SECTION I

STUDIES ON THE DEVELOPMENT OF NEW LABORATORY ANALYTICAL METHODS AND FIELD KITS FOR MONITORING FLUORIDE IN GROUND WATERS AND APPLICATION OF ALUMINA FOR DEFLUORIDATION
CHAPTER 1
GENERAL INTRODUCTION

1.0. Introduction

In view of importance of ground water as potential drinking water source and major pollution problems arising out of fluoride and toxic organic pollutants like phenol, chlorophenols etc., in ground water quality due to industrial and mining activities the author has taken up a systematic study for the last 4 years for developing methods for precise estimation of fluoride, cost-effective defluoridation technologies and innovative, insitu application of sonication for detoxification of groundwater's from phenolic pollutants.

The data of these results are presented in two sections. Section –1 comprises of details of investigations relating to methods for fluoride estimation, and defluoridation technologies while in Section –2 the data on application of sonication for insitu decontamination of ground waters from phenolic pollutants are presented.

1.0.1. Water resources of Andhra Pradesh

Andhra Pradesh is the fourth largest state in India in terms of geographical area (27.44 million hectares; 8.4% of the country’s territory), and the fifth largest in terms of population (75.7 million in 2001).
The major part of the state lies in the plateau zone lying about 600 m toward the west. There are few isolated hills in this plateau and it is underlain by Archean granitoids. The majority of this plateau (parts in the state) is drained by Krishna River and its tributary, Tungabhadra. The northern part of the state lies in the right bank of Godavari River. Towards the northwestern part of the state, Deccan traps and associated black cotton soils are found.

1.0.2. Ground Water Resources of Andhra Pradesh

About 84 percent of the state is underlain by crystalline and consolidated formations. The rest of the area either has alluvial formation or coastal sandy zones. Since most part of the hard rock regions, especially the Rayalaseema districts, are located in semi-arid areas, groundwater availability is likely to be low and competing demands from agriculture can put a severe strain on drinking water availability during summers. Most of the groundwater extraction for agriculture is carried out during the rainy and winter months and wells can go dry before the onset of summer season.

Since more than 80 percent of the population is situated in the hard rock regions, groundwater availability becomes a critical issue to ensure drinking water availability in this state. About 44 percent of the total population in the state, reside in the plains areas which are mostly the areas amenable to surface irrigation through large irrigation projects. The remaining 36 percent population is located in the uplands, plateaus, hills, and forested regions. Groundwater availability becomes critical for these regions since
they do not have surface water options. The rural population in all these regions is more than three fourths of the total population of these regions, except in case of uplands (64 percent, due to location of Hyderabad in this region type).

1.0.3. Water Quality of Andhra Pradesh

Andhra Pradesh has both coastal and semi-arid hardrock regions, therefore problems of coastal salinity and fluoride are the most common groundwater quality problems in the state. Fluoride is the major quality problem in the interior areas of the state. The fluoride affected districts are Nalgonda, Anantapur, Cuddapah, Guntur, Nellore, Chittoor and Krishna. In each of these districts, some villages do not have any groundwater source free of fluoride. The state government has commissioned many surface water based water supply schemes, to address this problem. In some of the affected areas, water treatment through the Nalgonda process has been attempted but these plants are reported to be mostly defunct now due to poor O&M (operation and maintenance). Activated alumina based household and village level treatment methods are being tried out now in the state. The Sathya Sai Trust has set up large surface water based piped water scheme for Anantapur district. The O&M of this system is large and the maintenance of the piped system running across the semi-arid countryside will not be sustainable. Inland salinity is also reported from the semi-arid regions, especially in the Rayalaseema region, but the problem is not very severe.
In respect of water supply, of the 69,732 rural habitations in the state, there are about 32,000 fully covered (FC) villages and 26,976 (39 percent) habitations are partially covered (PC). Fluoride problems are reported from 12,068 habitations and 8,519 habitations have problems of salinity or brackishness. Of the quality affected habitations, about 46 percent have been provided safe sources subsequently. This leaves more than fifty percent of the habitations needing to be provided with safe drinking water (James and Robinson, 2001).

1.1. Fluoride

The presence of fluoride, in quantities in excess of limits is a serious matter of concern from a public health point of view. Like any other pollutant the fluoride pollution can also occur due to both natural and man made reasons.

Fluoride in drinking water is known for both beneficial and detrimental effects on health. Fluorine, the most electronegative of all elements is so violently reactive that it is encountered in nature only in the chemically combined form. It is the seventeenth in the order of abundance of elements in the earth's crust constituting about 0.032%. It is widely distributed in both igneous and sedimentary rocks, soils and waters (Ramamohana Rao, 1997).
1.1.1. Sources of human and environmental exposure

Fluorides are released into the environment naturally through the weathering and dissolution of minerals, in emissions from volcanoes and in marine aerosols. Fluorides are also released into the environment via coal combustion and process waters and waste from various industrial processes, including steel manufacture, primary aluminium, copper and nickel production, phosphate ore processing, phosphate fertilizer production and use, glass, brick and ceramic manufacturing, and glue and adhesive production. The use of fluoride-containing pesticides as well as the controlled fluoridation of drinking-water supplies also contributes to the release of fluoride from anthropogenic sources. Based on available data, phosphate ore production and use as well as aluminium manufacture are the major industrial sources of fluoride release into the environment (Fluorides, EHC, 227, WHO, 2002).

Hydrogen fluoride is an important industrial compound that is used mainly in the production of synthetic cryolite (Na₃AlF₆), aluminium fluoride (AlF₃), motor gasoline alkylates and chlorofluorocarbons, with an annual world consumption in excess of 1 million tonnes. It is also used in etching semiconductor devices, cleaning and etching glass, cleaning brick and aluminium and tanning leather, as well as in commercial rust removers. Calcium fluoride is used as a flux in steel, glass, and enamel production, as the raw material for the production of hydrofluoric acid and anhydrous hydrogen fluoride, and as an electrolyte in aluminium production. Sodium fluoride is used in the controlled fluoridation of drinking water, as a preservative in glues, in glass and enamel production,
as a flux in steel and aluminium production, as an insecticide and as a wood preservative. Sulfur hexafluoride is used extensively in various electronic components and in the production of magnesium and aluminium. Fluorosilicic acid (H$_2$SiF$_6$) and sodium hexafluorosilicate (Na$_2$SiF$_6$) are used for the fluoridation of drinking-water supplies (Fluorides, EHC, 227, WHO, 2002).

1.1.2. Global distribution in Natural Waters

High fluoride concentration in groundwater is a natural phenomenon in close to 24 countries such as (1) Argentina (2) Algeria (3) Australia (4) African Nations viz. Senegal - Kenya - Tanzania - Ethiopia - Uganda (5) Bangladesh (6) China (7) Egypt (8) Iraq (9) Iran (10) India (11) Jordan (12) Japan (13) Libya (14) Morocco (15) Mexico (16) New Zealand (17) Pakistan (18) Palestine (19) Syria (20) Sri Lanka (21) Turkey (22) Thailand (23) UAE and (24) USA (Southern States). Fig 1.2 shows the countries affected by fluorosis worldwide (UNICEF, 1995).

The total number of people affected by fluorosis worldwide is not known, but a conservative estimate would number in the tens of millions. 19 of India's states were identified as endemic for fluorosis. In Mexico, 5 million people (about 6% of the population) are affected by fluoride in groundwater. Fluorosis is prevalent in some parts of central and western China, and caused not only by drinking fluoride in groundwater but also by breathing airborne fluoride released from the burning of fluoride-laden coal.
worldwide, such instances of industrial fluorosis are on the rise (UNICEF, 1995).

The fluorosis problem is most severe in the two largest countries of the world, China and India. In China, the WHO recently estimated that 2.7 million people have the crippling form of skeletal fluorosis, while in India, 15 of its 32 states have been identified as "endemic", with over 6 million people seriously afflicted. Fluoride has thus become a major public health problem in both of these countries. The countries affected with fluorosis are shown in the Fig 1.1

![Fig 1.1: Countries affected with fluorosis worldwide (UNICEF, 1995)](image-url)
1.1.3. Distribution of fluoride in waters in India

In India, fluorides are widely distributed in waters of different geographical regions having diverse hydro-geological settings. The distribution of fluoride in ground waters of India is shown in Fig 1.2.

Skeletal fluorosis is a crippling disability that has a major public health and socioeconomic impact, affecting millions of people in various regions of Africa, China, and India.

1.1.4. Fluoride Bearing Illness

Long-term consumption of water containing 1 mg of fluoride per liter leads to dental fluorosis. White and yellow glistening patches on the teeth are seen which may eventually turn brown. The yellow and white, patches when turned brown present itself as horizontal streaks. The brown streaks may turn black and affect the whole tooth and may get pitted, perforated and chipped off at the final stage.

1.1.4.1. Skeletal fluorosis

This has been observed in persons when water contains more than 3-6 mg/L of fluoride. Skeletal fluorosis affects young and old alike. Victims of the severe stages of fluorosis
often suffer from permanent hunch back as the result of an extreme immobilization of the spine. Joints throughout the rest of the body become extremely stiff, making movement of any kind (i.e. getting out of bed, sitting down) a difficult, painful, and belaboring experience, which is often not possible without the help of someone else. In the advanced stages patients cannot even squat and will be bedridden for the rest of their life.

1.1.5. Fluoride Analysis

Accurate determination of fluoride gained importance from 1930’s with the growth of the practice of fluoridation of water supplies as a public health measure. The quantity of fluoride ions present in potable waters assumed increasing importance since it was indicated by McCollum and co-workers in 1925 that the structure of the teeth of the long-time inhabitants of a community is affected by the fluoride ion concentration in that community’s water supply. Maintenance of an optimal fluoride concentration is essential in maintaining effectiveness and safety of the fluoridation procedure.

Among the methods suggested for determining fluoride ion (F⁻) in water, the electrode, and spectrophotometric methods are the most satisfactory. However, the cost is inhibitive because the instruments are expensive and the cost of detection is very high. The visual comparison methods are easy to use, and more economical. The scott-sanchis colorimetric method is the most widely used colorimetric method.
1.1.5.1. Alizarin Visual (Scott-Sanchis) Method

*Nessler-tube technique.* The basis for the alizarin visual method is the zirconium-alizarin reaction in which a red lake (a deep color) is produced by the combination of alizarin and zirconium. Any fluoride present in the water sample or standard solution removes zirconium from the reaction due to formation of colourless Zr-fluoride complex of higher stability, thus decreasing the intensity of red color present. In water samples, that are high in fluoride, the only color apparent is the yellow color of the unreacted dye. Conversely, in low fluoride samples, the color approaches the deep red of the zirconium-alizarin lake. Intermediate fluoride concentrations give colors that are intermediate between these two. A visual comparison is made between unknown samples and simultaneously prepared standards. The colour comparisons are made in 100-ml Nessler tubes—tall glass cylindrical tubes with flat bottoms. Usually, these are held in a rack with a reflector below the tubes so that light is reflected up through the longitudinal axis of the tubes to the eye of the observer. In practice, a number of tubes containing standard fluoride solutions at fixed concentration intervals are prepared in addition to the tubes containing the unknown samples.

The disadvantage is since the eye has poor memory sense color comparisons must be made simultaneously in order to judge the colour match. This requirement necessitates use of a series of color standards each time a determination is made, and since the colours change with time, the series of standards must be freshly prepared.
The reagent itself has limited stability, necessitating the preparation of fresh batches at relatively frequent intervals.

There is a need for a better visual comparison method for fluoride estimation for use in a field survey.

1.1.6. Methods of Defluoridation

The fact that the problems associated with the excess fluoride in drinking water is highly endemic and widespread in countries like India prompted many researchers to explore quite a good number of both organic and inorganic materials adopting various processes from coagulation, precipitation through adsorption, ion exchange etc. Some are good under certain conditions while others are good in other conditions. The process of removal of fluoride is generally termed as defluoridation or defluorination. Numerous methods have been described employing various materials for the fluoride removal since 1930s. Based on the nature of processes, the defluoridation techniques can be grouped under the following categories

(i) Precipitation
(ii) Adsorption and Ion exchange
(iii) Electrochemical method and
(iv) Membrane technique
1.1.6.1. Precipitation methods

They include the use of lime and alum, aluminium sulphate, gypsum, lime, magnesite, semi-calcined dolamite or calcium chloride.

1.1.6.1.1. Nalgonda Technology Using Lime And Alum

In this technology, raw water is mixed with adequate lime and alum. The dose of lime depends upon the alkalinity of the raw water. If the raw water has adequate alkalinity, the addition of lime is not required. Alum solution is added after the addition of lime, stirred gently for 10 minutes and the flocs formed are allowed to settle. This process of floc formation and settling requires an hour.

1.1.6.2. Adsorption or ion exchange

These methods include activated carbon, activated alumina, bone char etc.

1.1.6.2.1. Activated Alumina

Defluoridation of water by activated alumina is the method of choice in developed countries. Its affinity for fluoride is very high. It is a porous material with the surface comprised largely of active sites. It is prepared by dehydration of Al(OH)₃ in the
temperature of 300 – 600° C. Alumina, that is, aluminium oxide (Al₂O₃), is practically insoluble in water.

1.2. Cultivation with agrochemicals

Agricultural land-use and cultivation practices have been shown to exert major influences on groundwater quality. Under certain circumstances serious groundwater pollution can be caused by agricultural activities, the influence of which may be very important because of the large areas of aquifer affected. Of particular concern is the leaching of fertilizers and pesticides from regular, intensive cultivation, with or without irrigation, of cereal and horticultural crops. The impact of cultivation practices on groundwater quality is greatest, as are most anthropogenic effects, where relatively shallow, unconfined aquifers are used for potable supply in areas where there is no alternative.

The impact of modern agricultural practices on groundwater quality became fully apparent in some regions of industrialized countries during the latter part of the 1970s. Some of them can be biodegraded by means of the microorganism present in the water. Some others have a extremely low biodegradability and are called refractory contaminants. They can remain in water for long periods in which its chemical action and/or toxicity may constitute a potential hazard.
1.3. Industrial pollution

Phenols, pesticides, fertilizers, detergents, and other chemical products are disposed of directly into the environment, without being treated, via discharging, controlled or uncontrolled and without a treatment strategy.

Because of an increasing social and political concern on environment, the research field of water purification has been extensively growing in the last decades, comprising both polluted wastewaters and groundwaters from seas, rivers and lakes, as water quality control and regulations against hazardous pollutants have become stricter in many countries.

*Phenols* have been widely used in many industrial processes, as synthesis intermediates or as raw materials in the manufacturing of pesticides, insecticides, wood preservatives, and so forth. Because of the great diversity of their origins, they have a great ubiquity and can be found not only in industrial wastewaters but also in soils and surface and ground waters, as a consequence of their release in industrial effluents or improper waste disposal practices and accidental leakages (Benitez et al, 1997).

*Chlorophenols* constitute a group of organic substances that are introduced into the environment as a result of several man-made activities, such as waste incineration, uncontrolled use of wood preservatives, pesticides, fungicides and herbicides, etc, as well as by-products formed during bleaching of pulp with chlorine and in the disinfection by
chlorination to get drinking water (Ahlborg and Thunberg, 1980).

Elevated phenol levels have been reported in sediments and ground waters due to industrial pollution (Environmental Health Criteria 161: Phenol, World Health Organization, Geneva 1994).

4-chlorophenol has contaminated drinking water as well as the water and soil around sawmills. It remains in the water cycle for a long time period because its halogenation makes it a stable and toxic molecule, resisting biological and chemical degradation. 4-chlorophenol is known to be mutagenic to animals; it causes methemoglobinemia, liver and kidney damage, and skin and gastrointestinal irritation. Because of its toxicity, longevity, and the possibility that it is a carcinogen, 4-chlorophenol is undesirable in the water supply (Schwarz, 2002).

1.3.1. Removal of refractory organic pollutants from water

Refractory or recalcitrant compounds in this context are those, which resist aerobic microbial degradation in conventional biological treatment processes and the natural environment. Their low biodegradability makes necessary to find out other alternative techniques to the biological oxidation. The chosen method will depend on the characteristics of the contaminant itself.
For the last 25 years, the research field of water purification has been extensively growing. Rigorous pollution control and legislation in many countries resulted in an intensive search for new and efficient water treatment technologies.

Advanced Oxidation Processes (AOPs) for the degradation of non-biodegradable organic contaminants in wastewater are useful alternatives to established techniques like flocculation, precipitation, and adsorption on granular activated carbon, air stripping or reverse osmosis. Chemical treatment of wastewater by AOPs can effect a complete mineralization of the pollutants to \( \text{CO}_2 \) and in case of halogenated compounds to halide ions. On the other hand, partial decomposition of non-biodegradable organic contaminants, like halogenated aromatics, by these AOPs is straightforward, leading to biodegradable intermediates. Therefore, combinations of an AOP as a preliminary treatment, followed by an inexpensive biological process, seem very promising from an economical viewpoint. Although some authors claim that there are other species involved, the active species responsible for destruction of contaminants in most cases seems to be the hydroxyl radical (\(^*\text{OH}\)) with its very high oxidation potential. It ‘burns’ nearly all organic, but especially favors unsaturated compounds in aqueous solution. This unstable and therefore very reactive radical can be generated by various techniques (Bauer et al., 1999).

In respect to the harmful character of organic water contaminants and the fact that sonication is a chemical free technology, there has been a growing interest in the sonochemical destruction of organic contaminants in water in recent years. Thus,
ultrasound has been proved to degrade several organic contaminants in water (e.g. chlorinated hydrocarbons, phenols, and pesticides. An ultrasonic treatment may offer the following advantages: partial or complete destruction of pollutants, avoidance of disposal, recycling or combustion, full on-site process, physical treatment (i.e. no addition of chemicals) as well as the water has not to be translucent. Moreover, ultrasonic processing steps could also improve existing technologies (e.g. advanced oxidation processes) (Peters, 2001).

The softening (i.e., partial degradation) of the more recalcitrant organic compounds (e.g., SVOCs and nonvolatile organic compounds) in order to convert them into compounds that are more amenable to both vapor stripping and biological treatment is the feature of sonication in water treatment.

In view of the above, systematic study was taken up by the author for the last four years with the following objectives.

1.4. Objectives Of The Study

1. To develop new low cost spectrophotometric and visual colorimetric methods for precise estimation of fluoride in potable waters.
2. To improve the existing technologies available for defluoridation of fluorosis affected areas water; by comparing the removal capacity of F-1 activated alumina and γ-alumina.
3. To investigate ultrasound technology for treatment of contaminated ground waters.

The review of literature on methods of fluoride estimation are presented in Chapter 2.