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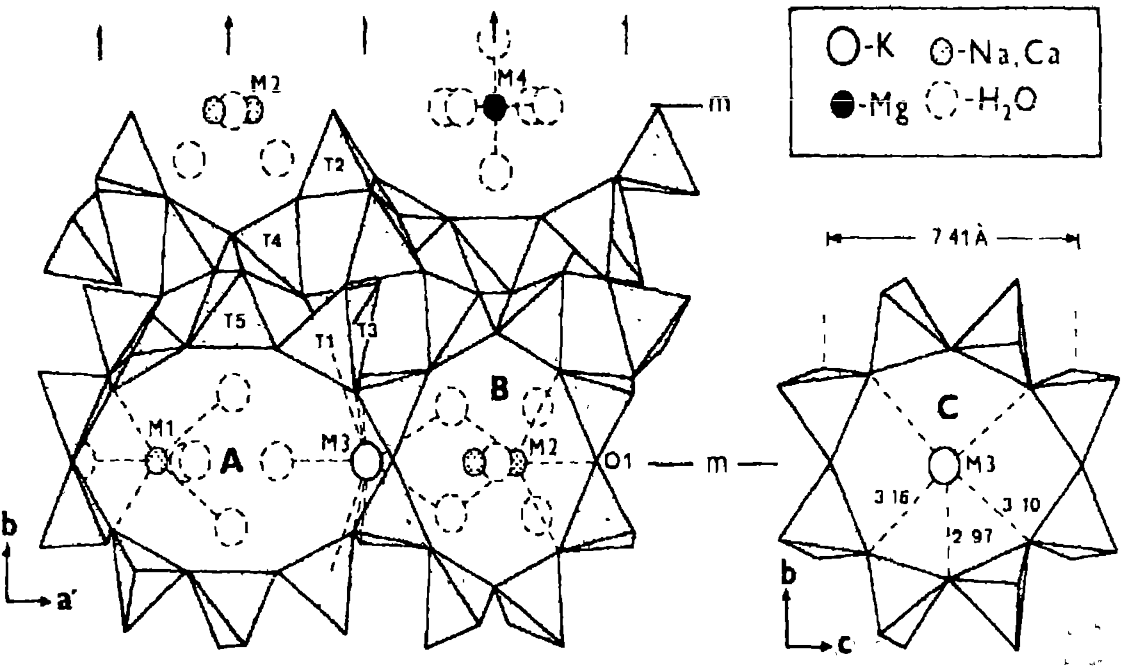

Main components in the Clinoptilolite structure

Defluoridation of Drinking Water By Conditioned Zeolite

Taddele Kibru Weldesemayat

M.Sc Thesis D.E.W. 080

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IHE
DELFT

Defluoridation of drinking water

by conditioned zeolite

by

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This Work is Dedicated to My Father,

Kibru Weldesemayat.

ABSTRACT

The intake of excessive amount of fluoride (above the WHO recommended level of 1.5 mg/l) causes pathological changes in the teeth (*dental fluorosis*), and at higher levels in the skeleton eventually causing permanent disability (*skeletal fluorosis*). Currently more than 80 million people suffer from fluorosis worldwide, mostly in developing countries.

Fluorosis as illness is not amenable to treatment. However, the cause of it can be combated at its source. Several methods of defluoridation exist. But, they have one or more of the following disadvantages: high-cost technology, limited efficiency, deteriorated water quality, taboo limitations, and difficulty to apply on individual well sites to serve at a household or a community level.

The use of conditioned zeolite (Clinoptilolite treated with calcium chloride salt in acidic conditions) for the treatment of water sources, containing fluoride concentrations ranging from 2.5 to 100.0 mg/l, was investigated. Batch experiments carried out with the material resulted in a successful reduction of the fluoride content from 2.5 mg/l and 5.0 mg/l down to below 0.4 and 1.0 mg/l respectively in contact times of less than 30 seconds. Column experiments also showed the possibility of treating 10.0 mg/l down to acceptable level. However, this method is not with side effects. These include: the conductivity of the treated water in batch experiments was high (>3000 µS/cm); re-mobilization of fluoride in to the water was observed when 'real' water samples were treated; and the capacity of the material, determined in column experiments, was limited.

The main conclusion which can be drawn from this study is that water containing up to 5.0 mg F^-/l can be treated by conditioned zeolite in S/L ratio 1:20. It is recommended, however, that the appropriate conditioning method should be devised so that the calcium and chloride ions loosely held to the surface of the zeolite should not impart high conductivity and further investigation is required for column experiments.

Key words: Defluoridation, zeolite, Clinoptilolite.

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Chapter 1

INTRODUCTION

1.1 General Background

The intake of excessive amount of fluoride (above about 1.5 milligrams per litre) causes pathological changes in the teeth (dental fluorosis), and at higher levels in the skeleton eventually causing permanent disability (skeletal fluorosis) (AWWA, 1971; HELMER, 1998; FRENCKEN, 1990). Fluoride (F^-), being an ion of an electronegative element and having a negative charge, is attracted by positively charged ions like calcium (Ca^{2+}). Bone and tooth having highest amount of calcium in the body, attracts the maximum amount of fluoride and is deposited as calcium fluoroapatite crystals. Currently more than 80 million people worldwide suffer from fluorosis. The Rift valley in Africa, parts of India, parts of China and parts of Central and Eastern Europe are places where millions of people are suffering from these effects (HELMER, 1998). In India alone an estimated 25 million people are leading a painful, crippled and vegetative life (PICKFORD, 1992).

If only drinking water, high in fluoride concentration, is available-as is the case in most of the affected areas, the water must be defluorinated. Literatures show that defluoridation of water is technically feasible, and can routinely be carried out in central water distribution systems (FRENCKEN, 1990). But, most of the problem areas have no central distribution systems. They are village communities, mainly in developing countries, depending on local wells. In order to provide defluorinated water under these conditions, a method must be devised that can be applied at individual well sites to serve at a household or at a community level and lower cost level.

1.2 The significance of the study

The significance of the study is that the removal of excessive fluorides from public water supplies to prevent dental disfigurement, loss of teeth, and increased cost of dental care is a sound economic investment. Current researches show that zeolites, conditioned by a fairly simple chemical process, could take up fluoride and bring fluoride levels down to approximately 1 mg/liter, which is within the WHO-norm for drinking water. Furthermore, if the technique is proved to be efficient, it can be used at individual well sites to serve a community or a family. Moreover, the use of zeolites for fluoride removal is technically as well as economically feasible.

1.3 Hypothesis

The natural zeolite, clinoptilolite, conditioned by calcium chloride salt, reduces the fluoride level from higher concentrations to below the WHO recommended level of 1.5 mg/l.

1.4 Objectives

The following objectives were considered:

- ☐ Testing of conditioned zeolite;
- ☐ Determination of optimal parameters for fluoride uptake by conditioned zeolite (residence time, solid to liquid ratio, washing);
- ☐ Testing of selectivity with respect to other ions in drinking water, by testing 'real' water samples;
- ☐ Testing of the unconditioned zeolite;
- ☐ Testing other alternative materials for fluoride uptake;
- ☐ Determination of the capacities of conditioned zeolite and the successful alternative materials, if any.

Chapter 2

BACKGROUND

2.1 Fluoride

2.1.1 Fluoride and Its Sources

Fluoride is an ion of the chemical element fluorine, which belongs to the halogen group. In nature, fluorine never occurs in an elemental form because of its electronegativity and high chemical activity. The fluoride ions can form complexes with metal ions, if the pH of the water is below 5. In higher pH ranges, the single fluoride ion (F^-) prevails. The geochemical behaviour of fluoride is similar to that of hydroxyl ion (OH^-).

The sources of fluorine in human environment can be divided into two categories (FRENCKEN, 1990):

1) Primary sources; and
2) Secondary sources.

The primary sources include the "natural" sources, such as fluoride bearing minerals and volcanic gases, which are related to the geological and the geochemical processes in a region. Out of the total of about 150 distinguished fluorine bearing minerals, fluorite (CaF_2) is the most important mineral containing fluorine in chemical bonding. Table 2.1 lists the number of fluorine bearing minerals in different chemical groups and shows the most important examples for each of these groups. Volcanic gases, produced during the degassing of magma usually contain fluorine such as HF, SiF_4 or H_2SiF_6 Though the total volume of HF in volcanic gases amounts only 1 to 2 %, the fluorine concentration may reach to several thousands of ppm.

TABLE 2.1 FLUORINE BEARING MINERALS

Group	Number	Examples
Silicates	63	Amphiboles, Micas
Halides	34	Fluorite, Villiaumite
Phosphates	22	Apatite
Others	30	Aragonite

Source: Frencken, 1990

The secondary sources include the "pollution" sources, which are related to the industrial and agricultural activities in a region. Significant industrial sources of fluoride are the production of coke, glass and ceramics, electronics, steel and aluminium processing, pesticides and fertilisers, and electroplating operations (BARTRAM and BALANCE, 1996).

Fluoride can enter the human body by ingestion, inhalation and absorption by the skin through a variety of sources viz. water, food, air, medicaments, and cosmetics. Of the total fluoride entering the body, a part is excreted mainly in the urine while the remaining part is absorbed in the tissues. Once retained, only a small percentage of fluoride can be slowly released. Repeated or continuous exposure to fluoride sources will therefore cause accumulation of fluoride in the body.

2.1.2 Fluoride in Drinking Water

Fluoride is well known as a substance effective in the struggle to prevent dental carries. However, the intake of excessive amounts of fluoride causes pathological changes in the teeth (dental fluorosis), and also in the skeleton (skeletal fluorosis or bone fluorosis) eventually causing permanent disability (BULSU and BISWAS, 1993; FRENCKEN, 1990; HELMER, 1998; SUSHELEELA, 1993). Usually the cause of the fluorosis lies in the use of drinking water that has a fluoride content in excess of 1.5 mg/l (WHO, 1984a), the WHO limit for drinking water.

In areas with fluoride containing geological formations, the ground water, through its direct contact with the fluoride minerals, usually has a higher fluoride content than the nearby surface water sources. Groundwater from boreholes, wells, and springs may have varying and/or fluctuating fluoride contents, ranging between 0.1 and >100 mg/l, depending on several influences, e.g.:

- In shallow groundwater, fluoride content usually is lower during the rainy season than the dry season, because of dilution by infiltrating rainwater;
- In deep groundwater, the fluoride content is more or less constant;
- Groundwater may show variation in fluoride content depending on the presence of fluoride-containing formations at different depths.

Surface water, including rivers, streams, lakes, etc., usually have a low fluoride content except when fluoride-containing waste products are discharged into these waters. Lakes in volcanic areas may contain extremely high fluoride values, e.g. a lake in Kenya with more than 2,800mg/l (FRENCKEN, 1990). WHO has published 'Guidelines for Drinking-Water Quality' (WHO, 1984a) and in Table 2.2 the fluoride values and possible health effects are given.

TABLE 2.2 FLUORIDE CONTENTS IN DRINKING WATER AND POSSIBLE EFFECTS

Concentration of fluoride	Possible effects
0.5 – 1.5 mg/l	Fluoride in water has no adverse effects, Incidence of caries decreases
Above 1.5 mg/l	Mottling of teeth may occur to an objectionable degree (Dental Fluorosis; incidence of caries decreases)
3 – 6 mg/l	Association with skeletal fluorosis
Above 10 mg/l	Crippling skeletal fluorosis

Source: WHO, 1984a

In the setting of a guideline limit of 1.5 mg/l and in defining possible effects for higher concentrations, WHO assumed that people consume a daily average of 2 litres of water. However, in tropical countries drinking water consumption is much higher than in countries with a temperate climate; the ambient temperature is higher and the physical workload is usually greater. Adults consume on average 2 to 5 litres per capita per day (lcd), sometimes even up to 10 lcd of drinking water. Apart from this fact, the urinary excretion of absorbed fluoride is lower and the transpiration is higher in tropical countries than in modest countries while the fluoride content of the sweat is higher that of urine.

The facts given above shows that the international guidelines and standards on fluorides are too high for tropical countries, an adjustment towards more realistic fluoride guidelines and standards is necessary. Results of a study carried out in Senegal suggest other guiding values for tropical regions (FRENCKEN, 1990). These are:

- Above 0.6 mg/l: mottling of teeth may occur to an objectionable degree, i.e. dental fluorosis;
- Above 7.0 mg/l: crippling skeletal fluorosis.

2.1.3 Areas with Higher Fluoride Concentration in Drinking Water

More than 260 million people all over the world consume drinking water with a fluoride content of more than 1.0mg/l (WHO, 1984b). A large part of this group lives in tropical countries. Some of the countries with areas facing the problem of a fluoride content above 1.5 mg/l in drinking water are listed below.

Africa: Ethiopia, Sudan, Kenya, Tanzania, South Africa, Nigeria, Senegal, Algeria, Egypt, Zimbabwe, Malawi, Morocco, Uganda, and Somalia. (In Kenya and Tanzania values far above 100mg/l are reported).
Asia: India, China, Korea, Thailand, Sri Lanka, Indonesia, Yemen, and Pakistan. (In India approximately 25 million people in 8,700 villages drink water with a fluoride content of more than 1.5 mg/l).
Latin America: Mexico, Peru, Ecuador, Chile, and Argentina.
Europe: Greece, Finland, Sweden, Great Britain, Germany, Poland, Moldavia, and Ukraine.

2.1.4 Existing Fluoride Removal Techniques

Fluorosis, as an illness, is not amenable to treatment. However, the cause of it (high fluoride concentration in local drinking water) can be combated. Most of the methods used for removing fluoride from drinking water sources can be broadly grouped in to precipitation, adsorption and ion exchange, osmosis, electrochemically stimulated coagulation and electrodialysis (FRENCKEN, 1990). Precipitation methods include the use of lime and alum (commonly known as Nalgonda technique), aluminium sulphate, gypsum, lime, magnesite, semi-calcined dolomite or calcium chloride (FRENCKEN, 1990), and a mixture of sodium dihydrogen phosphate and calcium chloride (known as Contact precipitation) (DAHI, 1996)[1]. The adsorption or ion-exchange media include activated alumina, activated bauxite, bone char, granulated bone media, tricalcium phosphate, super phosphate, zeolites, activated carbon, plant carbon, charcoal, clay pots, coconut shell and several commercially available ion-exchange resins such as Defluoron 1 and 2, Zeocarb 225, Tulsion, Carbion and Agrion O-100 (FRENCKEN, 1990).

The defluoridating capacity of kaolinitic clay, china clay, and serpentinite has been investigated recently. Furthermore, a number of electrochemical methods, reverse osmosis methods and a few new precipitation methods have been tested.

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[1] DAHI. ELI. Paper invited for presentation at the 5th National Conference for Fluoride and Arsenic Research; Taiyuan, China, October 16-21,1996.

The most extensively tested and used methods include activated alumina, reverse osmosis, and electrochemically stimulated coagulation. According to the review made in FRENCKEN, 1990 these methods are able to reduce the fluoride concentration in the treated water to below the recommended WHO level. However, they are only suitable for use in technologically advanced areas. The activated alumina, and the electrochemically stimulated coagulation method are applied presently only in municipal plants. The reverse osmosis method is applied presently at household level. Although the electrodialysis method has so far only been tested in the laboratory and at a pilot-plant, it appears to be promising for the removal of fluoride in technologically advanced areas. Other methods which are able to reduce the fluoride concentration to below the recommended WHO level and which seem to be suitable for application in municipal plants, are methods which use lime and alum, lime alone, the phosphate-calcium mixture used in the Andco process and semi-calcined dolomite. In general, the suitability of these materials for fluoride removal is not studied to the extent as done for activated alumina, reverse osmosis, and electrochemically stimulated coagulation.

There are methods such as lime and alum, polyaluminium chloride (PAC), gypsum and fluorite filter, clays, and use of bone media (granulated bone and bone char) that can be used in decentralised units, either at individual wells, in households, or at the community level. A disadvantage of several of these methods is that they do not achieve a fluoride reduction till the WHO recommended level of 1.5 mg/l. A further disadvantage of most of these methods is that, they have only been tested in the laboratory using artificial waters. Neither information on the life spans nor on the bacteriological quality is, unfortunately, available for these technologies. As most of these methods have not yet be tested under field conditions, it is not clear whether they will be acceptable to the population they are supposed to serve.

Here, only some of these defluoridation techniques will be discussed briefly.

(a) Lime and alum method

This method, commonly known as Nalgonda Technique, involves addition of lime and aluminium sulphate to fluoride containing water followed by rapid mixing, flocculation, sedimentation, filtration and disinfection (BULSU and BISWAS, 1993; FRENCKEN, 1990). Aluminium chloride can also be substituted for or used in conjunction with aluminium sulphate depending on the concentrations of sulphate and chloride ions to avoid exceeding their permissible limits (BULSU and BISWAS, 1993). The dose of aluminium sulphate and/or aluminium chloride depends on alkalinity pH, and the amount of fluoride in the raw water. It increases with fluoride content and alkalinity level of the raw water. The method is reported to reduce fluoride to levels lower than 1 mg/l from as high as 20 mg/l, although there are conflicting views with respect to its efficiency (FRENCKEN, 1990). The optimum removal of fluoride occurs at pH 6.5 and the dose of lime is empirically 1/20th that of the dose of aluminium salt (BULSU and BISWAS, 1993; FRENCKEN, 1990).

The method is tested in the village level in India and at a pilot plant in Kenya. According to FRENCKEN, 1990 the disadvantages of the method are listed as follows: it cannot be used in household units, the addition of chemicals requires trained staff, large amount of alum is required to obtain a good removal efficiency, it results in high residual aluminium levels of the drinking water and a sludge disposal device is needed. Figure 2.1 shows a schematic representation of the Nalgonda technique as used in India as a community defluoridation plant.

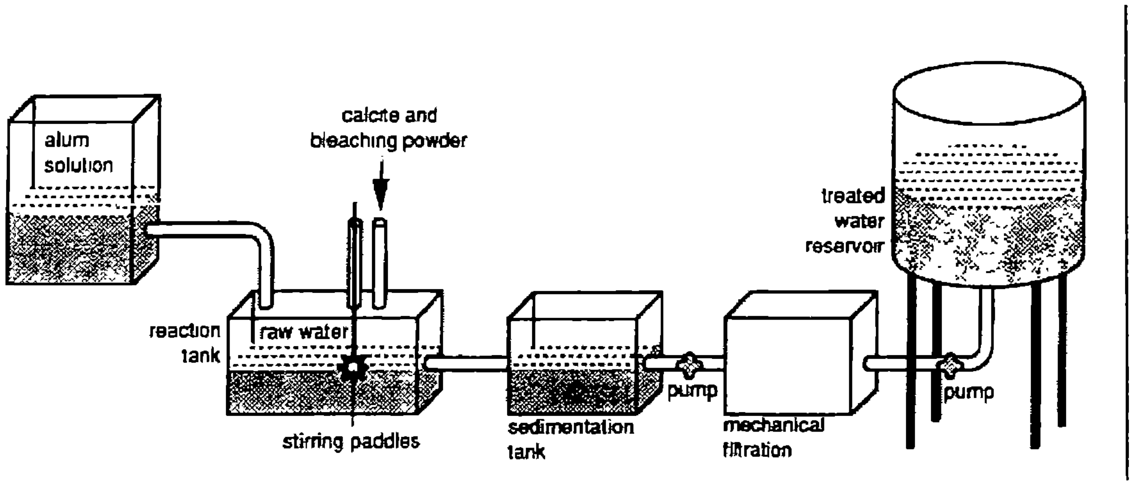

FIGURE 2.1 DEFLUORIDATION OF WATER WITH THE NALGONDA TECHNIQUE (FRENCKEN, 1990).

According to BULSU and BISWAS, 1993 the chemical reaction involving fluorides and aluminium species is complex. It is a combination of polyhydroxy aluminium species complexation with fluorides and their adsorption on polymeric aluminium hydroxides (floc). Besides fluorides, turbidity, colour, odour, pesticides and organics can also be removed and the bacterial load reduced significantly. All these occur due to adsorption on the floc. Lime or sodium carbonate ensures adequate alkalinity for effective hydrolysis of aluminium salts, so that residual aluminium does not remain in the treated water.

BULSU and BISWAS, 1993 suggested the following chemical reactions to take place:

1. $2Al_2(SO4)_3 \cdot 18H_2O + NaF + 9Na_2CO_3 \Rightarrow$

   $[5Al(OH)_3 \cdot Al(OH)_2F] + 9Na_2SO_4 + NaHCO_3 + 8CO_3 + 45H_2O$
2. $3Al2(SO4)_3 \cdot 18H_2O + NaF + 17\,NaHCO_3 \Rightarrow$

   $[5Al(OH)_3 \cdot Al(OH)_2F] + 9Na_2SO_4 + 17CO_2 + 18H_2O$

(b) Contact Precipitation

In this method, sodium dihydrogen phosphate ($NaH_2PO_4.H_2O$) and calcium chloride ($CaCl_2.2H_2O$) were mixed with raw water in a relatively large column (DAHI, 1996). The mix was then allowed to flow slowly through a contact bed consisting of bone char, already saturated with the fluoride water. The method was developed in Denmark and tested at village school level in Tanzania. It was reported that during one year of operation, 1200 bed volumes of water containing 11 mg F-/l was defluoridated 97.9 %, without any signs of deterioration of water quality or clogging of contact bed. The method was also reported to have high efficiency, high reliability, good water quality and very low cost (DAHI, 1996).

(c) Polyaluminium Chloride (PAC)

A summary of this method is shown in FRENCKEN (1990). PAC is an organic polymer with the general formula $Al_n(OH_mCl_{3(n-m)})$. The results of Jar test experiments performed using raw water with a fluoride content of 19mg/l and a pH value of 8.5 showed that 96.4 % removal could be achieved at a dosage of 6 ml PAC/500 ml raw water. This means a residual fluoride concentration of 0.7 mg/l. At optimum dose of 4 ml PAC/500 ml water, the fluoride level was reduced to 1.6 mg/l. However, the pH value dropped to 4.3 requiring adjustment by adding sodium carbonate and magnesite. Pre-treatment of the water with sodium carbonate followed by addition of 3 ml PAC/500 ml water resulted in a fluoride concentration of 1.5 mg/l and a pH value of 7.2.

The disadvantages of the method can be summarized as follows: inconvenient to apply it in household units, the addition of chemicals requires careful training of the user, the method had only been tested in the laboratory at the time, and information on the residual aluminium levels was not available.

(d) Gypsum and fluorite filter

This method involved passing of fluoride-rich water through a gypsum filter bed (figure 2.2) resulting in an increasing calcium concentration in the water to exceed the solubility product of fluorite, which was then precipitated according to the following simple reaction (SCHUILING *et al.*, 1994):

$$CaSO_4{\cdot}2H_2O + 2F^- \rightarrow CaF_2 + SO_4^{2-} + 2H_2O$$

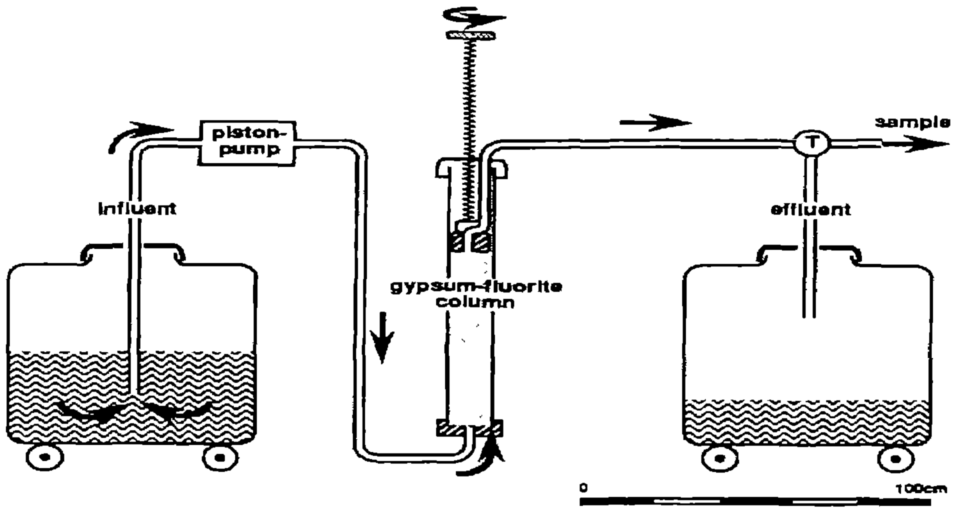

FIGURE 2.2 LABORATORY SET-UP FOR THE DEFLUORIDATION OF DRINKING WATER BY GYPSUM AND FLUORITE FILTER METHOD (FRENCKEN, 1990).

In order to help the reaction, it was found that small fluorite crystals had to be added to the gypsum bed as seed crystals for the crystallization of fluorite. The method was capable of defluoridating relatively large amounts of fluoride-rich water to a level of approximately 4 B 4.5 mg F^-/l, but, at the same time, increase the calcium and sulphate concentrations substantially (FRENCKEN, 1990). The method was relatively new and had not been tested in the field. Its in-expensiveness, use of locally available materials in the developing countries, possibility to apply in the household level and community level were some of the advantages of the method.

(e) Zeolites for fluoride removal

According to the review made on defluoridation techniques in FRENKEN (1990), it was stated that zeolites were tested and found to be impractical for fluoride removal. This was because; different zeolites showed selectivity to different ions. The review pointed out, however, that it could be possible that a zeolite exists, which more effectively removes fluoride, but concluded that the investigation does not seem to be promising.

However, current study on both natural and synthetic zeolites showed encouragingly good results (MPIA, 1998)[2] This study used natural zeolites (Clinoptilolite and Mordenite), synthetic zeolites (K-G, Na-P_1), and Fly ashes (AvL_2 and AvL_3) for fluoride removal. It was found out that modified Clinoptilolite has reduced the fluoride content by 70% when the concentration of fluoride in the water exceeded 2.5 mg/l. In the conditioning process, the zeolite was treated with a solution of $CaCl_2$ (2M) in acid condition (HCl, 2N) for different time intervals of 30 minutes, 2 hours and 24 hours and the pH was stabilised at 2. Then the treated zeolite was filtered and dried at 50°C.

It was believed that calcium-containing zeolites could liberate Ca^{2+}, which in turn react with F^- to form CaF_2 precipitate. The other process expected to have played a role was adsorption of fluoride on the surface of the zeolite. Batch experiments were done using standard solutions of NaF over a range of 5, 10, and 100 mg F^-/l. To each solution, a zeolite was added in a Solid to liquid ratios of 1:20 (1 g of zeolite in 20 ml of water) and 1:50 (1 g of zeolite in 50 ml of water). Then the mixture was shaken and the residual fluoride concentration was measured by a fluorometer at different intervals of contact times.

The main findings of this study can be summarised as follows:

1. Fly -ash AvL_2 and AsL_3 showed best results of fluoride uptake (81.3% and 83.4%), they couldn't be proposed for water treatment, due to high content of heavy metals.
2. Clinoptilolite showed better fluoride removal (73.3%) compared to Mordenite (68.0%) and other synthetic zeolites.
3. Treatment, with both $CaCl_2$ and acid, was necessary for the conditioning process.
4. Powdered zeolites (<0.1 mm) were more efficient than coarse zeolites.
5. Time of treatment also has an effect on adsorption. The more the time of zeolite treatment, the better the fluoride uptake.
6. The use of solid to liquid ratio of 1:20 gave a better result than ratio of 1:50. It was observed that fluoride removal using the ratio 1:50 is about 30% less than using the ratio1:20.
7. Fluoride uptake capacity of zeolite decreased for concentrations less than 2.5 ppm.

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[2] MPIA, Cyril R. MAMBOTE Preliminary study on the use of modified zeolite for the removal of fluorine from drinking water. Research report, University of Utrecht, Utrecht, The Netherlands.

8. Even though the decrease by about 10% in fluoride reduction occurred when water with high TDS content was used, it was clearly observed that modified zeolite, indeed, showed selectivity more to fluoride.

2.2 Zeolites

2.2.1 Definition

The use of the term "zeolite" has been loosely applied to all those materials which were used for water softening (AWWA, 1971). These materials included green sand, bentonitic clay, synthetic gel-type mineral, sulfonated coal, and the synthetic organic resins. Strictly speaking the term should include only those inorganic aluminosilicates which display ion-exchange properties. Today, the exchangers can be classified into two types: the naturally occurring and manufactured inorganic mineral zeolites and the synthetic organic resins.

Zeolites are defined as a group of hydrated, microporous, crystalline aluminosilicates containing exchangeable cations of Group 1A and Group 2A elements (i.e. Na^+, K^+, Mg^{2+} and Ca^{2+}) and which reversibly adsorb and desorb water (TOMLINSON, 1998). Or, they can be defined as aluminosilicates with a skeletal structure, containing voids occupied by ions and molecules of water having a considerable freedom of movement that leads to ion exchange and reversible dehydration (TSITSISHVILI *et al.,* 1992). They were first discovered in 1756 by Cronstedt, a Swedish mineralogist, who named them from two Greek words for 'boiling stone' (*zein* – boiling, *lithos* – stone) which well describes the escape of water molecules from the cavities in natural zeolites. Early in the history of the field, zeolites were characterised by the following properties (TOMLINSON, 1998):

- Low density and high void volume when dehydrated;
- High hydration degree;
- Generally stable structure when dehydrated;
- Cation exchange properties;
- Sorption properties;
- Catalytic properties;
- Uniform molecular channels in dehydrated crystals.

2.2.2 Occurrence

Since Cronsted's original discovery, 40 natural zeolites have been identified, although only 9 are known to occur in deposits large enough to mine (e.g. Heulandite, Clinoptilolite, Chabazite, Mordenite, etc.). Natural zeolites are available in both hydrated and activated (dehydrated) forms and may be enhanced in H^+ or Na^+ content by washing with acid or NaCl, respectively. They are the largest group of minerals among the silicates. Before the 1960s, zeolite minerals were thought to be mainly distributed in hydrothermal veins and geodes in basalts, andesites and other volcanic rocks. Zeolites in such settings form large, well-shaped crystals and druses. Due to the usual small size of the veins and because of polymineralility, these deposits have no practical importance, but samples of vein origin have been used to establish the properties of the minerals and the possibility of their utilization in industry. All known zeolites have been found in hydrothermal veins; some of them are major rock forming species.

Only in recent decades, first in Japan, and later in the USA and Europe, has a wide distribution of zeolites in certain sedimentary rocks been established. These deposits differ markedly from the primary type. They are frequently monomineralic, of huge dimensions and suitable for industrial mining. Zeolite crystals in sedimentary rocks, however, are usually microscopic in size.

More than 100 zeolites have been synthesized, but the principal commercial synthetics are Types A, X, Y, and ZSM-5. Synthetic siliceous gel-type zeolites are prepared by the mixing and reacting together of solutions of sodium silicate and sodium aluminate under such conditions that no precipitate forms. The whole reaction mass is poured into a shallow vat where it sets to a homogeneous gel, which contains all the constituent elements of the solutions. The gel is dried, crushed, and screened to a particle size of 0.3 to 0.5 mm without intermediate processing (AWWA, 1971).

2.2.3 Crystal Chemistry of the Zeolites

The primary building block of the zeolite framework is the tetrahedron, the centre of which is occupied by a silicon or aluminium atom, with four atoms of oxygen at the vertices. Each oxygen atom is shared between two tetrahedra. Hence, the tetrahedra form a continuous framework. Figure 2.3 shows a schematic representation of the joined SiO_4 and AlO_4 tetrahedra as given by SLANGEN, 1998. Here, only Na^+ is shown occupying the cation site.

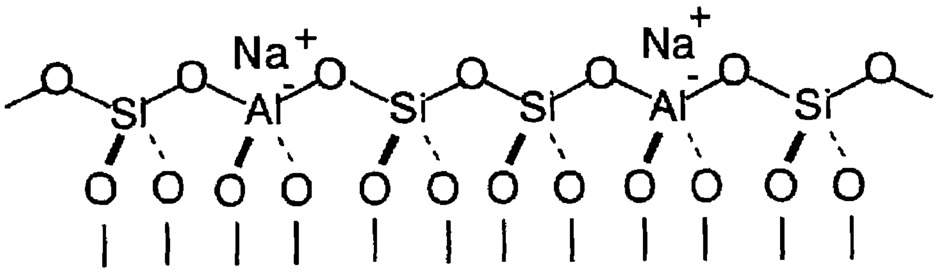

FIGURE 2.3. SCHEMATIC REPRESENTATION OF SiO_4 AND AlO_4 TETRAHEDRA MAKING UP ZEOLITE STRUCTURE

Since two aluminium atoms cannot share the same oxygen atom (Lowenstein's Rule), a zeolite unit cell contains at least as many, and usually more, silicon atoms as aluminium atoms (CIULLO, 1996). The presence of structural aluminium imparts a negative charge to the zeolite lattice. This is balanced in nature by alkali and alkaline earth cations located together with water molecules in structural channels.

Cations are substituted easily, and therefore are termed exchange or extra-framework cations, unlike Si and Al, which are not exchanged under ordinary conditions; the latter are termed tetrahedra (T) or framework cations. The channels or interconnecting voids of this framework, which may amount to as much as 50% of the zeolite by volume, normally contain cations and water molecules. When a zeolite is reversibly dehydrated by heating, the cations become co-ordinated to the oxygen along the inner surfaces of the cavities, while the crystalline structure remains intact (TOMLINSON, 1998). This leaves a porous zeolite crystal permeated with cavities interconnected by channels, which have a diameter ranging from 0.3 to 0.8 nm.

The formula of a zeolite can be written in several ways. TOMLINSON, 1998 expresses the structural formula of a zeolite based on a crystal unit cell as

$$M_{x/n}[(AlO_2)_x(SiO_2)_y].wH_2O.$$

Where, n is the valence of cation M, w is the number of water molecules per unit cell, and x and y are the total number of tetrahedra per unit cell. The ratio y/x usually has values from 1 to 5, although zeolites have been prepared where y/x ratio can reach 100 or higher. Thus, the unit cell formula of the widely distributed natural zeolite, Clinoptilolite is described in TOMLINSON, 1998 as $Na_6[Al_6Si_{30}O_{72}].24H_2O$.

However, TSITSISHVILI *et al.*, 1992 expresses the formula of the zeolite in two ways. The first one is the idealised chemical formula of the zeolites and which is expressed as

$$M_{x/n}[Al_xSi_yO_{2(x+y)}].pH_2O$$

Where M is (Na, K, Li) and/or (Ca, Mg, Ba, Sr), n is cation charge; $x/y = 1$ to 6, $p/x = 1$ to 4. The second way of expressing the zeolite composition, is by the so-called oxide formula as

$$M_{2/n}O.Al_2O_3.xSiO_2.yH_2O$$

The oxide formula of Clinoptilolite is expressed as $(K,Na,1/2Ca)O.Al_2O_3.10SiO_2.8H_2O$ and unit cell contents can be expressed as $(K_2,Na_2,Ca)_3\ (AlO_2)_6(SiO_2)_{30}.24H_2O$, or $(K_2,Na_2,Ca)_3[Al_6Si_{30}O_{72}]24H_2O$. The composition of the tetrahedral framework is usually given in square brackets.

2.2.4 Heulandite-Clinoptilolite

Four varieties are identified: heulandite, high-silica heulandite, and low- and high-silica clinoptilolites. According to tradition, high-silica clinoptilolite is called simply clinoptilolite, whereas low-silica varieties are known as Ca-Clinoptilolite (TSITSISHVILI *et al.*, 1992).

Minerals of the clinoptilolite group are the most widely distributed zeolites in nature. Huge occurrences of clinoptilolite are mined in many countries, and their interesting properties and varieties of application have attracted intensive investigation

As a rule, low-silica members are enriched with Ca and often contain Ba and Sr, whereas high-silica species are enriched with K, Na, and Mg. Of the alkali metal cations, sodium is more characteristic for heulandite and potassium for clinoptilolite, although there are clinoptilolites, which occur in nature with very high Na contents.

Simultaneous occupation of adjacent cations sites is prohibited due to their proximity. Analysis of these constraints showed that the maximum number of cations in the unit cell of clinoptilolite is 6, and this is attained in all natural samples (TSITSISHVILI *et al.*, 1992). The degree of occupation of the possible cation sites indifferent natural samples varies between 70 and 98 %. On ion exchange, cations occupy first the cation sites depending on cation radius, and if these sites are insufficient the cations can occupy water molecule sites as well.

Figure 2 .4 shows the main components of the clinoptilolite structure as presented in TSITSISHVILI *et al.* 1992.

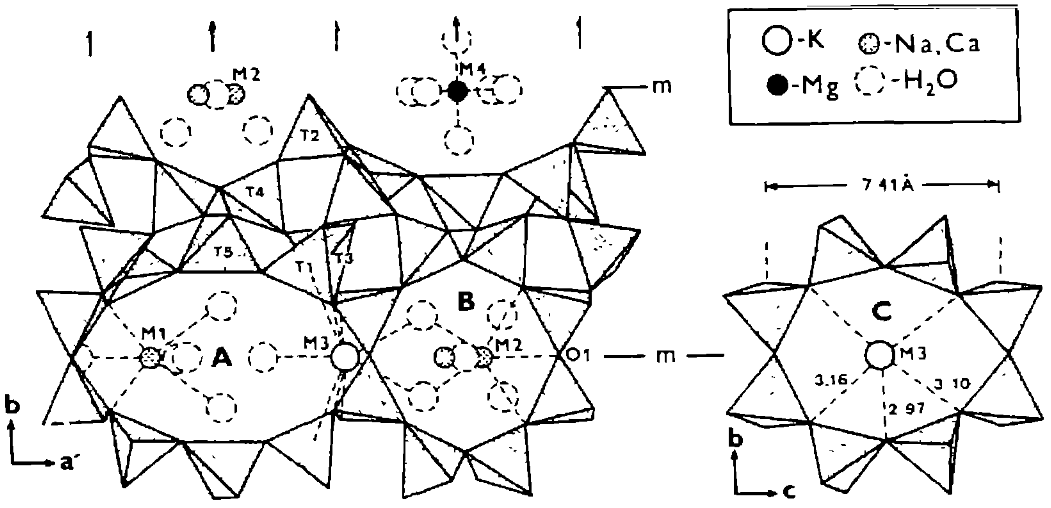

FIGURE 2.4. MAIN COMPONENTS IN THE CLINOPTILOLITE STRUCTURE

2.2.5 Uses

They can be utilised in various environmental systems against pollution with great success because of their unique adsorptive, molecular sieve, ion exchange and catalytic properties (TSITSISHVILI *et al*, 1992). The principal uses for natural zeolites are ammonia removal from organic wastes, removal of radioactive Cesium^{137} and Strontium^{90} from nuclear wastes, odour control, and soil treatment (CIULLO, 1996). Synthetic zeolites are used in catalytic cracking at petroleum refineries, for drying, purifying and separating industrial gas streams, and as detergent builders. The various applications of zeolites are briefly summarized below.

- *In Agriculture*:

  Zeolites, principally clinoptilolite, are used to remove ammonia from water at fish hatcheries and farms, in aquaria, and in live fish transport systems. They, mainly Clinoptilolite, are used as vehicles as a controlled release of ammonia in fertilizers and as carriers of insecticides, herbicides, and fungicides. They also are added to contaminated soils to scavenge radioactive Cs^{137} and Sr^{90}, plus Pb, Cd and other toxic metals (CIULLO, 1996). Zeolites are used as animal feed supplements to improve nutrient efficiency and growth rates for poultry and swine while reducing manure moisture and odour.

- *Waste Treatment:*

  Clinoptilolite, Chabazite, Mordenite, and Phillipsite remove radioactive Cs^{137} and Sr^{90} from nuclear waste streams and serve as encapsulants for these isotopes to facilitate solid waste disposal (CIULLO, 1996). Zeolites, particularly Clinoptilolite, are used in treating sewage and industrial waste streams to remove ammonia and heavy metals. Extracted ammonia is subsequently vented, recovered for chemical use, or converted with sulphuric acid to ammonium sulphate fertiliser.

- *Adsorption:*

  Zeolites with appropriate channel dimensions are used for selective removal of certain gases from gaseous mixtures. Mordenite and calcium Type A (NaA) are preferred for adsorbing nitrogen from the air to generate relatively pure oxygen for medical and industrial uses. The latter include oxygenation of pulp and paper mill effluents, waste and sewage treatment streams, and metal smelters. Natural gas and methane generated by animal waste, sanitary landfills, and sewage system are purified by treatment with synthetic zeolites, principally Type A, to remove H_2O, CO_2, SO_2, and H_2S. Clinoptilolite and Mordenite can be used to remove SO_2 from the stalk gases at fossil-fuel burning plants.

  The results of numerous investigators on the adsorption of different anions and cations are given in Table 2.3 below:

TABLE 2.3 ORDER OF ADSORPTION OF IONS

ANIONS			CATIONS	
1[*]	2	3	4	5
OH	OH		H	
CNS	CNS		Al	
I	I	I		
CLO_3			Cu	
NO_3	NO_3	NO_3	Zn	
CrO_4			Mg	
Br	Br	Br	Ca	
Cl	Cl	Cl		Cs
	HPO_4		NH_4	NH_4
SO_4	SO_4	SO_4	Rb	
			K	K
			Na	Na
			Li	

Source: Mantell, 1945.

- *Detergents:*

  The largest amount of zeolite, NaA, is used in detergents, where it is used as a solid exchanging agent to reduce water hardness (SLANGEN, 1998). The calcium and magnesium often found in tap water can deposit as salts on the laundry, giving it a greyish color. Apart from having a large exchange capacity for calcium, the zeolite also have a small average particle size (large active surface area), no sharp edges (low abrassiveness) and do not contain impurities. According to SLANGEN, 1998 zeolite NaA was the first zeolite to be used in detergents, but recently zeolite MAP (Maximum Aluminium NaP) started to be used. Which of the two zeolites, NaA or MAP, is the more effective ion exchanger, has not yet been settled.

  Reactions for removing hardness can be given as follows. Let Z be zeolite, then:

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[*] Each of the five columns shows the results of individual investigation.

$$\left.\begin{matrix} Ca \\ Mg \end{matrix}\right\}\text{Salts} + \text{Na}_2\text{Z} \Rightarrow \left.\begin{matrix} Ca \\ Mg \end{matrix}\right\}\text{Z} + \text{Na}_2\text{Salts}$$

The reversible regeneration reaction can be given as:

$$\left.\begin{matrix} Ca \\ Mg \end{matrix}\right\}\text{Z} + 2\text{NaCl} \Rightarrow \text{Na}_2\text{Z} + \left.\begin{matrix} Ca \\ Mg \end{matrix}\right\}\text{Cl}_2$$

- *Cracking catalysts:*

  Fluid Catalytic cracking is the primary conversion unit in many oil refineries, converting heavy fractions of crude oil into lighter fractions, mainly gasoline and middle distilates (SLANGEN, 1998; CIULLO, 1996). The active part of a cracking catalyst is generated through the acid sites of the zeolites. Usually, zeolite NaY, which is modified to create Ultra Stable Y (USY), is used as the starting material. The higher Si/Al ratio in USY gives the zeolite a greater stability at high temperatures (SLANGEN, 1998). USY also is used to improve the octane rating of gasoline, where as, ZSM-5 is used primarily to produce gasoline from methanol by both catalysis and molecular sieving, (CIULLO, 1996). Methanol is first converted to dimethyl ether, which is further converted by the zeolite to a mixture of hydrocarbons.

- *Other uses:*

  Zeolites find additional uses as desiccants, heat storage media, filters for air cleaning, and (in Japan) as paper fills.

Chapter 3

MATERIALS AND METHODS

3.1 Introduction

The materials used for the study include conditioned zeolite (Clinoptilolite), unconditioned zeolites (Clinoptilolite and Heulandite), synthetic Xonotlite ($Ca_6Si_6O_{17}(OH)_2$), Hydrotalcite ($Mg_6Al_2(CO_3)(OH)_{16}.4H_2O$), and precipitated silica ($SiO_2.nH_2O$). Both the conditioned and the unconditioned zeolites (Cliniptilolite and Heulandite) were obtained from Roscon Holland BV. Prof. R. D. Schuiling, the supervisor of the work, supplied the rest of the materials. The conditioning of the natural zeolite, Clinoptilolite was done by Roscon Holland BV. The process involved the treatment of Clinoptilolite with acidified Calcium chloride solution.

Basically, two different types of experiments were done: batch and column. The batch experiments were carried out for all the materials listed above. However, the column experiments were done only for conditioned zeolite and synthetic Xonotlite due to time limitations. All the batch experiments, except for very few cases, were done in duplicates. Moreover, all the experiments and measurements were carried out at room temperature.

3.2 Batch Experiment

3.2.1 General setup

In the batch experiments, a certain (pre-weighed) amount of the material under investigation was added to a known volume of water containing fluoride depending on the solid to liquid (S/L) ratios in use. In using S/L ratio 1:20, for example, the mixture was 50 g zeolite in 1 liter of fluoride water in a polyethylene beakers. The mixture was continuously stirred at 200 rpm by a Jar test apparatus with steel paddles, while taking samples at different specified time intervals. The samples were immediately filtered by vacuum filter using GF6 glass fiber papers (Ref. No 370019) with diameter 47 mm and pore size 0.50 – 1.49 µm. The resulting filtrate was analyzed by ISE25F fluoride electrode for determining the fluoride concentration remaining in the solution. The filtered samples were also analyzed for pH (by 691 pH meter made by Metrohm) and conductivity (by LF 340 conductivity meter made by WTW), whenever applicable. The Method is schematically described in Figure 3.1 below.

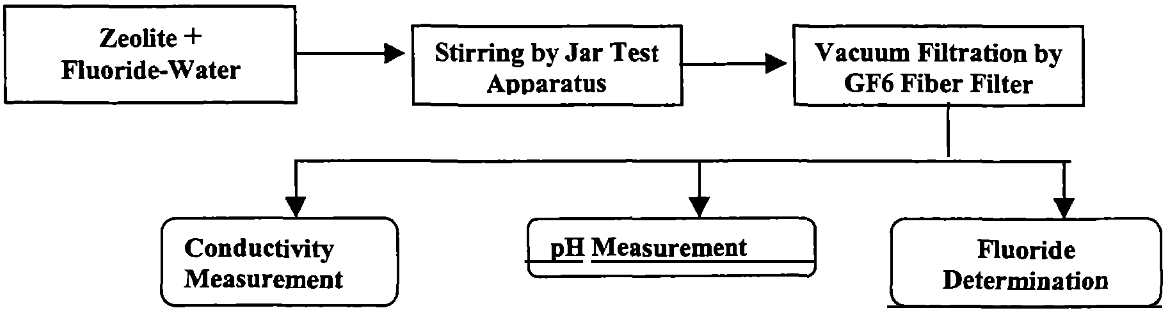


FIGURE 3.1 SCHEMATIC REPRESENTATION OF THE PROCEDURE IMPLEMENTED IN THE BATCH EXPERIMENTS

Except in few particular cases, where water samples from Greece were used, all the experiments were done using fluoride-containing water prepared by dissolving sodium fluoride, NaF (a product of J.T. Baker B.V. Deventer-Holland) in de-mineralized water produced in the IHE Laboratory. First, a stock solution of 1000 mg F^-/l was made; then, from this stock solution, the solutions containing the desired amount of fluoride ion were produced by dilution.

The types of batch experiments carried out in the study are given below.

3.2.2 The effect of conditioned zeolite on fluoride removal

Conditioned zeolite was investigated for fluoride uptake from concentrations of 2.5, 5.0, 10.0, 15.0, 20.0, 25.0, 50.0, 75.0, and 100.0 mg F^-/l. The following time intervals were used: 30 seconds, 1 minute, 2 minutes, 5 minutes, 10 minutes, 30 minutes, 60 minutes and 24 hours; all with a S/L ratio of 1:20. Additional batch experiment carried out with the conditioned zeolite included treatment of 10 mg F^-/l in two steps.

3.2.3 Varying the solid to liquid ratio on the efficiency of the conditioned zeolite

The conditioned zeolite was also tested for fluoride concentrations of 10.0 mg /l and 15.0 in S/l ratios of 1:15 and 1:10 and the results were compared with that obtained in the 1:20 S/L ratio.

3.2.4 The effect of washing of the zeolite on the removal efficiency

To evaluate the relationship between further washing of the zeolite and efficiency of removal, the conditioned zeolite was washed with de-mineralized water to different conductivity levels (114, 200, 430, 870, and 2610 μS/cm). These values were found after measuring the conductivity of the filtrates from each beaker. The zeolite-water mixture was allowed to settle and the supernatant water was decanted. This process of washing and decanting was repeated until the desired conductivity level is achieved. The resulting zeolite was dried in an oven (50 °C) over night and used to treat 10.0 mg F^-/l solution in S/L ratio of 1:20.

3.2.5 Two step treatment

10 mg F^-/l solution was first treated with conditioned zeolite, pre-washed to conductivity levels of 1560 and 2522 μS/cm, in a S/L ratio of 1:20 for 30 minutes. The remaining mix was filtered and treated again with fresh conditioned zeolite in similar conditions as the first step.

3.2.6 The effect of non-conditioned zeolite on fluoride removal

Unconditioned zeolite (Clinoptilolite) was investigated for fluoride concentrations of 2.5, 5.0, and 10.0 mg/l and S/L ratio and time intervals similar to that of the conditioned zeolite.

3.2.7 Testing 'real' water samples

Water sample from Nymphopetra village in Thessaloniki, Greece, containing 5.5 mg F^-/l was tested with conditioned zeolite in a S/L ratio 1:20 for 1 hour.

3.2.8 Alternative materials for fluoride removal

Materials tested as alternatives for fluoride removal included the natural zeolite, Heulandite, synthetic Xonotlite, Hydrotalcite, and precipitated silica. These materials were tested on 10 mg F^-/l in S/L ratio of 1:20 for treatment times of 0.5, 1.0, 1.0, 5.0, 10.0, and 30.0 minutes.

3.2.9 Varying the solid to liquid ratio on the efficiency of the synthetic Xonotlite

Synthetic Xonotlite was tested in S/L ratios 1:20, 1:50, and 1:100 for fluoride up take from water containing 10.0 mg F^-/l in 30 minutes contact time.

3.2.10 Others

Additional experiments performed include the effect of filter paper on fluoride adsorption, the relationship between continuous stirring of the zeolite in de-mineralized water and the conductivity, the relationship between washing the synthetic Xonotlite in de-mineralized water and pH, and using synthetic Xonotlite to treat 'real' water samples from Greece. To check the effect of membrane filtration on fluoride removal, solutions containing 1, 25, 50, 75, and 100 mg F^-/l were filtered using the GF6 glass fiber paper. The millivolt responses were measured for both filtered and unfiltered solutions and the values were compared for the presence of significant difference. The conditioned zeolite was mixed with only de-mineralized water in a S/L ratio of 1:20, and stirred for 1 hour and samples were taken, filtered and analyzed for electrical conductivity in time intervals of 0.5, 1.0, 2.0, 5.0, 10.0, 30, and 60.0 minutes. Similarly, synthetic Xonotlite was mixed with de-mineralized water in a S/L ratio of 1:50 and stirred for 30 minutes. Samples were drawn, filtered and analyzed for pH in time intervals of 0.5, 1.0, 5.0, 10, and 30 minutes. Synthetic Xonotlite was used in a S/L ratio of 1:50 to treat 'real' water samples from Greece. The material was mixed with the water sample, stirred for 30.0 minutes. Samples were drawn in 0.5, 1.0, 5.0, 10.0, and 30.0 minutes, filtered and analyzed for residual fluoride concentration, pH and electrical conductivity. This experiment was done only once due to time limitations.

3.3 Column Experiment

In the column experiments, a solution containing a desired fluoride content was pumped by peristaltic pumps (model Watson Marlow-101U) through the column packed with a mixture of inert silver sand and the material under question. The purpose of the sand was to increase permeability. Then samples were taken at different time intervals and analyzed for fluoride, pH and electrical conductivity. Due to problem of pressure development inside the columns, and hence leakage, down flow type was used instead of up flow through the columns. The plastic-made cylindrical columns used were obtained from the Technical University of Delft. They were about 50 cm long and 5 cm wide (internally), equipped with screw-packing parts on both ends fitted with polyethylene filter (pore size 10μm). The GF6 glass fiber papers were also put inside the filter of the column to give additional ability to retain the zeolite. The schematic representation of the column experiments has been described in Figure 3.2.

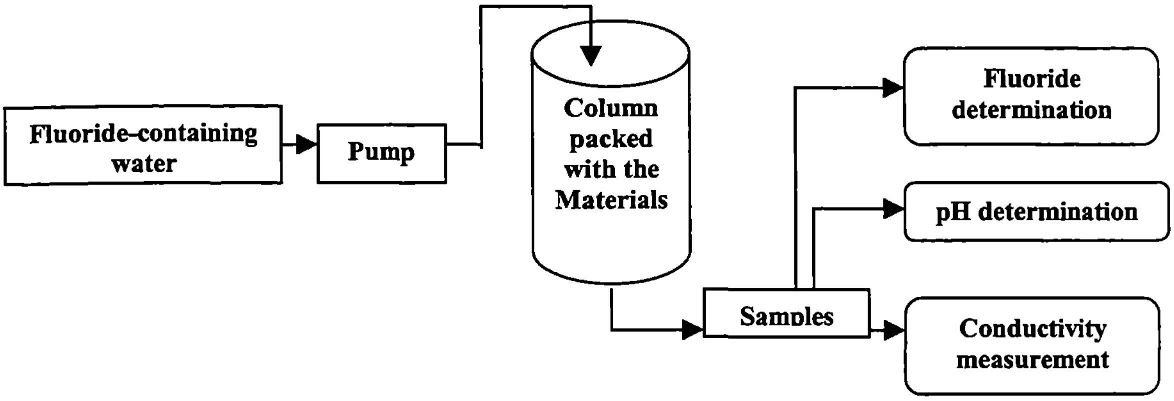


FIGURE 3.2. SCHEMATIC PRESENTATION OF THE COLUMN EXPERIMENT

The types of column experiments carried out in the study are given below.

3.3.1 The effect of sand on fluoride adsorption

Solution containing 100.0 mg F⁻/l was pumped through a column, packed with 300 g of inert silver sand (length 12.0 cm). The flow rate through this column was 0.12 m/h. Samples were checked for fluoride content for approximately three days.

3.3.2 The effect of conditioned zeolite on fluoride adsorption

Three columns were run with conditioned zeolite. The first two columns were run to have an insight on how long it takes to reach the break-through point, while the third one was monitored closely and used to determine the capacity of the zeolite. The first column was subsequently filled, from top to bottom, with 75 g sand, a mixture of 60 g zeolite with 210-g sand, and 75 g sand. Through this column was passed a solution containing 25.0 mg F⁻/l at a flow rate of 0.102 l/h. The second column was packed from top to bottom with 20-g sand, a mixture of 30 g zeolite with 300-g sand, and 20 g zeolite. Through this column was passed a solution containing 100.0 mg F⁻/l at a flow rate of 0.2 l/h. The third column was packed from top to bottom with 30 g sand, a mixture of 30 g zeolite and 300 g sand, and 30 g sand. 10 mg F⁻/l was passed through this column at a flow rate of 0.237 l/h. All the columns were run until the break through point was noticed.

3.3.3 The effect of synthetic Xonotlite fluoride adsorption

One of the columns was packed from top to bottom with 80-g sand, a mixture of 10g synthetic Xonotlite with 300-g sand, and 40-g sand. A solution containing 10.0 mg F⁻/l was passed through this column at a flow rate of 0.18 l/h until the break through point was noticed.

3.4 Fluoride Analysis by Ion Selective Electrode for Fluoride

The apparatus, reagents, and procedures used were the following:

Apparatus

- Digital pH meter (pH 96, Microprocessor pH meter, WTW).
- Reference electrode. REF201 single junction reference electrode filled with saturated KCL.

- Fluoride Electrode. ISE25F Fluoride electrode (made by Radiometer, Copenhagen).
- Insulated Magnetic stirrer and Teflon coated stirring bars.
- Stopwatch.
- Polyethylene reagent bottles and beakers.

Reagents

- De-mineralized water. All solutions were prepared in de-mineralized water of IHE Laboratory.
- Fluoride stock solution. 2.21 g of analytical grade anhydrous sodium fluoride, NaF, was dissolved in distilled water and diluted to a final volume of 1 liter to make 1000 mg F^-/l (1ml η 1 mg F^-)
- Working standards of 0.1, 0.5, 1.0, 10.0, and 100.0 mg F^-/l were prepared just before starting the analysis.
- Total ionic strength adjustment buffer. The total ionic strength adjustment buffer (TISAB) was prepared as follows: 14.3 ml glacial acetic acid (0.25 M) (99-100%, a product of Mallinckrodt Baker B.V.-Holland), 61.5 g anhydrous sodium acetate (0.75 M), 58.5 g sodium chloride (1 M) (made by ACROS ORGANICS), and 0.36436 g DCTA (trans-1,2-diaminocyclohexene-N,N,N',N'-tetraacetic acid) (0.001 M) were dissolved in distilled water and the final volume was adjusted to 1 liter.

Procedures

- 10 ml of the standard solution was mixed with an equal volume of the TISAB in a small plastic beaker. The mixture was let to stand until the room temperature was reached. Then the beaker was placed on magnetic stirrer, a stirring bar was added, the electrodes were immersed, and stirred for 3 minutes for equilibration. The millivolt responses were recorded from the pH meter when a stable value is reached; these took generally at least 3 minutes.
- The millivolt responses obtained for the standard solutions were plotted against the logarithm of their concentrations (calibration curve). The curve was mostly linear for fluoride concentrations of above about 0.2 mg/l. The process of calibration was repeated every day before analysis was done.
- The same procedures were followed to analyze samples for obtaining millivolt values. The fluoride concentrations of the samples were then determined from the calibration curves.

Chapter 4

RESULTS

This section presents only the summary of the major findings of the study. The detailed results are given in the Appendices. For practical reasons the results will be presented categorically by types of experiments. The first section presents information on the particle size and chemical analysis of the zeolite as obtained from Roscon Holland BV. The remaining sections are devoted to the results obtained from the study.

4.1 Analysis of conditioned and unconditioned zeolites

Table 4.1 presents the particle size determination of the raw (unconditioned) zeolite. From this Table it is apparent that 50 % of the raw zeolite is less than 24.3 μm whereas, 10 % is smaller than 2.1 μm and 90 % smaller than 105 μm. The residual zeolite amounted only 0.174 %. Compared to the pore size of the filter paper used (0.50 –1.49 μm), there are smaller fractions of the zeolite which still can pass through the filter paper. These smaller fractions include the residual and the fraction in the range between 0.1 and 2.0 μm, which is 9.6 % of the raw zeolite. In conditioned zeolite, however, the decanting of the supernatant after conditioning and washing has removed most of the fine-grained particles from the conditioned zeolite.

TABLE 4.1 THE PARTICLE SIZE MEASUREMENT OF THE UNCONDITIONED ZEOLITE.

FRACTION (μM)	FRACTION (%)	CUMULATIVE (%)
0.1-2.0	9.60	0.00
2.0-4.0	9.34	9.60
4.0 - 8.0	9.81	18.94
8.0 - 16.0	11.94	28.75
16.0 - 25.0	10.02	40.69
25.0 - 35.0	8.74	50.71
35.0 - 50.0	10.17	59.45
50.0 - 63.0	6.79	69.62
63.0 - 75.0	5.00	76.41
75.0 - 88.0	4.32	81.41
88.0 - 105.0	4.33	85.73
105.0 - 125.0	3.75	90.06
125.0 - 150.0	3.36	93.81
150.0 - 177.0	2.58	97.17
177.0 - 210.0	0.25	99.75
210.0 - 250.0	0.00	100.0

Residual = 0.174 %; $D_{50\%}$ = 24.3 μm; $D_{10\%}$ = 2.1 μm; $D_{90\%}$ = 104.8 μm.

This is in agreement with the facts observed during the rest of experiments:

- The filtered solution after treatment with conditioned zeolite was found to be relatively clearer than the one treated with unconditioned zeolite.

- The filterability of conditioned zeolite also was found to be better than for the unconditioned zeolite. The finer particles in non-conditioned zeolite caused clogging of the filter and made filtration slower.

Table 4.2 presents the chemical analysis made before and after conditioning of the zeolite. From this Table, we can see that conditioning process has considerably increased the content of some of the chemical species, such as CaO (32.2 %), Na_2O (56.5 %), As (65.5 %), Cu (23.8 %), Ni (31.1 %), and Sr (29.0 %) and decreased other species, such as MnO (55.9 %), Cr (65.2 %), Pb (42.4 %) and U (92.5 %). The increase in some of the heavy metals may be is due to the presence of impurities with the calcium chloride salt and the decrease is due to dilution during washing process. The increase in CaO must be to the conditioning material (calcium salt) and the increase in Na_2O to mobilization from the zeolite due to ion exchange with calcium. But their presence in an attached form shows the insufficiency of washing the conditioned zeolite to remove substance, that are no more part of the zeolite structure.

TABLE 4.2 CHEMICAL ANALYSIS OF THE ZEOLITE BEFORE AND AFTER CONDITIONING.

PARAMETERS	QTY	NATURAL ZEOLITE	CONDITIONED ZEOLITE
SiO_2	%	73.70	71.96
TiO_2		0.15	0.13
Al_2O_3		11.88	11.38
Fe_2O_3		1.66	1.56
MgO		0.32	0.30
MnO		0.03	0.01
CaO		3.85	5.08
K_2O		3.20	2.85
Na_2O		0.28	0.43
P_2O_5		0.02	0.02
Total		95.07	93.73
LOI		9.20	9.40
As	ppm	0.61	1.01
Co		37.50	34.90
Cr		2.30	0.80
Cu		5.13	6.35
Ni		6.21	8.14
Pb		14.90	8.58
V		9.00	9.70
Zn		33.72	28.57
S (not analyzed)		0.00	0.00
Ba		727.20	686.30
Ga		12.65	12.86
Nb		10.42	9.88
Rb		122.86	117.72
Sr		306.54	395.57
Th		15.78	15.98
U		1.72	0.13
Y		25.06	24.58
Zr		136.90	132.82

4.2 Results of the batch experiments

4.2.1 The effect of conditioned zeolite on fluoride removal

The detailed results for this experiment as well as others are given in detail in Appendix section. Usually duplicate results with 95 % confidence intervals were found, except in few particular cases like experiment with 50 mg F⁻/l. The summary of the results obtained after the treatment of selected fluoride concentrations for 60 minute using S/L ratio 1:20 are given in Figure 4.1. This shows that water, containing fluoride up to 5.0 mg/l can be treated by conditioned zeolite to below the WHO recommended level of 1.5 mg/l in less than 30 seconds of treatment. The electrical conductivity of the treated water, however, is very high making the water unacceptable for drinking. From this Figure we can also see that, as the fluoride concentration in the water to be treated is increased, the residual fluoride concentration is also increased.

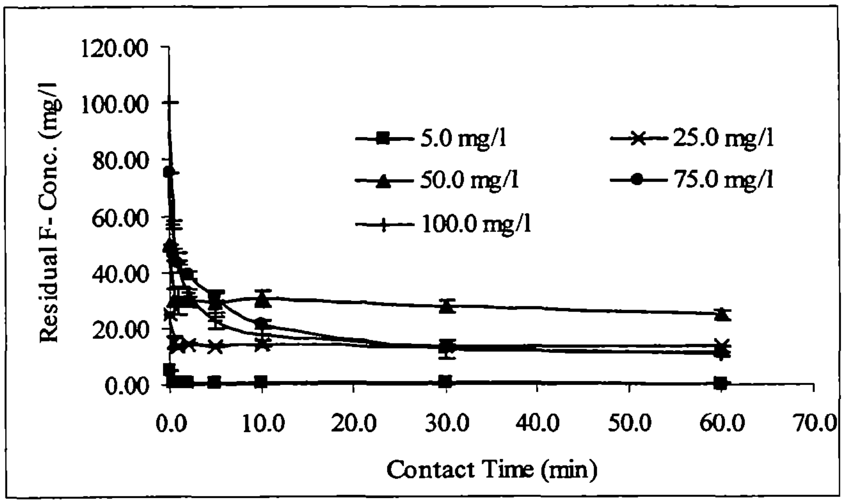


FIGURE 4.1. RESIDUAL FLUORIDE CONCENTRATION (MEAN ± STD) AGAINST TIME FOR THE TREATMENT OF SELECTED FLUORIDE CONCENTRATIONS.

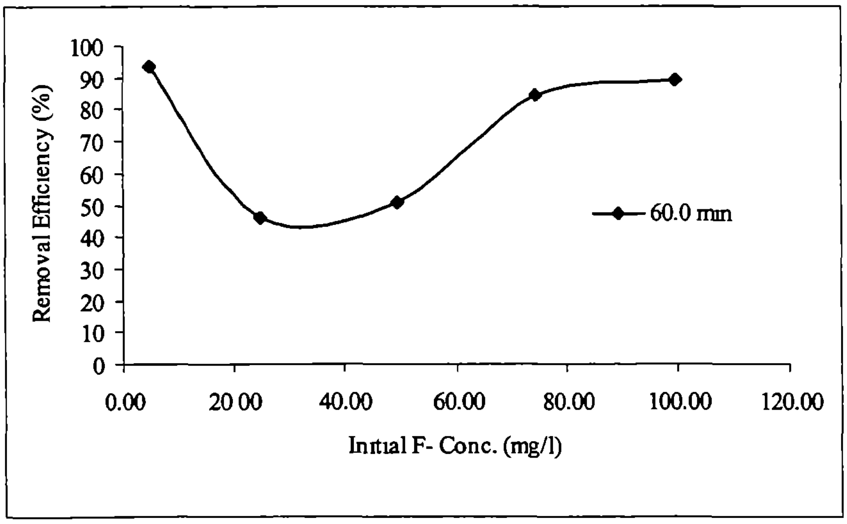


FIGURE 4.2. FLUORIDE REMOVAL EFFICIENCY OF THE CONDITIONED ZEOLITE AGAINST INITIAL FLUORIDE CONTENT OF THE WATER FOR 60 MINUTES OF CONTACT TIMES.

This pattern holds for concentration range from 2.5 mg F^-/l up to approximately 50.0 mg F^-/l. For concentration range from 50.0 mg F^-/l up to 100.0 mg F^-/l, a different some how reverse pattern is observed, i.e., when the fluoride concentration in the starting solution is increased the removal efficiency also is increased. This reversing pattern of the efficiency of the conditioned zeolite is plotted in Figure 4.2 for a 60.0 minutes of contact time. It clearly shows a U-shaped pattern of decrease followed by increase in efficiency, with a turning point at about 50.0 mg F^-/l. This pattern is probably connected to the mixed adsorption/precipitation reactions removing the F^- ions (See Chapter 5).

4.2.2 The effect of varying solid to liquid ratios on the efficiency of the zeolite.

The results found for the treatment of 10.0 mg F^-/l and 15.0 mg F^-/l by conditioned zeolite in S/L ratios 1:20, 1:15, and 1:10 are plotted in Figure 4.3 and Figure 4.4, respectively. Although the S/L ratio 1:10 showed that better performance is achieved by using more zeolite on both fluoride concentrations tested, there is hardly any difference in using 1:20 and 1:50 S/L ratios, especially on the 15.0 mg F^-/l solution. This may be is due to the relatively small difference in the amounts of zeolite used in these S/L ratios. The amounts of zeolite used are 100 g, 66.7 g, and 50.0 g, for S/L ratios of 1:10, 1:15, and 1:20 respectively. The residual fluoride concentration is higher than the WHO guideline even after the treatment of 10.0 mg F^-/l by a relatively higher S/L ratio of 1:10.

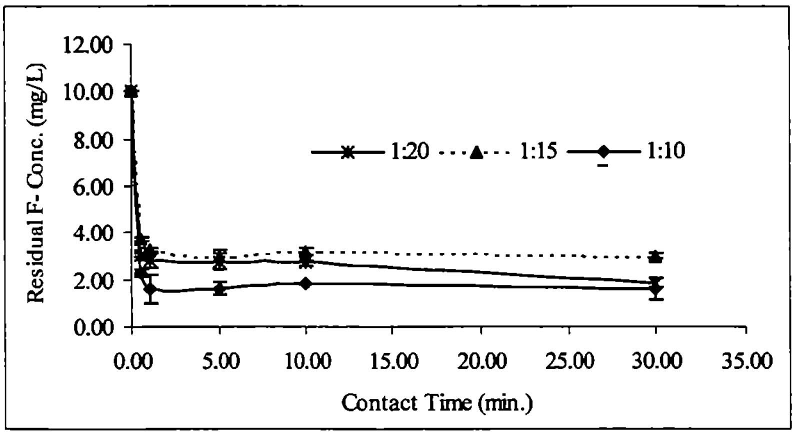


FIGURE 4.3. RESIDUAL FLUORIDE CONCENTRATION (MEAN ± STD) AGAINST TIME, AFTER TREATMENT OF 10.0 MG F^-/L BY S/L RATIOS OF 1:20, 1:15, AND 1:10.

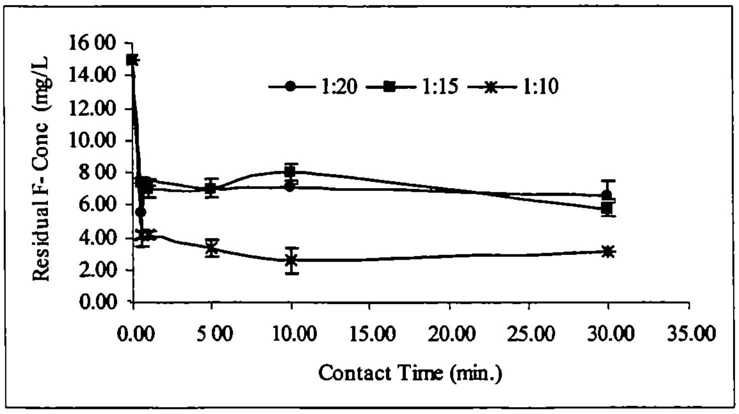


FIGURE 4.4. RESIDUAL FLUORIDE CONCENTRATION (MEAN ± STD) AGAINST TIME, AFTER TREATING 15.0 MG F^-/L BY S/L RATIOS OF 1:20, 1:15, AND 1:10.

4.2.3 The effect of washing of the zeolite on the efficiency of removal.

Some of results found for the treatment of water containing 10.0 mg F⁻/l by conditioned zeolites, pre-washed to different conductivity levels, are plotted in Figure 4.5. For details of all experiments see Appendix. The result of the unwashed zeolite (>3000 µS/cm) is also presented for comparison. The S/L ratio of 1:20 was used for the test. This shows that the more the zeolite is washed, the smaller the efficiency of fluoride removal becomes. This is probably because the conditioning process did not fix the calcium ion well in the structure of the zeolite. Instead, it is loosely held on the surface. Therefore, whenever it is washed, it is easily removed. The fluoride removal mechanism, however depends on the availability of calcium ions either attached or unattached to the zeolite surface for both adsorption and precipitation to take place.

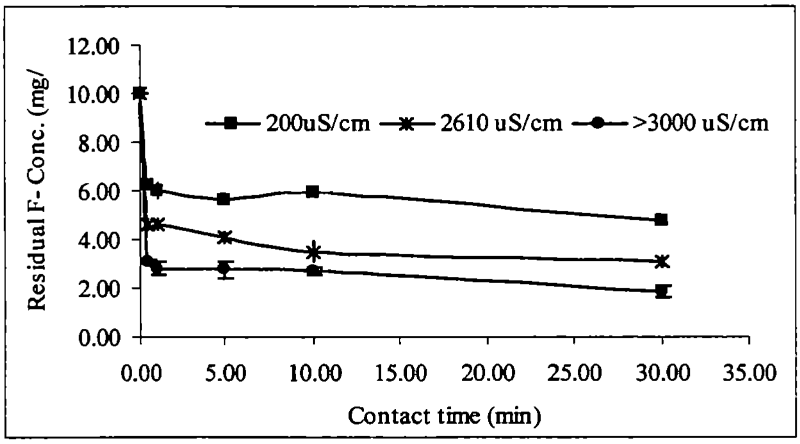


FIGURE 4.5. RESIDUAL FLUORIDE CONCENTRATIONS (MEAN ± STD) VERSUS TIME FOR THE TREATMENT OF WATER BY UNCONDITIONED ZEOLITE.

4.2.4 Two step treatment

It is found out that treating water, containing 10.0 mg F⁻/l, by conditioned zeolite did not reduce the fluoride level below 1.5 mg/l. Here a two step treatment process is done for water containing 10.0 mg F⁻/l by conditioned zeolite washed to 1560 µS/cm and 2522 µS/cm in S/L ratio 1:20. The results obtained for conditioned zeolite washed to 1560 µS/cm are given in Figure 4.6 below.

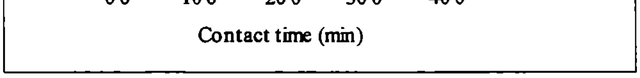
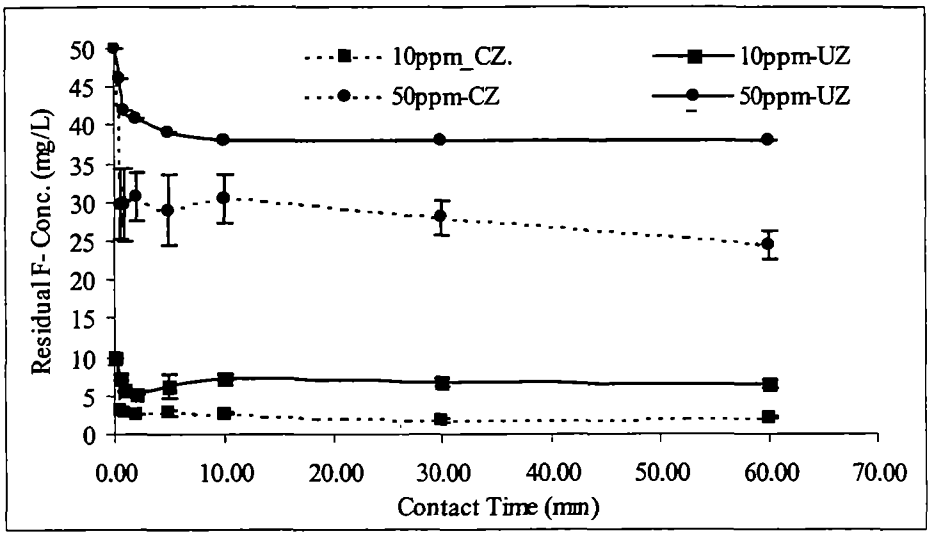


FIGURE 4.6 TWO STEP TREATMENT OF 10.0 MG F⁻/L BY CONDITIONED ZEOLITE

From this figure it is apparent that water containing 10.0 mg F⁻/l can be treated successfully to values below 1.5 mg/l, in two steps. The first step constitutes 30 minutes of treatment, whereas less than 1 minutes of treatment is sufficient for the second step.

4.2.5 The effect of non-conditioned zeolite on fluoride removal

Figure 4.7 gives the results found after the treatment of water containing 10.0, and 50.0 mg F⁻/l in a S/L ratio of 1:20 in comparison with the results obtained for the treatment of similar concentrations and by the same S/L ratio, but with conditioned zeolite. It can be seen from the figure that some reduction in fluoride was achieved by non-conditioned zeolite, but this was very much less than the one achieved by conditioned zeolite. For all fluoride concentrations tested, a remarkable rise in residual fluoride concentration is observed for non-conditioned zeolite after 24 hours of treatment.



CZ = with conditioned zeolite; UZ = with unconditioned zeolite

FIGURE 4.7. COMPARISON BETWEEN THE CONDITIONED AND UNCONDITIONED ZEOLITE FOR THE TREATMENT OF 10 MG F⁻/L AND 50.0 MG F⁻/L.

4.2.6 Testing 'real' water samples.

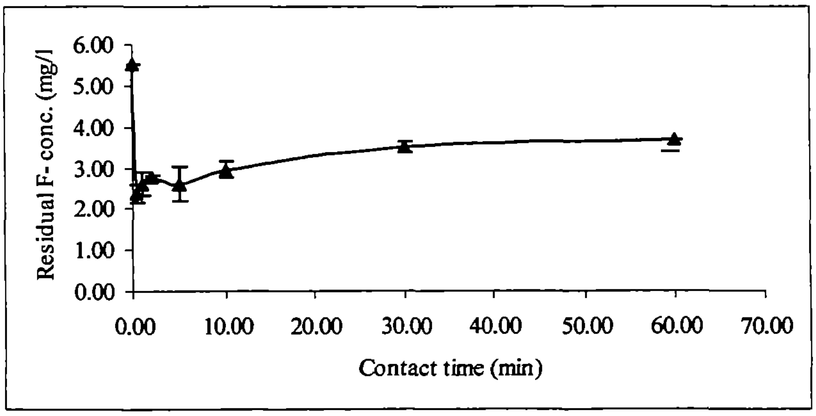


FIGURE 4.8 TREATMENT OF GREECE WATER SAMPLES BY CONDITIONED ZEOLITE.

The results obtained after the treatment of Greece water samples by conditioned zeolite are given in Figure 4.8 above. As we can see from this Figure, a fast reduction of fluoride from 5.5 mg/l to 2.35 mg/l (57.27 % reduction) in fluoride is occurred in about half a minute, but this is followed by an increase in fluoride concentration to 3.7 mg/l (32.73 % reduction) in 60 minutes. This may be is due to variety of competing ions present in the water sample.

4.2.7 Alternative materials for fluoride removal

Figure 4.9 gives a plot of the residual fluoride concentration versus time for the four materials tested as an alternative to zeolite for fluoride removal. These materials are Heulandite, synthetic Xonotlite, Hydrotalcite, and precipitated silica. Single tests on these materials show that synthetic Xonotlite can treat the water even more efficiently than the conditioned zeolite. While precipitated silica and Heulandite showed almost no reduction, a slow reduction was observed with Hydrotalcite.

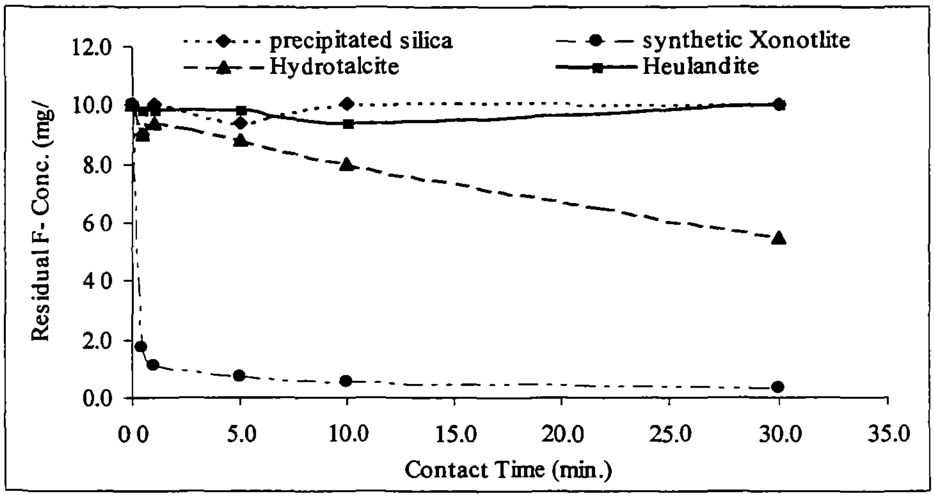


FIGURE 4.9 RESIDUAL FLUORIDE CONCENTRATION VERSUS CONTACT TIME FOR THE TREATMENT OF FLUORIDE-WATER BY ALTERNATIVE MATERIALS.

The better performance observed by the synthetic Xonotlite is may be due to displacement reaction or anion exchange reaction, the replacement of the hydroxide ion by an ion of the most electronegative element (F^-).

4.2.8 Varying the S/L ratio on the efficiency of the synthetic Xonotlite

Since interesting results were found for synthetic Xonotlite, it was further investigated on water containing 10.0 mg F^-/l in S/L ratios of 1:20, 1:50, and 1:100. The results obtained after these investigations are plotted in Figure 4.10. These results show that synthetic Xonotlite can reduce the fluoride level from 10.0 to below 1.5 mg/l in less than 30 seconds using the S/L ratio of 1:20 and in little more than 1 minute using the S/L ratio of 1:50. The only disadvantage of this material is that it imparts high pH (≅ 10) to the water after treatment. This is due to the presence of hydroxide (OH^-) ions in the structure of this material and it loses these ions whenever added to water. This fact is proved by other experiment given below.

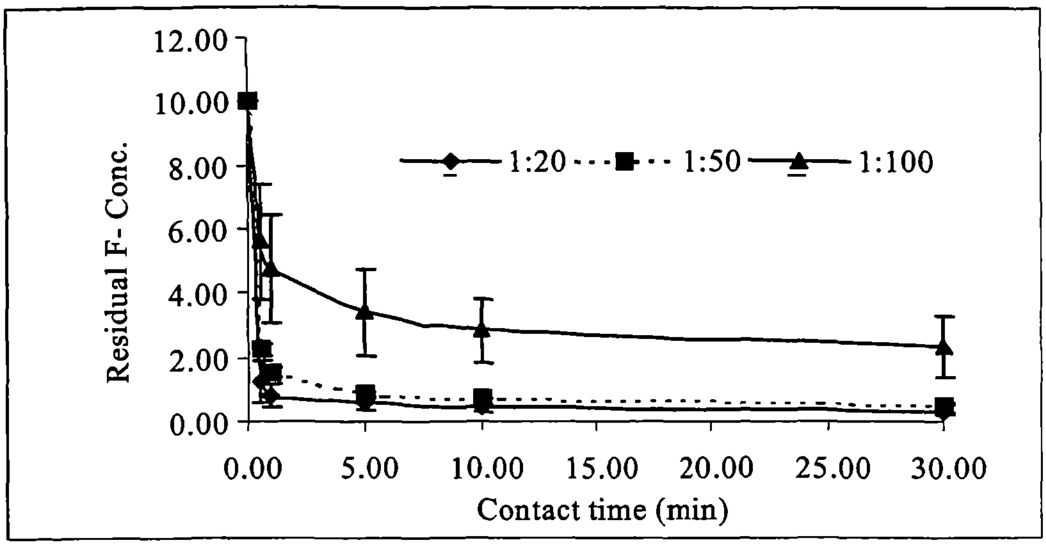


FIGURE 4.10 RESIDUAL FLUORIDE CONCENTRATION (MEAN ± STD) VERSUS TIME FOR THE TREATMENT OF FLUORIDE WATER BY SYNTHETIC XONOTLITE IN DIFFERENT S/L RATIOS.

4.2.9 Other batch experiments.

1. **The treatment of Greece water sample by synthetic Xonotlite.**

The results obtained for the treatment of Greece water sample by synthetic Xonotlite in a S/L ratio of 1:50 are plotted in Figure 4.11. This result shows that synthetic Xonotlite can also treat natural water sample accompanied with a lot of competing ions. Although the fate of the other ions is not studied, it is expected that the material selectively removed fluoride.

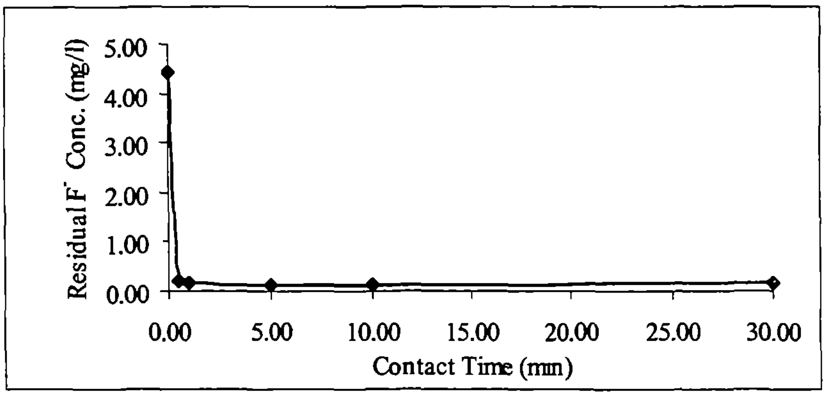


FIGURE 4.11 RESIDUAL FLUORIDE CONCENTRATION AGAINST TIME FOR THE TREATMENT OF 'REAL' WATER SAMPLE BY SYNTHETIC XONOTLITE.

2. **The relationship between washing the synthetic Xonotlite in de-mineralized water and pH**

Stirring synthetic Xonotlite with only distilled water and monitoring the pH proved that the release of the hydroxide ion occurs indeed. In this experiment, the synthetic Xonotlite was mixed in S/L ratio of 1:50 with distilled water and stirred continuously. The pH of the mix is raised to 9.99 in about 5 minutes.

3. The relationship between continuous stirring of the zeolite in de-mineralized water and conductivity

Mixing the conditioned zeolite with de-mineralized water in a S/L ratio of 1:20 resulted in a gradual increase in the conductivity of the water from 804 μS/cm, immediately after they are mixed, to 1454.5 μS/cm after 1 hour. This is presented in Figure 4.12 below.

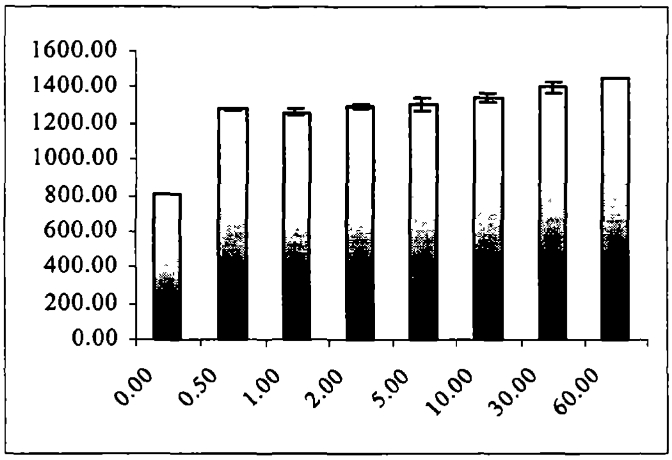


FIGURE 4.12 EFFECT OF WASHING CONDITIONED ZEOLITE AND CONDUCTIVITY.

4. Effect of GF6 glass fiber paper on fluoride reduction.

The effect of membrane filtration on fluoride removal was checked by measuring millivolt responses before and after filtration of solutions containing 1, 25, 50, 75, and 100 mg F^-/l by GF6 glass fiber paper. The results show that there is hardly any difference between the two measurements and the effect of filtration on fluoride removal can be considered to be insignificant. The millivolt response versus logarithm of the concentrations is plotted in Figure 4.13.

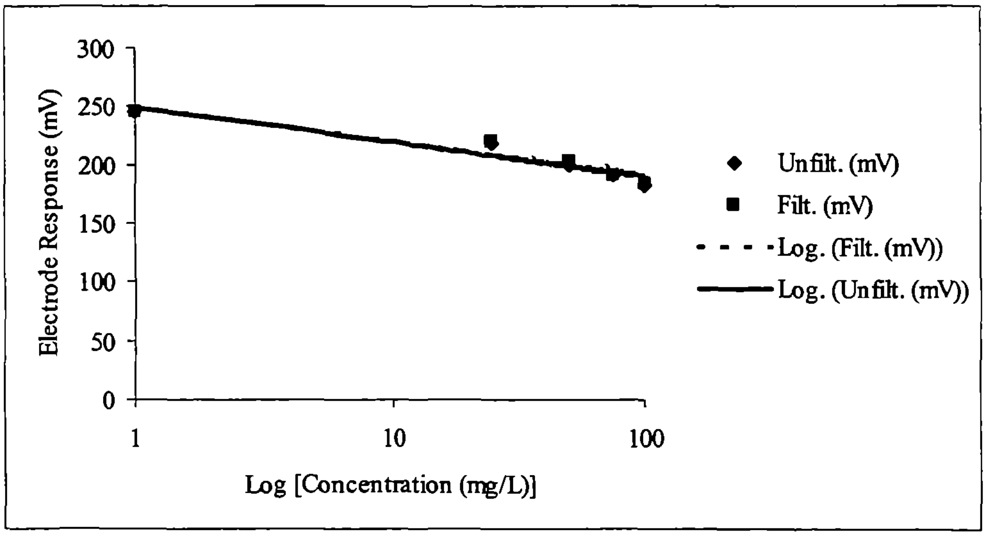


FIGURE 4.13 EFFECT OF FILTRATION ON FLUORIDE REDUCTION.

4.3 Column experiments

4.3.1 control

The column, which was run as a control, showed the absence of adsorption of fluoride by inert silver sand. The results are presented in Figure 4.14. The 100.0 mg F⁻/l solution that passed at a flow rate of 0.12 m/h through the column containing only silver sand remained mostly at 100 mg F⁻/l for some 70 hours.

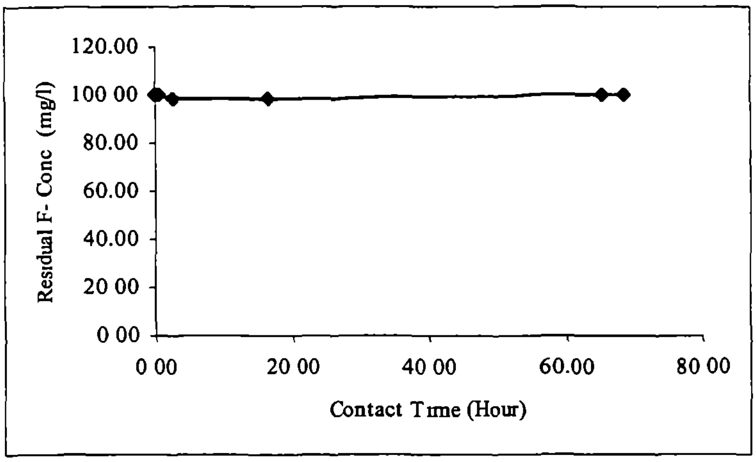


FIGURE 4.14. COLUMN WITH ONLY SAND (CONTROL).

4.3.2 Column with conditioned zeolite and 100.0 mg F⁻/l

One column was packed from top to bottom with 20-g sand, a mixture of 30 g zeolite with 300-g sand, and 20 g zeolite; and a solution containing 100.0 mg F-/l is run through it. The break-through point has occurred so fast that it cannot be used to calculate the capacity of the zeolite. The results of this experiment are plotted in Figure 4.15 below.

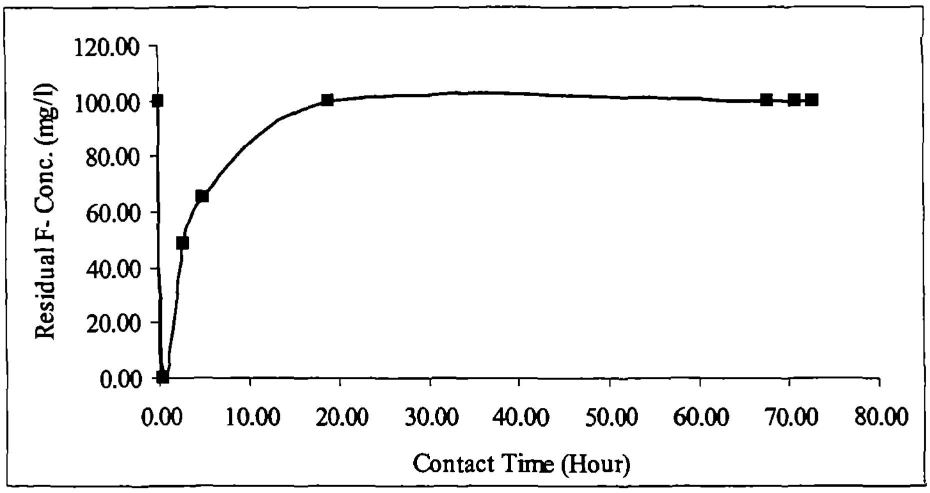


FIGURE 4.15 COLUMN WITH CONDITIONED ZEOLITE AND 100.0 MG F⁻/L

4.3.3 Column with conditioned zeolite and 25.0 mg F/l

Another column, subsequently filled from top to bottom with 75 g sand, a mixture of 60 g zeolite with 210-g sand, and 75 g sand, was also run with 25.0 mg F-/l solution. The results of this experiment are adequate to be used to calculate the capacity of the zeolite either, because of the fast occurrence of the break-through point. These results are presented in Figure 4.16.

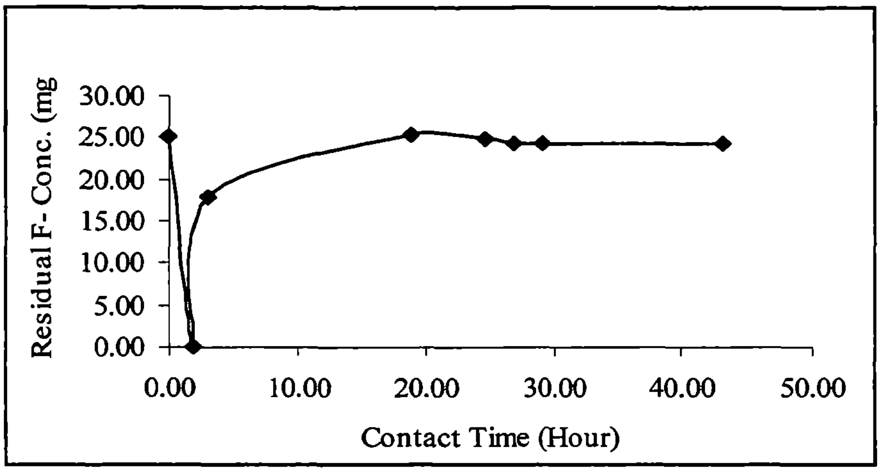


FIGURE 4.16 COLUMN WITH CONDITIONED ZEOLITE AND 25.0 MG F/L

4.3.4 Column with conditioned zeolite and 10.0 mg F/l.

A solution, containing 10.0 mg F/l was passed through a column packed from top to bottom with 30 g sand, a mixture of 30 g zeolite and 300 g sand, and 30 g sand, at a flow rate of 237 ml/h. This experiment was closely monitored by continuous sampling and used to determine the capacity of the zeolite. The results of this experiment are plotted in Figure 4.17 below.

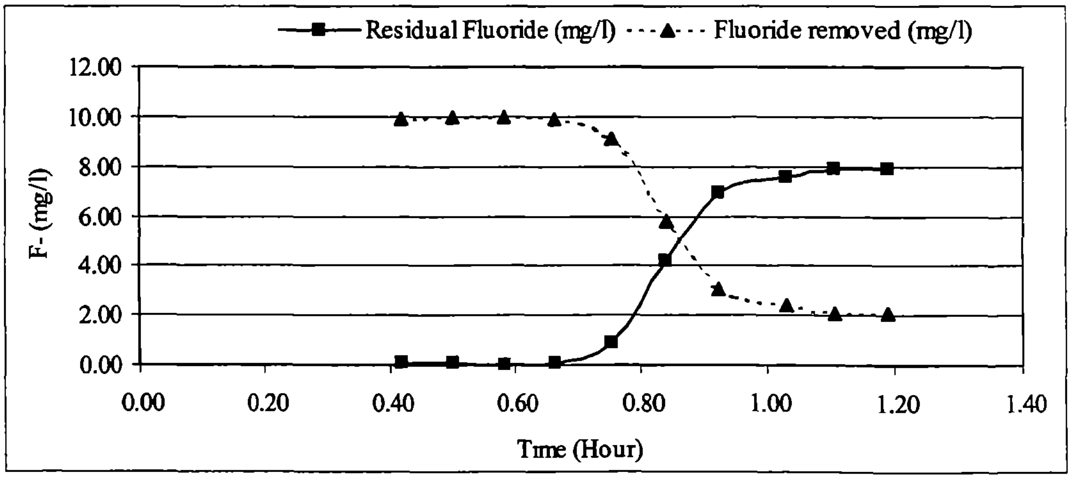


FIGURE 4.17 RESIDUAL AND REMOVED FLUORIDE CONCENTRATIONS AGAINST TIME FOR THE TREATMENT OF 10.0 MG F/L SOLUTION BY COLUMN EXPERIMENT WITH CONDITIONED ZEOLITE.

To calculate the capacity the following equation was used:

Capacity (mg/mg)=[(flow rate (l/h)×F⁻removed (mg/l)×Time (hr))/(mg of zeolite)]

To do this the curve showing the fluoride removed is divided in to two parts, a linear part and a polynomial part. The equations of the two curves were integrated to obtain the respective areas under the curves. These areas give the product of concentration removed and treatment times in mgh/l. Then the capacity of the zeolite was obtained by multiplying these values by the flow rate and dividing the new product by weight of the zeolite.

Therefore, the capacity of the conditioned zeolite determined in this way as **3.75×10^{-5}** mg F⁻/mg zeolite or **0.0375** mg F⁻/g Zeolite or **0.00375 %.** Details of the calculations are given in the Appendix.

4.3.5 Determination of the capacity of synthetic Xonotlite by column experiment.

A solution containing 10 mg F-/l was passed through a column containing a mixture of synthetic Xonotlite and sand, as described in chapter 3, at 180 ml/h to determine the capacity of the material for fluoride adsorption. The results are plotted in Figure 4.18 below.

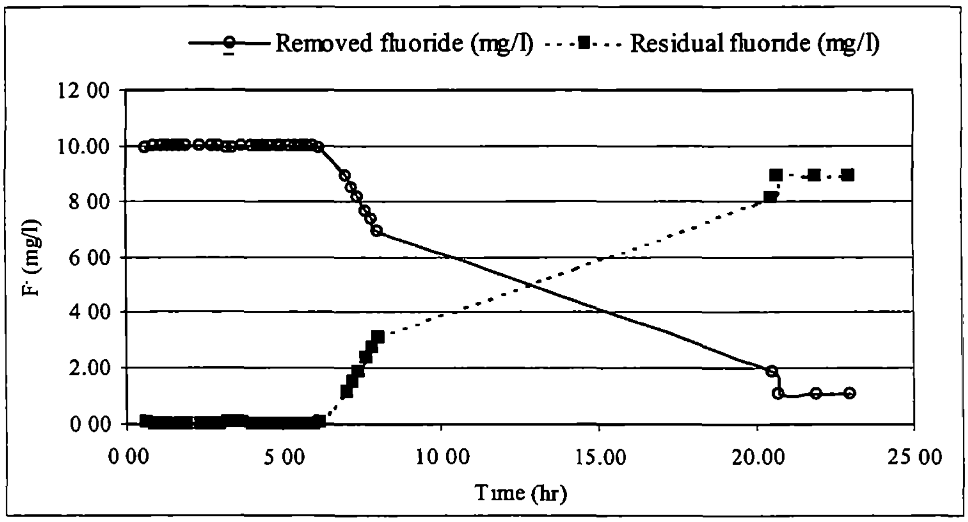


FIGURE 4.18 SYNTHETIC XONOTLITE IN COLUMN EXPERIMENT

The capacity of the synthetic Xonotlite is determined in the same way done for the conditioned zeolite as **0.002673** mg F⁻/mg synthetic Xonotlite or **2.6732** mg F⁻/g synthetic Xonotlite or **0.2%.**

Chapter 5

DISCUSSION

The results presented in the previous chapter indicate that conditioned zeolite is able to defluoridate water sources, which contain relatively small fluoride concentration (≅ 5.0 mg/l or less), down to below the WHO recommended level of 1.5 mg/l. The removal efficiencies of 86 % for 2.5 mg F^-/l and 81.2 % for 5.0 mg F^-/l were achieved in less than 1-minute treatment time using a solid to liquid ratio of 1:20. These efficiencies are higher than the one reported by MPIA, 1998 (73.3 %) for similar material, clinoptilolite. Water containing fluoride level as much as 10.0 mg/l can only be treated to an acceptable level in two steps using S/L ratio 1:20. This involves filtration of the water treated for 30 minutes and mixing it with fresh conditioned zeolite. The second step of the treatment need not take another 30 minutes; about half a minute is sufficient.

One disadvantage of using this material is that the conductivity of the water after treatment is so high (>3000 µS/cm). Further washing of the zeolite to reduce the conductivity well result in a reduction in the efficiency of the material. However, water containing fluoride concentrations as low as 5.0 mg/l can be treated well with the washed zeolite without causing the problem high conductivity.

The other disadvantage of this method is that the conditioned zeolite showed preference to other competing ions. This is observed when the conditioned zeolite is used to treat 'real' water samples This is in agreement with earlier findings (FRENCKEN, 1990). The question as which ions have exactly competed with fluoride is not answered in this study due to time limitations. This involves the complete analysis of the water before and after treatment with conditioned zeolite. Once the competing ions are determined, the removal of these ions should be considered first, before defluoridation is attempted.

Comparing the feasibility of using this method over existing methods is not done here. It involves knowing the exact cost of materials at a pilot plant scale. This is beyond the scope of this study.

The treatment of water containing fluoride concentrations above 10.0 mg/l for drinking purpose seems to be unreliable. However, the results obtained for fluoride concentrations as high as 100.0 mg/l can be applied for industries, which produce wastewater with very high fluoride concentration exceeding the discharge limits. They can treat their waste by conditioned zeolite to an acceptable level before discharge.

Generally, as the fluoride concentrations in the water to be treated gradually increased from 2.5 mg/l to 100.0 mg/l, the decrease in efficiency up to 50.0 mg/l and an increase afterwards up to 100.0 mg/l were observed. One explanation for this shifting of pattern may be because two processes play a role in fluoride removal, namely adsorption to surface of the zeolite and precipitation of fluorite by calcium. Although the two processes may occur simultaneously in each region, one seems to be dominant over the other in one of the two distinct regions.

In the region where the fluoride content is between 2.5 to 50.0 mg/l, the adsorption process is expected to be dominant; this adsorption will be higher for lower fluoride concentrations and lower for higher concentrations. This is because the surface area of the zeolite, which is available for adsorption is fixed. Therefore, as the fluoride content is increased, the adsorption process decreases. However, for precipitation process this is different, mainly in the range between 50.0 to 100.0 mg/l. The more fluoride is available, the more the precipitation process is favored. The precipitation process is due to the calcium ion available with the zeolite and the fluoride ion in the water to form calcium fluoride (fluorite).

Calcium fluoride is a sparingly soluble salt whose solubility is dependent on the pH of the solution in which it is dispersed. When fluorite is placed in water, the following equilibria are eventually established (GIMBLETT, 1998):

$CaF_2\ (s) \Leftrightarrow Ca^{2+} + 2\ F^-$ $K_s = 4\ \%\ 10^{-11}$

$Ca^{2+} + F^- \Leftrightarrow CaF^+$ $K_1 = 10$

$H^+ + F^- \Leftrightarrow HF$ $K_2 = 1.5\ \%\ 10^{-3}$

$HF + F^- \Leftrightarrow HF_2^-$ $K_3 = 3.9$

The equilibrium concentration curves (Figure 5.1) indicate that the predominant species present in the CaF_2 (s) / water system are HF, Ca^{2+}, and H^+, at pH values below 3.25. The concentrations of HF_2^- and CaF^- are much lower than those of the HF or Ca^{2+} species at and below this pH value; above this pH value, Ca^{2+} and F^- ions are more predominant.

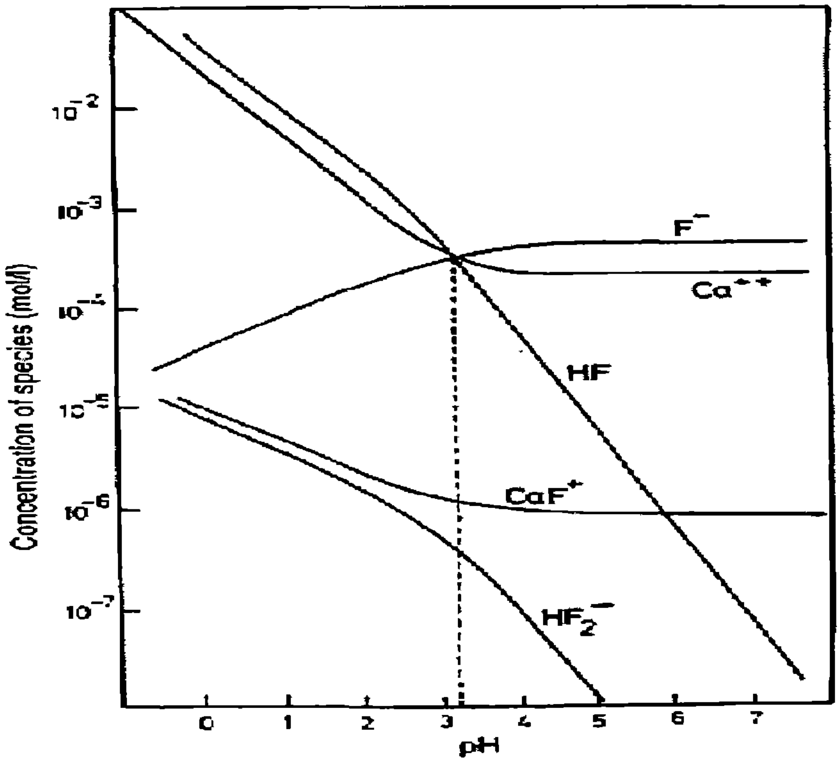


FIGURE 5.1 THEORETICAL SOLUBILITY FOR CaF_2 IN AQUEOUS SOLUTION AS A FUNCTION OF THE pH VALUE.

The average concentration of Ca^{2+} in filtered solution from a mixture of conditioned zeolite and distilled water in solid to liquid ratio of 1:20 was determined to be 230 mg/l. Therefore, the fluoride concentration required to precipitate fluorite can be determined from the solubility product:

$CaF_2\ (s) \Leftrightarrow Ca^{2+} + 2\ F^-$ $K_s = 4\ \%\ 10^{-11}$.

From this equation it can be easily calculated that the calcium ion which is present at this concentration would be sufficient to reduce F^- concentration to 1.6 mg/l. For washed zeolite, since the process remarkably reduces the Ca^{2+} concentration, precipitation starts at relatively higher fluoride concentrations and the effect of precipitation becomes insignificant for low fluoride concentrations.

Varying the S/L ratio indicated that fluoride-water can be defluoridated better by using more zeolite (S/L ratio of 1:10) than using less zeolite (S/L ratios 1:15 and 1:20). The results for S/L ratios 1:15 and 1:20 were combined because there is no marked difference between them due to the closeness of the amounts of zeolite used in each case.

In my opinion, the conditioning of the zeolite did not produce the desired conditioned zeolite, clinoptilolite with only Ca^{2+} occupying all the cation sites. The aim of the conditioning was to change the natural Na form of the zeolite to the Ca form according to the simplified ion exchange reaction (my suggestion):

$$Na_6[Al_6Si_{30}O_{72}].24H_2O + 3CaCl_2 = Ca_3[Al_6Si_{30}O_{72}].24H_2O + 6NaCl$$

However, the produced NaCl and unreacted $CaCl_2$ should be washed sufficiently so that only the zeolite remains and further washing should not change the conductivity of the water. Especially the unreacted $CaCl_2$ and the loosely held Ca^{2+} played a role in precipitating fluorite. Fluoride removal by Calcium chloride is one of the existing methods of defluoridation by precipitation.

The unconditioned zeolite can be used to treat water containing low fluoride concentration as 2.5 mg/l down to WHO recommended level. However, the contact time should be limited to less than one hour to avoid remobilization of fluoride back to the solution.

Among the alternative materials tested for fluoride removal, it was found out that synthetic Xonotlite worked much better for fluoride removal than conditioned zeolite. It successfully treated water containing fluoride concentrations as high as 10.0 mg/l in a S/L ratio of 1:50. It showed superiority in several ways over the use of the conditioned zeolite namely the use of smaller material to treat the same fluoride concentrations, the capability to treat higher fluoride concentrations, and the capability to treat the natural water sample without showing preference to other competing ions. The mechanism of fluoride by this material may be is due to the replacement of the hydroxide ions present in the structure of the material by fluoride ions (ion exchange), which can be depicted as (my suggestion):

$$Ca_6Si_6O_{17}(OH)_2 + 2F^- = Ca_6Si_6O_{17}F_2 + 2OH^-$$

The only disadvantage of the method is the rise in pH of the water to around 10 after treatment with the material due to the release of the hydroxide ion to the solution. This makes the water not acceptable for drinking, without subsequent neutralizations. Parallel experiments showed that the release of the hydroxide was apparent even when the material was mixed with only distilled water.

The column experiments indicated showed the capacities of both synthetic Xonotlite and conditioned zeolite are limited, i.e. 0.2% and 0.00375 %, respectively. Therefore, the application of these methods depends on the availability and cost of the materials in comparison to other defluoridation techniques.

Chapter 6

CONCLUSIONS and RECOMMENDATIONS

6.1 Conclusions

The following conclusions can be made:

- ☐ Conditioned zeolite can be used, in a solid to liquid ratio of 1:20, to reduce fluoride levels from water sources containing as much as 5.0 mg F^-/l down to below 1.0 mg/l in less than 1 minute of contact time with about 81 % efficiency. This efficiency is higher for fluoride concentrations lower than 5.0 mg/l (86 % for 2.5 mg/l).
- ☐ Water sources containing as much as 10.0 mg F^-/l can only be treated to an acceptable level by using the solid to liquid ratio of 1:20 after 24 hours of contact time. Alternatively, they can be treated in two steps comprising 30 minutes for the first step and less than a minute for the second step using the same solid to liquid ratio.
- ☐ For natural water sources, the efficiency of the conditioned zeolite was low and a gradual remobilization of the fluoride ion back to the water has occurred after few minutes of treatment, due to the preference of the zeolite for other ions.
- ☐ It was found out that the conditioning process of the zeolite leads to an increase of the electrical conductivity of the water after treatment, in fact too high for drinking. Washing the zeolite however resulted in a reduction in efficiency.
- ☐ Two processes have played a role in removing fluoride ion, namely adsorption and precipitation. Calculations show that the precipitation process can remove a portion of the zeolite. (See Discussion).
- ☐ Among the alternative materials tested, synthetic Xonotlite performed better than the conditioned zeolite both on 'artificial' and 'real' waters. It is capable of treating water containing as much as 10.0 mg F^-/l in less than half a minute using a S/L ratio of 1:20 (87.7 % reduction) and in less than 5 minutes using a S/L ratio of 1:50 (91.1 % reduction). For 'real' water sources, the material was capable of reducing the fluoride level to an acceptable level using S/L ratio of 1:50 in less than a minute.
- ☐ The pH of the water after treatment with synthetic Xonotlite was high for drinking (9 – 10).
- ☐ The Capacity of conditioned zeolite for fluoride removal was very low, i.e. 0.00375 %, while that of the synthetic Xonotlite was found to be 0.2 %.

6.2 Recommendations

The following points are recommended:

- ☐ The conditioning process needs to be studied more and an appropriate mechanism should be obtained so that the zeolite does not impart high conductivity on the treated water.
- ☐ More fundamental research is needed on the different mechanisms that play role on the fluoride removal by zeolites.
- ☐ The column experiment for the conditioned zeolite should be further investigated with more zeolite in the column and with up-flow type of treatment.
- ☐ The synthetic zeolite should be further studied with respect to neutralization before it is used or neutralizing the water after treatment.
- ☐ The column experiment for synthetic Xonotlite also needs further investigation by mixing it with relatively lighter material than sand, in order to avoid irregular distribution of the synthetic Xonotlite throughout the column.

REFERENCES

AWWA (1976). Water Quality and Treatment, A Handbook of Public Water Supplies, 3rd edition. *Mc Graw-Hill Book Company, USA.*

BARTRAM, JAMIE AND BALANCE, RICHARD (1996). Water Quality Monitoring, A practical guide to the design and implementation of freshwater quality studies and monitoring programmes. *E & FN Spon, London, UK.*

BUITEMAN, J.P. (1995). Water Treatment, Part 2, Treatment Methods for Rural Areas. *IHE Lecture note: EE085/95/1, (4:1-14), Delft, The Netherlands.*

BULSU, K.R. AND BISWAS, S.K. (Eds.) (1993). Prevention and Control of Fluorosis, Volume II, Water Quality and Defluoridation Techniques. *Rajiv Gandhi National Drinking Water Mission, New Delhi.*

CIULLO, PETER A. (1996). Industrial Minerals and Their Uses, A Handbook and Formulary. *Noyes Publications, Westwood, New Jersey, USA.*

FRENCKEN, J.E. (ed.) (1990). Endemic Fluorosis in Developing countries. Causes, Effects and Possible Solutions. *Report of a Symposium, Delft, The Netherlands.*

GIMBLETT, F.G.R. (ed.) (1998). Adsorption Science & Technology. Volume 6, Number 6. *Multi-Science Publishing Co. LTD., England.*

HELMER, R. (1998). Water Quality and Health. *IHE Lecture note, No. EE349/98/1, Delft, The Netherlands.*

HELMER, R. and HESPANHOL, I. (ed.) (1997). Water Pollution Control. *E & FN Spon, London.*

MARIER, J.R. AND ROSE, D (1971). Environmental Fluoride. *National Research Council Of Canada, Public. No. 12226, Ottawa, Canada.*

PICKFORD, J. (1992) Water, Environment and Management. *Proceedings of the 18th WEDC conference, Kathamandu, Nepal.*

SCHUILING, R.D., ANDRIESSEN, P.A.M., FRAPPORTI, G., KREULEN, R., de LEEUW, J.W., POORTER, R.P.E., de SMETH, J.B., VERGOUWEN, L., VRIEND, S.P., ZUURDEEG, B.W., AND NIJENHUIS, I.A. (1994). Introduction to Geochemistry. Sixth edition. *Department of Geochemistry, Institute of Earth Sciences, University of Utrecht, Utrecht, The Netherlands.*

SLANGEN, P.M. Zeolite Synthesis Using Rapid Heating Methods, Towards Continuous Synthesis. *Technical Univerisity of Delft, The Netherlands.*

SUSHELEELA, A.K. (ed.) (1993). Prevention and Control of Fluorosis. Volume I, Health Aspects. *Rajiv Gandhi National Drinking Water Mission, New Delhi.*

TOMLINSON, A.A.G. (1998). Modern Zeolites, Structure and Function in Detergents and Petrochemicals. *Trans Tech Publications Ltd., Switzerland.*

TSITSISHVILI, G.V., ANDRONIKASHVILI, T.G., KIROV, G.N., AND FILIZOVA, L.D. (1992). Natural Zeeolites. *Ellis Horwood Limited, England.*

WORLD HEALTH ORGANIZATION (1984a). Guidelines for Drinking-Water Quality, Volume 1: Recommendations, and Volume 2: Health Criteria and other Supporting information. *Geneva.*

WORLD HEALTH ORGANIZATION (1984b). Fluorine and Fluorides. Environmental Health Criteria 36. *Geneva.*

APPENDICES

APPENDIX-I. Conditioned zeolite

APPENDIX-IA. Treatment of water by conditioned zeolite (S/L ratio 1:20).

Contact Time (Min)	Residual Fluoride Concentration (mg/l)				Efficiency (%)
	Run 1	Run 2	Mean	Std	
On 2.5 mg F/l					
0.0	2.50	2.50	2.50	0.00	0.00
0.5	0.38	0.32	0.35	0.04	86.00
1.0	0.37	0.22	0.30	0.11	88.20
2.0	0.35	0.18	0.27	0.12	89.40
5.0	0.28	0.18	0.23	0.07	90.80
10.0	0.27	0.15	0.21	0.08	91.60
30.0	0.22	0.14	0.18	0.06	92.80
60.0	0.20	0.12	0.16	0.06	93.60
1440.0	0.10	0.10	0.10	0.00	96.00
On 5.0 mg F/l					
0.0	5.00	5.00	5.00	0.00	0.00
0.5	0.92	0.96	0.94	0.03	81.20
1.0	0.60	0.70	0.65	0.07	87.00
2.0	0.56	0.78	0.67	0.16	86.60
5.0	0.60	0.60	0.60	0.00	88.00
10.0	0.50	0.62	0.56	0.08	88.80
30.0	0.39	0.36	0.38	0.02	92.50
60.0	0.25	0.39	0.32	0.10	93.60
1440.0	0.29	0.36	0.33	0.05	93.50
On 10.0 mg F/l					
0.0	10.00	10.00	10.00	0.00	0.00
0.5	3.10	3.00	3.05	0.07	69.50
1.0	3.00	2.60	2.80	0.28	72.00
2.0	2.50	2.60	2.55	0.07	74.50
5.0	2.50	3.00	2.75	0.35	72.50
10.0	2.60	2.80	2.70	0.14	73.00
30.0	1.70	2.00	1.85	0.21	81.50
60.0	2.10	2.30	2.20	0.14	78.00
1440.0	1.20	1.50	1.35	0.21	86.50
On 15.0 mg F/l					
0.0	15.00	15.00	15.00	0.00	0.00
0.5	4.00	7.00	5.50	2.12	63.33
1.0	7.20	7.50	7.35	0.21	51.00
2.0	7.20	8.00	7.60	0.57	49.33
5.0	7.00	7.00	7.00	0.00	53.33
10.0	7.00	7.20	7.10	0.14	52.67
30.0	5.80	7.20	6.50	0.99	56.67
60.0	6.00	7.00	6.50	0.71	56.67
1440.0	4.60	4.60	4.60	0.00	69.33
On 20.0 mg F/l					
0.0	20.00	20.00	20.00	0.00	0.00
0.5	11.50	9.60	10.55	1.34	47.25
1.0	9.60	7.60	8.60	1.41	57.00
2.0	9.60	8.20	8.90	0.99	55.50
5.0	9.60	8.00	8.80	1.13	56.00
10.0	9.20	8.00	8.60	0.85	57.00
30.0	8.60	8.60	8.60	0.00	57.00
60.0	8.80	8.20	8.50	0.42	57.50
1440.0	5.20	5.20	5.20	0.00	74.00

APPENDIX-IA continued

Contact Time (Min)	Residual Fluoride Concentration. (mg/l)				Efficiency. (%)
	Run 1	Run 2	Mean	Std.	
On 25.0 mg F/l					
0.0	25.00	25.00	25.00	0.00	0.00
0.5	16.50	13.50	15.00	2.12	40.00
1.0	14.00	13.50	13.75	0.35	45.00
2.0	14.00	14.50	14.25	0.35	43.00
5.0	14.00	13.50	13.75	0.35	45.00
10.0	15.00	13.50	14.25	1.06	43.00
30.0	14.00	12.50	13.25	1.06	47.00
60.0	13.50	13.50	13.50	0.00	46.00
1440.0	9.50	10.50	10.00	0.71	60.00
On 50.0 mg F/l					
0.0	A total of four experiments were done and the mean values are the averages of the four results. This is because this experiment behaved so strangely inconsistent compared to others.		50.00	0.00	0.00
0.5			29.75	4.57	40.50
1.0			29.75	4.72	40.50
2.0			30.75	3.20	38.50
5.0			29.00	4.55	42.00
10.0			30.50	3.11	39.00
30.0			28.00	2.16	44.00
60.0			24.50	1.73	51.00
1440.0			9.15	3.96	81.70
On 75.0 mg F/l					
0.0	75.00	75.00	75.00	0.00	0.00
0.5	45.00	48.00	46.50	2.12	38.00
1.0	43.00	44.00	43.50	0.71	42.00
2.0	40.00	38.00	39.00	1.41	48.00
5.0	32.00	30.00	31.00	1.41	58.67
10.0	22.00	20.00	21.00	1.41	72.00
30.0	15.00	10.50	12.75	3.18	83.00
60.0	11.50	11.50	11.50	0.00	84.67
1440.0	7.30	8.00	7.65	0.49	89.80
On 100.0 mg F/l					
0.0	100.00	100.00	100.00	0.00	0.00
0.5	58.00	56.00	57.00	1.41	43.00
1.0	46.00	41.00	43.50	3.54	56.50
2.0	34.00	32.00	33.00	1.41	67.00
5.0	25.00	21.00	23.00	2.83	77.00
10.0	18.00	18.00	18.00	0.00	82.00
30.0	14.00	12.50	13.25	1.06	86.75
60.0	11.00	10.00	10.50	0.71	89.50
1440.0	9.60	7.20	8.40	1.70	91.60

APPENDIX-IB Summary of the Table above for residual fluoride concentrations (S/L ratio 1:20)

Contact Time (min)	Residual fluoride concentration (mg/) from initial concentrations								
	2.5 mg/l	5 0 mg/l	10 0 mg/l	15.0 mg/l	20.0 mg/l	25 0 mg/l	50.0 mg/l	75 0 mg/l	100.0 mg/l
0 0	2.50	5.00	10.00	15 00	20.00	25.00	50.00	75.00	100.00
0.5	0.35	0.94	3.05	5.50	10.55	15.00	29.75	46.50	57.00
1.0	0.30	0.65	2.80	7.35	8.60	13.75	29.75	43.50	43.50
2.0	0.27	0.67	2.55	7.60	8.90	14.25	30.75	39.00	33.00
5.0	0.23	0.60	2.75	7.00	8 80	13.75	29 00	31.00	23.00
10.0	0.21	0.56	2.70	7.10	8 60	14.25	30.50	21.00	18.00
30.0	0.18	0.38	1.85	6 50	8.60	13.25	28.00	12.75	13.25
60.0	0.16	0.32	2.20	6.50	8.50	13.50	24 50	11.50	10.50
1440.0	0.10	0.33	1.35	4.60	5.20	10.00	9.15	7.65	8.40

APPENDIX-IC Effect of Varying S/L ratio of conditioned zeolite.

Time (min)	10 0 mg F^-/l			15.0 mg F^-/l		
	1:20	1:15	1 10	1:20	1:15	1:10
0 00	10.00	10.00	10.00	15.00	15.00	15.00
0 50	3.05	3.75	2.30	5.50	7.40	4 15
1.00	2 80	3.25	1.63	7.35	7.00	4 15
5.00	2.75	3 00	1 63	7.00	7.00	3.35
10 00	2.70	3.20	1.80	7.10	8.00	2.55
30 00	1.85	3.00	1.60	6.50	5.70	3.10

APPENDIX-ID Washing of the zeolite and its efficiency (S/L ratio 1:20).

Time (min)	114 µS/cm	200 µS/cm	430 µS/cm	870 µS/cm	2610 µS/cm	>3000 µS/cm
0.00	10.00	10.00	10.00	10.00	10 00	10.00
0.50	7.40	6.20	5.80	6 40	3.05	4.60
1.00	6.80	6.00	5.80	6.70	2 80	4.60
5 00	6.00	5.65	4.90	5.85	2.75	4.10
10.00	5.50	5.90	5.25	5 65	2 70	3.50
30 00	4 90	4.80	5.35	5.30	1.85	3.10

APPENDIX-IE Two step treatment of 10.0 mg F^-/l (in S/L ratio 1:20)

Contact time (min)	Step 1			Step 2		
	F^- (mg/l)	Efficiency (%)	EC µS/cm	F^- (mg/l)	Efficiency (%)	EC µS/cm
Zeolite, pre-washed to 1560 µS/cm						
0 0	10.0	0 0	50 6	3 0	70 0	90 0
0 5	4 8	52 0	93 0	1 3	87.5	117 6
1 0	4 1	59 0	86 0	0 9	91.2	122 4
5 0	3 8	62 0	85.6	1 0	90 4	125 4
10 0	3.4	66 0	88 1	1 0	90.0	120.3
30 0	3 0	70 0	90 0	0 7	93.0	130.2
Zeolite, pre-washed to 2522 µS/cm						
0 0	10 0	0 0	50.6	3 6	64.0	660 0
0 5	4 0	60 0	489 0	1 3	87 3	1048 0
1 0	3 7	63.0	486 0	1 1	88 8	1090 0
5 0	2 9	71 0	551 0	1 0	90.0	1107 0
10 0	3 3	67.0	564 0	0 9	91.2	1172 0
30 0	2 7	73 0	626 0	0 8	92 2	1185 0

APPENDIX-IF Treatment of Greece water sample by conditioned zeolite (S/L ratio 1:20)

Contact time (min)	F^- (mg/l)	Efficiency (%)
0.00	5.50	0.00
0.50	2.35	57.27
1.00	2.60	52.73
2.00	2.75	50.00
5.00	2.60	52.73
10.00	2.95	46.36
30.00	3.50	36.36
60.00	3.70	32.73

APPENDIX-1G Stirring conditioned zeolite in demi-water and its conductivity (S/L ratio 1:20)

Contact time (min)	EC (µS/cm)			Std.
	Run 1	Run 2	Mean	
0.00	804.00	804.00	804.00	0.00
0.50	1279.00	1276.00	1277.50	2.12
1.00	1254.00	1274.00	1264.00	14.14
2.00	1305.00	1285.00	1295.00	14.14
5.00	1338.00	1282.00	1310.00	39.60
10.00	1362.00	1323.00	1342.50	27.58
30.00	1419.00	1380.00	1399.50	27.58
60.00	1458.00	1451.00	1454.50	4.95

APPENDIX-1H The effect of GF6 glass fiber paper on filtration

Concentrations tested (F^- mg/L)	Unfiltered (mV)	Filtered (mV)
1	246	245
25	219	220
50	200	202
75	191	191
100	182	184

APPENDIX-II Unconditioned Zeolite (S/L ratio 1:20)

Contact time (min)	Residual F^- Conc. (mg/l) from		
	2.5 mg/l	10.0 mg/l	50.0 mg/l
0.00	2.50	10.00	50.00
0.50	1.30	7.40	46.00
1.00	1.45	5.70	42.00
2.00	1.43	5.10	41.00
5.00	1.45	6.30	39.00
10.00	1.68	7.40	38.00
30.00	1.80	6.83	38.00
60.00	2.00	6.50	38.00
1440.00	2.30	8.05	45.50

APPENDIX-III Alternative materials

APPENDIX-IIIA. The four alternative materials tested (S/L ratio 1:20)

Time (min)	synthetic Xonotlite			Hydrotalcite			Precipitated silica			Heulandite		
	F^- (mg/l)	EC µS/cm	pH	F^- (mg/l)	EC µS/cm	pH	F^- (mg/l)	EC µS/cm	pH	F^- (mg/l)	EC µS/cm	pH
0.0	10.0	50.6		10.0	50.6		10.0	50.6		10.0	50.6	
0.5	1.7	244.0	9.6	9.0	212.0	8.7	9.0	65.8	6.0	9.8	93.1	6.9
1.0	1.1	235.0	9.2	9.4	266.0	8.8	10.0	67.9	6.3	9.8	98.9	6.9
5.0	0.7	244.0	9.2	8.8	537.0	9.2	9.4	70.8	6.4	9.8	118.7	6.9
10.0	0.5	261.0	9.6	8.0	638.0	9.1	10.0	70.1	6.6	9.4	94.2	6.9
30.0	0.3	277.0	9.8	5.5	930.0	9.4	10.0	69.4	6.5	10.0	95.0	6.9

APPENDIX-IIIB. The effect of Varying S/L of synthetic Xonotlite on fluoride removal

Contact time (min)	S/L ratio 1:20		S/L ratio 1:50		S/L ratio 1:100	
	F^- (mg/l)	pH	F^- (mg/l)	pH	F^- (mg/l)	pH
0.00	10.00		10.00		10.00	
0.50	1.23	9.97	2.24	9.71	5.61	9.4
1.00	0.83	9.83	1.56	9.82	4.75	9.47
5.00	0.55	9.87	0.89	9.93	3.41	8.97
10.00	0.41	10.05	0.74	9.97	2.82	9.31
30.00	0.26	10.10	0.55	9.97	2.32	9.52

APPENDIX-IIIC. Treating 'real' water sample by synthetic Xonotlite (S/L ratio 1:50)

Contact time (min)	F^- (mg/l)	pH	EC (µS/cm)
0.00	4.43		
0.50	0.22	9.39	164.20
1.00	0.16	9.45	161.90
5.00	0.14	9.65	155.30
10.00	0.14	9.79	154.10
30.00	0.16	10.00	155.30

APPENDIX-IIID. Washing synthetic Xonotlite in distilled water and pH (S/L ratio 1:50)

Contact Time (min)	pH
0.5	9.54
1.0	9.61
5.0	9.99
10.0	9.76
30.0	9.82

APPENDIX-IV Column Experiments

APPENDIX-IVA. Column filled with 300g sand 100 mg F^-/l (Control)

Time (Hr)	Conc.(mg/l)	Efficiency (%)	EC (µS/cm)
0.00	100.00	0 00	481
0.50	100.00	0.00	466
2.72	98.00	2.00	466
16 65	98 00	2.00	466
65.38	100.00	0.00	466
68 55	100.00	0 00	460

APPENDIX-IVB Column filled with 75g sand (bottom), mixture of 60g zeolite and 210g sand (middle), and 75g sand (top) through which is run a solution containing 25 mg F^-/l

Time (Hr)	Conc.(mg/l)	Efficiency (%)	EC (µS/cm)
0.00	25 00	0.00	
1.90	0.10	99.62	968.0
3 07	17.79	28.84	44.8
18.92	25.39	-1.55	130 0
24.62	24.86	0.55	134.0
26.90	24.35	2.61	129.4
29.12	24.35	2.61	128.2
43.05	24.35	2.61	128.2

APPENDIX-IVC. Column filled with 20g sand (bottom), mixture of 30g zeolite and 300g sand (middle), and 20g sand (top) through which is run a solution containing 100 mg F^-/l.

Time (Hr)	Conc.(mg/l)	Efficiency (%)	EC (µS/cm)
0 00	100.00	0.00	481
0 50	0.33	99.67	20100
2.78	48.56	51.44	236
5.00	65.08	34.92	307
18.93	100.00	0 00	460
67.67	100 00	0 00	463
70.83	100.00	0.00	460
72 92	100.00	0.00	472

APPENDIX-IVD. 10.0 mg F^-/l in conditioned zeolite column

Total Time (hr)	EC (µS/cm)	pH	Residual F^- (mg/l)	Removed F^- (mg/l)
0.42	26000.00	5.50	0 06	9.94
0.50	1098.00	5 30	0.04	9.96
0 58	368 00	5.51	0 03	9.97
0.67	202.00	5.51	0.06	9.94
0.76	136.00	5 41	0.87	9.13
0.84	101 00	5.47	4 22	5.78
0.93	44.50	5 46	6.96	3.04
1 03	41.70	5.51	7.56	2.44
1 11	38 20	5.50	7.88	2.12
1.19	38.00	5 55	7 88	2.12

APPENDIX-IVD. 10.0 mg F^-/l in synthetic Xonotlite column

Total time (hr)	EC (µS/cm)	pH	Residual F^-mg/l	Removed F^- (mg/l)
0.63	1160.00	10.83	0.07	9.93
0.87	364.00	10.65	0.03	9.97
1.12	208.00	10.41	0.03	9.97
1.33	163.40	10.34	0.02	9.98
1.53	158.70	10.07	0.02	9.98
1.72	154.80	10.12	0.02	9.98
1.92	150.00	10.10	0.02	9.98
2.35	143.50	10.11	0.01	9.99
2.77	151.00	10.21	0.01	9.99
2.95	150.10	10.18	0.01	9.99
3.17	153.30	10.34	0.06	9.94
3.38	158.40	10.46	0.05	9.95
3.68	156.00	10.40	0.04	9.96
4.00	174.80	10.52	0.03	9.97
4.20	177.00	10.57	0.02	9.98
4.40	178.00	10.60	0.02	9.98
4.62	180.20	10.06	0.02	9.98
4.82	183.03	10.60	0.02	9.98
5.00	182.00	10.61	0.02	9.98
5.20	165.30	10.54	0.02	9.98
5.40	177.20	10.29	0.03	9.97
5.58	128.20	8.11	0.03	9.97
5.78	180.60	10.19	0.02	9.98
5.98	192.00	8.80	0.02	9.98
6.17	191.40	10.00	0.06	9.94
7.05	178.50	9.88	1.12	8.88
7.25	185.40	10.00	1.52	8.48
7.47	184.40	10.00	1.90	8.10
7.70	152.10	9.18	2.37	7.63
7.90	160.20	10.00	2.70	7.30
8.08	164.20	9.78	3.09	6.91
20.52	146.30	10.34	8.14	1.86
20.72	147.20	8.90	8.89	1.11
21.97	146.60	8.45	8.89	1.11
23.00	148.20	10.00	8.89	1.11

APPENDIX-V Capacity Calculation

APPENDIX-VA. Capacity of the zeolite

For the reasons of convenience, the graph that shows the fluoride removed versus time is divided in to two parts, the linear part and the polynomial part. Then the equations of these two parts are integrated in respective time intervals to get the product of concentration and time in mgh/l. This product is multiplied by the flow rate and divided by the weight of the zeolite to get the capacity of the zeolite in each region. Then the values obtained for the two regions are added together to get the total capacity of the zeolite.

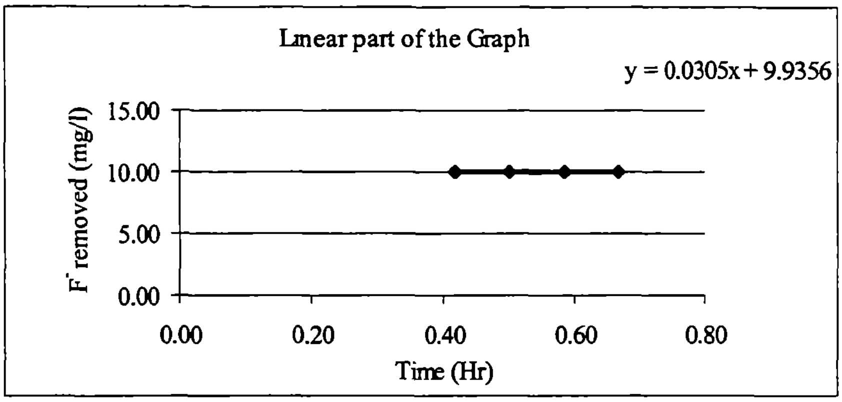


Figure App-1. Linear part of the graph

The equation of the curve is Y = 0.0305X + 9.9356. Integrating this equation in time intervals from 0.42 hr to 0.67 hr gives the desired product in mgh/l.

Conc. (mg/l) × Time (hr) = $\int_{0.42}^{0.67}(0.0305x + 9.9356) = 0.0305x^2/2 + 9.9356x$ from 0.42 hr to 0.67 hr

Conc. (mg/l) × Time (hr) = <u>2.488056 mgh/l.</u>

Capacity of the zeolite in this region is then calculated as,

Capacity (mg/mg) in the linear region = (2.488056 mgh/l × 0.23675l/h)/30000 mg zeolite

= **<u>1.96×10^{-5} (mg/mg)</u>**

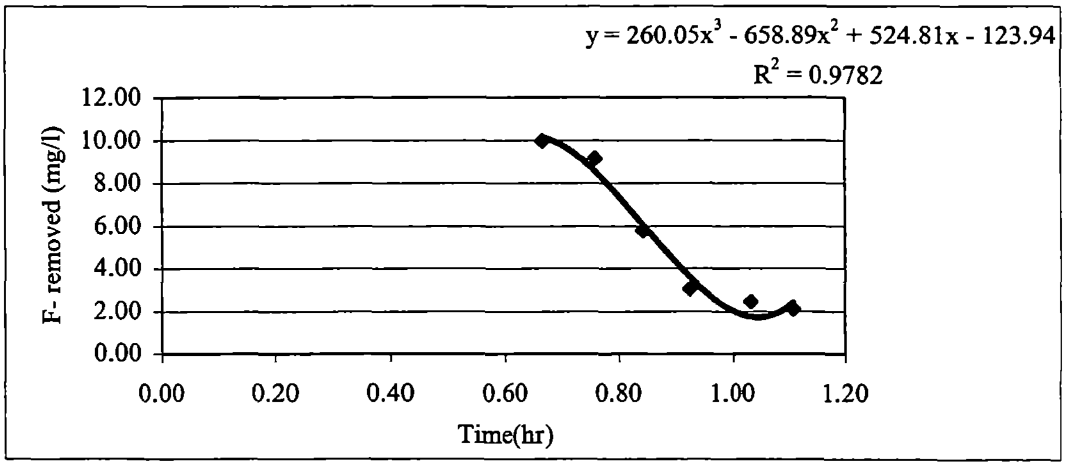


Figure App-2. Polynomial part of the curve

The capacity of the zeolite in this region is also calculated in the same way as the linear part. Equation: Y = $260.05x^3 - 658.89x^2 + 524.81x - 123.94$. Integration of this equation over time intervals of 0.67 hr to 1.03 hr gives:

Conc. (mg/l) × Time (h) = $\int_{0.67}^{1.03}(260.05x^3 - 658.89x^2 + 524.81x - 123.94)$

$= [9260.05/4)x^4 - (658.89/3)x^3 + (524.81/2)x^2 - 123.94x]$ from 0.67 hr to 1.03 hr

Capacity in the polynomial region = (2.258582 mgh/l × 0.23675l/h)/30000 mg zeolite

= **1.78×10^{-5} mg/mg**

Total capacity of the zeolite = 3.75×10^{-5} mg/mg
= 0.0375 mg F^-/g Zeolite
=0.00375%

APPENDIX-VA. Capacity of the synthetic Xonotlite

Similarly the graph which shows the fluoride removed is divided in to two parts and the area under each curve is calculated by integrating the curve in respective time intervals.

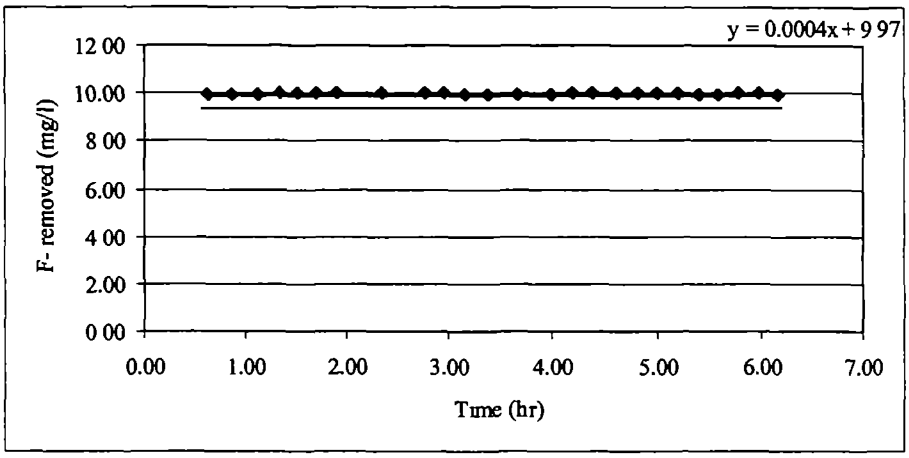


Figure 4.17 Linear part of the curve

Equation: Y = 0.0004x + 9.97

$$\text{Conc. (mg/l)} \times \text{Time (hr)} = \int_{0.63}^{6.17} (0.0004x + 9.97)$$

$= [(0.0004/2)x^2 + 9.97x)]$ from 0.63 hr to 6.17 hr

= 55.24133 mgh/l

Then, Capacity in the linear region = (55.24133 mgh/l × 0.1796575l/h)/10000 mg synthetic Xonotlite

= **0.000992 mg/mg**

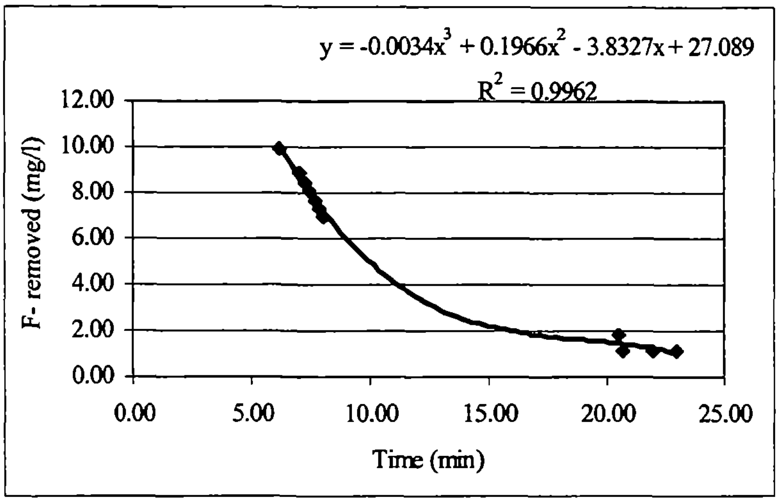


Figure 4.18. Polynomial part of the curve

Equation, $Y = -0.0034x^3 + 0.1966x^2 - 3.8327x + 27.089$. Integrating this equation from 6.17 hr to 23.00 hr gives us the product of conc. and time in mgh/l.

$$\text{Conc. (mg/l) x Time (hr)} = \int_{6\,17}^{23\,00} (-0.0034x3 + 0.1966x2 - 3.8327x + 27.089)$$

$$= (-0.0034/4)x^4 + (0.1966/3)x^3 - (3.8327/2)x^2 + 27.089x$$

$$= 93.552976 \text{ mgh/l}$$

Capacity in the polynomial region = [(93.55297 mgh/l x 0.179575l/h)/10000 mg synthetic Xonotlite]

<u>=0.001681 mg/mg</u>

Total capacity of synthetic Xonotlite = 0.002673 mg/mg

= 2.6732 mg F⁻/g synthetic Xonotlite

= 0.2%