CHAPTER I
GENERAL INTRODUCTION

1.1 SALT AND SALT PRODUCTION
1.1.1 Importance of salt

The story of salt is the story of mankind. Salt has played a predominant part in the development of man’s activities, trade, politics and culture from prehistoric times. One reason for its overwhelming influence is that it is the source for sodium and chlorine, two of the twelve dominant elements in the human body. These two elements have important functions in the metabolism of the body. Sodium is one of the highly reactive electropositive elements, and chlorine is one of the highly reactive electronegative elements known. Sodium chloride is formed by the complete transfer of an electron from sodium to chlorine, which is a classical example of ionic or electrovalent bond. Thus sodium chloride molecule is highly stable, and is widely distributed. All the properties of sodium chloride are due to the strong electrostatic force of attraction between the two ions. The mass number of sodium is 23 and chlorine is 35.45, and in one gram of sodium chloride, there are approximately 39.37% of sodium and 60.63% of chlorine.

Lack of these elements leads to decay and death. The other reason is that the science of chemistry has used this inexpensive and abundantly available commodity as an important raw material in today’s industry. Directly or in the form of derivatives, salt finds application in more than 14,000 ways. Salt is one of the best known minerals, and the first substance after water to have attracted human attention. Salt enjoys unique advantages as a vehicle for micronutrient fortification in most parts
of the world in terms of universal access, uniformity of consumption and low cost of fortification. Encouraged by the process made in several countries in implementing successful salt iodisation, efforts have been directed at examining the feasibility of fortifying salt with iron and other nutrients such as fluorine along with iodine. Fluoridation of edible salt profits from the experience gained in production, quality controle and monitoring in respect of the iodisation of edible salt\(^3\).

### 1.1.1.1 Salt for human consumption

Salt is a principal constituent of extracellular body fluids i.e fluids outside the cells as in the tissues, blood serum and saliva. Its concentration varies with the type of fluid being almost the same in blood serum, cerebral and spinal fluids, but less in tissue fluids, sweat and gastric juices. In the physiological system, salt functions as sodium ion and chloride ion.\(^a\) Sodium controls muscular movement including that of the heart muscles, the peristaltic movement of the digestive tract, and the transmission of message by nerve cells. The chloride ion produces hydrochloric acid required for digestion. A principal function of salt is to regulate pressure, and the exchange of fluids between the intracellular fluid and the extracellular fluid. On the otherhand excess of sodium contributes hypertension, heart, liver and stomach ulcer, stomach cancer and kidney diseases\(^4\).

For normal health, the salt concentration in the body can vary only within narrow limits. Salt that goes out of the system has to be replaced. Salt is lost mainly through sweating. It is also passed out through urine, but the amount is so regulated by the kidneys that the salt remaining in the system is maintained at the necessary level. The rice eating population of the world requires more salt than others because
salt is very deficient in rice. In temperate climate, the annual human requirement of salt is about 5 kg per year. In tropics like India, it is higher. Salt in the gastric juices and the digested food is mostly reabsorbed in the intestines, except in cases of frequent loose motions which result in salt depletion. Salt loss is high in the tropical summer under conditions of heavy manual work when excessive sweating takes place. Such loss of salt through sweating and other processes has to be made good by intake of fresh salt with food. The early man who subsisted on a meat diet had no need to add salt to his food as meat contains an adequate amount. Even today, certain Eskimo tribes living on seal meat or the Masai tribesmen of Kenya who drink the blood of cattle, do not need salt. Agricultural cereals became his staple food. These contain more potassium salts than sodium salts, and hence addition of salt to the diet became important. While herbivorous animals get their salt from salt lick, carnivorous animals get it from the flesh and the blood of the herbivorous ones.

Chronic inadequacy of salt produces loss of weight, loss of appetite, inertia, nausea and muscular cramps. Acute salt depletion as in gastroenteritis results in dehydration and reduction of blood volume, interfering with the supply of oxygen and other elements to the tissues. When this happens, the body, in an attempt to maintain the normal balance in the fluids, releases vital substances from within the cells, causing damage to health and hazard to life. Excessive heat, like the summer in deserts, results in salt depletion, and causes heat strokes especially among children. Water required to maintain sodium at the proper concentration in blood accumulates in the tissues leading to oedema. Patients are then advised to be on a low sodium diet.
1.1.1.2 Salt for animal consumption

Salt is as important for the health of animals just like of human beings. It is a part of an animal’s body fluid in almost the same concentration as in humans. Experiments indicate that insufficient salt stunts the growth of young animals, and in the case of fully grown ones produces lassitude, lowered production of milk, loss of weight and nervous diseases leading at times to death. Since fodder and plant life have little salt, domestic animals have to be given salt with their feed. In today’s modern farms, salt is also used as a vehicle for mineral supplements that are essential for good health of livestock.

1.1.2 Status of the solar salt industry in the world

The production of common salt is one of the most ancient and widely distributed industries in the world. Salt is produced by mining of solid rock deposits and by the evaporation of sea water, lake, and underground brines. The later method accounts for over 50% of world salt production today. The distribution of world salt production in 2012 surveyed by British Geological Survey (BGS) was as follows:

Table 1.1.1 Distribution of world salt production in 2012 by British Geological Survey (BGS)

<table>
<thead>
<tr>
<th>Rank</th>
<th>Country</th>
<th>2012 Salt production (Metric tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>China</td>
<td>62,158,000</td>
</tr>
<tr>
<td>2</td>
<td>United States</td>
<td>40,200,000</td>
</tr>
<tr>
<td>3</td>
<td>India</td>
<td>24,500,000</td>
</tr>
<tr>
<td>4</td>
<td>Germany</td>
<td>19,021,295</td>
</tr>
<tr>
<td>5</td>
<td>Canada</td>
<td>10,844,624</td>
</tr>
<tr>
<td>6</td>
<td>Australia</td>
<td>10,821,000</td>
</tr>
<tr>
<td>7</td>
<td>Mexico</td>
<td>10,100,935</td>
</tr>
<tr>
<td>8</td>
<td>Chile</td>
<td>8,057,130</td>
</tr>
<tr>
<td>9</td>
<td>Netherlands</td>
<td>6,513,000</td>
</tr>
<tr>
<td>10</td>
<td>Brazil</td>
<td>6,300,000</td>
</tr>
</tbody>
</table>
Country-wide production during the year 2012 is given in Table 1.1.1. Some countries depend entirely on rock salt, some on solar salt and there are a few countries where both forms are produced. While the process for solar evaporation of brines is the same all over the world manufacturing techniques and product quality vary considerably.

The demand for salt increases with growth of population as well as the development of industries. Apart from consumption for human use, heavy chemical industries chiefly chlorine, caustic soda and soda ash require salt as raw material. In the developed countries, industrial requirements of salt are more than the edible consumption. In the USA for instance, over 95 % of the total production of approximately 41 million tonnes is used for non-edible purposes. In the developing countries the trend towards increased industrial demand for salt has become apparent only during the past decades.

1.1.3 Solar salt manufacture
1.1.3.1 Salt from the sea

The oceans are the most prolific source of sodium chloride accounting for over 50 % of world production today. The reserves in the seas are estimated as 50 million billion tonnes. Apart from sodium chloride, the seas are an important source for potassium, magnesium and calcium. 65 % of magnesium metal produced in the world is from sea water. Many elements including iron and iodine are found in traces in sea water. Table 1.1.2 lists the major elements found in sea water giving their concentration and the amount present.
Table 1.1.2 Concentrations of various elements in natural sea water

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Atomic number</th>
<th>Seawater: Concentration range</th>
<th>Approximate weight concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>F</td>
<td>9</td>
<td>68 µm</td>
<td>1.3 mg/l</td>
</tr>
<tr>
<td>Sodium</td>
<td>Na</td>
<td>11</td>
<td>468 mm</td>
<td>10.8 g/ l</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg</td>
<td>12</td>
<td>53.2 mm</td>
<td>1.29 g/ l</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl</td>
<td>17</td>
<td>546 mm</td>
<td>19.4 g/ l</td>
</tr>
<tr>
<td>Potassium</td>
<td>K</td>
<td>19</td>
<td>10.2 mm</td>
<td>398 mg/ l</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca</td>
<td>20</td>
<td>10.3 mm</td>
<td>412 mg/ l</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr</td>
<td>24</td>
<td>2-5 nm</td>
<td>260 ng/ l</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn</td>
<td>25</td>
<td>0.2-3 nm</td>
<td>165 ng/ l</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>26</td>
<td>0.1-2.5 nm</td>
<td>140 ng/ l</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Co</td>
<td>27</td>
<td>0.01-0.1 nm</td>
<td>6 ng/ l</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni</td>
<td>28</td>
<td>2-12 nm</td>
<td>700 ng/ l</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>29</td>
<td>0.5-6 nm</td>
<td>380 ng/ l</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn</td>
<td>30</td>
<td>0.05-9 nm</td>
<td>590 ng/ l</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb</td>
<td>82</td>
<td>5-175 pm</td>
<td>36 ng/ l</td>
</tr>
</tbody>
</table>

Most of seawater’s constituents are inorganic ions. Figure 1.1.1 shows the primary ions present by weight. Sodium and chloride, the two ions in table salt, are the two primary ions in seawater. Salt consists of 19,000 ppm of chloride, and 10,500 ppm of sodium, and they comprise 54% and 30% of the total weight of ions in seawater respectively. The next two most common ions, sulphate (at 2700 ppm) and magnesium (at 1280 ppm) comprise 7.7% and 3.7% of the weight of seawater ions respectively. Together, these four ions comprise almost 96% of the weight of ions present.  

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1.1.4 Methods of crystallization of salt

1.1.4.1 Solar evaporation method

This is the oldest method of salt production. It has been used since salt crystals were first noticed in trapped pools of sea water. Its use is practical only in warm climates where the evaporation rate exceeds the precipitation rate, either annually or for extended periods, and ideally where there are steady prevailing winds. Solar salt production is typically the capturing of salt water in shallow ponds where the sun evaporates most of the water. The concentrated brine precipitates the salt which is then gathered by mechanical harvesting machines. Any impurities present in the brine are drained off, and discarded prior to harvesting.
Usually two types of ponds are used. The first is the concentrated pond, where the salty water from the ocean or salt lake is concentrated. The second is called the crystallizing pond, where the salt is actually produced.

Crystallizing ponds range from 40 to 200 acres with a foot-thick of salt resulting from years of depositions. During the salt-making season of four to five months, brine flows continuously through these ponds. This is a saturated brine solution, containing as much salt as it can hold.

1.1.4.2 Vacuum Evaporation Method

Another method of salt production is the evaporation of salt brine by steam heat in large commercial evaporators, called vacuum pans. This method yields a very high purity salt, fine in texture and principally used in those applications requiring the highest quality salt.

The first part of the operation is known as solution mixing. Wells are drilled from 100 to 1,000 feet apart into the salt deposit, and these wells are connected via lateral drilling, a recently developed technology. Once the wells are connected, the solution mining operation begins, and water is pumped down into a well. The salt below is dissolved, and the resulting brine is forced to the surface through the other well, and it is then piped into large tanks for storage.

The brine is pumped into vacuum pans, these are huge closed vessels under vacuum. They are normally arranged in a series of three, four or five with each one in the line under greater vacuum than the preceding one. This series of vacuum pans are operated on a very simple principle. Whenever pressure is lowered, the temperature at which water will boil is also lowered. For instance, under normal air pressure at sea
level, water boils at 212°F, but at ten thousand feet above sea level, where air pressure is much less, water boils at 194°F, and vacuum pans may operate at as low as 100°F.

In the vacuum pan process, steam is fed to the first pan, and this causes the brine in the pan to boil. The steam from the boiling brine is then used to heat the brine in the second pan, and the pressure is reduced still further in the previous pan to boil the brine in the next pan. While the boiling operation could be done with several pans in a row, produce more salt per pound of steam, thus allowing greater energy efficiency.

1.1.5 Crystallization of salt in salt pan

The order of separation of the dissolved salts depends on their relative solubility. Calcium carbonate being the least soluble separates out first and the highly soluble magnesium salts are separated last. In studying phase chemistry, brine concentration is given on the Baume scale which is defined as

\[ ^\circ\text{Be} = 145 - \frac{145}{\text{Specific gravity of the brine at } 15^\circ\text{C}} \]

The evaporation process is conveniently divided into four distinct phases\(^9\). The first phase is from 3\(^\circ\)Be to 13\(^\circ\)Be, and most of the carbonates are precipitated as salts of iron, magnesium and calcium. While iron carbonate and magnesium carbonate are crystallized completely at 13\(^\circ\)Be, calcium carbonate is crystallized up to 90%, and the remaining 10% precipitated at 15\(^\circ\)Be in the next phase. These carbonates have little practical value.

The second phase, extending from 13\(^\circ\)Be to 25.4\(^\circ\)Be, centers round gypsum, and this is crystallized as needle shaped crystals of CaSO\(_4\).2H\(_2\)O. 85% of the calcium
sulphate present is precipitated in this phase. The precipitation of the remaining 15 % is spread over the third and fourth phases in decreasing amounts, right until evaporation is complete. Gypsum is used in the production of cement and plaster of paris. It is also of immediate value in a solar salt works since its crystals are used to pave the pond floors, thus preventing leakage of brine into the soil.

![Fig: 1.1.2 Crystallization started in the salt bed](image)

The third phase extends between 25.6°Be and 30°Be. Common salt (NaCl) is precipitated out in this phase. Crystallization starts at 25.6°Be, and its rate rapidly increases in the initial stages (Fig. 1.1.2). 72% of the total amount is precipitated by 29°Be, and 79 % by 30°Be. At higher levels of salinity the crystallization slows down considerably, and is complete only with the completion of evaporation. The concentration at which sodium chloride starts to crystallize is known as the salting point, and the mother liquor at this point is called the pickle. At the end of the phase, when the concentration is 30°Be, the liquor is called bittern because of its characteristic bitter taste.
Sodium chloride is formed as cubic crystals, and it is colourless, odourless and has a characteristic taste. It has a specific gravity of 2.165 and a molecular weight of 58.45, and its solubility in water varies only slightly with temperature.

Though salt is the predominant precipitate in the third phase, it is not pure because gypsum is also precipitated especially in the earlier stages. At the higher concentration near 30°Be, some bromides, potassium chloride and magnesium sulphate from the fourth phase appear. The technique of salt manufacture involves fractional crystallization of the salts, and sodium chloride is obtained in the purest form.

According to typical standards adopted in developing countries, the purity required is 99.5% for grade I industrial salt, 98.5% for grade II industrial salt, 96.0% for edible common salt, 99.6% for dairy salt, and 97.0% for table salt. In advanced countries the specifications are more stringent, the minimum purity prescribed for table salt being 99.5%.

The considerable shrinkage in the volume of brine takes place during salt manufacture. The volume of water is 19% of the original at the beginning of phase I when gypsum starts crystallizing, 9% at the salting point when salt crystallizes, and 3% when phase III ends, and bittern is formed\textsuperscript{11}.

The relation of vapour pressure of brine vs vapour pressure of fresh water is dependent upon fresh water temperature and Mg\textsuperscript{2+} concentration. The relative rate of brine evaporation depends upon this vapour pressure of brine vs vapour pressure of water and the relative humidity. The evaporation of bittern to produce by products is known to salt makers to be a tediously slow process.
The chemistry of phase IV relating to the evaporation of the bittern is complex. A number of sulphates of potassium and magnesium and potassium chloride separate out either singly or as double crystals in equilibrium or in metastable conditions. The phase chemistry affects weather conditions. Normally bitterns are not utilized, but under certain conditions, recovery of byproducts of potassium, magnesium and bromine becomes economical. These conditions are that there should be an adequate market nearby, and the solar salt operations must be on a large scale, producing more than 100,000 tonnes of salt per year. The recovery processes are complex. A brief account of the chemistry is now given.

If the bittern is concentrated by evaporation without precipitating potassium salts, a mixture of the remanent sodium chloride and magnesium sulphate is separated out. This fraction is known as mixed salt I. The mother liquor is further evaporated when a mixture of sodium chloride, potassium chloride and carnallite called mixed salt II is obtained. Other potassium salts precipitating between 36°Be and 38°Be are kainite, schoenite, glasserite, sulphate and langbeinite. Beyond 38°Be, the mother liquor consists predominantly of magnesium chloride with a small proportion of bromides.

1.1.5.1 Underground brines

The salinity of underground brines is much higher than that of sea water, and sometimes as much as eight times. Underground brine is considered to be sea water cut off from oceans by early geological changes and concentrated by periods of sunlight before being covered by further geological deposits. There are also brines formed by the flow of underground water amongst weak salt deposits.
The composition of underground brines varies widely. The composition of brines close to sea coasts is similar to sea water evaporated to the same concentration with minor variations. Sometimes the calcium sulphate content is higher, and in other cases the KCl:NaCl ratio is higher than that of sea water. In certain inland underground brines, potassium and magnesium salts are totally absent, and sodium sulphate is the only constituent other than sodium chloride.

Fig. 1.1.3 Underground water is used for making salt.

Underground brines occur at varying depths from very shallow levels of 3 metres to the depths of more than 200 metres. Underground sources are tapped by sinking borewells (Fig.1.1.3), and pumping the brine to the surface and subjecting it to an evaporation process similar to sea brine.

1.1.6 New technologies employed in salt production

In many places in India old technologies are used for salt production. But Central Salt & Marine Chemicals Research Institute (CSMCR) and others launched new methods for the preparation of common salt of high purity from brines in solar salt pans.
1.1.6.1 Production of spherical small size salt

Nearly spherical morphology of solution-grown NaCl particles in the size range of 300–1000 μm was achieved at 55–60°C employing a suitable crystallizer equipped with a butterfly wing-shaped impeller operated at 250 rpm. Morphology control was equally effective with synthetic and natural brines and required no habit modifier. Sieved spherical salt of 350–500 μm size exhibited superior flow as compared to commercial vacuum evaporated free flow cubic salt of comparable dimension—upon treatment with potassium ferrocyanide anticaking additive. The superior flow characteristic was retained even after 3 months of storage. Scanning electron microscopic studies revealed that the round polycrystalline particles were derived from the stacking of minute NaCl cubes and the average size of the spheres was amenable to reduction through use of ethanol as antisolvent. The process was successfully scaled up to 10 kg level\(^1\)\(^2\).

1.1.6.2 Production of high purity salt

A process for production of high purity salt with reduced level of impurities by solar recrystallization of solar sea salt using seawater medium\(^1\)\(^3\), said process comprising the steps of:

i. Adding the salt prepared by known method into seawater upto saturation level to obtain saturated brine;

ii. Spreading the saturated brine as obtained in step (i) in a pre-crystallizer to effect solar evaporation till 27°Be saturated brine;

iii. Draining out the saturated brine of 27°Be as obtained in step (ii) into a second crystallizer;

iv. Heaping and washing the salt with water to obtain high purity salt;
v. Adding seawater into the pan to restore the original volume and thereafter adding more salt up to saturation point;
v. Repeating the process of evaporation in (ii) above;
vi. Once again harvesting more salt;
vii. Discharging the saturated brine of 27°Be into the pre-crystallizer.

1.1.6.3 Remote monitoring of brine density in salt works

This method relates to a novel device that enables a person to gauge the brine density in solar salt works from afar without recourse to sampling of the brine. The device—which can be considered as an improvisation over the conventional laboratory type Baume meter can be placed directly in the salt pan. The device remains sunk, and therefore invisible, until the desired density of brine is approached. Thereafter it gradually floats up and becomes visible from afar. From appropriate markings on the rod connected to the top end of the device, it can be gauged whether the brine is yet to attain the desired density, or has attained the desired density range, or has exceeded the desired density range. The device is resistant to corrosion and able to combat extreme weather conditions prevailing in solar salt works. The control of brine density from afar helps eliminate the need for frequent sampling of brine for density measurement that would make adherence to the optimum process of salt production easier.

1.1.6.4 Production of ultra pure salt

The method for producing ultra pure salt, containing below 500 parts per billion (ppb) of calcium and other multivalent metal ions, Comprises:

Acidifying primary treated brine from pH 9.5 to 12 to pH 2 to 4, thereby converting the calcium, barium, strontium, and other reactive multivalent metal
compounds to soluble chlorides. Such acidification also converts excess sodium carbonate and hydroxides to salt, water, and dissolved carbon dioxide, and removes the carbon dioxide by stripping. The stripped material is neutralised to a pH of at least 6 but not exceeding 8, thereby preventing metals corrosion at pH less than 6, and carbon dioxide uptake from the surroundings, at pH above 8. The neutralized stripped brine is concentrated, and the crystals produced are washed to produce ultrapure salt crystals\textsuperscript{15}.  

1.2 CHEMISTRY OF FLUORINE

Fluorine is the first element of VII A group, the halogen family in the periodic table. Halogen means salt producing element (Halo means salt, and gens means producer). Its electronic configuration is [He] 2s\textsuperscript{2}2p\textsuperscript{5}. The fluorine atom having no d orbital electrons in its valence shell, and cannot have any higher oxidation states and it has negative oxidation state of -1. It being the most electronegative element known. Fluorine exists as diatomic covalent molecule (F\textsubscript{2}). The force between the discrete molecules are only weak Vander walls forces which explain the volatile nature of fluorine. The small F\textsubscript{2} molecules absorb high energy radiation, and appear yellowish in colour. Fluorine’s atomic radius is 0.72 Å, and the ionic radius of fluoride (F\textsuperscript{-}) ion is 1.36 Å. The density of fluorine is 1.580 g cm\textsuperscript{-3}. It is having greater ionization energy (1681 kJ mol\textsuperscript{-1}) than other halogens. The bond energy, the heat of dissociation of fluorine molecule is very low, and it is about 159 kJ mol\textsuperscript{-1}. This is due to the repulsion between non-bonding electrons. Though electron affinity of fluorine (333 kJ mol\textsuperscript{-1}) is less than that of chlorine (348 kJ mol\textsuperscript{-1}), Fluorine is the strongest oxidizing agent. It oxidizes water to oxygen with large evolution of heat.
\[
\text{F}_2(g) + \text{H}_2\text{O}(l) \rightarrow 2\text{H}^+(aq) + 2\text{F}^-(aq) + \frac{1}{2} \text{O}_2(g); \quad \Delta G = -795 \text{kJ mol}^{-1}
\]

Fluorine is the most reactive element, and the reactivity decreases with increase in atomic number in the group. The reactivity of fluorine is due to high electronegativity, small size, extremely high oxidizing power and low energy of the F-F bond. Due to the high electronegativity it forms very strong bonds with other elements. Highly electropositive alkali metals and alkaline earth metals burn spontaneously in fluorine at room temperature forming fluorides, e.g., NaF and CaF₂. Affinity for hydrogen decreases from fluorine to iodine. Fluorine has such a high affinity for hydrogen that it explodes or reacts very vigorously with hydrogen, hydrogen compounds like water and hydrocarbons even in the dark. Its compounds have properties that are distinct relative to other halides structurally, and to some extent chemically, the fluoride ion resembles the hydroxide ion. The range of fluorine-containing compounds is vast because fluorine is capable of forming compounds with all the elements except helium and neon.

Living organisms are mainly exposed to inorganic fluorides through food and water. Based on quantities released and concentrations present naturally in the environment as well the effects on living organisms, the most relevant inorganic fluorides are hydrogen fluoride (HF), calcium fluoride (CaF₂), sodium fluoride (NaF), sulphur hexafluoride (SF₆), and sodium silicofluorides (Na₂SiF₆). Flouride is exposed to the atmosphere during the burning of coal also.
1.2.1 Anomalous nature of Fluorine

Ionization potential, electronegativity and electrode potential are higher than expected. Ionic radii, covalent radii, melting point, boiling point, bond dissociation energy and electron gain enthalpy are low.

1.3 FLUORIDE IN THE NATURAL ENVIRONMENT

The fluorides are widely distributed in nature, and it has been estimated that the element fluorine in the form of fluoride constitutes about 0.032 % of the earth’s crust in four kinds, such as rock forming minerals, rocks, commercial ores and soils. The fluorides are used industrially in the production of aluminum, and are commonly present in phosphate fertilizers, bricks, tiles, and ceramics. They are also used in metallurgy\(^{21}\).

\(^{22}\)The major fluoride bearing minerals found in the earth’s crust are fluorite (CaF\(_2\)), fluoroapatite (Ca\(_5\)(PO\(_4\))\(_3\)F), cryolite (Na\(_3\)AlF\(_6\)), and topaz (Al\(_2\)SiO\(_4\)(F,OH)\(_2\)).

\(^{23}\)Fluorine ranks thirteenth among the elements in the order of abundance in earth’s crust averaging 650 ppm. Fluoride is widely dispersed in the environment accounting for 0.38 g/kg of the earth’s crust\(^{25}\).

Fluoride is found not only in all kinds of rocks, igneous and sedimentary, and in water in various amounts, but also in many organisms. Generally the content of water is not dangerous for human, but in some cases weathering of rocks, specially volcanic rocks increases the amount of fluoride. Industrial dusts can also provoke some diseases\(^{25}\). Many fluoride minerals are known, but of paramount commercial importance are fluorite and fluorapatite\(^{26}\).
In the igneous rocks the major F-bearing minerals are apatite and fluorite. Apatite is more abundant but less rich in fluorine in the basic rocks (2 % in gabbros) than in the acid ones (3 to 4.5 % in granodiorites). Fluorite, a frequent mineral in hydrothermal veins, is present in a small proportion in the common igneous rocks.

It was analyzed that the waste emitted into the atmosphere from enameling plants polluted air with fluoride content varying from 50 to 80 %. Fluoride levels of rain water in industrial areas of Germany ranged from 0.28 ppm to 14.1 ppm depending up on the kind of industry.

1.4 SOURCES OF FLUORIDE

1.4.1 Rocks

In minerals the ions F$^-$ and OH$^-$ have very close ionic radii, and if F$^-$ can be the major anion of some minerals like fluorspar (CaF$_2$) and topaz (Al$_2$SiO$_4$(F,OH)$_2$), it is also in F-bearing minerals, an isomorphous replacement in the OH$^-$ position. For this reason many minerals usually contain fluoride. In sedimentary rocks there are few fluoride-bearing minerals, apatite, aragonite, clay minerals, opal, of which only the apatite contains more than 1% fluorine by weight.

1.4.2 Flora & fauna

The fluoride contents of plants are generally low except in tea which can contain up to 400 ppm. Roots and leaves generally have higher fluoride content than fruits, seeds, stems, woods or barks. Plants exposed to fluoride in the atmosphere accumulate it in their foliage, which may affect the growth and development of the plants. Plants absorb or release atmospheric fluoride by their above-ground parts because fluoride uptake is a reversible process governed by climatic conditions such
as exposure to rainfall and wind. All vegetation contains some $F^-$ which is absorbed from the soil and water$^{29}$.

The water with high fluoride content when used for irrigation in agricultural farms affects the vegetation$^{30}$. The fluoride levels in herbaceous vegetation leaf samples from perennial trees around 5 km of Indian Aluminium Company at Hirakud were studied. The fluoride level in herbaceous vegetation samples varied from 2.5 to 80 $\mu$g/g. The average fluoride contents were 24.4, 23.12, 18.33, 2.0 and 2.0 $\mu$g/g at 0-1, 1-2, 2-3 and 4-5 km distance respectively. The average fluoride content in herbaceous vegetation is 15.97 $\mu$g/g. Thus at the greater distance fluoride content is significantly less. The fluoride present in the soil contaminates all the water sources which in turn leads to accumulation of fluoride in all vegetation$^{31}$. Vegetation having high fluoride content is responsible for fluorosis in live stock$^{32}$.

Various plant biomasses are known to solubilize transport, and absorb several ionic species from the aqueous solution. Water – hyacinth has been known for its efficiency in removal of different metallic and mineral species from water bodies. Capability of fluoride biosorption by dry water hyacinth plant is less investigated and understood. This aquatic weed has great proliferation rate and property of adsorption of various ionic species from aqueous solution. Though every part of the hyacinth plant absorbs fluoride it is more with the root organ$^{33}$.

The water used for irrigation in the southern part of Moldova contains relatively high levels of fluoride. The effect of this water on the fluoride content in wheat was studied during a 5 year period. The irrigation of wheat with fluoride containing water increased the content of fluoride in plants especially at the stage of
tillering and in stems at the stage of booting. High levels of fluoride in soil were observed after irrigation with fluoride containing water\textsuperscript{34}.

Fluoride in the atmosphere enters plants through stomatal diffusion\textsuperscript{35}. Fluoride is also taken up by plant roots, and is then transported via xylem to different parts of the plant where it accumulates\textsuperscript{36-39}. Moreover, aquaporins may be involved in the transmembrane transport of F\textsuperscript{−}. The effect of F\textsuperscript{−} on germination and physiological and biochemical characteristics in different plant species is negatively correlated\textsuperscript{40,41}. Excess F\textsuperscript{−} absorption induces phytotoxicity symptoms with ultrastructural changes in leaves\textsuperscript{42}, and may enhance enzymes that mitigate reactive oxygen species\textsuperscript{43}.

Animals obtain their fluoride from plants that they eat, and water they drink\textsuperscript{32}. Aquatic organisms take up fluorides directly from water or to a lesser extent via food, and tend to accumulate fluoride in their exoskeleton or bone tissue. More than 2000 mg/kg of mean fluoride concentration have been measured in the exoskeleton of krill while, but bone fluoride concentration in aquatic mammals, such as seals and whales, ranged from 135 to 18600 mg/kg dry weight\textsuperscript{20}.

Fluoride toxicity to aquatic invertebrates and fishes increases with increasing fluoride concentration, exposure time, and water temperature. Fresh water invertebrates and fishes, especially net-spinning caddisfly larvae and up stream-migrating adult salmons appear to be more sensitive to fluoride toxicity than estuarine and marine animals\textsuperscript{44}. Samples of Antarctic krill (Euphausia superba), and Atlantic krill (Meganyctiphanes norvegica) were analysed for fluoride using a selective fluoride electrode method. Both species showed very high concentrations, a total of 1330-2400 mg F\textsuperscript{−}/kg on fat free dry weight basis in raw samples whereas deep sea
prawns (Pandalus borealis) showed a total of 18-91 and red feed (Calanus finmarchicus) 10-37 mg F/kg\textsuperscript{45}.

The concentrations of fluoride in dietary dry matter above which normal performance may be affected are beef 40 ppm, horses 60 ppm, and breeding hens 400 ppm\textsuperscript{34}. Fluoride levels in terrestrial animals and plants are higher. Lichens, which have been used extensively as biomonitor for fluorides, generally contain less than 1 mg fluoride/kg (background level), but at a distance of 2 to 3 km from fluoride emission sources, and its mean concentration ranges from 150 to 250 mg/kg. Bones of amphibians and cows were collected around 5 km radius INDIAL smelter at Hirakud. The bones of cows showed an average fluoride level of 20 μg/g, whereas amphibians showed 8.3 μg/g\textsuperscript{31}. Fluoride accumulates in the bone tissue of terrestrial vertebrates, depending on factors such as diet and the proximity of fluoride emission sources. For example, mean fluoride concentrations of 7000 to 8000 mg/kg have been measured in the bones of small mammals living near an aluminium smelter\textsuperscript{20}.

1.4.3 Water

The amount of fluoride present naturally in drinking water is highly variable depending on the specific geological environment from which the water is obtained. In non-fluoridated drinking water i.e., drinking water to which fluoride has not been intentionally added for the prevention of dental caries levels may reach up to about 2.0 mg/litre. However, some places can have fluoride levels in drinking water up to 20 mg/litre. The areas in which drinking water is fluoridated, the concentration of fluoride in drinking water generally ranges from 0.7 to 1.2 mg/litre\textsuperscript{20}.  

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The content of fluoride in ground water is generally lower than the critical limit of 1.5 mg/l or ppm, but in some places it can reach more than 1.5 ppm. The level of fluoride in bore well salt pan from a study at Ramanathapuram, Ramanathapuram District, India was around 1.5 mg/l\textsuperscript{16}. The ground waters associated with hot springs are special, and can reach some tens of ppm. Many authors studied about rivers and lakes around the world, and their results gave a content generally lower than 0.4 ppm fluoride. It is noted that with increasing use of fertilizers today, the fluorine content of surface water can also increase. Approximately 20 to 400 g fluoride per hect. are annually leached from soils. It means that the same amount is added to the soil from the atmosphere, but fertilizing adds 5 to 30 kg fluoride/hect. annually. A part of this fluorine can be absorbed by the minerals of soils especially clay mineral, but it is not known how it is retained\textsuperscript{25}.

Fluoride is considered as a major element being present in sea water at concentrations>1mg/kg. The average fluoride concentration in sea water is 1.3 mg kg\textsuperscript{-1} at salinity 35 \times 10\textsuperscript{-3}. Studies at Tamil Nadu, India also proved this\textsuperscript{47-52}. However, since it lies on the borderline between major and minor elements, its behaviour, conservative or non-conservative, is yet to be fully understood. Average fluoride concentration in river water is given as 0.1 mg/kg\textsuperscript{53,54}. Fluoride is ubiquitous in the environment, and therefore sources of drinking water are likely to contain at least some amount of fluoride. The amount of fluoride present naturally in non-controlled fluoridated drinking water (i.e. drinking water to which fluoride has not been intentionally added for the prevention of dental caries) is highly variable, being dependent upon the individual geological environment from which the water is obtained.
Fluorine is in the dynamic balance of two geochemical processes, enrichment and leaching, reflecting the adsorption and desorption of fluoride by clay minerals respectively. The two geochemical processes of fluorine in soil are influenced by factors including geochemical characteristics of soil and clay minerals, pH, climate, grazing and agriculture activities. Main factors controlling enrichment and leaching process of fluorine in soil can be found with interaction consideration.

Water is the principal medium of fluoride intake by the human population. The contribution of fluoride rich ground water is due to the leaching process of fluoride bearing minerals in the igneous, metamorphic and sedimentary rocks. High levels of fluoride in drinking water are found in some countries such as India, China, Japan and part of Middle East and Africa. In these areas cases of osteosclerosis and crippling fluorosis have been observed. In the U.S., two thirds of Americans tap water contains fluoride, which is added under the guise of preventing cavities, water fluoridation continues to occur in the majority of the U.S. even as research stack up that fluoride is a neurotoxin that can harm brain function. A study of Mexican women and children is among the latest to raise concern, showing that higher exposure to fluoride while in utero is associated with lower scores of tests of cognitive function in childhood, both at the age of 4 and 6 to 12 years.

Generally river water contains less fluoride than the ground water. When the river passes through the areas with fluoride bearing minerals, fluoride content in river water is significant. For example Kongal river of Nalgonda district, Andhrapradesh flowing over Achaean granites records 12 ppm of fluoride. In rain water presence of significant amount of fluoride is possible only in industrialised areas with fluoride emitting industries like phosphate fertilizer industry, aluminium manufacturing industry, poly tetrafluoro ethylene industry etc. Otherwise rain water consists less amount of fluoride.
Godavari river (16°-83°3’E) starts from Nasik district near the western ghats, and traverses across the Indian Peninsula shield. It covers an area of \(3.1 \times 10^5\) sq km in the central and southern parts of Indian subcontinent. It branches into two major distributaries, namely the Gouthami-Godavari and Vasishta-Godavari. The Gouthami-Godavari estuary covers a distance of 44 km, and it is tidal. The tide is semi-diurnal, and its range as recorded from the annual tide tables in the vicinity of the estuarine region was 1.9 – 4.0 m. The fluoride levels of various river waters in India are shown in the Table 1.4.1.

### Table 1.4.1 Fluoride levels of various river waters in India

<table>
<thead>
<tr>
<th>River</th>
<th>Location</th>
<th>Fluoride (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ganga</td>
<td>Rishikesh, UP</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>Rajmahal, Bihar</td>
<td>0.35</td>
</tr>
<tr>
<td>Hooghly</td>
<td>Dakshineswar, WB</td>
<td>0.35</td>
</tr>
<tr>
<td>Narmada</td>
<td>Jamtara, Jabalpur, MP</td>
<td>0.10</td>
</tr>
<tr>
<td>Netravati</td>
<td>Mangalore, Karnataka</td>
<td>0.10</td>
</tr>
<tr>
<td>Periyar</td>
<td>Alwaye, Kerala</td>
<td>0.10</td>
</tr>
<tr>
<td>Chalakudiyar</td>
<td>Chalakudiyar, Kerala</td>
<td>0.10</td>
</tr>
<tr>
<td>Mahanadi</td>
<td>Rajim, MP</td>
<td>0.10</td>
</tr>
<tr>
<td>Indravati</td>
<td>Chitrakut, MP</td>
<td>0.40</td>
</tr>
<tr>
<td>Vekkilu</td>
<td>Chagla marri, AP</td>
<td>1.50</td>
</tr>
<tr>
<td>Krishna</td>
<td>Vijayawada, AP</td>
<td>1.00</td>
</tr>
<tr>
<td>Paleru</td>
<td>Rajapet, AP</td>
<td>1.50</td>
</tr>
<tr>
<td>Sabri</td>
<td>Chittoor, AP</td>
<td>1.00</td>
</tr>
<tr>
<td>Indravati</td>
<td>Bhopal Patnam</td>
<td>1.00</td>
</tr>
<tr>
<td>Bhima</td>
<td>Yadgir, Karnataka</td>
<td>1.50</td>
</tr>
<tr>
<td>Pennar</td>
<td>Pamidi, AP</td>
<td>1.50</td>
</tr>
<tr>
<td>Vaigai</td>
<td>Madurai, Tamil Nadu</td>
<td>1.00</td>
</tr>
<tr>
<td>Amaravathi</td>
<td>Darapuram, Tamil Nadu</td>
<td>1.00</td>
</tr>
</tbody>
</table>
1.4.4 Food

Virtually all foodstuffs contain at least a trace amount of fluoride. Elevated levels are present in fish and in tea leaves, which are particularly rich in fluoride. Although the concentration of fluoride in food products is not significantly increased by the addition of superphosphate fertilizers containing fluorides as impurities to agricultural soil. The use of water containing relatively low levels (less than about 3 mg/litre) of fluoride for crop irrigation generally does not increase fluoride concentrations in foodstuffs, but this depends on plant species and fluoride concentrations in soil and water. However, the level of fluoride in foods is significantly affected by the fluoride content of the water used in food preparation or processing, particularly in beverages and dry foodstuffs to which water is added prior to consumption, such as powdered baby formula. The concentrations of fluoride in unwashed or unprocessed foods grown near industrial fluoride sources may be greater than the levels in the same foods grown in other non-industrially exposed areas. Fluoride has been detected in breast milk at concentrations up to 100 µg/litre, with most measurements ranging between 5 and 10 µg/litre\textsuperscript{20}.

There have been many incidences of fluorosis where fluoride in food was identified as the main source of fluorides. One extreme example is prevalence of dental fluorosis among the native people of South Atlantic Island consuming water with 0.2 ppm fluoride only, and fish with 7 mg/kg of fluoride\textsuperscript{61}. Weizan – dao et al discovered skeletal fluorosis in the Bijie country in western part of Guizhou Province, China where fluoride in the water was 0.18 ppm\textsuperscript{62}. The average fluoride consumed through food to an extent of 7.6 mg/day was established as
the cause of the disease. In all such cases food is identified as main source of fluorides, and food born fluorosis has been stressed up on recent times.

1.4.5 Tooth paste

Dental products such as tooth paste, mouth wash and fluoride supplements have been identified as significant source of fluoride. Tooth pastes for adults that are commercially available generally contain fluoride at concentrations ranging from 1000 to 1500 µg/g, whereas those designed for children contain 250 to 500 µg. The concentration of fluoride in mouth rinses varies with the recommended frequency of use from 230 to 1000 mg/litre20.

1.4.6 Industrial sources

Fluoride is released to the environment (air, water and soil) via exhaust fumes, process waters and waste from various industrial processes, including steel manufacture aluminum, copper and nickel production, phosphate fertilizer production, and use glass bricks and ceramic manufacturing glue and adhesive production. The use of fluoride containing pesticides as well as the fluoridation of drinking water supplies also contributes to the release from anthropogenic sources. Out of these the major contribution is from phosphate fertilizer production and phosphate ore production. Some of the important fluoride bearing compounds are given below.

1.4.6.1 Hydrogen fluoride (HF)

Hydrogen fluoride an important industrial compound with an estimate annual world consumption is more than 1 million tonnes62. It is manufactured from calcium fluoride, and is used mainly in the production of synthetic cryolite, aluminium fluoride, motor gasoline alkylates and chlorofluoro carbons. It is also used in the
synthesis of uranium tetra fluoride and uranium hexa fluoride, both of which are used in nuclear industry\textsuperscript{63}.

1.4.6.2 Calcium fluoride (CaF\textsubscript{2})

Calcium fluoride is used as flux in steel glass and hydrofluoric acid or hydrogen fluoride\textsuperscript{63}.

1.4.6.3 Sodium fluoride (NaF)

Sodium fluoride is prepared from hydrofluoric acid and sodium carbonate or sodium hydroxide. It is used in the controlled fluoridation of drinking water, as a preservative in certain glues in glass, and enamel production, as flux in steel and aluminum production, as an insecticide, and as a wood preservative\textsuperscript{64}.

1.4.6.4 Fluorosilicic acid (SiF\textsubscript{6})

Fluorosilicic acid is a liquid which is most commonly obtained as a coproduct in the manufacture of phosphate fertilizers. It is widely used for the fluoridation of drinking water.

1.4.6.5 Sodium hexafluoro silicate (Na\textsubscript{2}SiF\textsubscript{6})

Like fluorosilicic acid sodium hexafluoro silicate is also used in the fluoridation of drinking water.

1.4.6.6 Sulphur hexafluoride (SF\textsubscript{6})

Sulphur hexafluoride is used extensively as an insulation and current interruption medium in electrical switchgears, such as power circuit breakers and as protective inert gas over molten metals such as magnesium and aluminum.
1.4.6.7 Fluorapatite (Ca$_5$(PO$_4$)$_3$F)

Fluorapatite, an important calcium and fluoride–containing minerals, is used as a source of phosphate in the fertilizer industry$^{65}$. 

1.5 THE FLUORINE CYCLE IN NATURE

In nature, fluorine enters water bodies from rocks by weathering. In this process the solubility and the hydrolysis of minerals are important. These solubilities are different (CaF$_2$, 0.016 g/l, MgF$_2$, 0.13 g/l, Na$_3$AlF$_6$, 0.42 g/l, NaF, 40 g/l, HF and SiF$_4$ hydrates)$^{66}$, and of course, the most soluble mineral provides more fluorine to percolating water. But these solubilities are generally low and the fluorine goes very slowly in solution and during its travel it can be temporarily fixed on clay minerals. For this reason, in the most common cases, continental waters contain a low amount of fluorine and the transportation from continent to ocean is probably more efficient through particles floating in the river than through solution$^{67}$. In the oceans the fluorine is injected by rains and rivers and removed by incorporation into the carbonate of organisms or fixation on clay minerals. Formation of phosphorites plays, probably, an important role. The budget of fluorine in the oceans is with injection five to eight times more important than removal. Examples which show the influence of weathering are in the Black Greek aquifer system of Harry and Georgetown Counties in South Carolina, Zack$^{68}$ observed that variations of fluoride contents from 0.5 to 5.5 ppm, the highest amounts being found with the highest amounts of sodium bicarbonate. The fluoride would be provided by the fluorapatite of fossil shark teeth contained in a neighboring formation. Fluoride ions would be liberated to the groundwater system through anion exchange. In East Africa, where the problem of excess of fluorine in water is well known, Kilham and Hecky$^{69}$ examined lakes and rivers to
elucidate processes of fluoride acquisition, concentration, removal, etc… The range of concentrations (0.02 to 1617 ppm) is the greatest found anywhere. A strong correlation is found between the concentration of fluoride and the predominant crystalline rocks of particular drainage basin and the F/Cl ratio in surface waters. This fluoride is concentrated by evaporation in the lakes whereas it may be removed from pore waters as fluorite and more possibly as fluorapatite. In these countries, the high fluoride concentrations seem to have an influence on the distribution of zooplankton, phytoplankton, and even on higher aquatic plants. It was also reported that the concentration of fluoride in the ground water of Kenya was above 5 ppm in 20% of the 1286 boreholes studied, which is in close association with the distribution of volcanic rocks occurring in the Rift valley area.

Gaseous fluoride generally enters plant by diffusion through the stomata on leaf surface and it is generally considered to be retained in the leaves, with redistribution occurring predominantly towards leaf extremities. Uptake of gaseous fluoride through surfaces other than the stomatal pores is considered to be limited, and generally is ignored. Rates of fluoride uptake will generally be proportional to stomatal conductance and rates of transpiration.

A less common liquid pathway of atmospheric fluoride uptake is through diffusion of ions in solution across the cuticle of the leaf, stem or fruit surfaces, with accumulation again occurring in the organs into which the fluoride is absorbed. There are few reports of fluoride uptake by aerial plant parts from liquid although Zhang et al. and Zhang and Huang reported black tip and stunted fruit disorders of mango that could be replicated by immersing fruits in solutions containing fluoride at
150 mg/l or more. Fluoride may also be absorbed in sufficient quantities from solutions on the surface of leaves, flowers, and fruits to cause acute injury symptom or slower-developing growth defects.

Fluoride may be lost from vegetation as a result of leaching by rain or volatilization or by the shedding of plant parts. It may be sequestered in relatively non-toxic forms in soils and in the tissues of same plant species, but it is not metabolized to the same extent as sulphur or nitrogen. Therefore, intermittent exposure to fluoride in the environment will usually result in progressive increases in foliar fluoride concentration and its consequent effects. This progressive injury is most apparent where several annual cohorts of leaves may be retained on a plant. As a result, fluoride exposure may cause sensitive perennial plant species to show reduced foliage density in their crowns, with consequent reduction in the shoot growth and the capacity recover from other forms of stress such as fire, drought or defoliation by insects.

1.6 USES OF FLUORIDE

- Fluoridated drinking water is one of the most cost-effective means of delivering fluoride to large numbers of individuals. It requires a suitable community – wide drinking water delivery system along with a reasonable level of technological development. About 210 million individuals throughout the world consume such water.

- Fluoridated toothpaste, which usually contains approximately 1000 mg fluoride/kg, is considered to be one of the major factors responsible for the gradual decline in the prevalence of dental caries in most industrialized
countries. About 500 million individuals throughout the world use such toothpaste.

- Fluoridated mouth rinse is popular among public health care programmes for school aged children. Such rinses contain 0.05 or 0.2% of fluoride depending on whether they are recommended for daily or weekly use. It is not suitable for children below the age of six who might swallow significant amounts of the product.

- Fluoridated solutions, gels or varnishes, applied by dentists, may be effective for individuals with an elevated risk of dental caries. Because of the high level of fluoride contained (upto 22300 mg/kg), and to avoid acute toxic effects in younger children who may swallow them, such materials are applied according to strict protocols.

- Fluoridated salt is considered to act against the appearance of caries in a way similar to fluoridated drinking water.

- Fluoridated milk was formerly considered to be a suitable means of increasing children’s intake of fluoride; however, little information is available on the efficacy of this delivery method that requires close co-operation with the dairy industry as well as a widespread system of distribution.

- Fluoride supplements in the form of tablets, liquid drops or lozenges are intended to provide a source of fluoride when fluoridated drinking water is not available. There appears to be a growing consensus that fluoride supplements have a limited public health role in improving dental health.
- Hydrogen fluoride (HF) is a colourless, pungent smelling liquid or gas that is highly soluble in organic solvents (e.g., benzene) and in water. It is mainly used in the production of synthetic cryolite (Na$_3$AlF$_6$), aluminum fluoride (AlF$_3$), motor gasoline alkylates and chlorofluorocarbons (CFCs). It is also used in etching semiconductor devices, cleaning and etching glass, cleaning brick and aluminium and tanning leather, as well as in removing rust.

- Calcium fluoride (CaF$_2$) is a colourless solid that is relatively insoluble in water, dilute acids and bases. It lowers the melting temperature during the production of steel, glass and enamel. It is also used to produce hydrofluoric acid and anhydrous hydrogen fluoride as raw material, and aluminium as electrolyte.

- Sodium fluoride (NaF) is a colourless white solid that is moderately soluble in water. It is used in the fluoridation of drinking water and in the manufacture of dental preparations such as toothpaste. It is also used in the production of steel and aluminium to lower the melting temperature, and glass and enamel, or as an insecticide and a preservative for glues and wood.

- Silicofluorides such as fluorosilicic acid (H$_2$SiF$_6$) and sodium hexafluoro silicate (Na$_2$SiF$_6$) are also used for the fluoridation of drinking water supplies.

Fluoro polymers such as ploy tetrafluoro ethylene, and Teflon are used as chemically inert and biocompatible materials for a variety of bypass grafts$^{79}$, and a replacement for soft tissue in cosmetic and reconstructive surgery$^{80}$. Poly tetrafluoro ethylene is commonly used as non-stick surfaces in cookware and the fluoropolymer fabric Gore-Tex is used in breathable garments for outdoor use.
Fluoride containing compounds are used in systemic fluoride therapy for preventing tooth decay. They are used for water fluoridation, and in many products associated with oral hygiene. Originally, sodium fluoride is used to fluoridate water, however hexafluoro silicic acid (H$_2$SiF$_6$) and its salt sodium hexafluoro silicate (Na$_2$SiF$_6$) are more commonly used as additives, especially in the United States. The fluoridation of water is known to prevent tooth decay. Numerous drugs contain fluorine including antipsychotics such as fluphenazine, HIV protease inhibitors such as tipranavir, antibiotics such as ofloxacin and trovafloxacin and anaesthetics such as halothane.

Fluorine is incorporated in the drug structures to reduce drug metabolism, as the strong C–F bond resists deactivation in the liver by cytochrome P450 oxidases. Fluoride salts are commonly used to inhibit the activity of phosphatases such as serine/threonine phosphatases. Fluoride mimics the nucleophilic hydroxyl ion in these enzymes active sites. Beryllium fluoride (BeF$_2$) and aluminium fluoride (AlF$_3$) are also used as phosphatase inhibitors, since these compounds are structural mimics of the phosphate group (PO$_4^{3-}$), and can act as analogues of the transition state of the reaction.

1.7 FLUORIDE TOXICITY

Acute fluoride toxicity occurring from the ingestion of optimally fluoridated water is impossible. The amount of fluoride necessary to cause death for a human adult (155 pound man) has been estimated to be 5-10 grams of sodium fluoride ingested at one time.
1.7.1 Permissible limits of fluoride in drinking water

1ppm is the safe limit prescribed by I.C.M.R., and Committee on Public Health Manual and Code of Practice\(^5^9\). Today, oral fluoride is still considered as an effective means of reducing dental caries\(^2^0\).

Historically, populations consuming fluoridated drinking water have shown a much lower prevalence of dental caries than have those consuming non-fluoridated drinking water, but the difference in caries prevalence between those two groups has narrowed virtue of fluoridated drinking water may be explained by the fact that individuals who do not have access to fluoridated drinking water may consume other fluoridated products in significant amounts, for example beverages prepared elsewhere with fluoridated drinking water and dental products such as fluoridated toothpaste\(^2^0\).

Drinking water is considered to be the main source of fluorides, and standards are fixed by various authorities for the permissible limit of fluorides (Table 1.7.1). However, there have been many includes of fluorosis where F\(^-\) in drinking water is less than the prescribed standards. In all such cases, food is identified as main source of fluorides, and food born fluorosis has been stressed upon in the result times. In India also, certain cases of fluorosis were reported where water fluoride is less than 1 ppm, the prescribed limit by Indian Council of Medical Research (I.C.M.R.), and Committee on Public Health Engineering Manual and Code of practice. There was a suggestion in one of the papers to consider the safe limit of F as 0.5 ppm under the Indian conditions\(^9^0\).
Table 1.7.1 Drinking water standard for fluoride presented by various authorities

<table>
<thead>
<tr>
<th>Authority</th>
<th>Permissible fluoride (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U.S. Public Health Standard</td>
<td>0.8</td>
</tr>
<tr>
<td>I.C.M.R. Recommendation</td>
<td>1.0</td>
</tr>
<tr>
<td>Recommendation of the Committee on Public Health Engineering Manual and Code of Practice constituted by Government of India</td>
<td>1.0</td>
</tr>
<tr>
<td>I. S. I. Recommendation</td>
<td>1.5</td>
</tr>
<tr>
<td>W.H.O. International Standard by drinking water</td>
<td>1.5</td>
</tr>
</tbody>
</table>

1.7.2 Permissible limits of fluoride in salt

It is well known that excess fluoride ion intake beyond a limit is responsible for dental and skeletal fluorosis which is a serious public health problem in many areas of the world. The mandatory standard GB 5461-2000 “Table salt” specifies that the content of fluoride shall not exceed 5.0 mg/kg in salt.

1.7.3 Toxic fluoride compounds

Fluoride containing compounds are so diverse that it is not possible to generalize on their toxicity, which depends on their reactivity and structure, and in the case of salts, their solubility and ability to release fluoride ions. Soluble fluoride salts, of which NaF is the most common, are mildly toxic, but have resulted in both accidental and suicidal deaths from acute poisoning. While the minimum fatal dose in humans is not known, a case of a fatal poisoning of an adult with 4 grams of NaF is documented. For sodium fluoro silicate (Na$_2$SiF$_6$), the median lethal dose orally in rats is 0.125 g/kg, corresponding to 12.5 g for a 100 kg adult. The fatal period ranges from 5 minutes to 12 hours.
The mechanism of toxicity involves the combination of the fluoride anion with the calcium ions in the blood to form insoluble calcium fluoride, resulting in hypocalcemia. Calcium is indispensable for the function of the nervous system, and the condition can be fatal. Treatment may involve oral administration of dilute calcium hydroxide to prevent further absorption, and injection of calcium gluconate to increase the calcium levels in the blood.

Hydrogen fluoride is more dangerous than salts such as NaF because it is corrosive and volatile, and can result in fatal exposure through inhalation or upon contact with the skin; calcium gluconate gel is the usual antidote.\(^96\)

In the higher doses used to treat osteoporosis, sodium fluoride can cause pain in the legs and incomplete stress fractures when the doses are too high; it also irritates the stomach, sometimes so severely as to cause ulcers. Slow-release and enteric-coated versions of sodium fluoride do not have gastric side effects in any significant way, and have milder and less frequent complications in the bones.\(^97\) In the lower doses used for water fluoridation, the only clear adverse effect is dental fluorosis which can alter the appearance of children’s teeth during tooth development; this is mostly mild, and is unlikely to represent any real effect on aesthetic appearance or on public health.\(^98\)

The ingestion of fluoride is encountered among residents of areas consisting of high fluoride concentration in drinking water and food grains. Inhalation is the way of entry in occupational settings such as mining and manufacturing industry. Irrespective of the way of entry, fluoride induced changes are similar. Fluoride toxicity depends upon the following factors viz. (i) the total dose ingested (ii) duration of exposure (iii)
nutritional status and (iv) body’s response. It not only affects humans, but also animals like cattle. Fluorosis is a crippling disorder which affects every organ in the body. The presence of fluoride in water and food is universal, and therefore its intake in the diet virtually inevitable\(^99\).

### 1.7.4 Fluoridation and cancer

Numerous studies have shown that fluoride causes genetic damage\(^{100-106}\) at levels as low as one half part per million (0.5 ppm) in cell structures\(^90\) and at exposures as low as 1 ppm in drinking water\(^{105}\). It is generally agreed that substances which cause genetic damage are also likely to cause cancer. Since the level of fluoride used to fluoridate public drinking water is 0.7-1.2 ppm, individuals living in fluoridated areas may suffer an increased risk of genetic damage and cancer. More recently researchers have shown that increasing levels of fluoride transform white blood cells into cells “suggestive of reticuloendothelial malignancy”\(^{106}\). Others have found that fluoride transforms normal cell into cancer cells\(^{107-109}\) and that it promotes and enhances the carcinogenicity of other cancer causing chemicals\(^{108}\).

Studies by Procter and Gamble showed that the incidence of precancerous growth in oral tissues increased as exposure to fluoride level increased\(^{110}\). They also concluded that this was a compound (fluoride) related increase in osteoma in both male and female mice\(^{111}\). In addition they tabulated bone cancers and tumours in rats fed fluoride, but not in untreated rats\(^{112}\). Epidemiological studies have shown that from 1975 to 1977 ten thousand or more cancer death per year were due to water fluoridation in the U.S\(^{113-116}\).
1.7.5 Effect of fluoride on humans

Serious health problems associated with chronic fluorosis occur in many parts of the world\textsuperscript{117-121}, and endemic fluorosis has been identified in 20 states of India\textsuperscript{122,123}. About 62 million people, including 6 million children are at risk in India from endemic fluorosis\textsuperscript{124}.

There kinds of fluorosis are identified in humans, and they are:

1. Dental fluorosis.
2. Skeletal fluorosis.
3. Non-skeletal fluorosis.

1.7.5.1 Dental fluorosis

Fluoride can have both beneficial and potentially detrimental effects on dental health. While an increase in the concentration of fluoride in drinking water means less chances of developing dental caries, it also means greater chances of developing dental fluorosis. The “optimum” level of fluoride in drinking water, associated with the maximum level of dental caries protection and minimum level of dental fluorosis, is considered to be approximately 1 mg/litre\textsuperscript{20}.

Dental fluorosis is usually of endemic in nature. Although the presence of optimum levels of fluoride is essential for the prevention of dental caries excessive fluoride intake for a long period affect the teeth of human being\textsuperscript{125}.(Fig. 1.7.1).
Dental fluorosis depends on the concentration of fluoride in the drinking water during the years when the teeth are being formed. After eruption of the teeth, the fluoride content of drinking water has no visible effect on the enamel, but the fluoride content of the teeth increases\textsuperscript{126}.

During the year of tooth formation ameloblast cells in the jaws lay down a matrix called amelogen. This matrix form structured foundation upon which phosphate and calcium are deposited, giving rise to tooth enamel. Excess ingestion of fluoride interferes with amelogen laying mechanism of ameloblast cell. In the absence of the protective enamel the risk of tooth loss increases and the enamel may be pitted, rough and hard to clean. It becomes a permanent feature on the teeth, and it affects both the inner and outer surface of the teeth. Moreover incorporation of excessive fluoride makes the teeth brittle, and susceptible to flourapatite crystals during the mineralization of teeth.
Dean classified the degree of clinically observed mottling into seven categories ranging from normal to severe\textsuperscript{127,128}. The basis for such a classification of mottling is as follows:

1. **Normal**: The enamel is translucent, smooth, and presents a glossy appearance (Fig. 1.7.2).

2. **Questionable**: It is seen in areas of relatively high endemicity, and occasional cases are border line, and one would hesitate to classify them as apparently normal or very mild (Fig. 1.7.3)

3. **Very mild**: In very mild category white areas are seen, scattered irregularly over the labial and buccal tooth surfaces (Fig. 1.7.4)

4. **Mild**: The white opaque areas involve at least half of the tooth surface, and faint brown stains are sometimes apparent (Fig. 1.7.5)

5. **Moderate**: Generally all tooth surfaces are involved, and minute pitting is often present on the labial and buccal surfaces, and brown stains are frequently a disfiguring complication (Fig. 1.7.6)

6. **Moderately severe**: Pitting is marked more frequently and generally observed on all tooth surfaces, and brown stains are generally of greater intensity (Fig. 1.7.7)

7. **Severe**: The severe hypoplasia affects the form of the tooth, and stains are widespread, and vary in intensity from deep brown to black. This condition may sometimes be referred to as ‘corrosion’ type of mottled enamel (Fig. 1.7.8).
Fig. 1.7.2 Normal

Fig. 1.7.3 Questionable

Fig. 1.7.4 Very mild

Fig. 1.7.5 Mild

Fig. 1.7.6 Moderate

Fig. 1.7.7 Moderately severe

Fig. 1.7.8 Severe
1.7.5.2 Skeletal fluorosis

Skeletal fluorosis has been found to occur among individuals who have exposed to high intake of fluorides through drinking water for a prolonged period of time. Excessive fluoride deposition in the skeleton, and its consequence is known as skeletal fluorosis which can affect both the young and adults. This is due to constant exposure to fluoride over a long period of time. Unlike dental fluorosis, the skeletal fluorosis is not clinically obvious until the advanced stage of crippling fluorosis occurs. Skeletal fluorosis affects bones causing stinging pain in the neck, back and joints, followed by progressive restriction of movement. The fluoride gets accumulated in the vertebral discs resulting in the partial fusion of vertebrae. Density of the bone becomes abnormally high, and this causes stiffness of the back bone and hip. At this stage the affected persons have stiff necks, bow legs and bend frame, and after some time their movement becomes totally restricted (Fig.1.7.9). This stage is known as skeletal fluorosis. This disease is common in aged compared to children. Airbone fluoride and long term hemodialysis have been responsible for the development of skeletal fluorides. Cancellous bones (spongy bones) are more prone to fluorosis attack than the cortical bones (dense bones).

Fig. 1.7.9 Bones affected by skeletal fluorosis
1.7.5.3 Non - skeletal fluorosis

The conventional belief that fluoride affects only bone, and tooth has been neglected in recent years as the evidences on the involvement of soft tissues and organs of the body is convincing. Evidence from fluorosis patients is now available to demonstrate the damage or involvement of skeletal, muscle, erythrocytes, gastrointestinal mucosa and ligaments in human fluorosed parents. The soft tissue organs are affected by fluoride very easily, and they are arranged in the following order: aorta, thyroid gland, lungs, kidney, heart, pancreas, brain, spleen and liver. With advancing age, the fluoride content increases. For this reason early recognition of Non-skeletal fluorosis is important, and fluoride intoxication is essential.

Fluoride is a protoplasmic poison; in excess amounts it has definite toxic effects on the cells of animals, including humans. It enters the cells of various organ systems, and binds with protoplasm inside, ultimately causing damage to protoplasm. Aluminium fluoride has been shown to act as a phosphate analog, and stimulate G-protein receptors and signaling pathways, such as the phosphatidylinositol pathway which controls protein phosphorylation, the uptake of calcium into cells, and the release of calcium from intracellular stores. These processes are involved in hormonal and immunologic responses, transmission of nerve impulses, cell division, and even neoplastic transformations.

High fluoride ingestion through drinking water affects children’s IQ irrespective of the gender. Reproductive system of males living in fluorosis endemic areas is found to be adversely affected. Fluoride toxicity is suspected to promote kidney stone formation and a single dose intake of fluoride in the range,
2250 to 4500 mg, can be lethal. Fluoride like TSH has the ability to influence all aspects of thyroid hormone homeostasis in all tissues where the TSH receptor is expressed. It includes the brain and bone as well as the thyroid, including iodine uptake and utilization, thyroid hormone homeostasis, deiodination, and thyroid peroxidase (TPO) activity. Deiodination involves the conversion of the hormone produced in the thyroid gland, thyroxine or T4, to the active thyroid hormone triiodothyronine, T3.

Dr Russell Blaylock has suggested that fluoride may lead to excitotoxicity with cell death in the brain from overstimulation. It may also induce, via brain NMDA receptor stimulation, a chronic activation of the microglial cells in the brain, with the release of high levels of the excitotoxic aminoacids glutamate and aspartate, and the secretion of high levels of immune cytokines, and other immune factors, which can enhance excitotoxicity. An increase in the maternal urine F of 0.5 mg/l during pregnancy was associated with impaired cognitive development at ages 1-3 year (a 1.2 point decrease in the MDI). Fluoride ion adversely impacts the reproductive system in mammals. Fluoride ingestion leads to poly urea and poly atpsta (Tendency to urinate frequently) which are associated with fluoride toxicity. Among all soft tissues the aorta is affected more, and repeated abortions, and still birth have been reported from endemic areas.

The permissible level of fluoride content in drinking water by WHO is 1.0 ppm. High levels of fluoride in drinking water are found in some countries such as India, China, Japan and parts of Middle East and Africa. Ramamohana Rao investigated the fluoride content of 302 samples of water from Karnool District of Andhra Pradesh in relation to reports of endemic fluorosis in the area, and found only
69 samples contained more than 1.5 ppm of fluorides, calculated as fluoride\textsuperscript{141}. When the concentration is 2 ppm, it affects the enamel of the teeth and when it is 3 ppm, there is severe discolourisation, and the teeth almost look brown. At 4 ppm, there is defective formation of enamel apart from defective calcification, and when the fluoride content is 5 ppm or more, severe deformity results. Though this is the general rule, even with small quantity some people will be affected. Endemic fluorosis analysis in Kanyakumari District, Tamil Nadu revealed that it was not only associated with high content of fluoride in drinking water. But the socio economic status of the residents played some important role\textsuperscript{142}.

\textsuperscript{143}Fluorosis was first reported from India as early as 1937, but is only now that the environmental and biochemical effects of fluoride are beginning to be appreciated mainly due to modern analytical techniques for investigating the metabolism of skeletal tissues. Nevertheless, studies are now beginning to emerge and they indicate that fluoride exerts a major influence on the metabolism of the organic components of enamel and dentine. Fluoride can inhibit the synthesis of proteins by ameloblasts in developing enamel. It also appears that fluoride is able to inhibit the proteases involved in the transitional phase of protein mineral interaction during enamel development.

\textsuperscript{144}Seventeen Indian states have been identified with the problem of excess fluoride in ground water resources till 1999. The fluorosis problem is severe in India as almost 85 % of the rural population depends on untreated ground water for potable water supplied\textsuperscript{145}. The most detailed studies, however, have centered around the influence of fluoride\textsuperscript{146}. Excessive concentration of fluoride in drinking water leads to crippling fluorosis in endemic areas\textsuperscript{147}. More than a million people in India are
affected with skeletal and dental fluorosis. The fluoride absorbed through the gastrointestinal tract is rapidly distributed to all the tissues by simple diffusion. The quantum of water drawn from the aquifers exceeds aquifer re-charge that aids the concentration of fluoride in aquifers\textsuperscript{144}.

Fluorine can rapidly cross the cell membrane, skeletal and cardio muscle, liver, skin\textsuperscript{148} and the erythrocytes\textsuperscript{149}. Even placental transfer of fluoride by diffusion is known which can impose deleterious effects on foetal development\textsuperscript{150}. Since the origin of endemic fluorosis is hydrogeochemical, its effective control and prevention can only be achieved through providing low fluoride drinking water from alternate sources. Fluoride exerts an effect on bones during the period of fast growth and the continuous remodeling of bone structure. Incorporation of fluoride has been shown to alter slightly the chemical composition of tooth and bone mineral\textsuperscript{138}. The carbonate and citrate contents decrease slightly, whereas the magnesium level increases. The calcium phosphate ratio, however, remains essentially unchanged.

The extend of fluoride uptake by hard tissues is dependent upon the amount ingested and absorbed, the duration of exposure and the type, region and metabolic activity of the tissue concerned\textsuperscript{151}. Consequently there is a great disparity in fluoride levels both between individuals and between types of mineralized structures. Even when tissues appear structurally homogeneous; concentration may vary markedly over distance of a few microns.

\textsuperscript{152}Topical application of fluoride to the tooth surface for prevention of caries commenced in 1941. Some of these topical fluoride agents are sodium fluoride, stannous fluoride, acidulated phosphate fluoride, sodium monofluorophosphate and
amino fluoride. Commercial preparations are mouth rinses, gels, varnishes, dentifrices and tablets. Incorporation of fluoride into toothpaste as a cariostatic agent and its commercialization on a large scale has generated concern particularly where fluorosis is endemic. Ingredients and concentration of fluoride is not specified in most products, moreover some toothpastes although not labelled, contain fluoride.

The toxicity of fluoride will occur even when only 1.0 mg/l is received for a period of time. Acute poisoning produces a clinical syndrome characterized by nausea, vomiting, diarrhoea, abdominal pain, and paresthesia, and is usually associated with accidental ingestion of fluoride-containing insecticides and other home use products. The accumulative effect can cause many toxicities depending on the concentration and duration of intake above the standard levels.

Even drinking water is considered as the main source of fluoride, however there have been many incidences of fluorosis where fluoride in drinking water is less than the prescribed standards. A high level of F in drinking water can be harmful with accumulation over time in both the hard and soft tissues including the cardiovascular system.

1.7.6 Effect of fluoride on animals

Ultra structural studies have also shown that fluoride has the ability to induce cell ultra structure, changes in both plants and many species of animals including humans, mice, rats, rabbits, guinea pigs, pigs and chickens. The effectiveness of low fluoride intake leads to dental caries in animals, rats, and hamsters is well documented. Excessive intake of fluoride affects animals more. Many studies have indicated that excessive fluoride can induce free radical toxicity and oxidative damage.
to the brain, muscle, thyroid, ovary, liver and kidney in mice\textsuperscript{157-159}. Oral administration of Na F for 30 days causing significant reduction in the body weight of mice has been attributed to lower food consumption resulting in decreased protein synthesis and lower energy metabolism\textsuperscript{160}. A group of rats received silymarin followed by NaF, in which silymarin has a potent ameliorative effect on Na F-induced oxidative stress in rat erythrocytes\textsuperscript{161}.

The effects of 600 ppm NaF (271 ppm Fluoride ion) in the drinking water of the rats for one week significantly decreased the serum levels of the thyroid hormones thyroxine (T4) and triiodothyronine (T3) to $0.95 \pm 0.076 \mu g/ml$, and $88 \pm 1.64$ ng/dl respectively. Treatment intraperitoneal for one week with 20 mg curcumin/kg body weight actually increased the serum total T4 level to $5.25 \pm 0.089 \mu g/ml$, which was significantly higher ($P<0.05$) than in normal controle level, and significantly higher ($P<0.001$), and greater than in the NaF controle\textsuperscript{162}.

The broilers grew much slower in all high fluoride groups than those in controle groups. Meanwhile broilers in high fluoride groups showed decreased feed intake and depression. The malondialdehyde content increased significantly in high fluoride groups when compared with that of the controle group\textsuperscript{163}.

The mortality of the zebra mussels or mollusks rose with the increase of both fluoride concentration and exposure time. No mortality occurred in the first 24 hours at fluoride concentrations up to 360 ppm, while in the same period, 60% of animals exposed to 720 mg F-/l died\textsuperscript{164}. 78
In aquatic animals, fluoride uptake occurs either through exposure to the surrounding water or feeding. Chronic exposure of fingerlings of Indian major carp to 15 mg NaF-/l in water has been found to cause soft tissue damage.165

1.7.7 Fluoride toxicity: World scenario

Fluoride is a geochemical contaminant, and natural sources account for much of the fluoride found in surface and ground waters. Drinking water is considered to be the main source of fluorides. An attempt has been made to highlight the problem of fluorosis, by compiling the work carried out by various researchers in fluoride affected areas, against the background of present day developments.

In Kenya endemic fluorosis has been chronic for over 30 years. Above 30% of Kenya’s population suffers from dental fluorosis, and in isolated regions where the people depend on ground water for domestic use, nearly 100% of the population manifestes varying degrees of dental fluorosis. Drinking water is only Kenya’s major source of fluoride ion, especially in those regions of the country associated with volcanic rocks and hot springs.166 Fluorosis cannot be clinically treated, and prevention of its spread is of paramount importance. It is well known that excess fluoride intake is responsible for dental and skeletal fluorosis which is a serious public health problem in many areas of the world.167

1.7.8 Fluoride toxicity: Indian scenario

Fluorosis was first detected in India by Shortt (1937) when the disease was prevalent in four states namely Andhra Pradesh, Tamil Nadu, Punjab and Utter Pradesh.112 Skeletal fluorosis was observed from the villages in the southern part of India as early as 1937 by Shortt et al.143 During the period 1960 – 1986, nine
more states have been identified as endemic for fluorosis, and during 1990 – 1992 two additional states, Kerala and Jammu and Kashmir have also been identified as endemic for the disease. Thus the total number of states declared endemic for fluorosis at present are fifteen. The affected states are Jammu and Kashmir, Punjab, Haryana, Delhi, Uttar Pradesh, Rajasthan, Gujarat, Madhya Pradesh, Maharashtra, Karnataka, Andhra Pradesh, Kerala, Tamil Nadu, Orissa and Bihar of which Gujarat, Uttar Pradesh, Rajasthan, Andhra Pradesh and Tamil Nadu are the worst affected states.

Concentrations of fluoride in drinking water in different parts of the country varies from 0.5 to 50 ppm. Excessive ingestion of fluoride for a prolonged period of 6 months to several years causes fluoride toxicity in the form of dental, skeletal and gut fluorosis. The latter is also known as fluoride toxicosis, osteo-fluorosis, hydrofluorosis, fluoride osteopathies and endemic fluorosis. Fluoride toxicity also affects the soft tissues and the enzyme system, but its effect on teeth, bones and gut are of practical importance. Out of 6 lakh villages in India, at least 50 % have fluoride content in drinking water exceeding 1.0 ppm. An extensive survey of community water supplies showed that 25 million people in 8700 villages are consuming water with more than 1.5 ppm of fluoride. More than one million people in India are affected with skeletal fluorosis, and several times more than this figure are exposed to the risk of developing skeletal fluorosis.

The degree of manifestation of fluorosis has been related to concentration of fluoride in drinking water, and the period of consumption. In endemic areas fluoride from other sources may intensify the clinical manifestation of fluorosis. Fluoride
content of 1.0 ppm in drinking water has no biological side effects. However, in endemic areas around the world, various levels of fluoride in drinking water above 1 ppm has been recorded. Studies in these areas revealed that fluoride level between 1.5 and 3.0 ppm in the drinking water consumed over a period of 5-10 years caused mild form of dental fluorosis, between 4 and 8 ppm consumed over a period of 5-10 years or more caused severe form of dental as well as skeletal fluorosis\textsuperscript{167}.

1.7.9 Fluoride toxicity: Tamil Nadu scenario

The dental fluorosis survey made from the school children in Salem District includes 21 places like Pottiyapuram, Kondayanur, Sattur, Annadarampatti, Udajanpatti and Karipatti etc. The dental fluorosis survey was carried out at five schools in Salem District. From the results received from the age group of 9-10, 98 children were affected to a maximum extent out of 574 male children and 452 female children examined. 191 male and 161 female children were affected by the disease. The percentages of victims of male and female children are 33.27 and 37.26.

A preliminary survey of the people in the study area, namely Sivakasi and Aruppakottai taluks of Kamarajar district, Tamil Nadu, was undertaken. The diseases, like dental caries and mottled enamel, dental and skeletal fluorosis, and other complaints, like neck, collar, back, spinal and joint pains were noted to be common among the few respondents of some of the areas of these two taluks. About 60 % of the respondents were found to be affected by dental fluorosis from mild to moderate extent. All the available drinking water sources in these Fluorotic areas and other areas, where there is no such symptoms were identified\textsuperscript{168}. In Tamil Nadu fluorosis was reported in Coimbatore (Pollachi area), Salem, Tanjore, South Arcot and Kanyakumari Districts\textsuperscript{124}.
1.7.10 Factors affecting fluoride toxicity

Climatic variation plays an important role on endemic fluorosis. In the USA mottling is reported to be associated with at least 3 to 4 ppm at which many workers in India have recorded cases of skeletal fluorosis. Any substance which is able to combine or complex with fluoride hinders fluoride absorption from the gastrointestinal tract. Thus calcium and magnesium in large amounts reduce the absorption of fluoride owing to the formation of less soluble fluorides. Vitamin-C intake also is found to reduce the fluoride toxicity\(^{59}\). Presence of iron and aluminium reduces the concentration of ionic fluoride in water, by forming the complexes AlF\(_6^–\) and FeF\(_6^–\).

1.8 DISTRIBUTION OF FLUORIDE IN DIFFERENT ESTUARIES

The estuarine water is a simple mixture of river water and seawater. The fluoride concentration in Chesapeake Bay surface water was found to predict the distribution depending on the variability of input fresh water sources. This approach allows identification of non-conservative species, and can be useful for the quick identification of the probable directions, and magnitude of sources of conservative polluting substances. Variations in input waters can be reliable inferred from measurements in the body of the estuary from the source\(^{169}\).

1.9 DEFLUORIDATION

\(^{170}\)In some parts of India, the fluoride levels are below 0.5 mg/l, while at certain places fluoride levels are as high as 35 mg/l. To encounter this fluoride menace, the quantification of fluoride ions in environment is important, followed up with suitable adaptation of an effective defluoridation methodology. During recent years, several methods have been developed to remove fluoride ions from water.
namely adsorption\textsuperscript{171-176}, chemical treatment\textsuperscript{177,178}, ion exchange\textsuperscript{179,180}, membrane separation\textsuperscript{181,182}, electrolytic defluoridation\textsuperscript{183}, electro dialysis\textsuperscript{184,185}, membrane filtration\textsuperscript{186}, precipitation, nanofiltration\textsuperscript{187}, electro-coagulation\textsuperscript{188}, etc. Among these methods, adsorption is still one of the most extensively used methods for the defluoridation of water due to its low cost and viability. Researches were carried out in adsorption technique using sunflower plant dry powder, steam of phytomasshollyoke, neem bark powder, activated cotton jute carbon, bagasse ask, burnt bone powder, phosphate-treated saw dust, bone char, etc. as adsorbents, Nalgonda technique, activated alumina process and ion exchange process\textsuperscript{189}. The polymer composites showed considerable potential for the removal of fluoride ions from aqueous solution. Lower pH and higher temperature ranges were found as the favorable condition for maximum fluoride removal\textsuperscript{190}. In recent years considerable attention has been focussed on fluoride removal using natural biomass materials such as egg shell and calcareous solutions\textsuperscript{191,192}, but these adsorbents have limitations\textsuperscript{193}, and there is still need for an effective, low cost adsorbent. This findings of an investigation on the use of seeds and seed powder from Prosopis juliflora the defluoridation of saline water. The seeds of Prosopis juliflora, used as biosorbent in this experiment, generally grows in the dry lands of India, and its availability is easy without any practical investment.

1.10 AIMS AND OBJECTIVES OF THE PRESENT STUDY

The specific objectives of the present study are

i. To evaluate the physico chemical parameters, and assess the brine solutions, and salt quality.

ii. To study the level of fluoride content of brine solutions, salt and pan soil.

iii. To propose model studies to remove the concentration of fluoride ion in the salt.