treatment, the remaining F^- concentration (10-20 mg/L) could be removed using granular CaCO_3 . The removal performance was found to be better at low pH due to the high dissolution of CaCO_3 ²⁷⁵. Fluorite precipitation lead to the renewed limestone surfaces of limestone which increased the number of adsorption sites. Thus, F^- was removed through both adsorption of F^- along with the precipitation²⁴⁷, which was revealed from a saturation index (SI) calculation of fluorite using Eq. (1.7):

$$\text{SI}_{\text{fluorite}} = \log[\text{Ca}^{2+}][\text{F}^-]^2/\text{K}_{\text{sp}} \quad (1.7)$$

where, K_{sp} is the solubility product of CaF_2 in $(\text{mol/L})^3$ and $[\text{Ca}^{2+}]$ and $[\text{F}^-]$ are molar concentrations in mol/L before reaction. If $\text{SI}_{\text{fluorite}} < 0$ then the adsorption is the dominant mechanism and if $\text{SI}_{\text{fluorite}} > 0$ then precipitation is the main mechanism for fluoride removal since it reaches the supersaturation level of F^- and Ca^{2+} necessary for precipitation. The precipitation of fluorite dominates at lower pH and lower surface area (or particle size greater than 850 μm) whereas the adsorption of F^- dominates at higher pH and higher surface area (or particle size 150-300 μm)^{247, 275}.

Turner, et al. studied the impact of PO_4^{3-} on F^- removal by calcite and suggested that the removal of F^- by PO_4^{3-} was due to the precipitation as fluorite, FAP and HAP²⁷⁶. They reported that a small amount of PO_4^{3-} , viz., 17 mg/L had little effect on fluoride removal and can reduce only 20%, whereas, higher PO_4^{3-} concentration (500 mg/L) completely inhibited the fluoride removal.

1.10 Limestone defluoridation in presence of acid

Research has been done to increase the efficiency of limestone for fluoride removal. Turner et al. studied batch experiments using crushed limestone in presence of acid, viz., HNO_3 and H_2SO_4 for fluoride removal. The results with evidences from atomic force microscopy, X-ray photoelectron spectroscopy and ζ potential measurements and

revealed that combination of both adsorption and precipitation played an important role for fluoride removal.

1.10.1 Acid-enhanced limestone defluoridation

Nath and Dutta reported an acid-enhanced limestone defluoridation (AELD) method. They used a plug-flow fixed-bed reactor which consists of a plexiglass column of length 44 cm with a diameter of 4 cm containing fixed bed of limestone chips size of 2-3 mm. With a 200 mL void volume of the reactor, the influent water was pre-acidified of fluoride containing water with weak edible acids, viz., acetic acid (AA), citric acid (CA) or oxalic acid (OA) and allowed to react with fixed-bed crushed limestone column for different contact time²⁷⁷⁻²⁸⁰. The effluent water was withdrawn after 3h, 6h and 12 h and used for the measurement of residual fluoride and remaining pH of the treated water. The results showed that fluoride was efficiently removed from initial 10 mg/L to below 1.0 mg/L and the final pH of the treated water was found to be within the acceptable range for drinking. However, fluoride removal efficiency decreased with increase in the number of repeated use of same limestone bed. The mechanism of fluoride removal in the AELD method was studied using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), X-ray photoelectron spectra (XPS), scanning electron micrographs and energy dispersive X-ray spectra (SEM-EDX) analysis. The dominant mechanisms for fluoride removal were reported to be precipitation of fluorite (CaF_2) by Ca^{2+} ions formed by dissolution of limestone and through adsorption of fluoride on the limestone surfaces. On the basis of the results of fluoride removal, the order of performance of the acids can be arranged as: AA<CA<OA. Though the efficiency of fluoride removal was satisfactory, the capacity of limestone for fluoride removal was low.

Nasr et al. carried out a batch experiment using limestone particle of size 2-10 μm in presence of citric acid (CA) which removed fluoride from initial 2.7 mg/L to 1.2 mg/L. They reported that adsorption of fluoride on available surface area of limestone particle along with precipitation of fluoride as CaF_2 are the major mechanism for defluoridation of water²⁸¹.

1.10.2 Phosphoric acid-enhanced limestone defluoridation

Nath has also carried out a column study using PA an acid for PA-enhanced limestone defluoridation (PAELD)²⁸⁰. For the column experiment, groundwater containing different initial F⁻ concentrations ([F⁻]₀), viz., 5, 10 and 20 mg/L pre-acidified with 0.01 M, 0.05 M and 0.10 M initial PA concentration ([PA]₀), was allowed to react with fixed-bed of limestone column of chip size of 2-3 mm. The water was partially withdrawn at 3 h, 6 h, 12 h and 24 h from the outlet of the bottom of the column and filtered through Whatman 42 filter paper and used for analysis of the respective parameters. The fluoride concentration was reported to be reduced from an initial 10 mg/L to as low as 0.01 mg/L in 3 h in the presence of [PA]₀ in the range 0.01-0.10 M. There was however hardly any further reduction in the fluoride concentration after 3 h. On the other hand, the other edible acids, viz., AA, CA and OA could not remove fluoride to below 1.0 mg/L. Thus, Nath reported PA to be much more efficient in enhancing the fluoride removal by limestone than the other edible acids. Nath also reported that the quantity of water, which could be defluoridated by PAELD, increased with decrease in [F⁻]₀.

Here, PA is neutralized by limestone as shown in the following equation²⁸⁰:



In the PAELD method, Nath reported a rapid fluoride removal in the beginning which slowed down gradually and attained equilibrium at 3 h whereas the neutralization of the acid continued up to 24 h, i.e., even after the equilibration of fluoride concentration. On the other hand, in AELD with other organic acid, both fluoride removal and neutralization of the acid continued up to 12-24 h²⁷⁷⁻²⁸⁰. The interference by the co-existing anions was found to increase in the order: NO₃⁻ < Cl⁻ < Br⁻ < SO₄²⁻. Based on information obtained from the XRD, FTIR, TGA, XPS and SEM-EDX analyses, Nath suggested formation of fluorite (CaF₂) and hydroxyapatite (HAP) in the presence of PA in the limestone column. He also concluded that in PAELD, both limestone and HAP contributed towards fluoride removal through precipitation of CaF₂, and adsorption of F⁻ on limestone surface and HAP.

Nath reported that the efficiency of the four edible acids in increasing the capacity of limestone for fluoride removal by AELD process increased in the order: AA<CA<OA<<PA. He also estimated the cost of AELD with these aids to be in the range of US\$ 1.2-48.8 per m³ with the minimum of US\$ 1.2 per m³ estimated for 0.01 M

initial PA concentration. With a high efficiency, capacity, low-cost and environment-friendliness, the PAELD in the batch mode was shown to have a great potential for application²⁸⁰

1.11 The Lacuna

In India, vast areas are contaminated with fluoride much above the WHO and BIS value of 1.5 mg/L and 1.0 mg/L, respectively. Fluoride contamination of groundwater in Assam, a north-eastern state of India, came to light in 1999⁴². But, till now, a very little effort has been taken to mitigate fluoride menace. It is obvious from the literature that there are a large number of fluoride removal methods that have been evaluated till now and among them a few methods have been tried in practical field. In fact, a fluoride removal method which is efficient, cost-effective, safe, environment-friendly and at the same time simple enough to be used by rural people is still not available.

Many adsorbents have been successfully used in fluoride removal, but they have some limitations due to their non-availability and high cost. If a material has a high potential for fluoride removal and is easily available at a particular place, the material obviously gets the priority. Limestone, a readily available geomaterial which is also available naturally in vast areas of fluoride affected areas has added its advantage. As it is evident from previous discussions, several works have been done for defluoridation of water using limestone, which is abundant and low-cost material. However, limestone alone cannot remove fluoride efficiently. Addition of different edible acids in the limestone treatment for fluoride removal increases Ca^{2+} activity of limestone facilitating fluoride removal^{249, 250, 277-280}. In addition, PA has recently been shown to greatly enhance the fluoride removal by limestone²⁴⁹.

Use of phosphoric acid as the acid for this purpose has certain advantages. PA is easily acceptable to people since it is an edible acid, used as a common ingredient in many popular beverages, and used in refining of sugar and vegetable oils, etc²⁸². PA is also approved by the US-EPA for use in water purification²⁸³. The treated water also does not have any objectionable odour. Moreover, PA being a weak acid can be handled conveniently. In PA-limestone treatment PA is expected to play important roles in fluoride removal. Aqueous PA to the fluoride solution is expected to degrade the limestone to Ca^{2+} and CO_2 gas and neutralization of PA takes place. The free Ca^{2+} is expected to precipitate the fluoride in the water as CaF_2 and reaction between PA and

limestone resulting HAP produced in-situ in the reactor which adsorb fluoride. Adsorption of fluoride on HAP may also take place through an ion-exchange between F^- and OH^- of HAP. Thus, the combined effect of precipitation and adsorption is expected to give a better capacity of defluoridation. Therefore, it was thought worthwhile to systematically investigate fluoride removal and the mechanisms of fluoride removal using PA-limestone combination in different ways, i.e., limestone powder and modified limestone powder prepared by hydrothermal treatment of limestone powder in presence of PA.

Murutu et al. reported good fluoride removal by calcined phosphoric acid treated lime^{249, 250}. Nath observed very good defluoridation of water by AELD using PA in a study using crushed limestone in plug-flow fixed-bed column²⁸⁰. The fluoride removal was suggested to occur through precipitation of calcium fluoride and adsorption of fluoride by HAP, produced in situ in the reactor. He reported fluoride removal from 10 mg/L to less than 1.0 mg/L showing the PA-crushed limestone treatment (PACLT) as a potential defluoridation method for rural applications. Seeing these results the author thought that it was interesting to study the performance of PACLT in a continuous-flow mode also. Considering the potential for rural application to assess the field performance of the PACLT method in plug-flow mode in field it was also decided to carry out a detail study of PACLT method through a laboratory-scale pilot test and, subsequently, a user trial in some fluoride affected villages of Assam.

1.12 Aim of the present work

The aim of this work was to find a solution to the drinking water fluoride contamination problem, based on PA-limestone treatment, through development of an efficient and a low-cost fluoride removal unit for domestic and small community use in rural fluoride affected areas.

1.13 Objectives

The author proposed to meet this aim with objectives set as follows:

- (i) Study of defluoridation with PA-limestone powder
 - (a) Laboratory evaluation of fluoride removal performance and suitability of PA-limestone powder method with respect to various operational

parameters including initial PA and fluoride concentrations, limestone dose, contact time, etc.

- (b) Evaluation of fluoride removal mechanism in PA-limestone powder defluoridation through equilibrium and kinetic study.
 - (c) Evaluation of the effect of operational parameters and competing ions on fluoride removal in the above studies.
- (ii) Study of defluoridation with hydrothermally modified limestone powder
- (a) Hydrothermal modification of limestone powder at different initial PA concentrations and its characterization and study of fluoride adsorption behaviour of the modified products with respect to different experimental parameters.
 - (b) Evaluation of fluoride removal mechanism by the hydrothermally modified limestone powder through equilibrium and kinetic study.
 - (c) Evaluation of the effect of operational parameters and competing ions on fluoride removal in the above studies.
- (iii) Study of defluoridation by PA-crushed limestone in continuous-flow mode
- (a) Laboratory evaluation of performance of fluoride removal in PA-crushed limestone treatment in continuous-flow mode.
 - (b) Evaluation of the effect of operational parameters and competing ions on fluoride removal in the above studies.
- (iv) Study of defluoridation by PA-crushed limestone in plug-flow mode
- (a) Evaluation of the performance and process optimization of the PA-crushed limestone treatment method for fluoride removal in plug-flow mode through a laboratory pilot-scale pilot study using model system.
 - (b) Evaluation of the effect of operational parameters and competing ions on fluoride removal in the above studies.

- (v) Field trial of defluoridation by PA-crushed limestone treatment method
 - (a) Designing and setting up of small community and domestic units of the PA-crushed limestone defluoridation in plug-flow mode in fluoride affected areas for a field trial.
 - (b) Evaluation of fluoride removal performance of the PA-crushed limestone treatment method in plug-flow mode units in the field at small community and household levels.
 - (c) Evaluation of suitability of the PA-crushed limestone treatment method in terms of potability of treated water, cost, etc.

1.14 The strategy

In order to meet this aims and objectives, the author prepared a plane of work as follows:

- (i) Study of equilibrium and kinetics of fluoride sorption on limestone powder in presence of PA.
- (ii) Synthesis of HAP hydrothermally using limestone powder and PA and study of the fluoride sorption behaviour of the hydrothermally modified limestone.
- (iii) Study of the effectiveness of fluoride removal in continuous-flow mode of operation for PA-crushed limestone treatment of fluoride-contaminated water.
- (iv) Carry out a laboratory-scale pilot test of the best performing PA-crushed limestone treatment method chosen out of those mentioned above and the plug-flow mode PA-crushed limestone treatment method developed by Nath²⁸⁰ for optimizing the PA dose and other process parameters.
- (v) Conducting a field trial of the method of PA-crushed limestone treatment in plug-flow mode in domestic and small community level at some fluoride

affected rural areas so that the author can deliver some finished products applicable for fluoride removal in low income rural areas. The field trial will involve the following steps:

- (a) Selection of sites for field trial on the basis of available data and fresh verification of them by testing samples of groundwater collected from some villages of fluoride-affected areas.
- (b) Apprising the users of our method about the health-hazards of consuming excess fluoride through drinking water and training them the application of our method for fluoride removal.
- (c) Designing and installation of the fluoride removal units at the selected villages.
- (d) Monitoring the performance of the units by collecting treated water samples for fluoride and other relevant water quality parameters.
- (e) Evaluation of the performance of the fluoride removal method.
- (f) Assessment of the suitability of the method based on on-field fluoride removal performance, environmental impact and cost aspects of the method.