INVESTIGATION OF MEDIA FOR REMOVING FLUORIDE FROM THE ETHIOPIAN RIFT VALLEY GROUND WATER

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BY
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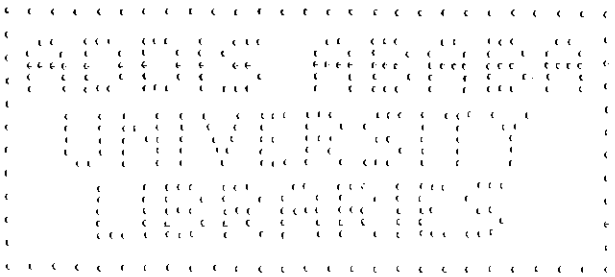
DEDICATION

To my wife, Admaswork Arega and my children Lidia and Fra'ol



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ABSTRACT

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By

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The chemical properties of fluorine, fluoride in the human environment; the fluoride absorption, distribution, and excretion in the human system are briefly reviewed. The beneficial and toxic effects of fluoride to human, plants, and animals; and several defluoridation methods have also been briefly reviewed.

Aluminium oxide, alumina, was prepared from aluminium sulphate (hydrate), produced locally in Awash Melkasa. The defluoridation capacity of 2% HCl treated laboratory product alumina was compared with commercial acidic alumina. The amounts of acidic alumina required to bring the fluoride concentration to less than the recommended value by WHO (1.5 mg/L F^-) were determined for different concentrations of fluoride. Studies were also made for local kaolin (beneficiated kaolin), commercial kaolin, and diatomaceous earth. Local kaolin was found to be a promising defluoridating material. The parameters investigated were contact time, mass, and volume effect. To some extent the pH effect was also considered. The overall result shows that acidic alumina and local kaolin are very efficient defluoridating material.

1. INTRODUCTION

1.1. Fluorine

Fluorine is in the VII A group of the periodic table. Its electronic configuration is $1s^2 2s^2 2p^5$; at room temperature it is a pale, yellow-green gas. It is the most electronegative and reactive of all elements and thus, in nature, is rarely found in its elemental state. Fluorine combines directly at ordinary temperature or elevated temperatures with all elements other than oxygen and nitrogen and therefore reacts vigorously with most organic compounds. Fluoride ions have a strong tendency to form complexes with metal ions in aqueous solutions,e.g. FeF_6^{3-},AlF_6^{3-},MnF_5^{2-}, MnF_3^-, ZrF_6^{2-}, and ThF_6^{2-}. The toxic potential of inorganic fluorides is mainly associated with this behaviour and the formation of insoluble fluorides [1,2].

Fluorine reacts with metallic elements to form compounds that are usually ionic, both in the crystalline state and in solution. Most of these fluorides are readily soluble in water; however, lithium, aluminium, strontium, barium, lead, magnesium, calcium, and manganese fluorides are insoluble or sparingly soluble [2].

1.2. Fluoride in the Human Environment

1.2.1. Fluoride in rocks and soil

Fluorine is widely distributed in nature and occurs in continental rocks of the earth's crust to the extent of about 0.065 % by weight. Among the elements, fluorine is thirteen in abundance. It exists in the form of fluorides in a number of minerals. The main fluoride containing minerals are fluorspar (CaF_2), cryolite (Na_3AlF_6), and fluorapatite [$Ca(F,Cl,OH)Ca_4(PO_4)_3$], but in most soils it is associated with mica and other clay minerals [1,2].

The volcanic rocks of East Africa are richer in fluoride content than analogous rocks in other parts of the world. These are most probably responsible for the East Africa Rift and is known to be a natural high fluoride zone. For example high fluoride concentration (400 mg/kg) is reported for the obsidian of the Chabbi volcano, Corbetti, which is consistent with the high fluoride in the surrounding waters [3].

The mean fluoride content of mineral soils is 0.2-0.3 g/kg, whereas that of organic soils is usually lower. However, in soils which have developed from fluoride containing minerals it

may range from 7 to 38 g/kg. The fluoride content of top soil may be increased by the addition of fluoride containing phosphate fertilizers, pesticides, irrigation water, or by deposition of gaseous and particulate emission [2].

1.2.2. Fluoride in water

Drinking water is by far the most important source of fluorine, which is present usually in the form of dissolved fluoride but occasionally in the form of suspended fluoride particles. Fluorides are present in both surface and ground waters owing to the solvent action of water on rocks and soil. The natural concentration of fluoride in ground water depends on such factors as the geological, chemical, and physical characteristics of the water supplying area, the consistency of soil, the porosity of rocks, the pH, the temperature of interaction between rock and water [2,3]. Owing to these factors, fluoride concentration in ground water fluctuate within wide limits. It is reported that the fluoride content of water in different areas of the Ethiopian Rift Valley ranges from 0.2 to 295 mg/L. Surface waters are generally low in fluorides (less than 1 mg/L),while underground or subsoil waters, which have a greater opportunity to contact fluorine bearing rocks, usually contain higher levels of fluoride [4].

1.2.3. Airborne fluoride

Traces of fluoride in the air of rural communities and cities arise from both natural sources and human activities. Natural sources of fluoride, including volcanic activity, in the air are the dust from soils, and sea-water droplets, carried up into the atmosphere by winds. However, most of the airborne fluoride in the vicinity of urbanized areas is generated through human activities including aluminium industry, steel production plants, superphosphate plants, ceramic factories, coal-burning power plants, brick works, glass works and oil refineries. Atmospheric dust contributions are not considered significantly in Ethiopia; however, in many of these industries airborne fluorides from dusts and gases are potential health problem in several parts of the world, as the fluoride ions are almost completely absorbed from the lung [2,4,5].

1.2.4. Fluoride in food

Food almost always contains at least traces of fluoride. All vegetation contain some fluoride, which is absorbed from soil and water. Tea leaves, for example, are usually very rich

in fluoride, and levels ranging from 3.2 to 400 mg/kg dry weight have been reported [2]. The fluoride content of water used in industrial food production and home cooking may also affect the fluoride content of ready-to-eat products.

1.3. Fluoride Absorption, Distribution, and Excretion

Fluorides are absorbed from gastrointestinal tract, the lung, and the skin. The gastrointestinal tract is the major site of absorption. The degree of absorption of a fluoride compound is best correlated with its solubility. The relatively soluble compounds, such as sodium fluoride, are rapid and almost completely absorbed from gastrointestinal tract. Fluorides from insoluble or sparingly soluble compounds, such as calcium fluoride and cryolite, are less efficiently absorbed [2,6]. However, some fluorides may be more easily dissolved in the stomach because of the low pH and hydrogen fluoride will then be formed. This compound may easily penetrate biological membranes, and its chemical reactivity is the probable cause of the resulting gastrointestinal symptoms when large amounts have been ingested. The simultaneous presence of strongly fluoride binding ions, especially calcium ions, will reduce the absorption of fluoride by forming low soluble complexes in the gastrointestinal tract [7]. Traditional milk feed up of children in some part of Wonji/Shoa may be related with the reduction of absorption of fluoride. The second most common route of absorption is by way of the lungs. Pulmonary inhalation of fluoride present in dusts and gases constitutes the major route of industrial exposure. A third, and relatively rare, route of absorption is through the skin [8].

Fluoride has been detected in all organs and tissues examined, however, there is no evidence that it is concentrated in any tissue except bone, thyroid, aorta, and perhaps kidney [9]. Fluoride is preponderantly deposited in the skeleton and teeth. The amount of fluoride present in bone depends on the fluoride intake, age, bone type and the specific part of the bone. Young animals store more of the daily intake than older ones, which is related to the skeletal growth. Trabecular bone contains more fluoride than compact bone, and the biologically active surfaces of bone take up fluoride more readily than the interior [2]. The amount of fluoride in bone increases up to the age of 55 years [10].

Because prolonged exposure to excessive quantities of fluorides can lead to ill effects, their excretion from the body is of great importance. The major route of fluoride excretion is by way of the kidneys; however, some excretion takes place through faeces and sweat. In adults,

excess of the fluoride absorbed is excreted through urine. Fluoride appears rapidly in the urine after absorption, and the level is recognized as one of the best indices of fluoride intake. Several factors may influence the urinary excretion of fluoride, such as age, urinary flow, previous exposure to fluoride, urine pH and kidney status. Young persons who are actively forming bone minerals excrete less fluoride, i.e., a lower proportion of the absorbed dose, than adults. In chronic renal failure, the urinary excretion of fluoride is diminished. In such case, the impairment of urinary fluoride excretion is reflected by an increase in the fluoride content of the bone [11]. Faecal excretion accounts for the loss of some 10% of the daily intake, but when the diet includes relatively insoluble fluorides (e.g. cryolite and calcium salt) the proportion may be as high as 30%. Under conditions of excessive sweating, the fraction of total fluoride excretion contributed by sweating can reach nearly one half [4,6].

1.4. Beneficial Effects of Fluoride on Human Beings

1.4.1. Fluorides in bones

The fluoride ion is unique in that it continues to be deposited in calcified structures after other bone constituents (calcium, phosphorus, magnesium, carbonate, and citrate) have reached a steady state. Even if large amounts of these other constituents are administered, their concentrations, which reached their maximum early in life, remain essentially unchanged. Fluoride in bone, on the other hand, increases very rapidly with higher fluoride levels in drinking water. However, age is an important factor in the extent to which fluorine is incorporated into the skeleton.

The current theory of bone formation postulates that collagen (the chief protein of bone fibre) forms a matrix for a nucleation process in which calcium and phosphorus are deposited. This is followed by the formation of the mineral phase called hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$. Thus the collagen fibres act as a template for the deposition of the hydroxyapatite crystals. As fluoride ions are much the same size and shape as the hydroxyl ions, they are able to replace hydroxyl ions, either partially or totally, in the apatite crystals; so that hydroxyapatite and fluorapatite are able to coexist in the mineral phase. The role of fluoride in the skeleton is not completely understood; though, low fluoride concentrations are beneficial for the formation of healthy apatite structure and reduce their solubility, thus stabilizing the whole skeletal system [4].

1.4.2. Fluoride in teeth

The concentration of fluoride in teeth follows a similar pattern to that in bone. The age of the individual and fluoride intake in food and water are the chief factors. But in dental enamel, which has no cells and no circulation, the uptake almost ceases after about the age of 30 years [4].

The carries inhibiting capacity of fluoride ions was discovered in 1930s, but the mechanism by which fluorides give protection against dental carries is not yet settled. In general terms, it is thought that fluoride reduces carries through influencing the morphology of teeth by reducing the solubility of the enamel and promoting remineralization, and through its effect on plaque bacteria. Remineralization (apatite-precipitation) occurs during relatively neutral periods being promoted by fluoride ions present in the bio-system constituted by dental plaque, saliva and the enamel surface. An increase in fluoride in this system will facilitate apatite formation and consequently stabilize already precipitated crystals, thereby counteracting dissolution processes that lead to carious cavities. In addition to influencing the formation of apatite, fluoride has also influence on the composition and retard the growth of bacterial plaques and the enzymatically conducted production of acids and polysaccharides in the plaque. Demineralization (apatite-dissolution) is effected by acids produced from carbohydrates, especially sucrose, by microorganisms in the bacterial (dental) plaques on the tooth surfaces [4,6]. In Ethiopia, studies related to dental carries and the uses of fluoride in carries prevention are not available.

1.4.3. Fluorides in the treatment of osteoporosis

Osteoporosis is defined as the loss of bone accelerated beyond the normal "physiological" rates [12]. Most adults lose minerals from bone steadily throughout their life. In women, this bone loss is accelerated for a year or two after the menopause, so that bone mass may ultimately be less than half of that in young adults. In males, a corresponding acceleration appear at 60-65 years of age. Severe clinical manifestation of osteoporosis are: loss of cortical bone, which leads to fracture of long bones, and loss of trabecular bone, which may cause fractures in the spine. However, it was found that sodium fluoride has been used as a potential treatment for osteoporotic disease [4,13].

1.5. Effect of Fluoride on Plants and Animals

1.5.1. Plants

Plants are exposed to fluoride in the soil and in the air as a result of volcanic activity, natural fires, wind-blown dusts, pesticides or an emissions from processes in which fluoride containing minerals are burned, manufactured, handled or used. Fluoride is taken up from the soil by passive diffusion, then it is carried to the shoot by transpiration. Where soils are saline or enriched by fluoride-containing minerals or the atmosphere contains elevated fluoride concentrations, the concentration may be much higher. In such areas, there may be sufficient plant uptake of fluoride to contribute significantly to the human or animal diet. There are also a number of species that accumulate high concentration, even when grown on low-fluoride soils, as a result of complex formation with aluminium. The tea family, Theaceae, is the best known of these accumulators [2]. Gaseous and particulate fluorides in the air deposit on exposed plant surfaces, whilst gaseous fluoride enters leaves through stomatal pores. Though such deposits are of negligible toxicity to the plant, they may present a hazard for grazing animals. Fluoride that penetrates the internal tissue of leaves or that is deposited on active surfaces such as stigmata may affect a variety of metabolic processes and result in effects on appearance, growth, or reproduction. The visible effects of toxic concentrations of fluoride on plants are chlorosis, peripheral necrosis, leaf distortion and malformation or abnormal fruit development [14].

1.5.2. Animals

The major route of fluoride uptake by domestic animals is through ingestion. Chronic manifestations of excess fluoride exposure are similar to those found in human, i.e., severe dental fluorosis and lameness; this limits feeding and therefore impairs performance. Symptoms in livestock develop progressively at total dietary fluoride concentrations above 20-30 mg/kg dry matter [1,2].

1.6. Toxic Effects of Fluoride on Human Beings

1.6.1. Acute toxic effect

Most cases of acute poisoning in human beings have been associated with accidental ingestion of fluoride containing insecticides and other products used in the home. Poisoning has

most frequently been in the form of sodium fluoride, sodium fluorosilicate (Na_2SiF_6) or hydrofluoric acid. In the case of acute fluoride poisoning, practically all the organs and systems are affected. The manifestations include vomiting (some times blood-strained), abdominal cramps, diarrhoea, severe weakness, cyanosis, cardiovascular disorders, convulsions and coma. There is no specific treatment in fluoride poisoning except for the administration of calcium salt [1,4,6].

1.6.2. Chronic toxic effect

Intake of excess fluoride ions are the causes of fluoride poisoning, often known as fluorosis [1] when the condition is chronic. The disease is known as "shakiso" in the victimized areas of Ethiopian Rift Valley, particularly Wonji/Shoa. Many people in the world, especially in developing countries, are suffer from fluorosis. Depending on the climatic conditions and daily water intake, the optimal range of fluoride concentration recommended by the World Health Organization, WHO, is from 0.6 to 1.5 mg/L [4,15].

Mottled enamel or dental fluorosis is a well-recognized entity that was first described in 1901 and first associated with fluorides in drinking water in 1931 [4,6]. Dental fluorosis involves discolouration, weakening and possible eventual loss of the teeth. The condition particularly affect growing teeth and so is most pronounced in young children between the age of 1-12 years. Mottling is one of the first visible signs of an excessive intake of fluoride during childhood.

Skeletal fluorosis connected with drinking water containing fluoride in excess of 10 mg/L was reported in 1937 in India [16]. Dental fluorosis is easily recognizable entity, whereas skeletal fluorosis does not become clinically obvious until crippling occurs. Early harmful effect (symptoms) of fluoride include pains in the small joints of the hands and feet, in knee joints, and in the joints of the spine. In later stages there is stiffening of the spine and limitation of movement, followed by curvature of the spine. The advanced stage of skeletal deformity and crippling results from continuous exposure for 10-20 years to a daily intake of 10 mg/L fluoride in drinking water. In skeletal fluorosis, the bones are heavy and irregular. The sites of muscle and tendon insertions are abnormally prominent, irregular bone may be seen along the attachment of muscles and tendons, there is thickening and calcification in most of the ligaments, and the thyroid cartilage is often calcified. Apart from these gross changes, fluorotic bones increase in

weight; the fluorotic skeleton may be more than twice as heavy as a normal skeleton of similar proportions. The chemical composition is also altered with a marked increase of fluoride in the bone. Moreover, poor nutrition including calcium deficiency, protein deficiency and hard manual labour increase individual susceptibility to fluorosis [2,4,6].

Both dental and skeletal fluorosis are prevalent in the Ethiopian Rift Valley, owing to high fluoride waters that originate from ground waters (spring and boreholes) [17]. Though the population affected by fluorosis is not known, those ingest ground water in the Rift Valley are adversely affected by the disease. Similarly, the possible effects of fluorosis on animals living in the region are not so far well studied.

1.7. Optimum Concentration of Fluoride in Water

Water requirements increase in hot climates. Based on the mean maximum temperature a generalized formula has been derived for the calculation of the "optimum" fluoride concentration in drinking water in different climatic regions [18].

$$\text{Optimum F} = 0.34/A \quad \text{mg L}^{-1} \tag{11}$$

where $A = (-0.038 + 0.0062\ t)$, t = the annual mean of daily maximum temperature (°F).

1.8. Detection of Fluoride

The spot test method of analysis (drop analysis) is one of the recent methods of qualitative chemical analysis [19]. The most commonly used procedures for fluoride detection, in different forms of fluoride containing substances, are the following.

1.8.1. Test with zirconium-alizarin solution

The addition of alizarin or alizarin sulphonate to dilute solutions of zirconium chloride containing hydrochloric acid results in a red-violet colour due to the formation of hydrosols of a zirconium lake with these dyestuffs. The dispersions turn yellow as soon as they are treated with excess fluoride. The zirconium combines with the latter to form colourless complex $[ZrF_6]^{2-}$ anions and withdrawn from the alizarin lake. Consequently, only the yellow colour of the alizarin remains.

1.8.2. Test with zirconium azoarsonate

The brown insoluble zirconium azoarsonate, formed by the action of p-dimethylaminoazobenzenearsonic acid on zirconium salts, reacts with fluorides to produce colourless $[ZrF_6]^{2-}$ ions and red azobenzenearsonic acid. Thus, if a drop of an acidic fluoride solution is placed on filter paper impregnated with zirconium azoarsonate, the colour change from brown to red indicates the presence of fluoride (in the absence of interfering compounds).

1.8.3. Test by conversion into silicomolybdic acid

Both soluble and insoluble fluorides are converted into silicon tetrafluoride (b.p. -65 °C) on warming with quartz sand (silica) and concentrated sulphuric acid.

$$MF_2 + H_2SO_4 \rightarrow MSO_4 + 2HF$$
$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

The gas may be absorbed in a drop of water; it reacts to produce silicic and fluorosilicic acids:

$$3SiF_4 + 4H_2O \rightarrow H_4SiO_4 + 2H_2SiF_6$$

Ammonium molybdate converts these products into silicomolybdic acid, $H_8[Si\ (Mo_2O_7)_6]$. The latter, unlike free molybdic acid, oxidizes benzidine in acetic acid solution to a blue dyestuff, with concurrent production of molybdenum blue. A blue colour shows the presence of silicic acid and hence the presence of fluoride in the original sample.

1.8.4. Test by etching glass

Vapours of hydrofluoric acid librated from fluorides by heating with concentrated sulphuric acid have a corrosive effect on glass. The decrease in transparency accompanying this change is the basis of the etching test for fluoride. Large amounts fluoride give the required result even without heating.

1.9. Determination of Fluoride

The determination of elementary fluoride is difficult mainly because of the great reactivity of this element. Many methods and modifications have been developed for the liberation of fluoride from samples of various origins as well as for the subsequent determination of the separated fluoride. Some of these methods are presented below.

1.9.1. Colourimetric method

With certain multivalent ions, fluoride ions form stable colourless complexes such as AlF_6^{3-}, FeF_6^{3-}, ZrF_6^{2-}, and ThF_6^{2-}. Most of the colourimetric methods for the determination of fluoride ions are based on such complex formation, i.e., on the bleaching resulting from reactions of fluoride ions with coloured complexes of these materials and organic dyes. The degree of colour change can be assessed by comparison with a standard either by visual titration or by spectrophotometry [20-22].

1.9.2. Chromatographic method

Gas chromatography has recently been introduced for the determination of fluoride in a variety of media. For instance, fluoride ion in water and urine samples is extracted with trimethylchlorosilane (TMCS) and converted to trimethylfluorosilane (TMFS) in toluene. The extracted toluene solution is injected into a gas chromatography and detected by atmospheric pressure helium microwave induced plasma (MIP) emission spectrometry. The emission line of fluorine at 685.6 nm is used for detection.

1.9.3. Fluoride ion-selective electrode

Fluoride ion-selective electrode has become an important method for determining fluoride in a wide variety of fluoride sample because of its excellent performance, speed, convenience and economy. The selectivity of the electrode is based on the properties of a membrane of sparingly soluble single crystals of lanthanum fluoride. It gives an electrochemical response that is proportional to the fluoride ion activity in the sample. The concentration response range for fluoride ion ranges from 0.1 to 10^{-6} mol L^{-1} [24,25]. Several measurement techniques have been used for the determination of fluoride ion concentration [26]. Some of the technique chosen for this particular application are:

Calibration method. Empirical calibration curves, whereby the electrode potential is related to the logarithm of activity or concentration of the ion of interest is most straight forward technique and is the technique of choice whenever possible. The sample to be analysed is pretreated as required and the electrodes immersed in it. The equilibrium cell potential is then measured and related to the determined activity or concentration by means of the calibration curve [26] and also the concentration of analyte (fluoride) in the sample can be calculated by the formula derived from the Nernest equation (single point calibration) as follows:

$$E_S - E_X = \Delta E = S \log C_X/C_S \qquad (1.2)$$

which can be rearranged to :

$$C_X = C_S\, 10^{\Delta E/S} \qquad (1.3)$$

where C_X = concentration of the analyte,

C_S = concentration of the standard solution,

E_S = electrode potential of the standard solution (mV),

E_X = electrode potential of the analyte (mV),

S = slope per decade (mV) /experimentally determined.

Standard addition method. In this method a known volume, V_S, of the standard solution of concentration, C_S, is added to the sample solution, V_X, containing unknown concentration, C_X, and the potential change of the electrode is recorded [27], then the concentration of unknown analyte (fluoride) in the original solution is given by:

$$C_X = C_S . V_S \left[(V_X + V_S)\, 10^{\Delta E/S} - V_X \right]^{-1} \qquad (1.4)$$

1.10. Defluoridation Methods

Excess fluoride in drinking water causes skeletal and dental fluorosis which is encountered in endemic proportion in several parts of the world. Due to the unavailability of effective therapeutic measures, defluoridation of drinking water appears to be the best method

for combatting the disease. Several methods, using a variety of materials, have been suggested from time to time. Methods practised for removal of excess fluoride from drinking water can be broadly divided into two categories, namely precipitation and adsorption. Precipitation method depends on the addition of chemicals to the water, which leads to the formation of fluoride precipitates or adsorption of fluoride onto the formed precipitate. In the adsorption method, water containing fluoride is retained on the adsorbent due to physical, chemical or ion-exchange interactions.

1.10.1. Fluoride removal by carbon

Defluoridation method reported by McKee *et al.* [28] involves the adsorption of fluoride by carbon. This method is simple and considered to be economical, but the process is handicapped by the fact that the water being treated must have a pH of 3 or less at the time of treatment.

Another method reported for the defluoridation of fluoride water was with carbonised sawdust [29] after soaked in a 2% $Al_2(SO_4)_3$ solution. However, the adsorption efficiency is decreases with increasing the temperature. It can be reactivated by treating with a 0.2 to 0.5% $Al_2(SO_4)_3$ and not affected by other ions normally present in water.

1.10.2. Fluoride removal by alum and lime

Nalgonda technique, that requires the addition of alum and lime was developed in India in 1975 [30]. It has been used in domestic as well as at community level in India. The limitations of this method are: the daily addition of chemicals; large volume of sludge production; ineffective with water sources having high total dissolved solid; and defluoridated water should be checked to ensure that there is no aluminium content arising from the alum [31]. In addition, the technique was found to be ineffective in removing fluoride from drinking water because in the defluoridation process fluoride was converted into a solution of aluminium complex and only 18-33% removed in the form of precipitate. The hitherto positive assessment of the method results from an analytical error [32].

1.10.3. Fluoride removal using $Ca_3(PO_4)_2$, MgO or $Mg(OH)_2$

Defluoridation of drinking water was also proved to be successful by $Ca_3(PO_4)_2$, MgO or $Mg(OH)_2$ [33]; however, the method is somewhat costly. In the case of magnesite particularly, since it is used extensively in building operations and for various other purpose, it may be possible to utilize the material after its availability for fluoride removal has been exhausted and thus indirectly reduce the cost of treatment.

1.10.4. Fluoride removal by aluminium sulphate

Precipitation methods that have been employed to defluoridate water with the aids of aluminium sulphate is reported in the literatures [34,35] and also preliminary study was conducted in our laboratory [36]. This material is manufactured in Ethiopia, readily available and relatively cheap (approximately 3.43 Eth. Birr per kg). But, apart from the acidity of water which govern the removal of fluoride, it may be inconvenient method as reported by Apparao *et al.* [32] for Nalgonda technique. A simple and better technique suggested for removing fluoride is the boiling of water than treatment with aluminium salts [37], but the cost of energy source made it dormant to gain wide acceptance in household or at community levels.

1.10.5. Fluoride removing with bone

Appropriate and promising techniques developed by various researchers are the methods based on the adsorption of fluoride by bone and bone char [38-41]. The methods require readily available materials, simple process, and repeatedly regeneration of charred bone without significant loss of binding capacity for fluoride or loss of efficiency. These techniques are recommended by World Health Organization, WHO, to be used in developing countries where drinking water contains excessive fluoride [42]. The problem connected with the bone char method is the disagreeable smell of burning fats released from bone meal in the furnace.

1.10.6. Fluoride removal by ion-exchange

Removals of fluoride from drinking water using ion-exchange materials such as zeolite consist of SiO_2 : Al_2O_3, (5:1), and resins have also been reported in the literatures [43-45]. The fluoride removal of zeolite, for example, involves by first converting negative radicals to acids by replacing metal with H^+ and then replacing acid ions by OH^- in the second bed of the system.

One treatment of this system reduces the fluoride content from 9 to 2 mg/L and a second treatment to 0.25 mg/L; and the exhausted material can be regenerated by means of 5% HCl. Although, the methods reduce the concentration of fluoride from 9 to 0.25 mg/L, they are not technically and economically feasible in developing countries like Ethiopia.

1.10.7. Fluoride removal using china clay and fired clay chips

Other materials suggested by various authors for removing fluoride from drinking water are china clay [46] and fired clay chips [47]. Adsorption of fluoride ion on china clay is favoured by low concentration of fluoride, high temperature and the acidity of fluoride rich water. The fluoride removal by the material, therefore, goes parallel with the appropriate optimization of different parameters and low fluoride content of the water. Therefore, china clay may not be successful for removal of fluoride from highly fluoridated ground waters of the Ethiopian Rift Valley. Moreover, a research report that has been published from the preliminary investigation on the defluoridation of water using fired clay chips was found to have low defluoridating capacity besides the difficulty of attaining high temperatures between 600-800 °C.

1.10.8. Fluoride removal by activated alumina

The most popular method for defluoridation of drinking water in developed countries is the activated alumina. This technique is reported by various researchers as the most promising and convenient technique for reliable specific removal of fluoride [48-52]. Activated alumina which involves the adsorption of fluoride has been practised even in developing countries like India [53] and in some parts of the Ethiopian Rift Valley (Wonji/Shoa and Mathahara Sugar Estates). The method has found to be attractive because the filtration capacity of the material can be fully restored by regeneration with NaOH and H_2SO_4 (HCl) at acceptable costs; and the material is relatively effective in fluoride removal in the pH range (6.5-8.5) stated by WHO as the guideline value for drinking water [54].

1.11. Objectives of the Project

Defluoridation of drinking water in the third world has generally been unsuccessful in spite of many attempts to implement projects. At the same time it has in many cases been avoided to initiate defluoridation in areas where fluorosis is prevalent. This has been due to lack

of knowledge of appropriate technologies or lack of means to provide all the project components associated with defluoridation.

In general, programmes directed towards prevention of fluorosis are not being practised in Ethiopia. No measures have been taken by the government to defluoridate drinking water on national basis, and therefore the problem of fluorosis still continues in most of high fluoride areas. Hence, to prevent this major health problem, the need to find and investigate locally available defluoridation media for safe and easy utilization at both household and community levels have to be practised. Furthermore, appropriate and economic technologies for removal of excess fluoride from drinking water, motivation of users and proper organizational set up shall be some of the immediate future programmes.

The objectives of the present study were thus undertaken to:

1. To prepare alumina from indigenously manufactured aluminium sulphate ($Al_2(SO_4)_3.14H_2O$) in laboratory.

2. To investigate defluoridating media for removing fluoride from the Ethiopian Rift Valley ground waters using;

    a) commercial acidic alumina,
    b) laboratory made acidic alumina,
    c) kaolin (kaolinite mineral), and
    d) diatomaceous earth.

2. EXPERIMENTAL

2.1. Reagents and Materials

Aluminium oxide, alumina (acidic form, Merck), hydrated aluminium sulphate ($Al_2(SO_4)_3.14H_2O$, from Awash Melkasa), beneficiated kaolin (from Awash Melkasa), commercial kaolin (Aldrich), diatomaceous earth (from Adami Tulu), NaCl (Riedel-de Haen), HCl (Riedel-de Haen), and $CaCO_3$ (BDH) were used as defluoridation and as raw materials for the preparations of defluoridating media. Natural waters used for defluoridation studies were obtained from Mathahara (Abadir 3rd) and Wonji/Shoa (CCY-camp). The water samples collected from selected areas of the Ethiopian Rift Valley are given in Table 1.

Table 1. Fluoride water samples collected from selected areas of the Ethiopian Rift Valley.

No.	Place of sample collection	Fluoride content (mg/L)	pH	Remark
1	Awash Melkasa ground water	1.68	8.0	untreated
2	Nazareth tap-water	4.00	8.2	"
3	Awasa ground water	9.79	8.0	"
4	Mathahara ground water			
	i. Abadir 2rd	3.23	8.0	"
	ii. Abadir 3rd	5.27	8.2	"
5	Wonji/Shoa ground water			
	i. Hospital	2.55	8.2	treated
	ii. CCY-camp	12.46	8.2	"
	iii. CCY-camp	12.51	8.2	untreated

Stock solution of 0.1 mol L^{-1} fluoride was prepared by dissolving known weight of NaF (Riedel-de Haen) in distilled water. Solutions of $1x10^{-5}$-$1x10^{-2}$ mol L^{-1} fluoride were prepared from the stock solution by serial dilution with distilled water for calibrating the electrode and for the defluoridation studies.

Total ionic strength adjustment buffer (TISAB) was prepared by dissolving 57 mL of glacial acetic acid (BDH), 58 g of sodium chloride (Riedel-de Haen), 7 g of sodium citrate

(BDH) and 2 g of EDTA (BDH) in 500 mL of distilled water; (and before dilution to volume) the pH was adjusted to 5.5 by adding 10 mol L^{-1} NaOH (BDH) solution [55,56].

2.2. Equipments

Naber electric furnace (Model L 51/S) which has a temperature range up to 1200 °C was used for heating aluminium sulphate ($Al_2(SO_4)_3.14H_2O$) and diatomaceous earth. Harris standard magnetic stirrer was used for stirring the sample and adsorbent. Heraceus centrifuge was used for the separation of adsorbed fluoride from supernatant. An Orion combination fluoride ion-selective electrode (Model 96-09) with an Orion portable pH/ISE meter (Model 250) was used for the determination of fluoride in the defluoridation studies.

2.3. Fluoride Determination

Electrode potentials of standard and sample solutions, in the presence of TISAB, were measured with fluoride ion-selective electrode. The cell consisted of 25 mL of magnetically stirred solution containing 20 mL of sample and 5 mL of TISAB. The residual fluoride concentration in the supernatant was then calculated using equation 1.3 and 1.4 (where its concentration found to be below 10^{-5} mol L^{-1}).

The quantities of fluoride adsorbed in a given period of contact time and removal efficiencies were calculated as [57]

$$Q_t = (C_o - C_t)/D \qquad (2.1)$$

or

$$\text{defluoridation capacity mg } F^-/kg = \frac{\text{mg of } F^- \text{ removed x } 1000}{\text{amount of adsorbent taken (g)}}$$

$$\% \text{ of removal efficiency} = (C_o - C_t) \times 100/C_o \qquad (2.2)$$

where t = contact time;

Q_t= the amount of adsorbate adsorbed within the given period of contact time, mg adsorbate per g of adsorbent;

C_o= the initial concentration of the adsorbate in the solution, i.e. at t = 0, mg/L;

C_t = the final concentration of the adsorbate in the centrifuged or/and filtered solution after the contact time of t, mg/L;

D = the adsorbent dosage, g/L.

2.4. Preparation of Alumina

Thermal decomposition of hydrated aluminium sulphate is one of the methods for the preparation of alumina [58]. This method was used in the present study. Ten g of weighed indigenously manufactured aluminium sulphate ($Al_2(SO_4)_3.14H_2O$) was placed into a china clay and calcined in a muffle furnace in the temperature range 900-950 °C for 2 h. The decomposed product was cooled to room temperature in a desiccator. The cooled material was weighed and found to be 1.7375 g.

Aluminium oxide prepared by heating the aluminium sulphate was treated with various concentration of HCl to obtain acidic alumina. The product was first transferred into two nylon mesh bags which were then dipped separately in 50 mL of 0.1 and 0.65 N HCl for 12 h (overnight). After HCl drain from nylon bags excess acid was removed by rinsing with tap water for 2 min. The rinsed alumina was dried in an oven at 100 °C for 6 h and stored in a desiccator before use in the defluoridation experiments.

2.5. Removal of Fluoride from Water

2.5.1. Experimental procedures and parameters

i. Batch system experiment

Mass effect. The fluoride removal efficiencies of various amounts of adsorbents from fixed volume of fluoride waters were investigated at constant period of contact time. At the end of a fixed period of contact time the adsorbed fluoride was removed by centrifugation and filtration.

Study 1. 0.1-1.5 g of commercial and laboratory made acidic alumina were separately added to each of 100 mL of 4.75, 9.5, 19 mg/L standard fluoride (pH = 6.2-6.5) and 5.27, 12.51 mg/L of ground waters (pH = 8.2); and kept with stirring for 90 and 45 min, respectively.

Study 2. 1-30 g of local kaolin (a raw material used for the manufacturing of $Al_2(SO_4)_3.14H_2O$ in Awash Melkasa) was added to 100 mL of fluoride waters containing 4.75-19 mg/L fluoride and allowed to stand for 30 min and 14 h including 3 min stirring time. For comparative study 2-15 g of commercial kaolin (Aldrich) was added to 100 mL of 19 mg/L standard fluoride solution and kept for 14 h of adsorption time.

Study 3. 5-15 g of untreated diatomaceous earth was mixed with 100 mL of 19 mg/L standard fluoride solution and allowed to stand for 13 h.

Study 3.1. 8 g of calcined diatomaceous earth (between 450-880 °C for 2 h without addition of any chemical) was mixed with 100 mL of 19 mg/L standard fluoride solution and kept for 3 h contact time.

Study 3.2. 10-30 g of calcined diatomaceous earth with equal amount of NaCl and $CaCO_3$ (heated between 450-880 °C for 2 h) was added to 100 mL of fluoride waters containing 5.27-19 mg/L fluoride and allowed to stand for 30 min including 3 min stirring time.

Study 3.3. 5 g of calcined diatomaceous earth (with equal amounts of NaCl and $CaCO_3$ heated between 450-880 °C) was treated with 25 mL of 2% HCl for 13 h (overnight). The HCl treated calcined diatomaceous earth was mixed with 100 mL of 19 mg/L standard fluoride solution and kept for 30 min.

Volume effect. The volume effect of fluoride water samples on fluoride removal at constant mass of adsorbent was studied at a fixed period of contact time.

Study 4. A fixed mass of 0.5 g of commercial and laboratory made acidic alumina was separately added to varied volumes (50-200 mL) of standard fluoride and ground waters containing 4.75-19 mg/L fluoride and allowed to stand for 45 min of contact time.

Study 5. The following constant masses of local kaolin were separately added to 50-200 mL fluoride waters and kept for 30 min (a, b) and 5 h (c) contact time.

a) 15 g of kaolin to Mathahara ground water (5.27 mg/L),
b) 30 g of kaolin to Wonji/Shoa ground water (12.51 mg/L), and
c) 15 g of kaolin to 19 mg/L standard fluoride water.

Study 6. 20 g of calcined diatomaceous earth (with equal amounts of NaCl and $CaCO_3$ heated between 450-880 °C for 2 h) was mixed with 50-200 mL of various concentrations of fluoride waters and kept for 30 min of contact time.

Time effect. The effect of contact time was investigated by adding a fixed amount of adsorbent to a constant volume of various concentrations of fluoride waters at different periods of contact time. Immediately after a given period of contact time the mixture was separated.

Study 7. 0.5 g of commercial and laboratory made acidic alumina were separately added to each of 100 mL of fluoride waters containing 4.75-19 mg/L fluoride and stirred for 3-45 min contact time.

Study 8. The following constant mass of kaolin was mixed with 100 mL of fluoride waters.
a) 4 g of local kaolin to 4.75 mg/L standard fluoride water,
b) 15 g of commercial and local kaolin to 19 mg/L standard fluoride water,
c) 15 g of local kaolin to Mathahara ground water, and
d) 30 g of local kaolin to Wonji/Shoa ground water.

Study 9. 20 g of calcined diatomaceous earth (with NaCl and $CaCO_3$ between 450-880 °C for 2 h) was added to 100 mL of fluoride waters containing 5.27-19 mg/L fluoride and kept for 30-120 min.

pH effect. The fluoride removal efficiencies of alumina and local kaolin were studied after the pH of natural water was adjusted to 6.5 with 0.1 N HCl.

ii. Column system experiment

Packed-column experiments were conducted to remove fluoride from water by adsorption on acidic alumina. A 2 mL "ISOLATES" column (3.2 cm height, 9 mm internal diameter) was packed with 2.1 g commercial and 0.55 g laboratory made acidic alumina separately. Fluoride water (5.27-19 mg/L F^-) was continuously pumped with "ALTEA U-8 R" pump into the column at a flow rate of 1 mL/min. The fluoride concentration of the different fraction of effluent was determined.

3. RESULTS AND DISCUSSION

3.1. Preparation of Alumina

Thermal decomposition of hydrated aluminium sulphate is one of the methods for the preparation of alumina [58]. This method was used in the present study. A weight loss of 82.6% was observed on heating indigenously manufactured aluminium sulphate, $Al_2(SO_4)_3.14H_2O$. The results are given in Table 2. Sato *et al.* [58] reported the weight loss of 83.7% on heating $Al_2(SO_4)_3.18H_2O$ at a temperature of 900 °C for 2 h. The theoretical value of weight loss for $Al_2(SO_4)_3.18H_2O$ and $Al_2(SO_4)_3.14H_2O$ are 84.7 and 82.9%, respectively. The mechanism suggested [59] for the thermal decomposition of aluminium sulphate is :

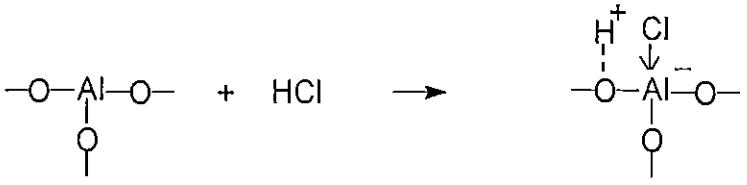
$$Al_2(SO_4)_3.14H_2O \text{ ---------> } Al_2O_3 + 3SO_3 + 14H_2O$$

Table 2. Weight loss of $Al_2(SO_4)_3.14H_2O$ on heating at 900-950 °C for 2 h.

Weight of $Al_2(SO_4)_3.14H_2O$ (g)	Weight loss (g)	% of weight loss
10	8.2566	82.57
10	8.2690	82.69
10	8.2618	82.62
Mean*	8.2627± 0.006	82.63

*Mean ± standard deviation for triplicate analysis.

The laboratory made aluminium oxide was treated with 0.1 and 0.65 N HCl to obtain acidic alumina. The Bronsted acidity induced by treatment with HCl can be represented as shown below [60]:



The fluoride uptake capacity of acid untreated, 0.1 and 0.65 N HCl treated alumina were evaluated on 100 mL of 19 mg/L standard fluoride solution at a contact time of 1:30 h. The defluoridation capacity of 0.65 N (2%) HCl treated alumina was found to be higher than the others two types of alumina (Table 3). Therefore, acidic alumina that has been treated with 2% HCl was selected to carry out the defluoridation studies throughout the investigation.

Table 3. Defluoridation capacity of different types of laboratory made alumina (dosage 1 g).

Type of alumina	Residual F^- concentration (mg/L)*	% of F^- removed	Defluoridation capacity (mg F^-/kg)
Untreated	5.46 ± 0.17	71.3	13,540
0.1 N HCl treated	2.06 ± 0.05	89.2	16,940
0.65 N HCl treated	1.25 ± 0.03	93.4	17,750

*Mean ± standard deviation for triplicate analysis.

3.2. Fluoride Removal by Acidic Alumina

3.2.1. Effect of mass

The results shown in Tables 4 and 5 are indicate that the residual fluoride concentrations in each of standard fluoride and ground water samples decreased with the increased amounts of acidic alumina. However, both the commercial and laboratory made acidic alumina showed remarkable decrease in the defluoridation efficiency for the ground water as compared to the standard fluoride solution. One factor which is responsible for this variations is due to the presence of other interfering ions [50] in natural water such as OH^-, Cl^-, SO_4^{2-}, HCO_3^-, and PO_4^{3-}. A report from Mathahara Sugar Estate confirmed that bicarbonate, sulphate, and chloride ions are the major constituents of Abadir 3rd ground water. The fluoride removal efficiency of acidic alumina is, therefore, severely inhibited by those ions owing to their competing effect with fluoride ion for the adsorption sites of alumina. The second factor that can affect the fluoride removal of alumina is the pH effect of natural water which have pH of 8.2. This effect was studied for Mathahara ground water after pH was adjusted to 6.5 with 0.1 N HCl.

The laboratory made acidic alumina was found to be better defluoridating material for

natural water than commercial acidic alumina. This may be due to the difference in the preparation processes of alumina. It was observed that the laboratory made acidic alumina was much lighter than the commercial acidic alumina, i.e., the laboratory made alumina has larger surface area than the commercial alumina and hence it exhibited greater efficiency for fluoride removal than the commercial alumina. From the observed results, the amount of acidic alumina required to reduce high concentration of fluoride to less than the maximum optimal limit (< 1.5 mg/L, as recommended by WHO) at specified period of contact time can be estimated (Tables 4 and 5) and accordingly used to defluoridate large volume of fluoride water.

Table 4. Effect of mass of commercial and laboratory made acidic alumina on fluoride removal from 100 mL of standard fluoride solution at contact time of 1:30 h and pH = 6.2-6.5.

Amount of alumina (g)	Initial F^- concentration (mg/L)	Residual fluoride concentration (mg/L)	
		laboratory made alumina	commercial alumina
0.1	19	4.80	14.42
	9.5	2.39	4.77
	4.75	0.98	1.57
0.5	19	1.90	4.58
	9.5	0.73	0.32
	4.75	0.42	0.30
1.0	19	0.83	0.30
	9.5	0.39	0.30
	4.75	0.36	0.30
1.5	19	0.54	0.30
	9.5	0.35	0.30
	4.75	0.33	0.29

Table 5. Effect of mass of commercial and laboratory made acidic alumina on fluoride removal from 100 mL of Wonji/Shoa (12.51 mg/L F^-) and Mathahara (5.27 mg/L F^-) ground water at contact time of 45 min and pH of 8.2.

Amount of alumina (g)	Initial F^- concentration (mg/L)	Residual F^- concentration (mg/L)	
		laboratory made alumina	commercial alumina
0.1	12.51	10.54	11.84
	5.27	4.22	4.73
0.5	12.51	4.37	6.17
	5.27	2.13	3.34
1.0	12.52	1.50	3.76
	5.27	1.12	1.80
1.5	12.57	0.52	1.90
	5.27	0.35	1.31

3.2.2. Effect of volume

The results are shown in Tables 6 and 7. The residual fluoride concentrations of defluoridated waters were found to increase with increased volume of water samples. The substantial decrease in the fluoride removal is due to the decrease in the active sites of the acidic alumina. Therefore, the residual fluoride can be decreased by increasing the dosage of acidic alumina proportional to the volume of water to be defluoridated. However, the residual fluoride concentration observed for various volumes (50-200 mL) of 4.75 mg/L of standard fluoride solution is still below the tolerance limit of fluoride concentration. This implies that the fluoride removal efficiency of acidic alumina is not significantly affected by increasing volume of fluoride solution.

Table 6. Effect of volume of standard fluoride solutions on fluoride removal with 0.5 g of commercial and laboratory made acidic alumina at contact time of 45 min.

Volume of sample (mL)	Initial F^- concentration (mg/L)	Residual F^- concentration (mg/L)	
		laboratory made alumina	commercial alumina
50	19	1.34	0.30
	9.5	0.55	0.30
	4.75	0.39	0.30
100	19	2.75	4.66
	9.5	0.93	0.72
	4.75	0.45	0.34
150	19	3.11	8.55
	9.5	1.23	1.31
	4.75	0.67	0.34
200	19	4.27	10.56
	9.5	1.55	2.76
	4.75	0.70	0.40

Table 7. Effect of volume of Wonji/Shoa (12.51 mg/L F^-) and Mathahara (5.27 mg/L F^-) ground water on fluoride removal on 0.5 g of commercial and laboratory made acidic alumina at contact time of 45 min.

Volume of sample (mL)	Initial F^- concentration (mg/L)	Residual F^- concentration(mg/L)	
		laboratory made alumina	commercial alumina
50	12.51	1.61	4.32
	5.27	1.27	1.82
100	12.51	4.37	6.17
	5.27	2.13	3.34
150	12.51	5.23	7.61
	5.27	3.19	4.16
200	12.51	6.02	8.66
	5.27	3.40	4.43

3.2.3. Effect of time

The results obtained for the influence of contact time on fluoride removal by acidic alumina are shown in Tables 8, 9 and Figs. 1 and 2. The fluoride uptake capacities of both commercial and laboratory made acidic alumina increased up to 30 min of contact time and then remained constant, i.e.,the amount of fluoride adsorbed after 30 min did not significantly add to the efficiency of fluoride removal (Tables 8 and 9). On the other hand, conflicting results were observed for Wonji/Shoa and Mathahara ground waters (Figs. 1 and 2, respectively), because the removal efficiencies were decreased with the increased periods of contact time. However, the controversies were reconciled after the pH of Mathahara ground water was adjusted to 6.5 with 0.1 N HCl. At this pH the results showed that an increase in the fluoride removal efficiency of alumina similar to the behaviour observed for standard fluoride solution. Therefore, this suggests that fluoride removal with alumina is probably governed by chemisorption in acidic medium and by physisorption in basic medium.

Table 8. Effect of contact time on the fluoride removal with 0.5 g commercial and laboratory made acidic alumina from 100 mL of 4.75 mg/L standard fluoride solution.

Contact time (min)	Residual F^- concentration (mg/L)	
	laboratory made alumina	commercial alumina
20	0.52	0.41
30	0.51	0.38
40	0.50	0.38
45	0.45	0.34

Table 9. Effect of contact time on the fluoride removal with 0.5 g of commercial and laboratory made alumina from 100 mL of 19 mg/L standard fluoride solution.

Contact time (min)	Residual F^- concentration (mg/L) using	
	laboratory made alumina	commercial alumina
3	3.76	12.97
5	3.40	10.32
10	3.14	9.22
15	3.05	8.40
20	2.98	6.51
30	2.96	5.42
40	2.92	4.83
45	2.90	4.58

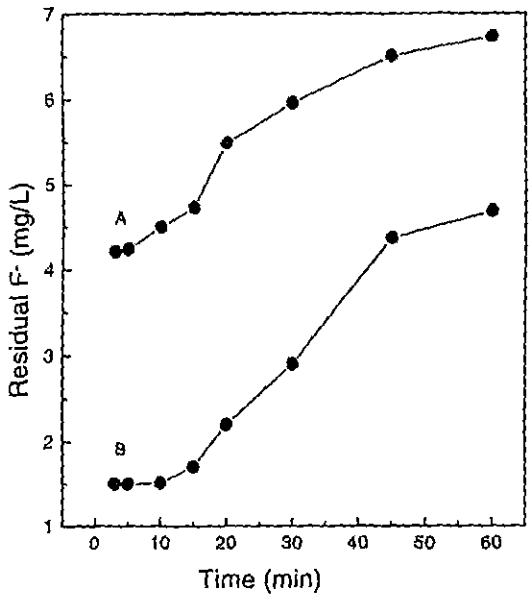


Fig. 1. Fluoride removal with commercial (A) and laboratory made (B) acidic alumina as a function of time; dosage, 0.5 g; 100 mL of Wonji/Shoa ground water (12.51 mg/L F^-); pH= 8.2.

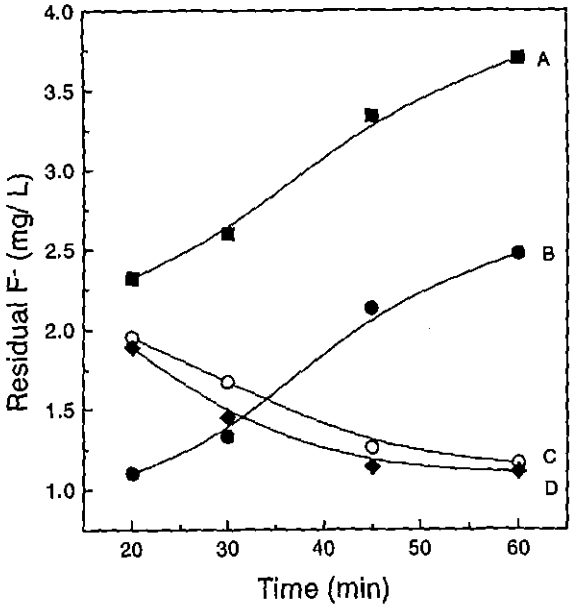


Fig. 2. Fluoride removal by commercial (A, C) and laboratory made (B, D) acidic alumina as a function of time; dosage, 0.5 g; 100 mL Mathahara ground water (5.27 mg/L F^-); A and B at pH = 8.2; C and D at pH = 6.5.

3.3. Fluoride Removal by Kaolin

3.3.1. Effect of mass

The results obtained for fluoride removal on local kaolin as a function of mass are presented in Tables 10-13. The residual fluoride concentration decreased with increased amount of kaolin added (as seen for the mass effect of acidic alumina). However, the material is by far less efficient than both commercial and laboratory made acidic alumina. Results observed for Abadir 3rd ground water (Table 13) after the pH was adjusted to 6.5 showed that the dosage of kaolin required to bring high fluoride concentration to desired value (< 1.5 mg/L F^-) is decreased by less than half (cf. Table 11). This observation suggests that the fluoride uptake capacity of kaolin is more favoured in acidic medium than in basic medium, most probably due to the development of positive sites at the crystal edges of kaolin [61].

Table 10. Effect of mass of local kaolin on fluoride removal from 100 mL of 4.75 mg/L standard fluoride solution at contact time of 30 min and pH between 6.2-6.5.

Amount of kaolin added (g)	Residual F^- concentration (mg/L)	% of F^- removed
1	3.22	32.2
3	1.61	66.1
5	1.00	79.0
7	0.56	88.2

Table 11. Fluoride removal efficiencies of various amounts of local kaolin from 100 mL of Mathahara ground water (5.27 mg/L F^-) at contact time of 30 min and pH = 8.2.

Amount of kaolin added (g)	Residual F^- concentration (mg/L)	% of F^- removed
5	2.94	44.2
7	2.49	52.8
10	1.87	64.5
15	1.41	73.2

Table 12. Effect of mass of local kaolin on fluoride removal from 100 mL of Wonji/Shoa ground water (12.51 mg/L F^-) at contact time of 30 min and pH = 8.2.

Amount of kaolin added (g)	Residual F^- concentration (mg/L)	% of F^- removed
10	3.72	70.3
15	2.61	79.1
20	2.17	82.7
25	1.78	85.8
30	1.43	88.6

Table 13. Effect of mass of local kaolin on fluoride removal from 100 mL of Mathahara ground water (5.27 mg/L F^-) after pH adjusted to 6.5; at contact time of 30 min.

Amount of kaolin added (g)	Residual F^- concentration (mg/L)	% of F^- removed
2	3.17	39.8
5	1.83	65.3
8	1.39	73.6
10	1.13	78.6

Defluoridation tests made to compare the defluoridating capacity of local kaolin with commercial kaolin are shown in Fig. 3. The percentages of fluoride removal with 2, 5, 10, and 15 g of local and commercial kaolin were 25.1, 54.3, 83.6, 86.4; and 14.2, 34.0, 57.8, 71.5, % respectively. Therefore, local kaolin is more efficient than commercial kaolin in removing fluoride from water.

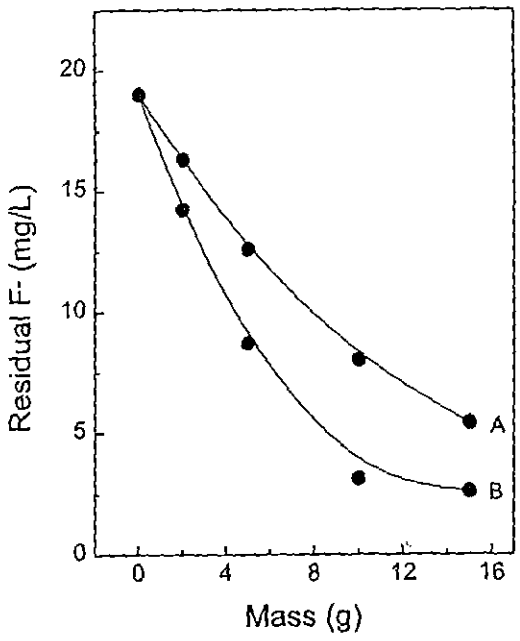


Fig. 3. Fluoride removal as a function of mass of commercial (A) and local (B) kaolin from 100 mL of 19 mg/L standard fluoride; contact time, 14 h.

3.3.2. Effect of volume

The results obtained are given in Table 14 and Figs. 4 and 5. The residual fluoride concentrations increased with the increased volume of fluoride water. Thus the fluoride removal efficiency can be increased by increasing the amount of kaolin proportional to the volume of fluoride water.

Table 14. Effect of volume of Wonji/Shoa ground water (12.51 mg/L F^-) on fluoride removal with 30 g of local kaolin at contact time of 30 min.

Volume of water (mL)	Residual F^- concentration (mg/L)
50	difficult to separate supernatant
100	1.42
150	2.27
200	3.01

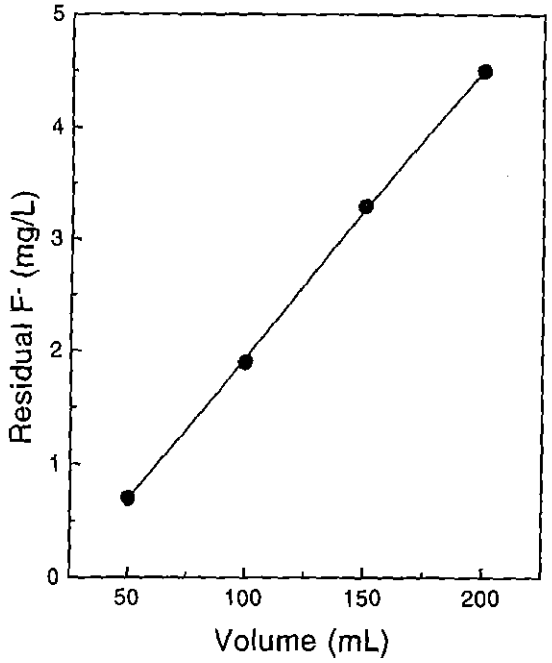


Fig. 4. Effect of volume on fluoride removal with local kaolin; initial fluoride, 19 mg/L; contact time, 5 h; dosage, 15 g.

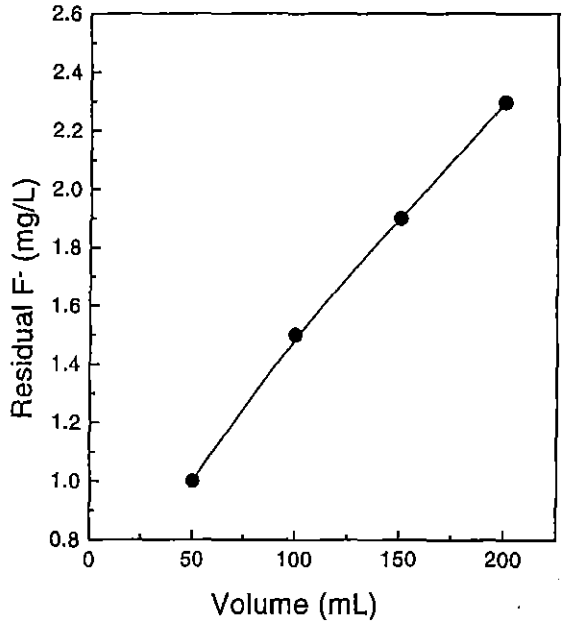


Fig. 5. Effect of volume on fluoride removal with local kaolin; initial fluoride, 5.27 mg/L (Abadir 3rd); contact time, 30 min; dosage, 15 g.

3.3.3. Effect of time

The results observed for fluoride removal with kaolin as a function of time are shown in Tables 15-17 and Fig. 6. The fluoride removal efficiency of kaolin was almost constant from 30 min up to 2 h contact time, after that the adsorbed fluoride was released into defluoridated water, Fig. 6. The factor which can be responsible for this reversible process is not clear; however, the fluoride removal with kaolin is probably governed by physisorption.

Table 15. Effect of contact time on fluoride removal with 4 g of local kaolin from 100 mL of 4.75 mg/L standard fluoride solution.

Contact time (h)	Residual F^- concentration (mg/L)	% of F^- removed
0:30	1.13	76.2
1:00	1.11	76.6
1:30	1.11	76.6
2:00	1.11	76.6

Table 16. Effect of contact time on fluoride removal with 30 g local kaolin from 100 mL of Wonji/Shoa ground water (12.51 mg/L F^-).

Contact time (h)	Residual F^- concentration (mg/L)	% of F^- removed
0:30	1.43	86.5
1:00	1.42	86.6
1:30	1.42	86.6
2:00	1.42	86.6

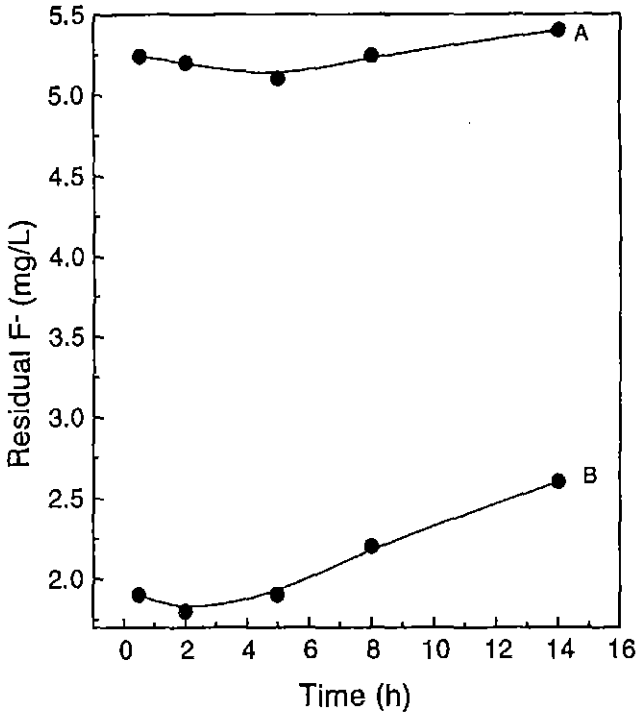


Fig. 6. Residual fluoride after treatment with commercial (A) and local kaolin (B) as a function of time; initial fluoride, 19 mg/L standard fluoride; dosage, 15 g/100 m

Table 17. Effect of contact time on fluoride removal from 100 mL of Mathahara ground water (5.27 mg/L F^-) on 15 g of local kaolin.

Contact time (h)	Residual F^- concentration (mg/L)	% of F^- removal
0:30	1.44	72.7
1:00	1.42	73.0
1:30	1.38	73.8
2:00	1.37	74.0

3.4. Fluoride Removal by Diatomaceous earth

This material was obtained from East Shoa Region, Adami Tulu. Its original place is known as "Gobejjecho Gulanta" which is found in the Rift Valley of Ethiopia. Four different approaches have been done for the fluoride removal with this material.

3.4.1. Effect of mass

Step 1. Defluoridation without heating diatomaceous earth (raw material). The data obtained for mass effect of the material are shown in Table 18 (Study 3). The results indicate an increase of fluoride concentration in the water sample by the amount of 1.52-4.46 mg/L fluoride. This suggests that the material itself contaminated by fluoride which was released into the solution. This was confirmed by the release of 1.76 mg/L fluoride from the original sample after 5 g of diatomaceous earth was mixed with 100 mL of distilled water and suspended solution was analysed.

Table 18. Effect of mass of diatomaceous earth on fluoride removal from 100 mL of standard fluoride water at contact time of 13 h.

Amount of diatomaceous earth added (g)	Residual F^- concentration (mg/L)	Excess F^- in the sample (mg/L)
5	20.52	1.52
10	21.98	2.98
15	23.46	4.46

Step 2. Defluoridation with calcined diatomaceous earth. The material was heated in a muffle furnace between 450-880 °C for 2 h without addition of any chemical and the calcined material (8 g) was tested for fluoride removal from 100 mL of 19 mg/L standard fluoride solution (Study 3.1). However, the observed result still showed an excess of 1.52 mg/L fluoride in the sample. Thus the calcination did not improve the fluoride removal efficiency of diatomaceous earth.

Step 3. Defluoridation after heating the diatomaceous earth with NaCl and $CaCO_3$. Equal amounts of diatomaceous earth, NaCl and $CaCO_3$ were taken and mixed together in a china clay. The mixture was heated in a muffle furnace between the temperature of 450-880 °C for 2 h [62]. The result obtained for fluoride removal of this material (Study 3.2) are shown in Table 19. In this case the fluoride removal efficiency is somewhat improved. This may due to the loss of fluoride from the original diatomaceous earth on calcination in the presence of NaCl and $CaCO_3$. The fluoride removal efficiency was increased with the increasing dose of the material. However, its removal efficiency is very poor relative to acidic alumina and kaolin.

Step 4. Defluoridation with acid treated calcined diatomaceous earth. Calcined diatomaceous earth (with equal amounts of NaCl and $CaCO_3$) was treated with (or soaked in) 2% HCl for 13 h (overnight). 10 g of acid treated material was evaluated for fluoride removal from 100 mL of 19 mg/L standard fluoride solution at the same experimental conditions. But the residual fluoride concentration observed was 16.10 mg/L fluoride which is the same result as obtained for acid untreated calcined diatomaceous earth (cf. Table 19). Therefore, acid treatment of the material has no effect on fluoride removal of calcined diatomaceous earth.

Table 19. Effect of mass of calcined diatomaceous (with NaCl and $CaCO_3$) on fluoride removal from 100 mL of fluoride waters at contact time of 30 min.

Amount of diatomaceous earth (g)	Initial F^- concentration (mg/L)	Residual F^- concentration (mg/L)
10	19 (standard)	16.12
	12.51 (Wonji/Shoa)	7.00
	5.27 (Mathahara)	3.82
20	19	13.53
	12.51	5.80
	5.27	3.68
30	19	12.40
	12.51	5.54
	5.27	3.38

Among the four approaches examined for the removal of fluoride by diatomaceous earth, the calcined diatomaceous earth (with NaCl and $CaCO_3$) gave better results. Therefore, the volume and time effect were studied using calcined (with NaCl and $CaCO_3$) diatomaceous earth.

3.4.2. Effect of volume

The data obtained are listed in Table 20. The observed results showed similar behaviour as seen for acidic alumina and kaolin, i.e., the residual fluoride concentrations increases with the increasing the volume of fluoride water.

Table 20. Effect of volume of fluoride water on fluoride removal with 20 g of calcined diatomaceous earth at contact time of 30 min.

Volume of sample (mL)	Initial F^- concentration (mg/L)	Residual F^- concentration (mg/L)
50	19 (standard)	10.65
	12.51(Wonji/Shoa)	4.30
100	19	13.53
	12.51	6.11
150	19	15.67
	12.51	6.37
200	19	16.19
	12.51	7.05

3.4.3. Effect of time

The data obtained for the effect of time on fluoride removal of calcined (with NaCl and $CaCO_3$) are presented in Table 21. The results indicate that the residual fluoride concentrations remained constant throughout with randomly selected contact time, 30 min-2 h. This suggests that the defluoridation capacity reaches saturation after a minimum contact time of 30 min.

Table 21. Effect of contact time on fluoride removal with 20 g of calcined diatomaceous (with NaCl and $CaCO_3$)earth from 100 mL of fluoride water.

Contact time (min)	Initial F^- concentration (mg/L)	Residual F^- concentration (mg/L)
30	19 (standard)	13.53
	12.51 (Wonji/Shoa)	5.96
	5.27 (Mathahara)	3.56
60	19	13.51
	12.51	5.96
	5.27	3.52
120	19	13.50
	12.51	5.92
	5.27	3.52

3.5. Packed Column Experiment

The fluoride removal efficiency of both commercial and laboratory made acidic alumina was also studied on column experiment. Alumina packed in "ISOLATES" column showed that 0.55 g laboratory made acidic alumina can defluoridate 120 mL of 19 mg/L standard fluoride, 80 mL of Wonji/Shoa (12.51 mg/L F^-) and 150 mL of Mathahara (5.27 mg/L F^-) ground waters till the fluoride content did not exceed 1.5 mg/L, which is the tolerance limit as prescribed by WHO. Similarly 2.1 g of commercial acidic alumina can defluoridate 250 mL of 19 mg/L standard fluoride, 120 mL of Wonji/Shoa (12.51 mg/L F^-) and 300 mL of Mathahara (5.27 mg/L F^-) ground waters. The results, therefore, suggest that column adsorption system is more economical than batch adsorption system. The plots of residual fluoride versus volume fraction of effluent for certain column system experiments are shown in Figs. 7 and 8.

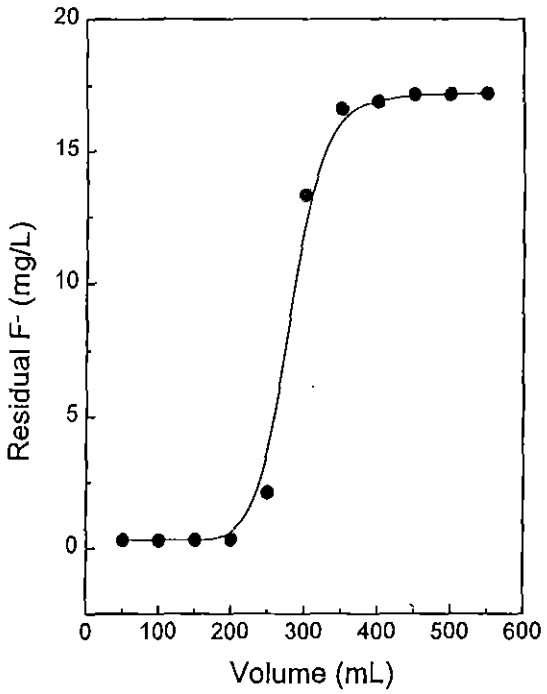


Fig. 7. Residual fluoride as a function of volume of effluent from commercial acidic alumina packed column; initial fluoride, 19 mg/L; flow rate, 1 mL/min.

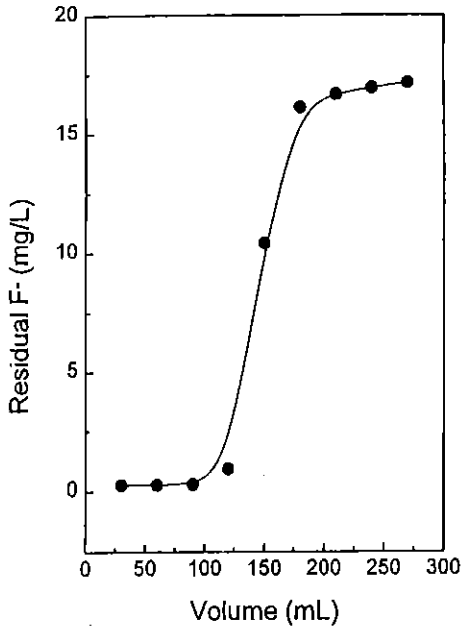


Fig. 8. Residual fluoride as a function of volume of effluent from laboratory made acidic alumina packed column; initial fluoride, 19 mg/L; flow rate, 1 mL/min.

3.5. Defluoridation Mechanisms

The mechanisms for fluoride removal by acidic alumina and kaolin are shown below. However, the mechanism is not clear for diatomaceous earth. When neutral (water-washed) alumina [61] is treated with acid, e.g. HCl, acidic alumina is formed in accordance with reaction (a):

$$\text{Alumina.HOH} + \text{HCl} \text{ --------> } \text{Alumina.HCl} + H_2O \qquad \text{(a)}$$

If this acidic form is contacted with fluoride ions, they displace the chloride ions, provided that hydroxide ions are absent (i.e., slightly acidic feed solution) as in reaction (b):

$$\text{Alumina.HCl} + \text{NaF} \text{ ---------> } \text{Alumina.HF} + \text{NaCl} \qquad \text{(b)}$$

To regenerate the fluoride-containing alumina, a dilute solution of hydroxide is used. The regeneration occurs in accordance with reaction (c):

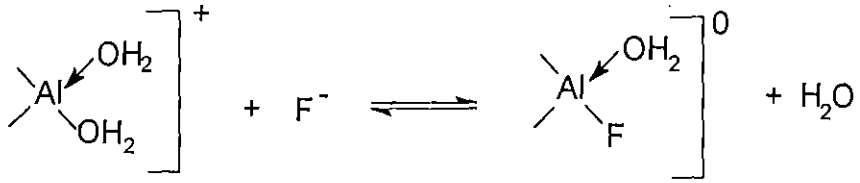
$$\text{Alumina.HF} + 2\text{NaOH} \text{ --------> } \text{Alumina.NaOH} + \text{NaF} + H_2O \qquad \text{(c)}$$

To restore the fluoride removal capacity, the basic alumina is contacted with an excess of dilute HCl as shown in reaction (d):

$$\text{Alumina.NaOH} + 2\text{HCl} \text{ --------> } \text{Alumina.HCl} + \text{NaCl} + H_2O \qquad \text{(d)}$$

The acidic alumina, Alumina.HCl, is now ready for another fluoride adsorption.

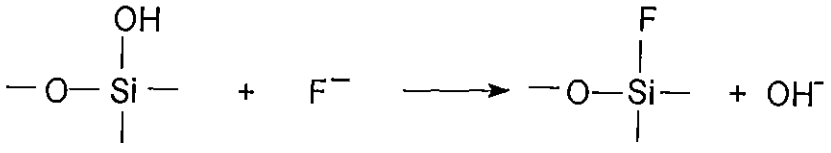
Many researchers have found that anion adsorption sites on clay minerals are aquo groups (-M-OH_2^+) and hydroxo groups (-M-OH) [63]. Therefore, adsorption of fluoride by kaolin (kaolinite mineral) may involve either equilibrium (i) or (ii) depending up on the surface chemistry of the mineral.



(i)

(ii)

The exposed -OH groups of solid phase of diatomaceous earth (hydrated silica skeletons of algae [64]) may be exchanged with F^- ions by an ion exchange mechanism as shown bellow:



4. CONCLUSIONS AND RECOMMENDATIONS

The results of the present investigation may have important practical implications for fluoride removal from various water by adsorption. The acidic alumina and local kaolin are considerably superior to diatomaceous earth and commercial kaolin for fluoride removal. Both commercial and laboratory made acidic alumina are superior to local kaolin because of its higher removal capacity. Even though, local kaolin is inferior to acidic alumina, it is a promising candidate. Because it is readily available and requires a simple defluoridation technique, i.e., by simply mixing fluoride water with kaolin.

Promising results obtained for laboratory made alumina would be a grant for the production of the medium at National level and then to promote defluoridation of water both at household and community level. In fact discouraging ideas may arise due to the emission of SO_3 during calcination; however, there might be a possibility of solving the emission problem of the gas by using it as a bleaching agent in both Mathahara and Wonji/Sugar Estates Factories instead of igniting sulphur.

The removal of excess fluorides from community water supplies to prevent dental disfigurement, loss of teeth, and physiological structure should be adopted as fast as possible. The pre-requisite for this is a comprehensive plan for the defluoridation in all areas of endemic fluorosis. Concurrently with these aims, the following points should be considered for implementation:

i. a consolidated information on the fluoride levels in underground water where the incidence of fluorosis is available. All available data should be compiled and systematic surveys will have to be initiated where such data is not available;
ii. detailed maps showing the level of fluoride at District, State, and Nationals level are to be prepared for delineating the problem zones;
iii. establishment of "Fluorosis Index" for conditions prevailing in Ethiopia is necessary;
iv. while there is a few data available on fluoride in water, practically no information is available on fluoride content of food material. A need therefore exists to the analysis of food material all over Ethiopia for fluoride content.

5. REFERENCES

1. Stacey, M.; Tatlow, J.C.; Sharpe, A.G. *Advances in Fluorine Chemistry*, Butterworths, London; 1961, pp. 35,183.
2. WHO, *Fluorine and Fluorides*, World Health Organization, Geneva, 1984.
3. Gizaw, B. *J. Afr. Earth Sci.* **1996**, 22, 391.
4. WHO, *Fluorides and Human Health*, World Health Organization, Geneva, 1970 (Monograph Series No. 59).
5. ILO, *Encyclopedia of Occupational Health and Safety*, 3rd ed., International Labour Organization, Geneva, **1989**, 1, 891.
6. Goodman and Gilman, *The Pharmacological Bases of Therapecities*, 6th ed., Macmillan, New York; 1980, p.1546.
7. Ekstrand, J.; Ehrnebo, M. *Eur. J. Clin. Pharmacol.* **1979**, 16, 211.
8. Burke, W.J.; Hoegg, U.R.; Phillips, R.E. *J. Occup. Med.* **1973**, 15, 39.
9. Armstrong, W.D. *J. Dent. Res.* **1967**, 46, 60.
10. Jackson, D.; Weidmann, S.M. *J. Path. Bact.* **1958**, 76, 451.
11. Parsons, S.V.; Choudhury, A.A.; Wass, J.A.H.; Vernon, A. *Br. Med. J.* **1975**, 1, 128.
12. Dixon, A.St.J. *Br. Med. J.* **1983**, 286, 999.
13. Mooradian, A.D.; Clements, N.C.Jr. *J. Drug Ther.* **1989**, 19, 69.
14. Weinstein, L.H. *J. Occup. Med.* **1977**, 19, 49.
15. WHO, *International Standards for Drinking Water*, World Health Organization, Geneva, 1971.
16. Pandit, C.G.; Raghavachari, T.N.S.; Rao, D.S.; Krishnamurti, V. *Indian J. Med. Res.* **1940**, 28, 533.
17. Haimanot, R.T.; Fekadu, A.; Bushra, B. *Trop. Geog. Medicine* **1987**, 39, 209.
18. Galagan, D.J.; Vermillion, J.R. *Public Health Rep.* **1957**, 72, 491
19. Feigl, F.; Anger, V. *Spot Test in Inorganic Analysis*, 6th ed., Elsevier, Amsterdam; 1972, p. 211.
20. Mellon, M.G.; Curry, R.P. *Anal. Chem.* **1956**, 28, 1567.
21. Bumsted, H.E.; Wells, J.C. *Anal .Chem.* **1952**, 24, 1595.
22. Bellack, E.; Schouboe, P.J. *Anal. Chem.* **1958**, 30, 2032.

23. Chiba, K.; Yoshida, K.; Tanabe, K.; Ozaki, M.; Haraguchi, H.; Winetordner, J.D.; Fuwa, K. *Anal. Chem.* **1982**, 54, 761.
24. Venkateswarlo, P. *Anal. Chem.* **1974**, 46, 878.
25. Kennedy, J.H. *Analytical Chemistry: Principles*, 2nd ed., Sauders College Publishing, New York; 1990, p. 529.
26. Bailey, P.L. *Analysis with Ion-Selective Electrodes*, 3rd ed., Heyden, London, 1980, p. 196.
27. Lakshminarayanaiah, N. *Membrane Electrodes*, Academic Press, London, 1976, 127.
28. McKee, R.H.; Johnston, Wm.S. *Ind. Eng. Chem.* **1934**, 26, 849.
29. Bhakuni, T.S.; Sharma, N.N. *Environ. Health (India)* **1962**, 4, 11.
30. Nawlake, W.G.; Kulkarni, D.N.; Pathak, B.N.; Bulusu, K.R. *Indian J. Environ. Health* **1975**, 17, 26.
31. Watsan, M.M. UNICEF, Ethiopia, unpublished data (private communication, 1995).
32. Apparao, B.V.; Meenakshi, S.; Karthikeyan, G. *Indian J. Environ. Prot.* **1990**, 10, 292; *Chem. Abstr.* **1991**, 114, 88322 n.
33. Elvove, E. *U.S. Pub. Health. Rep.* **1937**, 52, 14.
34. Boruff, C.S. *Ind. Eng. Chem.* **1934**, 28, 1429.
35. Kempf, C.A.; Galligan, W.E.; Greenwood, D.A.; Nelson, V.E. *Proc. Iowa Acad. Sci.* **1936**, 43, 191; *Chem. Abstr.* **1938**, 32, 4259.
36. Birru, B. *Senior Student Project*, A.A.U. Unpublished data (private communication, 1996).
37. Spira, L.; Grimbley, F.H. *J. Hyg.* **1943**, 43, 142; *Chem. Abstr.* **1943**, 37, 5174.
38. Smith, H.V.; Smith, M.C. *Water Works Eng.* **1937**, 90, 1600; *Chem. Abstr.* **1938**, 32, 1824.
39. Smith, H.V.; Davey, W.B. *Ariz. Agr. Expt. Sta. Tech. Bull.* **1939**, 81, 249; *Chem. Abstr.* **1940**, 34, 2977.
40. Burwell, A.L.; Case, L.C.; Goodnight, C.H. *Okla Geol. Survey, Circ.* 1945, No. 25, p.1; *Chem. Abstr.* **1945**, 39, 3863.
41. Christoffersen, J.; Christoffersen, M.R.; Larsen, R.; Moller, I.J. *Water Res.* **1991**, 25, 227; *Chem. Abstr.* **1991**, 114, 192153u.
42. Phantumvani, P.; Songpaisan, V.; Moller, I.J. *Appropriate Technology*, World Health Forum, Geneva, **1988**, 9, 555.

43. Oda, R.; Shimizu, H. *Chem. High Polymers (Japan)* **1949**, 6, 337; *Chem. Abstr.* **1952**, 46, 1186.

44. Venkataramanan, K.; Krishnaswamy, N.; Ramakrishnan, J. *Indian J. Med. Res.* **1951**, 39, 211.

45. Benson, R.E. *Iowa State College J. Sci.* **1941**, 16, 28.

46. Chaturvedi, A.K.; Pathak, K.C.; Singh, V.N. *Appl. Clay Sci.* **1988**, 3, 337; *Chem. Abstr.* **1988**, 109, 196836p

47. Moges, G.; Zewge, F.; Socher, M. *J. Afr. Earth Sci.* **1996**, 22, 479; *Chem. Abstr.* **1996**, 125, 230011h.

48. Lee, J.A. *Chem. Eng.* **1952**, 59, 400; *Chem. Abstr.* **1952**, 46, 9237.

49. Mazounie, P.; Mouchet, P. *Rev. Fr. Sci. Eav.* **1984**, 3, 29; *Chem. Abstr.* **1984**, 101, 235316a.

50. Schoeman, J.J.; MacLead, H. *Water SA* **1987**, 13, 229.

51. Bulusu, K.R.; Nawlakhe, W.G. *Indian J. Environ. Health* **1990**, 32, 197; Chem. Abstr. **1991**, 115, 56829n.

52. Rubel, F.; Woosley, R.D. *J. Am. Water Works Assoc.* **1979**, 71, 45.

53. Anil, S.; Lal, P.M.; Beena, V.T.; Monjo, M. *Fluoridation vs. Defluoridation Challenges Facing India*, Report on second International Workshop on Fluorosis and Defluoridation of Water, 1997.

54. WHO, *Guidelines for Drinking Water Quality*, World Health Organization, Geneva, 1984.

55. Ref. 26, 107.

56. Koryta,J. *Ion-Selective Electrode*, Cambridge University Press, London; 1975, p. 102.

57. Choi, W.-W.; Chen, K.Y. *Am. Water Works Assoc.* **1979**, 71, 562.

58. Sato, T.; Ozawa, F.; Ikoma, Sh. *J. App. Chem. Biotechnol.* **1978**, 28, 811.

59. Taylor, F.Sh. *Inorganic and Theoretical Chemistry*, 9th ed., William Heinemann, London; 1952, p. 394.

60. Campbell, I.M. *Catalysis at Surfaces*, Chapman and Hall, London; 1988, p. 152.

61. Bohn, H.L.; McNeal, B.L.; O'Connor, G.A. *Soil Chemistry*, 2nd ed., John Wiley, New, York 1985, p. 124.

62. Ref. 5, p. 617.

63. Rao, S.M.; Sridharan, A. *Clays and Clay Minerals* **1984**, 32, 414.
64. Harris, D.C. *Quantitative Chemical Analysis*, 4th ed., W.H. Freeman and Company, New, York; 1995, p. 647.