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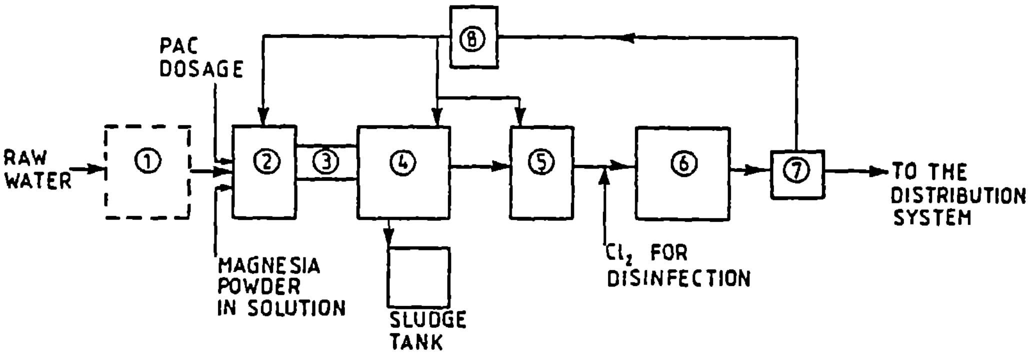
Singano, J.

DEFLUORIDATION OF DRINKING WATER BY USING MAGNESIA AND POLYALUMINIUM CHLORIDE



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DEFLUORIDATION OF DRINKING WATER BY USING MAGNESIA AND POLYALUMINIUM CHLORIDE

by Singano Joseph

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APPENDICES

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ABSTRACT

Defluoridation of drinking water by using magnesia and polyaluminium chloride (PAC) was investigated in the laboratory and at the pilot plant. The method has shown very good and encouraging results.

The results show that, for defluoridation by filtrating through magnesia the most appropriate magnesia particle sizes are 0.2 - 0.6 mm. Through filtration, fluoride can be removed from 22.0 mg/l to 0.3 mg/l at the filtration velocity of 0.3 m/h. Fluoride reduction in this method is more favourable when the pH in the raw water is below 7. The optimum contact time with magnesia for defluoridation is 4 - 8 h. The use of magnesite raises the pH to an unacceptable level for domestic use. Thus pH adjustment is inevitable after the filtration.

When using PAC as a coagulant in defluoridation the flocs are formed very fast, within 10 - 30 s. Fluoride can be removed from 22.0 mg/l to 0.2 mg/l. The use of clay bentonite or magnesia powder as coagulant aid improves the floc formation and floc settlement. The flocs are formed when the pH is 4.8 and above. PAC removes fluoride at a wider pH range of 2.3 - 10.3, however, the optimum pH value for fluoride removal is 5 - 7. PAC reduces the pH of water to an unacceptable value for domestic use requiring pH adjustment after the coagulation.

The combined use of magnesia and PAC for defluoridation allows to reduce the quantity of magnesia and the dosage of polyaluminium chloride. It adjusts the pH of the treated water to the acceptable level for domestic use.

The use of magnesia increases magnesium, sulphate and hardness and it reduces the bicarbonates of water. The use of polyaluminium chloride raises the chloride content in water.

Although the use of magnesia and PAC is very effective in defluoridation, it is very expensive. It costs 0.14 TZS to remove 1 mg of fluoride in 1 l of water.

1 INTRODUCTION

Defluoridation of drinking water is essential for water which has higher fluoride content than recommended. There are many methods of fluoride removal. However, there is no single defluoridation technique which is effective for all waters polluted with fluoride.

To find the most appropriate and feasible defluoridation technology, good knowledge of how fluoride occurs in water, how it reacts with other compounds, parameters affecting the reactions, and how it is adsorbed in the body, are assisting researchers. The good knowledge of the fluoride chemistry will guide scientists, chemists and engineers to find and design the appropriate and feasible fluoride removal technology for a particular area.

Fluoride has a great effect in the human body (WHO 1970, Mcharo 1986 and Mjengera 1988). Males seem to suffer from fluorosis more than females. The level of haptoglobin in blood provides information on the susceptibility of fluoride toxicity to individuals. If the haptoglobin is low the individual may not suffer from fluoride, even if high fluoride content is ingested or inhaled. Males normally have high haptoglobin as males' sex hormone stimulates its production while females' sex hormone inhibits it (Susheela 1986 b).

People who have malnutrition especially in protein and calories are more prone to fluorosis. High fat and fatty foods enhance proper adsorption and utilization of fluorides in the body (Kisanga et al 1987). Also low intakes of protein, vitamin A, C and D enhance the severity of fluoride toxicity (McClure et al 1962, WHO 1984 b and Massler and Schour 1952). Therefore the nutritional status must be assessed and guarded in areas with high fluoride content. In these areas people should be educated on the importance of taking balanced diet.

In the latest researches (Mjengera 1988) it was found that defluoridation by using polyaluminium chloride (PAC) as coagulant with magnesia as filter media could be feasible in areas where magnesia is locally available. The experiments were made in the laboratory only. In this work the experiments were made in the laboratory level and in the treatment models at the site. The use of clay bentonite, and the use of magnesia powder as coagulant aid were experimented. Combined dosage of magnesia powder solution and PAC was also made.

The overall objective is to find out materials and methods which are effective in defluoridation. The method should be suitable for the conditions, and economic and human resources for developing countries. The method should utilize the locally available materials as much as possible.

2 CHEMISTRY OF FLUORIDE

2.1 Occurrence of fluoride

Fluorine is the most electronegative of all elements due to its electrons configuration. It has an atomic number of 9 (Appendix 1 and 2). The element has an electronic configuration of $1s^2\ 2s^2\ 2p^5$. It exists naturally in the form of fluoride compounds in a number of minerals, in soils, rocks, waters and in the atmosphere (WHO 1970, WHO 1984 a, WHO 1984 b and Handbook of Geochemistry 1978).

The main sources of fluoride ions in soils and rocks are fluorite or fluorspar (CaF_2), topaz [$Al_2(FOH_2)SiO_4$], fluorapatite [$Ca_5(PO_4)_3F$], cryolite ($NaAlF_6$), etc. (Table 1). Most fluoride bearing mineral compounds in soils and rocks occur due to volcanic activities (Handbook of Geochemistry 1978 and Nanyaro et al 1984). The fluoride contents in water are due to the chemical weathering of fluoride from the fluoride bearing mineral compounds (Ramesam and Rajagopalan 1985, and Kilham and Hecky 1983).

The various factors which govern the release of fluoride ions into natural waters from the fluoride bearing minerals in the rocks and soils are:

- presence and accessibility of fluoride in rocks and soils
- pH, alkalinity and hardness of water
- temperature
- basic chemical composition of water
- time of contact between the minerals and water
- solubility of the aquifer material
- amount of dissolved gases in soil
- contact area between water and rock
- porosity of rocks or soils through which water passes and flow speed of water.

Table 1. Fluoride bearing mineral compounds found in soils and rocks (Karunakaran 1974).

Name	Formula	Fluorine content	
		Theoretical %	Range in analytical values %
A. Fluorides:			
Fluorite	CaF_2	48.67	48.18 - 48.61
Sellaite	MgF_2	60.98	
Fluocerite (Tysonite)	$(Ce\ La\ Dy)\ F_3$	29.00	19.49 - 29.44
Cryolite	Na_3AlF_6	54.29	53.55 - 54.88
B. Phosphates:			
Fluor-apatite (Carbonate-apatite)	$Ca_5(PO_4)_3F$	3.80	2.57 - 5.60
Wagnerite	$Mg_2\ PO_4\ F$	11.68	5.06 - 11.48
Triplite	$(Mn,Fe,Mg,Ca)2\ FPO_4$		6.02 - 9.09
Amblygonite	$(Li\ Na)\ Al(PO_4)\ (F,\ OH)$	12.85	0.57 - 11.26
C. Silicates:			
Topaz	$Al\ (F,OH)_2\ SiO_4$	20.70	13.23 - 20.37
Humite group	$Mg\ (OH,F)_2,\ n\ Mg_2\ SiO_4$		Tr. - 13.55
Sphene	$Ca\ Ti(SiO)_4\ (O,OH,F)$		0.61 - 1.40
Vesuvianite	Calcium-magnesium silicate with $(OH,F)_4$		Tr. - 3.22
Tourmaline	Complex boro-silicate with $(OH,F)_4$		0.07 - 1.16
Mica group	Sheet silicates with $(OH,F)_4$		
Muscovite	Potash mica		0.00 - 2.06
Phlogopite	Magnesian mica		0.56 - 9.20
Biotite	Iron-Magnesian mica		0.32 - 5.02
Lepidolite	Lithium mica		4.39 - 8.09
Amphibole group	Chain silicates with $(OH,F)_2$		Tr. - 2.95

Other factors which affect the concentration of fluoride ions in rocks and soils are the run-off in fluoride contaminated areas, for example in farms that use phosphate fertilizers, and rains in the areas where the atmosphere is polluted with soluble fluoride.

High temperature and humidity in tropical environments promote high rates of weathering (Kilham and Hecky 1983). Hence it is likely to have also high fluoride contents in tropical environments like in Tropical Africa, China, India, Japan, Australia, etc.

In the atmosphere fluoride occurs due to industrial emissions, volcanic activity, and evaporation of water. Plants take up fluoride from the atmosphere, soil and water (Mcharo 1986). The sources of fluoride can also be certain industrial products like fluoridated tooth pastes and drugs.

Fluoride sources for human beings and animals are either inorganic or organic. In the case of soluble inorganic fluoride compounds only fluoride ions are adsorbed in the body while in the case of organic fluoride compounds the whole compounds are adsorbed or inhaled into the body (WHO 1970). In the body fluoride penetrates biological membranes as the undissociated acid, hydrogen fluoride the absorption rate of which is pH-dependent (Susheela and Jain 1985).

Some fluoridated tooth pastes have high fluoride content in the range of 800 - 1 000 mg/l. Because children normally swallow tooth paste while brushing their teeth, the use of this type of tooth paste for children below four years should be prohibited (Susheela 1986 a). More detailed information of occurrence of fluoride in the body is discussed for example in the thesis reports by Mcharo 1986 and Mjengera 1988.

2.2 Physical and chemical properties of fluoride

Fluoride ion (F^-) has an ionic radius of 1.33 Å (0.133 nm) where Å = Ångstrom (10^{-8} cm). The ion is strongly hydrated. It does not loose an electron easily. None of the ordinary chemical oxidizing agents is capable to extract electron from fluoride ions (Sienko and Robert 1974). Thus fluoride ion is a poor reducing agent.

The fluoride ion has a similar ionic radius with hydroxyl ion (OH^-) 1.4 Å and oxyl ion (O^{2-}) 1.32 Å. Due to this similarity, fluoride ion may substitute easily the OH^- ion in crystal structure. The replacement of hydroxyl ion by fluoride ion can be strongly hindered if the hydroxyl ions are involved as donors in the hydrogen bond O-H---X. The co-ordination and kind of ligands of the hydroxyl ion generally control the degree of replacement.

The OH^- ion may escape as H_2O simply by combining with a hydrogen ion (H^+) from a second nearby OH^- ion. That is why sometimes F^- ion can replace O^{2-} ion (Handbook of Geochemistry 1978).

Most simple fluoride salts formed with monovalent cations are soluble for example villaumite (NaF), carobbiite (KF) and silverfluoride (AgF). These salts give weak basis solutions because of the hydrolysis of F^- ion to hydrogen fluoride (HF). However, fluoride salts formed with divalent cations are usually insoluble, for example fluorite (CaF_2) and leadfluoride (PbF_2) but their solubility is a bit increased in acidic solution.

Fluoride forms complex ions with silicon and aluminium SiF_6^-, SiF_4^o and AlF_6^{-3}, in which the small size of fluoride ion permits relatively large numbers of them to be attached to another atom. The formation of insoluble inerty fluorides as surface coatings is apparently the reason why fluorine and its compounds can be stored in containers made of metals like copper.

Fluoride ion can substitute the hydrogen ion to form fluoricarson and polymer species. Some fluoride complex compounds such as platinum fluoride (PtF_6) react with noble-gas element (Sienko and Robert 1974).

Normally when fluoride compounds are dissolved in water, fluorine element will occur as fluoride ion. Depending on the ionic concentration and on pH of the solution it can occur as HF_2^- and undissociated HF. In the lower concentration and neutral pH all the fluoride will be present as fluoride ion. However, when pH of the solution decreases, the proportion of F^- present also decreases while the proportion of HF_2^- and undissociated HF increases (WHO 1970).

When calcium fluoride is dissolved in water it ionizes as in Equations 1, 2 and 3 (Handa 1974):

$$CaF_2 \quad <====> \quad Ca^{++} + 2F^- \tag{1}$$
$$F^- + H^+ \quad <====> \quad HF \tag{2}$$
$$HF^- + F^- \quad <====> \quad HF_2 \tag{3}$$

Sodium fluoride will ionize as calcium fluoride.

Before the solubility product is reached in Equation 1, there is a positive correlation between Ca^{++} and F^-, while after the solubility product has been attained the negative correlation between the two ions may occur.

Fluoride forms complex compounds with several cations because it is a strong ligand. It can form complexes with magnesium, iron and aluminium as shown in Equations 4, 5 and 6 (Nordström and Jenne 1977):

$$Mg^{2+} + 2F^- \quad <====> \quad MgF_2 \tag{4}$$
$$Fe^{3+} + nF^- \quad <====> \quad FeF_n^{(3-n)}, \quad n=1,2,3 \tag{5}$$
$$Al^{3+} + nF^- \quad <====> \quad AlF_n^{(3-n)}, \quad n=1,2,3,4,5,6 \tag{6}$$

2.3 Geochemistry of fluoride

Fluoride ion is liable to be camouflaged in hydroxily ion bearing minerals. In metarmorphic, sedimentary and magnetic rocks fluoride occurs mainly in the $+OH^-$ bearing minerals. The fluoride rock-forming minerals can be distinguished in two groups. In the first group, the fluoride content is in the OH-position as a constituent of a mixed crystal. In the second group, fluoride is contained only in relatively small amounts, camouflaged in the OH^- and rarely in the O^{2-} position. Factors which govern the content of fluoride in such minerals are the physical properties of the lattice position of the OH^- ion or O^{2-} and the amount of fluoride available in the rock-forming environment.

In clay minerals the F^- and OH^- exchange adsorption reactions that occur during weathering are overlapped by chemical decomposition of silicates. In acidic environments, chemical decomposition and exchange adsorption act in the opposite direction. The adsorption of F^- prevails in the acidic range while F^- desorption takes place in the alkaline environment (Handbook of geochemistry 1978). Fluoride ions attack the lattice aluminium ion of day mineral causing mineral decomposition forming complex solids of F^- phases and release of OH^- into solution (Bower and Hatcher 1967).

Hydrothermal fluids, which form part of residual magnetic solution can contain fluoride. If the hydrothermal fluids with fluoride come in contact with limestone causing a silification reaction, the reaction given in Equation 7 may result (Nyambok 1978):

$$3\ CaCO_3 + H_2SiF_6 \text{ ----> } 3\ CaF_2 + SiO_2 + 3\ CO_2 + H_2O \qquad (7)$$

When granite magma erupts, the residue solutions might contain high fluoride concentration. The fluoride might get mixed with connate water to form hydrogen fluoride as shown in Equation 8 (Balasubramaniam and Kumar 1974):

$$F_2 + H_2O \text{ ----> } 1/2\ O_2 + 2\ HF \qquad (8)$$

The solution formed in equation 8 is hydrofluoric acid. It will react with impure limestone to form fluorite (CaF_2) as shown in Equation 9 (Balasubramaniam and Kumar 1974):

$$2\ HF + CaCo_3 \text{ ----> } CaF_2 + H_2O + CO_2 \qquad (9)$$

The hydrofluoric acid which is a weak acid can dissolve glass. The reaction is attributed to the formation of fluorisilicate ions as shown in Equation 10 (Sienko and Robert 1974):

$$SiO_2 + 6\ HF \text{ ----> } SiF_6^{--} + 2\ H_2O + 2\ H^+ \qquad (10)$$

2.4 Chemical reactions of fluoride with other compounds during defluoridation

Chemical reactions in some of the fluoride removal methods are discussed as follows (Mjengera 1988):

i) Granular activated alumina:
During fluoride removal by using granular activated alumina, the fluoride removal is maximum when the solution is in acidic state. The activated alumina is also adsorbing some organic molecules and heavy metal ions, at the optimum fluoride removal pH. Those ions compete for the same adsorption sites with fluoride ions, their presence depletes the alumina capacity for fluoride. The following are simplified reactions of alumina adsorption and regeneration (Rubel et al 1984):

Alumina HF + HOH ---> Alumina HOH (neutral alumina) (11)
Alumina HOH + HCl ---> Alumina HCl + HOH (acidification) (12)
Alumina HCl + NaF ---> Alumina HF + NaCl (ion exchange in acid solution) (13)
Alumina HF + 2 NaOH ---> Alumina NaOH + HOH (regeneration) (14)
Alumina NaOH + 2 HCl ---> Alumina HCl + NaCl + HOH (acidification) (15)

When the reaction reaches the stage presented in Equation 15 it then goes back to Equation 13.

ii) Lime:
Lime is used to remove fluoride by forming a precipitate of calcium fluoride. The reaction is as shown in Equations 16 and 17 (Mjengera 1988):

$$CaO_2 + H_2 \text{ ---> } Ca(OH)_2 \qquad (16)$$
$$Ca(OH)_2 + 2F^- \text{ ---> } CaF_2 + 2(OH)^- \qquad (17)$$

iii) Andco process:
Andco process is the process of removing fluoride as a high insoluble fluorapatite compound. It involves the addition of phosphate, calcium mixture and adjustment of pH to the range of 6.2 to 7.0 by using calcium hydroxide (slaked lime). The chemical equation is as follows in Equation 18 (O'Brien 1983):

$$2\ NaF + 6\ H_3PO_4 + CaCl_2 + 9\ Ca(OH)_2 \text{ ----> } 2\ Ca_5(PO_4)_3F + 2\ NaCl + 18\ H_2O \qquad (18)$$

iv) Bone char filter:
Granular bones react with fluoride as bones and teeth of human being, by ion exchange process. The reaction is as in Equation 19 (Mjengera 1988):

$$Ca_5(PO_4)_3OH + F^- + H_2O \text{ ---> } Ca_5(PO_4)_3F + OH^- + H_2O \qquad (19)$$

In Equation 19 it is assumed that the concentration of fluoride is not very high, otherwise double decomposition might occur and decompose the fluorapatite to phosphates as indicated in Equation 20:

$$Ca_{10}(PO_4)_6(OH)_2 + 20\ NaF \text{ ---> } 10\ CaF_2 + 6\ Na_3PO_4 + 2\ NaOH \qquad (20)$$

v) Nalgonda technique:
Aluminium sulphate or alum [$Al_2(SO_4)_3 \times 14\ H_2O$] and slaked lime $Ca(OH)_2$ are added to water which contains fluoride. The chemical reaction involving fluorides and aluminium species is complex. The water should have sufficient alkalinity and pH range of 5 - 7. Defluoridation is taking place during coagulation and followed by flocculation, clarification, filtration and disinfection (Gitonga 1985 and NEERI 1987).

In order to find the appropriate fluoride removal technology more research should be carried on the chemistry of fluoride; how it reacts and behaves with other elements or compounds.

3 PARAMETERS AFFECTING REACTION OF FLUORIDE WITH OTHER COMPOUNDS

Some of the parameters which affect the reaction of fluoride with other compounds are pH, alkalinity, hardness, temperature, solubility, time of contact, presence of other minerals, etc. The effects of some of these parameters are briefly discussed below.

3.1 Effects of solubility, alkalinity and hardness of water in defluoridation

In order to understand thoroughly the concentration of fluoride ions in water, the principle of solubility products has to be known. Simple basic rule of solubility is that "The solubility of a compound increases as concentration of various ions increases in solution" (Fuhong and Shugin 1988).

Compounds which mostly affect the concentration of fluoride in natural waters are:

i)	fluorapatite	$[3Ca_3(PO_4)_2\ CaF_2]$
ii)	fluorite	(CaF_2)
iii)	magnesium fluorite	(MgF_2)

Their ionic products are as follows:

Fluor-apatite $(Ca^{2+})^{10}\ (PO_4{}^{3-})^6\ (F^-)^2$

$= 1.4 \times 10^{-119}$ at 25°C

Fluorite $(Ca^{2+})\ (F^-)^2$

$= 10^{-10.57}$ at 25°C (2.7^{-11})

Magnesium fluoride $(Mg^{2+})\ (F^-)^2$

$= 7.1 \times 10^{-9}$ at 18°C and
6.4×10^{-9} at 27°C

The figures in brackets represent the activities of the ions. The solubility products value of fluorite differs from one reference to the other, it differs from $10^{-10.40}$ to $10^{-9.94}$ $(3.98^{-11}$ to $1.15^{-10})$ (Handa 1974). The differences may be due to different temperatures of solubility.

In the following example Handa used a solubility product of $10^{-10.57}$ (2.7^{-11}): The solubility product values given above show that the fluor-apatite would control the concentration of fluoride ions in the natural waters, provided the phosphate ions are present. When only fluorite and magnesium fluoride are assumed to be in water, fluorite which has lower solubility product value will control the concentration of fluoride ion in natural water. When fluorite is in water it will dissolve gradually until the saturation is reached. However, when the saturation is reached, the aqueous solution will contain about 2.0×10^{-4} moles/l of CaF_2. In other words; when the solubility balance, $(Ca^{2+})(F^-)^2 = 2.7^{-11}$ (at 25°C), is reached no more minerals will dissolve. When the saturation point has been reached and there is an addition of calcium ions (Ca^{2+}) from some other external sources, they will form a precipitate as CaF_2 with fluoride ions (F^{-1}), which will result in the removal of some fluoride, so that the solubility product is not exceeded. Similarly addition of F^- ions at this stage will remove some Ca^{2+} ions to keep the solubility product 2.7^{-11}. After the saturation stage has been reached the increase in the activity of one ion is being accompanied by a corresponding decrease in the activity of the other ion and vice versa (Handa 1974).

When there is calcite ($CaCO_3$) in water which contains fluorite, the solution formed can be represented by Equations 21 and 22:

$$CaCO_3 + H^+ \Longleftrightarrow Ca^{2+} + HCO_3^- \Longrightarrow \frac{(Ca^{2+})\ (HCO_3^-)}{(H^+)} = K_1 \qquad (21)$$

$$CaF_2 \Longleftrightarrow Ca^{2+} + 2\ F^- \Longrightarrow (Ca^{2+})\ (F^-)^2 = K_2 \qquad (22)$$

where K_1 and K_2 are equilibrium constants and the concentrations in the brackets are the activities of the ions.

When dividing Equation 21 by Equation 22 we get

$$\frac{(HCO_3^-)}{(H^+)\ (F^-)^2} = \frac{K_1}{K_2} \qquad (23)$$

Equation 23 above shows that if the hydrogen ion concentration or the pH of the water does not vary much, i.e. (H^+) is constant, then an increase of fluoride ion concentration should be accompanied by increase in HCO_3^- ion concentration in order to make the relation

$$\frac{(HCO_3^-)}{(F^-)^2} = \text{constant}$$

This relation is independent of calcium ion concentration (Handa 1974). However, when fluoride ions and bicarbonate ions increase, the calcium ions should decrease in order to have constant K_1 and K_2 (Equations 21 and 22). The above inter-relation between Ca^{2+}, F^- and HCO_3^- ions also applies to the Mg^{2+}, F^- and HCO_3^- ions.

The above explanation implies that natural water with high alkalinity values and low hardness will tend to have high fluoride concentration.

The removal of fluoride by using calcium salts is a formation of the carbonate ion (CO_3^{2-}) species from the bicarbonate (HCO_3^-) which are pH dependent. The inverse relation between F^- ion removal and pH is caused by the presence of CO_3^{2-} and the competition it exerts for the available Ca^{2+} cations in solution to precipitate as $CaCO_3$.

The defluoridation efficiency is also inversely proportional to CO_3^{2-} concentration at high pH value (Miller and James 1986).

With increasing fluoride content in water there is an increase in pH, alkalinity and the ratio of alkalinity/hardness, but a decrease in hardness and hardness/fluoride ratio. This is clearly shown in Table 2 (Teotia et al 1981 and Chandra et al 1981).

Table 2. F^- content and relationship with chemical constituents of natural drinking water (Teotia et al 1981).

Range of F (mg/l)	0.0	0.1-1	1-5	5-10	10-25
pH	6.5	7.1	8.3	8.5	8.5
Alkalinity (mg/l) (as $CaCO_3$)	20.0	193.6	402.0	450.0	530.0
Hardness (mg/l) (as $CaCO_3$)	0.0	242.0	192.0	80.0	28.0
$\frac{\text{Alkalinity}}{\text{Hardness}}$	0.0	0.84	2.16	5.60	18.90
$\frac{\text{Hardness}}{\text{Fluoride}}$	0.0	242.0	56.8	9.4	1.1
Ca (mg/l)	0.0	70.2	75.3	16.0	8.0
Mg (mg/l)	0.0	19.8	20.2	20.0	11.0
Cl (mg/l)	0.0	24.5	75.5	90.3	31.0
Na (mEq/l)	0.0	1.2	1.5	15.0	15.0

When fluoride level in water becomes higher, the water becomes more alkaline and softer. Water with low hardness i.e. low calcium and magnesium concentration and high HCO_3^- and CO_3^- concentrations and pH level presents the highest fluorosis hazard.

3.2 Effect of pH in defluoridation

The effect of pH values during the removal of fluoride depends on the methods used. In most cases when the precipitation or adsorption methods are used, the pH value has a strong effect. Precipitation methods involve the addition of chemicals and the formation of fluoride precipitates. The chemicals used are lime, aluminium sulphate, PAC, etc.

Adsorption methods utilize the passage of water with fluoride through a contact bed. Fluoride is removed by ion exchange or by chemical reaction with adsorbent. Sometimes it is very difficult to separate experimentally the effect of adsorption or precipitation. Thus the word removal in this text refers to total mechanism of adsorption or precipitation. Many researchers have found that the anion adsorption sites on different minerals are aqua group ($-M-OH_2^+$) and hydroxo groups ($-M-OH$) (Wu and Nitya 1979, Choi and Chen 1979, and Hao and Huang 1986).

The general principals of the surface chemistry of oxides in contact with an aqueous solution are as follows: The hydroxo groups behave amphoterically. The hydroxly ion association reaction for positively charged surface is as shown in Equation 24 and neutral surface is as shown in Equation 25 or Equation 26 while for negatively charged surface it is as shown in Equation 27:

$$-M\ -OH_2^+ \quad <====> \quad -M\ -OH + H^+ \qquad (24)$$
$$-M\ -OH_2^+ \quad <====> \quad -M\ -OH + H_2O \qquad (25)$$
$$-M\ -OH \quad <====> \quad -M\ -O^- + H^+ \qquad (26)$$
$$-M\ -OH + OH^- \quad <====> \quad -M\ -O^- + H_2O \qquad (27)$$

Equation 24 is favoured at low pH, while Equation 27 is favoured at high pH (Choi and Chen 1979). The surface concentration, surface acidity constants, surface charge and the acidity capacity can be found by alkalimetric titration technique (Hao and Huang 1986).

Despite the high affinity of F^- for the metal ions on the surface of adsorbents, fluoride ions are adsorbed mainly by the positively charged surface as shown in Equations 28 and 29. However, to some extent it can be adsorbed by an ion exchange mechanism even when the surface is neutral as shown in Equation 30 (Choi and Chen 1979).

In positive surface:

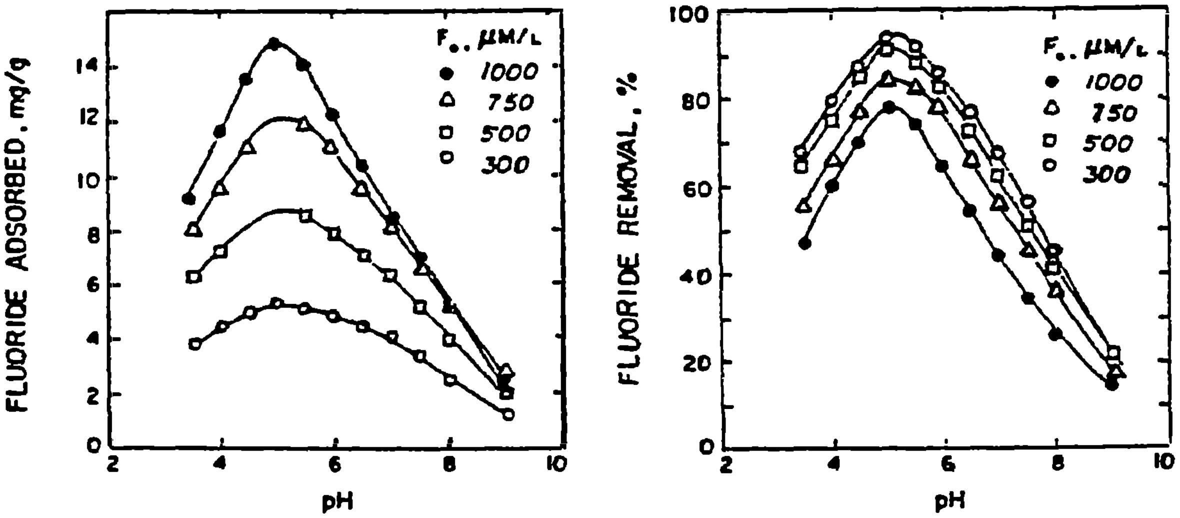
$$-M\ -OH + Hx \quad <====> \quad -M\ -OH_2^+ \ldots x \qquad (28)$$
$$-M\ -OH_2^+ \ldots x + F^- \quad <====> \quad -M\ -F + x^- + H_2O \qquad (29)$$

In neutral surface:

$$-M\ -OH + F^- \quad <====> \quad -M\ -F + OH^- \qquad (30)$$

As the pH decreases, positively charged complexes are formed and at the same time the hydroxyl ion association will be further positively charged. Thus there will be an electrical repulsion between the positively charged complexes and the positively charged surface. This is the reason why the fluoride removal efficiency decreases as the pH value decreases below the optimum value as illustrated in Figure 1. On the other hand, when the pH increases beyond the optimum value, the hydroxo groups ($-M-OH$) will gradually disappear forming more negatively charged surface as shown in Equation 26. In addition, OH^- will compete with fluoride ions for the available sites left on the surface (Choi and Chen 1979).

Hao and Huang (1986) found out that the formation of negative surfaces when using activated alumina is when pH is greater than 7. When the pH is less than 6 the alumina-fluoro complexes are formed. As the pH decreases more stable complexes are formed. Therefore, the fluoride removal should be operated at pH values when alumina-fluoro complexes are unstable. When the surface loading increases, the adsorption density of fluoride increases, but the percentage of fluoride removal decreases, as it can be seen in Figure 1.



a) Adsorption density of fluoride per unit weight of activated alumina

b) Percentage of fluoride removal

Figure 1. Effects of pH and surface loading on removal of fluoride by activated alumina (Hao and Huang 1986).

During defluoridation of drinking water by using clay it was found that the fluoride removal efficiency decreases at both high and low pH values. The decrease of fluoride removal at low pH is due to the formation of complexes between fluoride and the cations e.g. Al in solution. While the decrease of fluoride adsorption at high pH is caused by the increasingly unfavourable electrostatic potential (Jinadasa et al 1988).

In filtration through activated alumina it shows that fluoride removal is more favourable in acidic conditions, the optimum pH being 5.5 (Barbier and Mazounie 1984).

3.3 Effect of temperature in defluoridation

In any reaction, work must be done to separate positive and negative ions from each other. The amount of energy required per mole is called the "lattice energy". As water molecules are separated from each other and attracted to the added ions the energy which is liberated is called "hydration energy". When hydration energy is greater than the lattice energy, the overall dissolving process liberates energy to the surroundings (exothermic reaction). When the opposite occurs the reaction is endothermic. If the reaction is endothermic the solubility increases with rising temperature. In general the increase of temperature increases the rate of reaction except for a few extraordinary cases. For reactions which are endothermic, a rise in temperature will also increase the equilibrium constant, while for the exothermic reactions the increase in temperature decreases the equilibrium constant. It is a general principle of chemical kinetics that the rate of a reaction is increased by an increase in temperature (Sienko and Robert 1974).

It is obvious that most reactions in defluoridation are endothermic since the lattice energy is higher than the hydration energy. Thus increasing the temperature increases the rate of fluoride removal.

When magnesia (magnesium oxide, MgO) was used in India in defluoridation, 2 g of MgO/l removed 20 mg/l fluoride in 2 min at 100°C, while the same amount of magnesia per litre removed 20 mg/l in 20 - 30 min at 40°C (Venkateswarlu and Rao 1953).

3.4 Effect of other parameters in defluoridation

Fluoride removal capacity is affected by the particle size of the filtering material used. Fluoride removal capacity increases as the surface area per unit volume of the medium increases. The surface area per unit volume increases as the size of the particles in medium is reduced. Hence smaller particles are more efficient for fluoride removal than large (Bishop and Sansoucy 1978).

Other chemical species which have effects on fluoride removal are sulphate, silica, salinity, etc. The effect of salinity in defluoridation is due to the competition for adsorption sites and the increase of salinity in the solution decreases the activity of fluoride ions (Jinadasa et al 1988).

Silica affects the removal of fluoride when activated carbon is used. The effect depends on the inorganic contents and other impurities in the filter media which can reduce more sites for fluoride ions. Sulphate ions (SO_4^{2-}) also decrease the efficiency of activated carbon during defluoridation. Due to higher fluoride affinity for metals than SO_4^{2-} ions, there is no effect of sulphate ions in methods of defluoridation where metal compounds are used as adsorbent, while in non-metal compounds like activated carbons the available sites are subjected to the competition between the F^- ions and SO_4^{2-} ions (Choi and Chen 1979 and Barbier and Mazounie 1984).

Other parameters which affect the efficiency of fluoride removal are turbidity and the rate of flow during defluoridation. The high turbidity lowers the efficiency of fluoride removal (Barbier and Mazounie 1984).

4 REVIEW OF DEFLUORIDATION BY USING POLYALUMINIUM CHLORIDE AND MAGNESIA

Many fluoride removal methods have been tested and investigated in laboratory scale in several countries. Different defluoridation methods have been discussed in details in the following references: Dhalla (1973), Gitonga (1985), Mcharo (1986), Gumbo (1987), Mjengera (1988), Solsona (1989), etc. Research studies on defluoridation techniques have, however, shown that no single technique is effective for all waters contaminated with fluoride. Hence an appropriate defluoridation method needs to be selected according to local situations.

Mjengera (1988) has suggested that a possible defluoridation method in Tanzania could be combined use of magnesia (MgO, or calcined magnesite) and PAC.

4.1 Magnesia as filter media in defluoridation

Magnesite (= magnesium carbonate, $MgCO_3$) is the least soluble compound of magnesium. It occurs naturally in large deposits in various parts of the world. When magnesite is calcinated at high temperature above 600°C it yields magnesia (magnesium oxide) with a chemical formula MgO, as shown in Equation 31. Sometimes MgO is called also calcinated magnesite.

$$MgCO_3 \xrightarrow{\text{heating}} MgO + CO_2 \qquad (31)$$

In northern Tanzania there are many rich natural deposits of magnesite at Loborosite Longido and Chambogo Same. The magnesite from Loborosite Longido constitutes the following compounds shown in Table 3. However, at present there is no mining at Loborosite.

Table 3. Analysis of Longido magnesite (Removal of Excess Fluorides 1955).

	% by weight
Matter insoluble in hydrochloric acid	1.3
Iron and alumina (as Fe_2O_3 or Al_2O_3)	1.2
Calcium as ($CaCO_3$)	3.8
Magnesium as ($MgCO_3$)	93.7

The required specification of impurities of the calcinated magnesite (MgO or magnesia) is shown in Table 4.

Table 4. Specification of impurities in magnesia (Industrial Minerals 1988).

SiO_2	not more than	4.00 %
Al_2O_3	not more than	0.25 %
CaO	not more than	1.50 %
SO_2	not more than	0.02 %
Fe_2O_3	not more than	0.10 %

The chemical composition of commercial magnesia in India is shown in Table 4.

Table 5. Chemical composition of commercial magnesia in India (Viswanadham et al 1974).

Loss on ignition	2.00 %
Insoluble residue	6.00 %
Ferric oxide	0.25 %
Alumina	0.40 %
Calcium oxide	2.10 %
Magnesia	89.25 %

Crushed magnesia removes excess fluoride from water but it raises the pH of water to unacceptable level for domestic use (Mjengera 1988, Viswanadham et al 1974 and Removal of Excess Fluorides 1955). The rise of pH value during defluoridation can be attributed by the formation of hydroxylion (OH^-) in the following reactions

$$MgO + H_2O \text{ ----> } Mg(OH)_2 \quad (32)$$

$$Mg(OH)_2 + 2F^- \text{ ----> } MgF_2 + 2OH^- \quad (33)$$

Smaller size particles have better removal efficiency than bigger size particles (Mjengera 1988 and Removal of Excess Fluorides 1955).

4.2 Polyaluminium chloride as coagulant in defluoridation

PAC is a polynuclear complex of polymerized aluminium ion and chloride anion. It is manufactured in Finland by Kemira Oy. The chemical is commercially known as Kempac. It is an inorganic polymer with a general formula of $Al_n(OH)_mCl_{3n-m}$. (n has a value of 3 to 10 and m has a value of 5 to 20.) The value of n and m is pH-dependent. When the pH is high the value of n and m is low and vice versa. The chemical is in liquid form and has physical and chemical properties as summarized in Table 6 (Kemira Oy 1987).

Table 6. Physical and chemical properties of polyaluminium chloride (PAC) (Kemira Oy 1987).

Aluminium oxide	(Al_2O_3)	10 %
Chloride	(Cl^-)	9 %
Sulphate	(SO_4^-)	2 %
Density		1 200 kg/m^3
Viscosity		15 mPas at -10°C 8 mPas at 5°C 5 mPas at 25°C
Freezing point		-15°C
pH		2.7 ± 0.3
Colour		colourless or yellowish

The chemical contains sulphate because sulphuric acid is used in manufacturing PAC. The chemical is a new coagulant mainly used in drinking water production and in water and wastewater treatment in industry. In water treatment the chemical has been referred to have the following advantages over other coagulant chemicals (Kemira Oy 1987):

- It forms flocs very fast.
- It forms large flocs which endure handling.
- It precipitates very fast.
- It removes turbidity efficiently.
- It acts in wider pH area than other coagulants (i.e. aluminium sulphate, ferric sulphate).
- It needs less alkal for pH adjustment since it can act in a wide pH area between 2 and 10.

PAC has been found to be very effective in fluoride removal. The jar test experiments conducted in the laboratory show that it can remove up to 96 % of fluoride from water. In spite of good fluoride removal it lowered the pH level of the water to unacceptable value for domestic use as illustrated in Table 7 (Mjengera 1988).

Table 7. Results obtained after a jar test experiment using polyaluminium chloride (PAC). Raw water: fluoride concentration 19.0 mg/l, pH 8.5 (Mjengera 1988).

PAC added	pH	Fluoride content		Removed
		Residual	Removed	
ml/500 ml		mg/l	mg/l	%
1.0	6.0	4.7	14.3	75.3
2.0	5.0	5.0	14.0	73.7
3.0	4.6	2.6	16.4	86.3
4.0	4.2	1.7	17.4	91.3
5.0	4.2	1.2	17.8	93.7
6.0	4.1	0.7	18.3	96.4

4.3 Combined use of polyaluminium chloride and magnesia in defluoridation

When combined magnesia and PAC were used in defluoridation, fluoride content was removed from 19 mg/l to 0.4 mg/l which is 98 % removal with acceptable pH value for domestic use as shown in Table 8 (Mjengera 1988).

Table 8. Results of fluoride reduction using magnesite and polyaluminium chloride (PAC) (Mjengera 1988).

Type of water collected	pH	Fluoride content		Removed
		Residual mg/l	Removed mg/l	%
Raw water	8.6	19.0		
After filtration	10.0	6.4	12.6	66.3
Filtrate plus 24 ml PAC	5.9	0.5	18.5	97.4
After filtration	9.9	8.1	10.9	57.4
Filtrate plus 16 ml PAC	7.2	0.4	18.6	97.9

The jar test experiments show that the results are very promising for further investigations.

However, the use of magnesia reduces calcium content in water (Viswanadham et al 1974) and, on the other hand, when calcium content is high in the body the absorption and toxic effects of fluoride in human being are reduced (Chandra et al 1981). Hence more research is needed to justify this type of defluoridation techniques.

5 METHODOLOGY OF EXPERIMENTS

Experiments of fluoride removal using both magnesia and PAC were performed in the laboratory using jar test equipment and small scale filtration. The results from the laboratory tests were transferred to the field for further trials. Field tests were performed using manufactured model plants where pretreatment, chemical feeding, hydraulic rapid mixing, hydraulic flocculation, sedimentation and filtration were the processes involved.

The chemical quality of the materials used in the treatment were checked. Observations were made on the following: effects of pH in both magnesia and PAC in fluoride reduction, effects of pH in flocs formation, the quantity of both raw water required and the amount of magnesia needed in the process. Furthermore observations were made on the time required before the filter media is exhausted and has to be replaced in the fluoride adsorption process. The quality of raw water was analysed before experiments started. During the experiments the treated water was analysed for residual fluoride and pH, and a few treated samples were analysed. The limits of fluoride content in treated water were mainly aimed at the acceptable World Health Organization (WHO) standards of less than 1.5 mg/l. However, the temporary Tanzanian standard in areas with highly fluoride contaminated water, 8 mg/l, was also considered.

5.1 Physical and chemical properties of magnesite

Samples of magnesite were sent to the University of Dar-es-Salaam in Tanzania and Tampere University of Technology in Finland for physical and chemical analyses. Tables 9 and 10 illustrate the results of the natural magnesite ($MgCO_3$ or magnesium carbonate) and the calcinated magnesite (magnesia or MgO) after heating them up to 1 000°C at the University of Dar-es-Salaam.

Table 9. Chemical analysis of natural magnesite ($MgCO_3$) from Chambogo Same.

	% by weight
SiO_2	11.64
Al_2O_3	0.06
Fe_2O_3	0.14
MnO	0.02
MgO	42.70
CaO	0.25
Na_2O	0.07
K_2O	0.02
loss of ignition	46.60

Theoretically pure commercial magnesite has magnesium oxide about 47 %. The results show less percentage of magnesia than the anticipated quantity of about 45 %. The reason for this might be the long exposure to the rain and sunlight of the raw magnesite. However, the results show that magnesite from Chambogo mines can be used commercially in producing magnesia. Table 10 shows the results of at 1 000^{o}C calcinated magnesite.

Table 10. Chemical analysis of at 1 000^{o}C calcinated magnesite.

	% by weight
SiO_2	21.90
Al_2O_3	0.11
Fe_2O_3	0.26
MnO	0.04
MgO	80.35
CaO	0.47
Na_2O	0.13
K_2O	0.04

There is a minor error in the percentage calculation in Tables 9 and 10, i.e. the summations are 101.5 % and 103.3 % respectively instead of 100 %. The percentage of SiO_2 is 21.9 % and that of Fe_2O_3 is 0.26 % more than the specification of impurities in magnesia as illustrated in Table 4. In Table 4 SiO_2 is not more than 4.0 % and Fe_2O_3 not more than 0.10 %. Other possible reason for the differences is overheating since very high temperature, above 900^{o}C, can cause overburning of magnesite (Removal of Excess Fluorides 1955). More research on the calcination temperature ranges is required.

The results from Tampere University of Technology show that raw magnesite is 100 % $MgCO_3$ and magnesia used in the experiment is 98.8 % MgO and 0.02 % other impurities.

5.2 Preparation of filter media

Magnesite was obtained 230 km east of Arusha town at Chambogo mines in Same district in Kilimanjaro region. At Chambogo, the magnesite mines are producing 100 t of magnesite per month according to the present demand. The mines have a large deposit of magnesite which can last for more than 30 years, depending on the demand. At present only raw magnesite is being produced. The calcination of magnesite has stopped since 1973 due to lack of fire wood around the area. Thus the collected magnesia used in the experiments was an old stock of 1973. The magnesite was heated at high temperature, above 600^{o}C, by using fire wood. One ton of magnesite requires between 0.5 m^3 to 1 m^3 of fire wood depending on the type of the wood. From 1 t of magnesite about 0.45 t of magnesia was obtained. The calcination process normally took 3 days heating and cooking (Anderson 1989).

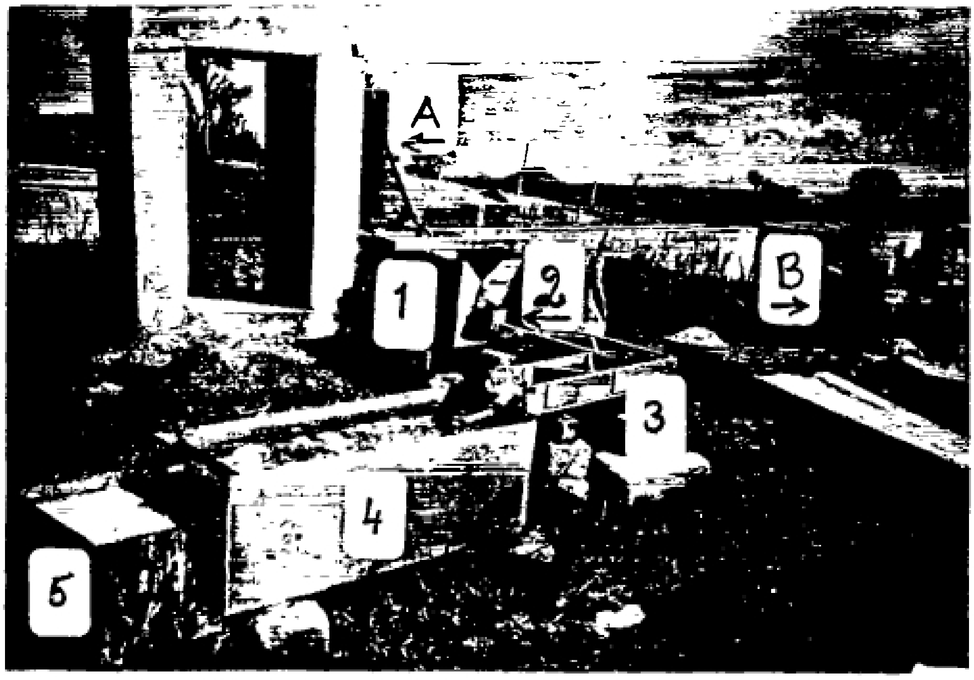
For good fluoride removal, the magnesite should be calcinated at a temperature above 600°C and below 900°C in order to avoid the use of undercomposed magnesite or overheated magnesia (Jones 1954 and Removal of Excess Fluorides 1955).

During defluoridation magnesia was used as filter media and in the powder form it was used as a coagulant aid when using PAC. The material was crushed and sieved manually at the working site at Ngurdoto, 30 km away from Arusha town along Moshi-Arusha road. The particle sizes used in the experiment were of diameters less than 0.2 mm (magnesia powder), 0.2 - 0.63 mm, 0.63 - 1.0 mm, 1.0 - 2.0 mm and greater than 2.0 mm (coarse particles). The media was washed thoroughly by using tap water to remove dust and organic materials before use for defluoridation.

5.3 Preparation of test model plants

Simple working models were prefabricated at as local garage in Arusha town. Two cylindrical filter units each fitted with water meter were prefabricated by using cast ion pipes 300 mm diameter and plate sheet. The cylindrical models were of 0.3 m diameter x 0.7 m height, and 0.3 m diameter x 0.54 height. One of the two cast iron pipe models for conventional downflow unit, while the second model was for upflow filtration unit.

The pretreatment tank, chemical dosing and hydraulic rapid mixing units with a V-notch, sedimentation and filtration tanks were prefabricated by using plate sheets. Figure 2 shows all prefabricated models used in the experiment. The pretreatment filter tank had the following dimensions: length 0.65 m, width 0.45 m and depth 0.40 m. The chemical dosing and hydraulic rapid mixing chamber was 0.10 m long, 0.10 m wide and 0.20 m deep. The hydraulic baffled 45° channel flocculation was made of timber. The flocculator was 2.00 m long, 0.23 m wide and 0.12 m deep. The sedimentation tank was 1.13 m long, 0.45 m wide and 0.40 m deep, while the filtration tank was 0.60 m long, 0.30 m wide and 0.30 m deep.



1) Pretreatment filter tank
2) Hydraulic rapid mixing chamber
3) Hydraulic baffle channel flocculation
4) Sedimentation tank
5) Filtration tank
A) Downflow filtration unit
B) Upflow filtration unit

Figure 2. Defluoridation treatment plant models when using magnesite and polyaluminium chloride (PAC).

The upflow filtration unit was installed at Sekei Jard temporarily for three weeks and transferred to Ngurdoto afterwards. The remaining models were installed at Ngurdoto. Sekei Jard has the main storage reservoirs for Arusha town. Ngurdoto (Figure 3) is among the highly fluoride contaminated areas in northern Tanzania (Figure 4).

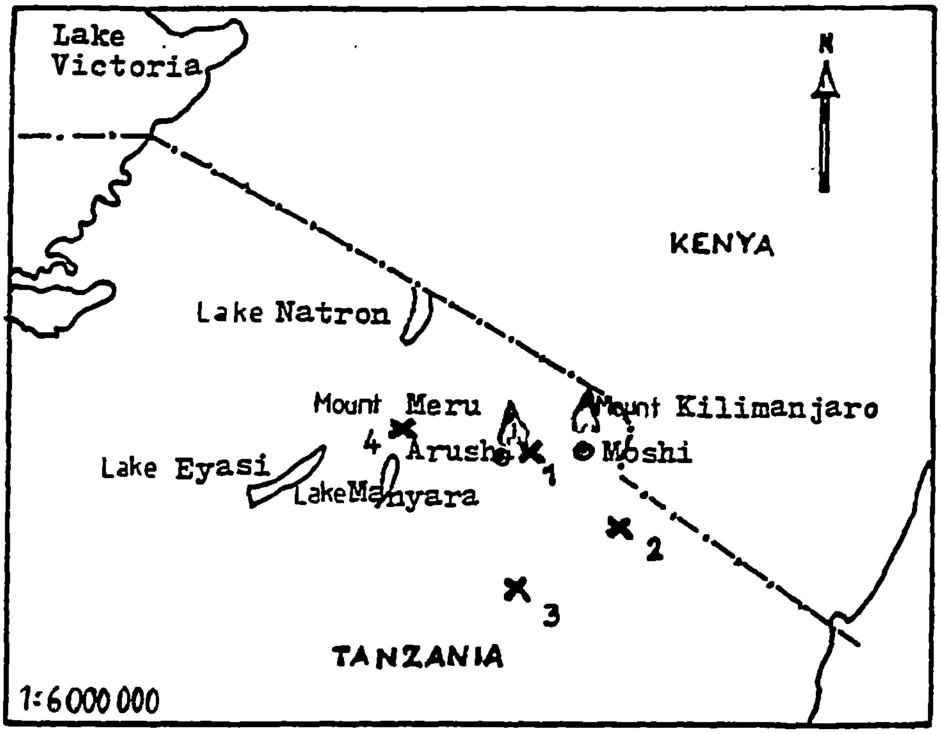


Figure 3. A map of northern Tanzania showing Ngurdoto defluoridation pilot plant (1), Chambogo Same magnesite mining area (2), Laborosite magnesite area (3) and Longido magnesite area (4).

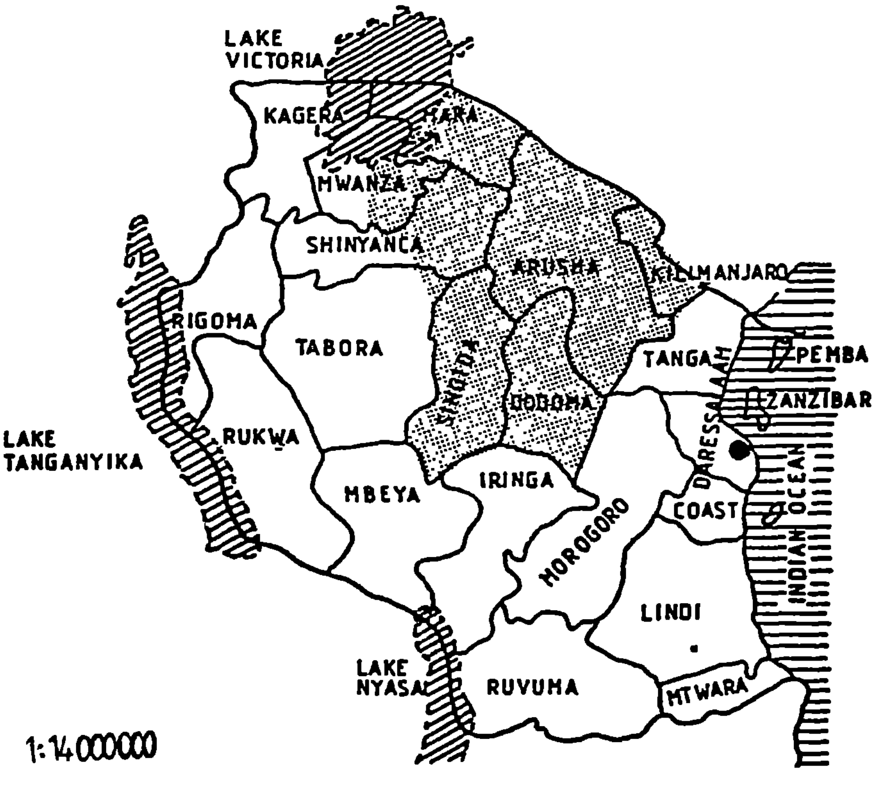


Figure 4. A map of Tanzania showing the fluoride belt.

5.4 Filtration tests using magnesia

In the laboratory magnesia particles with diameters less than 0.20 mm, 0.20 - 0.63 mm and 0.63 - 1.00 mm were used to determine the effect of pH in fluoride reduction. Different pH values of the raw water were obtained by sodium hydroxide for raising pH and sulphuric acid for lowering pH before filtering it through the filter media. In the laboratory the plastic device was used as a filtering unit (Figure 5).

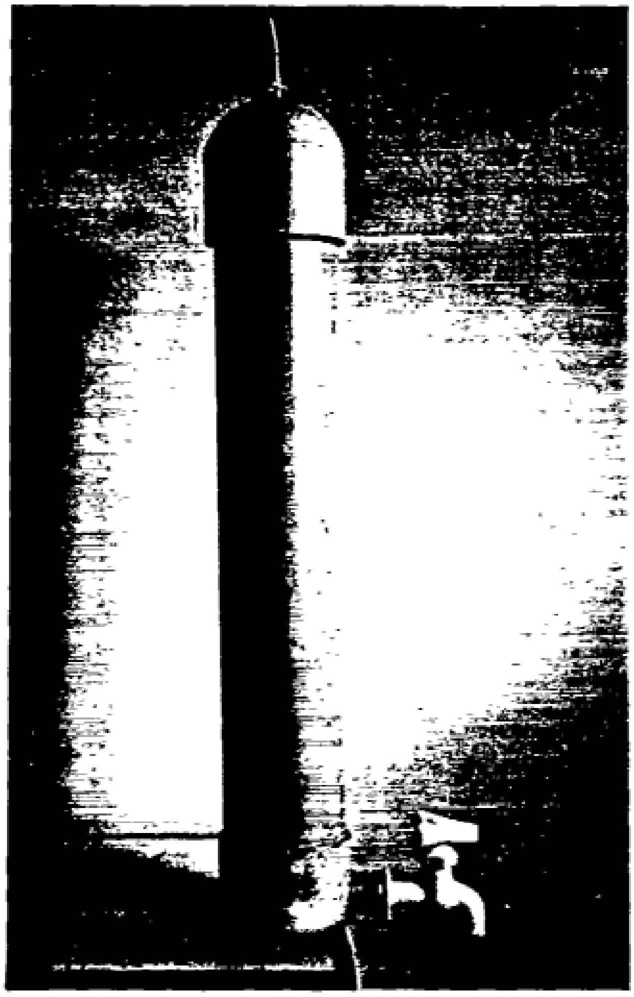


Figure 5. A picture of the plastic device from Thailand used for fluoride removal by filtering water through magnesia.

At the site several trial runs were performed by putting the desired quantity and particle sizes of magnesia into the respective filtering units and the desired quantity of water was then allowed to flow through the filter media. The particle sizes used in the field were less than 0.20 mm, 0.20 - 0.63 mm, 0.63 - 1.00 mm, 1.00 - 2.00 mm and greater than 2.00 mm. The filtrate was collected for fluoride residual and pH analysis.

The quantity of magnesite required to remove fluoride to the acceptable WHO standard of 1.5 mg/l was obtained by using different quantities and particle sizes of magnesia. The quantity of water required to be treated in a certain quantity of magnesia was also obtained by allowing the water to flow through the filter media until the media was exhausted with fluoride. Trials to regenerate the exhausted magnesia were made by washing the media manually. The washed magnesia was then sundried before being reused.

5.5 Coagulation tests using polyaluminium chloride

In the laboratory the most beneficial dosage of PAC, the optimum pH range for flocs formation, adjustment of pH during fluoride removal were performed by using jar test equipment (Figure 6).

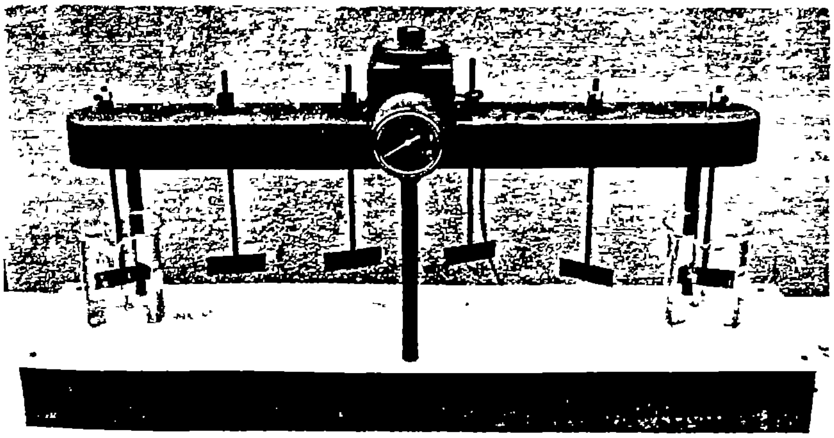


Figure 6. Jar test apparatus used in determining coagulant dosages. To avoid vortexing and to achieve effective mixing and flocculation, beakers equipped with internal baffles, as shown in the photograph, or square (battery) jars should be used.

The jar test was carried out by settling the six 1 l beakers each containing equal quantity of raw water under a stirring paddle (Figure 6). Different quantities of PAC were added to each beaker by means of measuring pipette. The stirring paddles were immersed in the beakers before starting the stirrer. The contents were slowly stirred for about 3 min at the speed of 30 revolutions/min. The time taken to form flocs was recorded as well as the time taken for flocs settlement at the bottom of the beakers after stopping the stirrer. The supernatant was filtered through filter paper and sample taken for fluoride and pH analysis.

pH adjustment of the raw water was done by adding sodium hydroxide or concentrated hydrochloric acid before performing the jar test. Magnesia powder was used for both adjusting the pH and improving the flocs formation and settlement. Clay bentonite which was locally available was tested as a coagulant aid.

At the site dosage of PAC was done in the chemical dosing and hydraulic rapid mixing chamber, where coagulation took place. Flocculation took place in the hydraulic baffle channels. Sedimentation and filtration took place in sedimentation and filtration tanks respectively. Trials to adjust pH after sedimentation was made in the filtration tank by using magnesia.

5.6 Testing of combined use of magnesia and polyaluminium chloride for defluoridation

Different particle sizes and quantities of magnesia were packed in the pretreatment chamber for reducing fluoride and raising pH of the raw water. PAC was added after the V-notch weir in the hydraulic rapid mixing chamber (Figure 2). The flow of water was recorded by reading the water meter. It was not possible to have accurate flow readings in the V-notch because the flow was very low. Dosage rate of PAC was adjusted for good flocs formation in the flocculator and good settlement of flocs in the sedimentation tank. The rate of PAC dosing was also recorded.

The use of magnesia powder or the supernatant of the magnesia powder solution in the rapid mixing chamber instead of using magnesia as a pretreatment filter media were attempted for improving flocs formation, pH adjustment and fluoride reduction. Bentonite clay powder and its supernatant, when in solution, were used as coagulant aid. Dosage rate of both magnesia and bentonite were recorded. Apart from analysing the residual fluoride and pH in treated water a full physical and chemical analysis of some of the samples was done. The advantages and disadvantages of using magnesia and bentonite powders are discussed in detail in Chapter 6.

The magnesia in the pretreatment tank was also used for determining the quantity of water required to be filtered through the magnesia media before the media is exhausted. The effect of using magnesia in the filtration tank after the sedimentation units was attempted as well.

The settled sludge in the sedimentation tank was discarded in the bush. The exhausted magnesia was stored for other uses i.e. in block making, blinding, plastering, etc.

5.7 Water sample analysis

a) <u>Fluoride ion analysis</u>

Fluoride concentration analysis was done by using an electrode method. Two electrodes were used, one of the electrodes was a fluoride sensing electrode while the second one was a single junction reference electrode. The sensing fluoride electrode was model Orion 9409 and reference electrode was model Orion 90.01. The electrodes were connected to the Orion research ionanalyzer specific pH/mV ion meter model 701A.

Reference standards were made from appropriate dilution of a stock solution of sodium fluoride (NaF), 100 mg/l fluoride and total ionic strength adjusting buffer (TISAB). Reference standards of fluoride concentration of 100 mg/l, 10 mg/l and 1 mg/l were prepared and their respective millivolts (mV) measured in the specific pH/mV ion meter. The standard curve was prepared from the mV results of the reference standards in a semi-logarithmic graph paper.

Buffer solution was used for neutralising the interfering ions in the water samples. The standard and the TISAB solutions were prepared by an analyst in the laboratory and stored in plastic bottles to preserve their stability.

Ten millimeters of water sample was transferred into 100 ml plastic beaker by means of 10 ml measuring pipette. After rinsing the pipette by using distilled water, 10 ml of TISAB was measured and transferred into the 100 ml beaker containing water sample. The electrodes were immersed into the sample and stirred slowly for 30 s and then the specific ion meter was switched on for reading the millivolts when the meter reading was steady. The concentration of fluoride in mg/l was obtained from the standard curve. After each water sample reading the electrodes were rinsed with distilled water and wiped dry with a tissue paper.

b) pH value analysis

The pH readings were recorded by using pH meter type 91 with electrode type E50. The meter was calibrated using pH buffer solutions with values of 4.0 and 7.0 before being used. The electrode was stored in 3 moles potassium chloride (3 m KCl), when not in use. The water sample to be tested was put into 100 ml plastic beaker, the electrode was immersed and stirred slowly before noting the stable reading from the meter. After reading the pH value of the sample the electrode was rinsed and wiped dry with a tissue paper for the next sample to be analysed.

c) Physical and chemical water sample analysis

The full physical and chemical analyses were carried out on selected raw water samples and on filtrate of both fresh and exhausted magnesia. Furthermore a physical and chemical analysis was carried out on the magnesia-PAC treated water. The analysis was done using DR 2000 spectrophotometer and digital titrator both from Hach company. Aluminium could not be determined due to absence of the necessary reagents.

6 RESULTS AND DISCUSSION

6.1 Defluoridation by using magnesia

6.1.1 Effect of pH

Table 11 shows that fluoride reduction efficiency by using magnesia powder was better in acidic range. Initial pH values of the samples were lowered by using sulphuric acid and raised up by using sodium hydroxide. At normal pH value of raw water 8.6, magnesia reduced the fluoride content of water from 19 mg/l to 6 mg/l (68 %). When the pH of raw water was lowered to 0.2, fluoride was reduced from 19 mg/l to 1.5 mg/l (92 %). When initial pH of the sample was raised to 10.9, fluoride was removed from 19 mg/l to 7.4 mg/l (61 %). The results are illustrated graphically in Figure 7.

Table 11. Effect of pH on fluoride removal by using magnesia.
Raw water: fluoride content 19 mg/l
pH 8.6
Material used: magnesia powder
Contact time: 30 s

Sample no.	MgO added ml/500 ml	Initial pH of samples	Final pH of treated water	Fluoride content Residual mg/l	Fluoride content Removed mg/l	Removed %
1	150	0.2	10.5	1.5	17.5	92
2	150	1.3	10.8	3.3	15.7	83
3	150	3.2	11.0	5.0	14.0	74
4	150	4.9	11.1	5.2	13.8	73
5	150	6.4	11.2	5.5	13.5	71
6	150	7.3	11.3	5.9	13.1	70
7	150	8.6	11.4	6.0	13.0	68
8	150	9.3	11.4	6.8	12.2	64
9	150	10.9	11.5	7.4	11.6	61

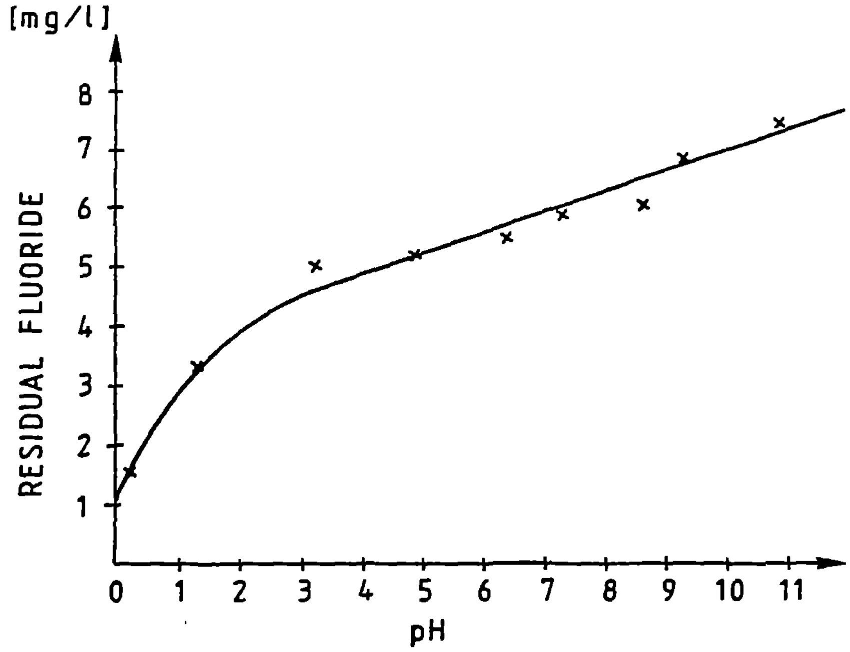


Figure 7. Effect of pH on defluoridation by using magnesia. Initial fluoride content of water samples was 19 mg/l.

Fluoride removal by filtration through magnesia was more favourable when pH of the raw water was lowered to very acidic condition of 0.2. However, with this initial pH value, the filter media raised the pH of treated water to 10.5. Thus this local available material can be used on pH adjustment in either drinking or wastewater treatment plants.

6.1.2 Effect of temperature

The effect of temperature in fluoride reduction was experimented by heating different quantity of magnesia powder (diameter less than 0.2 mm) with 500 ml of raw water up to 90^{o}C. The results revealed that fluoride was reduced from 22 mg/l to 1.1 mg/l which was 95 % removal instead of 32 % reduction at room temperature in Table 12. Figure 8 represents the results graphically.

Table 12. Effect of temperature in fluoride reduction by using magnesia.
Raw water: fluoride content 22 mg/l
pH 8.5
temperatures 20°C and 90°C

Sample no.	Quantity of MgO used g/500 ml	Final pH	Fluoride content Residual mg/l	Removed mg/l	Removed %	Remarks
10	50	9.7	15.0	7.0	32	at 20°C
11	50	9.2	1.1	20.9	95	after boiling to 90°C
12	40	9.2	2.2	19.8	90	after boiling to 90°C
13	30	9.2	3.0	19.0	86	after boiling to 90°C
14	25	9.2	5.5	16.5	75	after boiling to 90°C
15	10	9.2	10.5	11.5	52	after boiling to 90°C
16	5	9.2	12.0	10.0	45	after boiling to 90°C

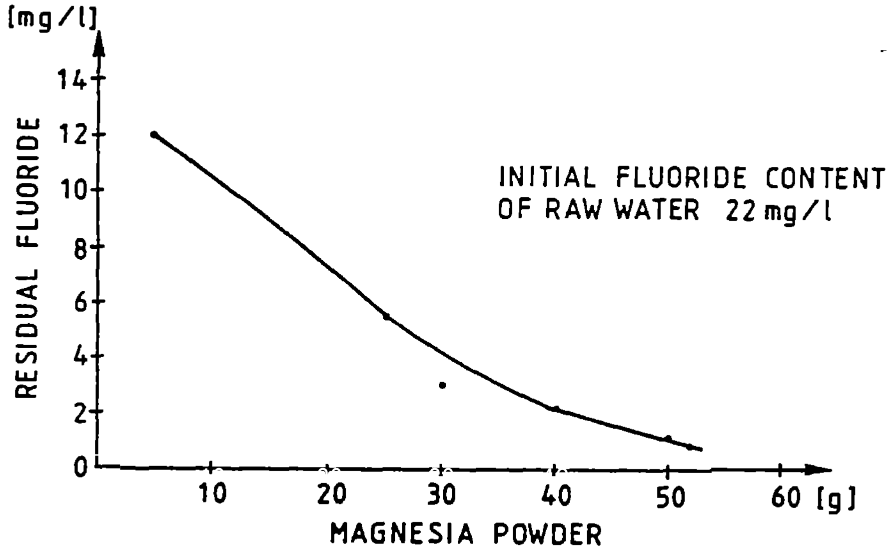


Figure 8. Removal of fluoride when heating raw water with magnesia to 90°C.

The results show that by increasing the temperature the rate of fluoride removal also increases. Since the reaction is endothermic, increase of temperature increases the rate of reaction or the adsorption rate of fluoride ions and magnesium ions or magnesium complexes ions.

The method of heating raw water with magnesia can be used in the household in case there is no other simple or cheap feasible household fluoride reduction method. In most developing countries it is advisable to disinfect water in the rural area by boiling it and filtering for domestic use. Hence during boiling for health aspect water can be boiled with magnesia for fluoride reduction. By boiling raw water with magnesia the pH raises to 9.2 which is in the upper limit in WHO or Tanzanian temporary standards

(Appendix III). The disadvantage of this method is that it requires at least 1 kg of magnesia powder for treating 20 l of raw water to diminish the fluoride content of 22 mg/l to 1.5 mg/l which is within the WHO standards. However, only 0.5 kg is required to treat 20 l with 22 mg/l of fluoride content to 8 mg/l which is within the Tanzanian temporary standards. More researches are required to determine the quantity of water which can be treated by 1 kg of magnesia before it expires for fluoride removal before this method can be adopted.

6.1.3 Effect of contact time

The results of optimum detention time analysis carried out in the research are presented in Table 13. 500 ml of raw water with fluoride content of 18 mg/l was treated with different quantity of magnesia. 10 ml were filtered for analysis after 30 min, 2 h, 4 h and 22 h. Figure 9 shows the results graphically.

The most beneficial contact time when using magnesia as filter media in fluoride removal is 4 - 6 h. The efficiency of fluoride reduction increases as the quantity of magnesia increases.

Table 13. Effect of contact time on fluoride removal when using magnesia.
Raw water: fluoride content 18 mg/l
pH 8.5
Filter media: grain sizes 0.63 - 1.00 mm

Sample no.	Contact time	Quantity of MgO in 500 ml raw water		pH	Fluoride content		Removed
		Volume	Weight		Residual	Removed	
	h	ml	g		mg/l	mg/l	%
17	0.5	50	57	10.1	16.0	2.0	11
18	0.5	100	113	10.2	14.0	4.0	22
19	0.5	150	170	10.2	12.0	6.0	32
20	0.5	200	226	10.2	11.0	7.0	39
21	0.5	250	283	10.3	9.5	8.5	47
22	2.0	50	57	10.1	14.0	4.0	22
23	2.0	100	113	10.2	9.0	9.0	50
24	2.0	150	170	10.3	8.3	9.7	54
25	2.0	200	226	10.4	7.5	10.5	58
26	2.0	250	283	10.5	6.3	11.7	65
27	4.0	50	57	10.1	13.0	5.0	28
28	4.0	100	113	10.2	8.0	10.0	56
29	4.0	150	170	10.3	7.0	11.0	61
30	4.0	200	226	10.4	5.0	13.0	72
40	4.0	250	283	10.5	3.8	14.2	79
41	22.0	50	57	10.2	11.5	6.5	36
42	22.0	100	113	10.2	6.5	11.5	64
43	22.0	150	170	10.4	4.8	13.2	73
44	22.0	200	226	10.5	3.5	14.5	81
45	22.0	250	283	10.5	2.8	15.2	84

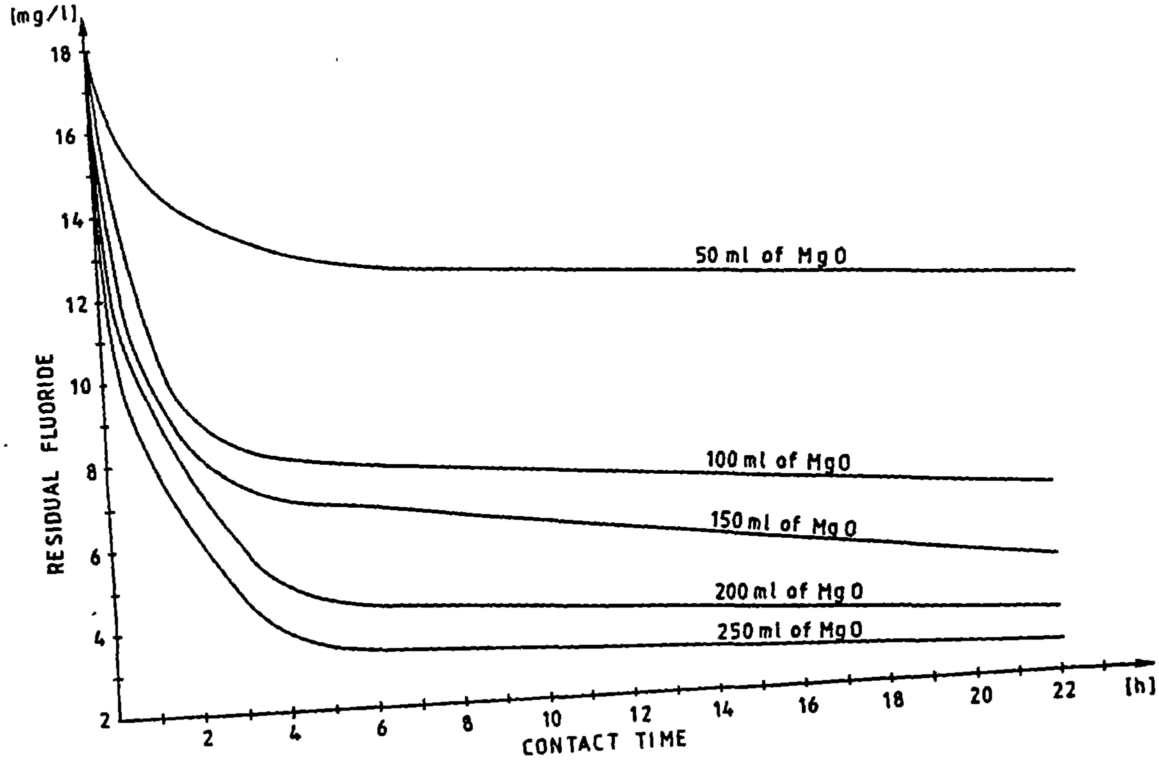


Figure 9. Effect of contact time in fluoride removal by magnesia. The raw water amount was 500 ml and the initial fluoride content was 18 mg/l.

6.1.4 Quantity of water required before filter media exhausts

Fluoride removal by filtration through magnesia was tested in laboratory scale. Table 14 shows the results. Fluoride was removed from 23.0 mg/l to 3.0 mg/l (87 %). The contact time between the raw water and the filter media was 30 min. Flow in the media was 0.02 l/s. The experiment was stopped after sample no. 55 due to the break down of the plastic filter device. There were no physical changes, i.e. colour, in the filter media after using it for defluoridation.

Table 14. Removal of fluoride by filtration through magnesia.

Raw water: fluoride content 23 mg/l
pH 8.6
Filter media: grain sizes 0.63 - 1.00 mm
volume 0.002 m^3
Flow rate: 0.02 l/s (72 l/h)

Sample no.	Time min	Water filtered l	Cumulative water filtered l	pH	Fluoride content Residual mg/l	Fluoride content Removed mg/l	Removed %
46	30	0.5	0.5	10.2	3.0	20.0	87
47	60	0.5	1.0	10.3	5.5	17.5	76
48	90	0.5	1.5	10.3	5.5	17.5	76
49	120	0.5	2.0	10.3	6.8	16.2	70
50	150	0.5	2.5	10.3	7.0	16.0	70
51	180	0.5	3.0	10.3	7.5	15.5	67
52	210	0.5	3.5	10.3	7.5	15.5	67
53	240	0.5	4.0	10.3	7.5	15.5	67
54	270	0.5	4.5	10.3	7.5	15.5	67
55	300	0.5	5.0	10.3	8.0	15.0	65

Attempt to reduce fluoride in Arusha municipal water supply using magnesia was done at Sekei. The raw water with initial fluoride content of 3.2 mg/l was filtered through magnesia. The filter media was 0.007 m^3 coarse particles of diameter 0.63 - 1.00 mm. The upflow filtration flow was 38.4 l/h. Table 15 shows the results. The filter media exhausted when about 2.9 m^3 of water was filtered through.

Table 15. Fluoride removal by using magnesia in Arusha water supply.

Raw water: fluoride content 3.2 mg/l
pH 7.4
Filter media: particle sizes 0.63 - 1.00 mm
volume 0.007 m^3
particle sizes greater than 2.00 mm
volume 0.008 m^3
Filtration rate: 38.4 l/h

Sample no.	Time of sampling	Cumulative water filtered through	pH	Fluoride content		Removed
				Residual	Removed	
	h	l		mg/l	mg/l	%
56	0.5	22	10.1	1.8	1.4	44
57	3	115	10.3	2.0	1.2	38
58	12	460	10.4	2.1	1.1	34
59	15	522	10.4	2.3	0.9	28
60	24	922	10.5	2.6	0.6	19
61	29	1 122	10.5	2.8	0.4	13
62	36	1 522	10.4	2.5	0.7	22 *)
63	43	2 523	9.9	2.6	0.6	19
64	48	2 900	9.4	2.8	0.4	13
65	60	4 292	9.4	2.8	0.4	13
66	72	6 362	9.4	3.0	0.2	6

*) After collecting the water sample no. 61 the filter media was mixed manually for about 1 min.

The exhausted filter media was replaced with fresh magnesia of the same quantity and grain size. The filtration rate was the same. Table 16 shows that the filter was exhausted when 2.7 m^3 was filtered through. The filter unit was thereafter transferred with its exhausted media to Ngurdoto. The exhausted magnesia from Sekei was able to reduce fluoride from 23 mg/l to 15 mg/l (35 %).

Table 16. Quantity of water which can be defluoridated by using magnesia.

Filter media: particle sizes 0.63 - 1.00 mm
volume 0.007 m^3
particle sizes greater than 2.00 mm
volume 0.008 m^3

Filtration rate: 38.4 l/h

Sample no.	Cumulative water filtered through l	Initial pH	Final pH	Fluoride content			Removed	
				Raw water mg/l	Residual mg/l	Removed mg/l	%	
67	30	7.4	10.2	3.2	1.8	1.4	44	
68	650	7.4	9.5	3.2	2.8	0.4	13	
69	2 690	7.4	9.5	3.2	2.8	0.4	13	
70	4 920	7.4	9.6	3.2	2.9	0.3	9	
								1)
71	6 300	7.4	9.9	3.2	2.4	0.8	27	
72	6 553	7.4	10.3	3.2	2.9	0.3	9	
								2)
73	6 580	8.6	9.9	23.0	15.0	8.0	35	
74	6 603	8.6	10.1	23.0	15.5	7.5	33	
75	6 970	8.6	10.5	23.0	16.0	7.0	30	
76	7 433	8.6	9.8	23.0	19.0	4.0	17	
77	7 533	8.6	9.6	23.0	19.0	4.0	17	
78	7 720	8.6	9.3	23.0	20.0	3.0	13	
79	8 400	8.6	9.2	23.0	21.0	2.0	9	
80	10 050	8.6	9.1	23.0	23.0	0	0	
								3)
81	10 070	8.5	9.4	22.0	17.0	5.0	23	
82	10 180	8.5	9.4	22.0	18.0	4.0	17	
83	10 490	8.5	9.4	22.0	18.0	4.0	17	
84	12 290	8.5	9.5	22.0	20.0	2.0	9	
85	14 300	8.5	9.5	22.0	22.0	0	0	

1) The filter media was agitated manually for 1 min.
2) The exhausted filter media from Sekei was transferred into filter treating water with high fluoride content of 23 mg/l.
3) The exhausted filter media was washed with tap water and replaced back for defluoridation.

The results show that agitating or mixing manually the filter media for a while increases the fluoride removal efficiency. Stirring or agitating increases the efficiency of reaction because the filter media is not heterogenous.

After sample no. 80 (Table 16) the exhausted filter media was regenerated by washing it with tap water and replaced back to the unit for defluoridation. The washed media was not dried in the sun. The results show that the regenerated media reduces fluoride from 22 mg/l to 17 mg/l (23 %).

The exhausted filter media after sample no. 85 (Table 16) was replaced with fresh media of different particle sizes of 1.00 - 2.00 mm and greater than 2.00 mm with the quantities 7 l and 6 l respectively. The results (Table 17) show that fluoride was reduced from 21 mg/l to 8 mg/l when the filtration rate was 119 l/h. However, the filter media exhausted when only 80 l was filtered through it.

Table 17. Fluoride removal by using particles with bigger diameter.

Raw water:	fluoride content 21 mg/l pH 8.9
Filter media:	particle sizes 1.00 - 2.00 mm volume 0.007 m^3 particle sizes greater than 2.00 mm volume 0.006 m^3
Filtration rate:	119 l/h

Sample no.	Cumulative water filtered through l	pH	Fluoride content Residual mg/l	Fluoride content Removed mg/l	Removed %
86	80	10.4	8.0	13.0	62
87	330	10.5	18.0	3.0	1
88	2 090	10.5	21.0	0	0

Fresh magnesia filter media was packed in the filtration unit of length 0.6 m, width 0.3 m and depth 0.3 m. The particle sizes of 0.63 - 1.00 mm and particles greater than 2.00 mm with the volumes 0.02 m^3 and 0.02 m^3 respectively were used. The results in Table 18 show that fluoride was reduced from 18 mg/l to 3.4 mg/l which is within the Tanzanian temporary standard of 8 mg/l. The filter media was being filled with raw water of 12.5 l, and drained completely after 30 min, from sample no. 89 to sample no. 111. Thereafter water was allowed to flow continuously at the flow rate of 23.6 l/h. The filter media was able to reduce fluoride to Tanzanian temporary standard after filtered only about 88 l.

Table 18. Defluoridation by using magnesia in bigger quantity.
Raw water: pH 8.5
Filter media: particle sizes 0.63 - 1.00 mm
volume 0.02 m^3
particle sizes greater than 2.00 mm
volume 0.02 m^3
Detention time: 30 min

Sample no.	Volume collected	Cumulative water filtered through	pH	Fluoride content			Removed	
				Raw water	Residual	Removed		
	l	l		mg/l	mg/l	mg/l	%	
89	12.5	12.5	9.6	18.0	3.4	14.6	81	
90	12.5	25.0	9.7	18.0	5.0	13.0	72	
91	12.5	37.5	9.7	18.0	7.5	10.5	58	
92	12.5	50.0	9.8	18.0	5.5	12.5	69	1)
93	12.5	62.5	10.0	18.0	5.3	12.7	71	
94	12.5	75.0	9.9	18.0	7.0	11.0	61	
		75.0	9.7	18.0	5.5	12.5	69	6)
95	12.5	87.5	9.9	18.0	7.5	10.5	59	
96	12.5	100.0	9.9	21.0	10.0	11.0	53	
97	12.5	112.5	9.9	21.0	11.5	9.5	45	4)
98	12.5	125.0	10.0	22.0	9.5	12.5	57	
99	12.5	137.0	10.0	22.0	10.8	11.2	51	
100	12.5	150.0	10.0	22.0	10.8	11.2	51	
		150.0	10.0		8.2			6)
101	12.5	167.5	10.0	22.0	12.0	10.0	45	
102	12.5	175.0	9.9	22.0	12.0	10.0	45	
103	12.5	187.5	9.9	22.0	12.0	10.0	45	2)
104	12.5	200.0	10.0	22.0	11.0	11.0	50	
105	12.5	212.5	10.0	22.0	10.2	11.8	54	
106	12.5	225.0	10.0	22.0	9.5	12.5	57	
107	12.5	237.5	10.0	22.0	10.8	11.2	51	
108	12.5	250.0	10.1	22.0	10.2	11.8	54	
109	12.5	267.5	10.2	22.0	11.0	11.0	50	
110	12.5	275.0	10.2	22.0	13.5	8.5	39	
111	12.5	287.5	10.2	22.0	14.0	8.0	36	
112	5.0	297.0	10.0	22.0	14.0	8.0	36	
113	5.0	302.0	10.2	22.0	16.0	6.0	27	
114	54.0	355.0	10.2	22.0	18.0	4.0	18	3)
115	21.0	376.0	10.2	22.0	17.0	5.0	23	
116	80.0	456.0	10.2	22.0	19.0	3.0	14	
117	20.0	476.0	9.6	22.0	7.0	15.0	68	5)
118	94.0	570.0	9.6	22.0	9.5	12.5	57	
119	31.0	601.0	9.9	22.0	16.0	6.0	27	
120	136.0	737.0	9.9	22.0	19.0	3.0	14	
121	27.0	764.0	9.9	22.0	20.0	2.0	9	

1) After sample no. 92 the media was stirred for 1 min.
2) After sample no. 103 the media was stirred for 1 min.
3) After sample no. 114 the media was stirred for 1 min.
4) Next morning: After sample no. 97 the media was left dry and in the morning the experiment started again.
5) Regeneration: The exhausted media was washed manually and dried in the sun for 10 h before packed for defluoridation again.
6) Cumulative water.

After sample no. 116 the media was completely exhausted. The exhausted media was removed from the model and washed thoroughly manually by turning it around and dried it in the sun for about 10 h. Thereafter the media was packed back into the model for fluoride removal. Fluoride was removed from 22 mg/l to 7 mg/l (68 %). About 100 l was filtered before the media was exhausted and the residual fluoride was again 8 mg/l. During regeneration 40 l of tap water with fluoride content of 8 mg/l was used in washing the filter media.

There was a fluctuation of fluoride concentration in the raw water from 18 mg/l to 22 mg/l. The fluctuation was due to changes of weather. The fluoride concentration is minimum during the rainy season and maximum during dry season (Gauff 1980).

The experiment was done using the pretreatment tank with fresh magnesia of the same particle sizes and quantity as in Table 18. The results (Table 19) show that about 80 l was filtered at the flow rate of 48.6 l/h before the filter media exhausted in fluoride reduction to 8 mg/l.

Table 19. Fluoride removal by magnesia as a filter media.
Raw water: fluoride content 18 mg/l
pH 8.6
Filter media: particle sizes 0.63 mm- 1.00 mm
volume 0.02 m^3
particle sizes greater than 2.00 mm
volume 0.02 m^3
Flow rate: 49 l/h

Sample no.	Cumulative water filtered through l	pH	Fluoride content Residual mg/l	Fluoride content Removed mg/l	Removed %	
122	18	10.2	5.5	12.5	69	
123	71	10.4	8.5	9.5	53	
	71	10.3	7.2	10.8	60	*)
124	83	10.4	8.6	9.4	52	
125	108	10.4	10.0	8.0	44	
126	483	10.4	14.0	4.0	22	
127	2 811	10.2	17.0	1.0	6	
128	4 050	10.2	17.0	1.0	6	

*) cumulative water

The exhausted magnesia in the pretreatment tank was removed and replaced with fresh magnesia particles with diameter of 0.20 mm- 0.63 mm. The fluoride content was reduced from 22 mg/l to 5.5 mg/l. The results in Table 20 show that about 70 l of raw water was filtered before the defluoridation efficiency reduced so that residual fluoride was on the limit of 8 mg/l. However, water was allowed to flow through the media for checking how long it will take before the media is 100 % exhausted, and how it behaves after it has exhausted. The results show that 6 120 l can be filtered before fluoride removal efficiency of the media becomes 0 (i.e. in sample no. 142 in Table 20).

Regeneration of the media was attempted again by washing thoroughly the exhausted media with tap water and dried it in the sun for 24 h before replacing it back to the unit for more filtration. The results in Table 20, samples no. 143 and 144, show that the regenerated magnesia removed fluoride from 22 mg/l to 11 mg/l (50 %). However, 400 l was filtered before the fluoride removal efficiency was less than 14 %.

Table 20. Results showing fluoride removal by filtration through magnesia.
Raw water: fluoride content 22 mg/l
pH 8.5
Filter media: particle sizes 0.20 - 0.63 mm
volume 0.02 m^3
particle sizes greater than 2.00 mm
volume 0.01 m^3
Flow rate: 49 l/h

Sample no.	Cumulative water filtered through	pH	Fluoride content		Removed
			Residual	Removed	
	l		mg/l	mg/l	%
129	5	9.8	5.5	16.5	75
130	50	9.9	8.5	13.5	61
131	70	9.9	8.0	14.0	64
132	90	9.9	10.0	12.0	55
133	214	10.2	12.0	10.0	45
134	861	10.0	15.5	6.5	30
135	978	10.0	15.5	6.5	30
136	998	10.2	15.5	6.5	30 1)
138	1 194	9.9	16.0	6.0	27
139	2 088	9.7	17.5	4.5	21
140	3 987	9.8	17.5	4.5	21
141	4 080	9.9	18.0	4.0	18
142	4 325	9.7	19.5	2.5	11
143	5 319	9.6	20.0	2.0	9
142	6 120	9.6	22.0	0.0	0
143	6 128	9.9	11.0	11.0	50 2)
144	6 138	9.9	11.0	11.0	50
145	6 140	9.9	10.0	12.0	55 3)
146	6 147	9.9	11.5	10.5	48
147	6 150	9.9	12.0	10.0	46
148	6 160	9.9	14.0	8.0	36
149	6 224	9.8	18.0	4.0	18
150	6 244	9.8	16.0	6.0	27 4)
151	6 529	9.8	19.0	3.0	14

1) After sample no. 137 the media was agitated for 1 min.
2) Regeneration: The media was removed, washed and dried in the sun for 24 h and then packed back in the unit for removal.
3) After sample no. 144 the media was agitated for 3 min.
4) After sample no. 149 the media was agitated for 1 min.

Fresh magnesia was packed again in the filtration tank. The results show that magnesia can remove fluoride content from 22.0 mg/l to 0.3 mg/l which is 99 % reduction (Table 21). Filter media with smaller particle sizes of 0.20 - 0.63 mm and volume of 0.05 m^3, and 0.63 - 1.00 mm with volume of 0.01 m^3 were used. The filtration rate in the experiment was 51 l/h. With this filter media 960 l was filtered before the media exhausted in fluoride reduction from 22 mg/l to 8 mg/l.

Table 21. Results showing the efficiency of magnesia in fluoride removal.

Raw water: fluoride content 22 mg/l
pH 8.5
Filter media: particle sizes 0.20 - 0.63 mm
volume 0.05 m^3
particle sizes 0.63 - 1.00 mm
volume 0.01 m^3
Filtration rate: 51 l/h
Detention time: 30 min

Sample no.	Cumulative water filtered through l	pH	Fluoride content Residual mg/l	Removed mg/l	Removed %	
152	2.5	10.2	2.0	20.0	91	
153	5.0	10.2	1.4	20.6	94	
154	7.5	10.2	1.1	20.9	95	
155	10.0	10.2	0.8	21.2	96	
156	12.5	10.1	0.8	21.2	96	
157	15.0	10.1	0.7	21.3	97	
158	17.5	10.2	0.7	21.3	97	
159	20.0	10.3	0.6	21.4	97	
160	22.5	10.3	0.5	21.5	98	
161	25.0	10.3	0.5	21.5	98	
	25.0	10.2	0.9	21.1	96	1)
162	27.5	10.3	0.4	21.6	98	
163	30.0	10.3	0.4	21.6	98	
164	32.5	10.3	0.4	21.6	98	
165	52.5	10.4	0.6	21.4	97	
166	55.0	10.5	0.3	21.7	99	
167	359.0	10.3	5.5	16.8	77	
168	960.0	10.2	9.5	12.5	57	
169	1 600.0	10.2	10.0	12.0	56	
170	2 112.0	10.2	12.5	9.5	43	
171	2 362.0	10.2	12.0	10.0	46	
172	2 705.0	10.2	12.0	10.0	46	
173	2 915.0	10.2	13.5	8.5	39	
174	3 271.0	10.2	14.0	8.0	37	
175	3 582.0	10.3	11.0	11.0	50	2)
176	4 634.0	10.3	11.0	11.0	50	
177	5 030.0	10.4	13.0	9.0	41	
178	5 690.0	10.4	14.0	8.0	36	2)
179	5 854.0	10.4	13.0	9.0	41	

1) Cumulative water from sample no. 152 to 161 was mixed in the container and the pH and fluoride residual were analysed.
2) After samples no. 174, 175 and 178 the media was agitated for 3 min.

Filtration velocity

The filtration velocity from Tables 15 to 21 was calculated from the following calculations:

$$\text{Filtration velocity} = \frac{\text{Discharge rate}}{\text{Surface area of the filter media}}$$

In Tables 15 and 16

$$\text{Filtration velocity} = \frac{0.038\ m^3/h}{0.070\ m^2} = 0.54\ m/h$$

In Table 17 $$\text{Filtration velocity} = \frac{0.119\ m^3/h}{0.070\ m^2} = 1.7\ m/h$$

In Table 18 $$\text{Filtration velocity} = \frac{0.024\ m^3/h}{0.18\ m^2} = 0.13\ m/h$$

In Table 19 $$\text{Filtration velocity} = \frac{0.049\ m^3/h}{0.509\ m^2} = 0.096\ m/h$$

$$= 0.10\ m/h$$

In Table 21 $$\text{Filtration velocity} = \frac{0.051\ m^3/h}{0.18\ m^2} = 0.29\ m/h$$

Table 22 summarizes the results of Tables 14 - 21 on particle sizes, quantity of magnesia used and the quantity of water before magnesia exhausted.

Table 22. Summary of particle sizes and quantity of magnesia used, and water filtered before the filter media exhausted.

Table no.	Particle sizes used	Quantity of MgO used	Filtration rate	Fluoride concentration			Quantity of water filtered at the exhausted point in column 7
				Raw water	Minimum residual achieved	Residual when media taken as exhausted	
	mm	m3	l/h	mg/l	mg/l	mg/l	l
14	0.63-1.00	0.002	72.0	23.0	3.0	8.0	5
15	0.63-1.00 > 2.00	0.008 0.007	38.4	3.2	1.8	2.8	2 900
16	0.63-1.00 > 2.00	0.008 0.007	38.4	3.2	1.8	2.8	2 690
17	1.00-2.00 > 2.00	0.007 0.007	119.0	21.0	8.0	8.0	80
18	0.63-1.00 > 2.00	0.02 0.02	23.6	18.0	3.4	7.5	88
19	0.63-1.00 > 2.00	0.02 0.02	49.0	18.0	5.5	8.6	83
20	0.20-0.63 > 2.00	0.02 0.01	49.0	22.0	5.5	8.0	70
21	0.20-0.63 0.63-1.00	0.05 0.01	51.0	22.0	0.3	9.5	960

The most efficient particle sizes for fluoride removal by filtration through magnesia are particles of 0.20 - 0.63 mm. Fluoride was removed from 22.0 mg/l to less than 1.5 mg/l when 60 l of raw water was filtered through 0.05 m^3 filter bed with this size of particles. The media has a capacity of reducing fluoride from 22 mg/l to 8 mg/l for 1 000 l of raw water.

The results show that the most appropriate filter media and filtration rate for fluoride removal when using magnesia are the ones recommended for slow sand filter. The specification of slow sand filter media is: grain size of sand 0.25 - 0.35 mm and the filtration velocity of 0.1 - 0.4 m/h (Schulz and Okun 1984).

Regeneration of magnesia in defluoridation was very laborious. The filter media was removed from the filter unit, washed with tap water thoroughly and then dried in the sun before replacing back to the unit.

The mechanism of removing fluoride from the exhausted magnesia by washing, is probably mechanical removal of MgF_2 from the surface of MgO particles during washing. However, the regeneration method of magnesia requires more detailed researches.

Defluoridation by filtration through magnesia alone at this stage is obviously not appropriate for large scale treatment plants. The method is appropriate for a small water supply scheme, village level water projects and for household unit. Another disadvantage of this method was high pH value value of the treated water. There should be a method of reducing pH value to the acceptable range when using magnesia alone in defluoridation.

6.2 Defluoridation by using polyaluminium chloride

6.2.1 Dosage of polyaluminium chloride and flocs formation

The jar test results in the laboratory show that PAC can remove fluoride from 22 mg/l to 0.2 mg/l (99 % reduction) (Table 23, Figure 10). The disadvantage of the good results was that there were no flocs in samples no. 183, 184 and 185 where the fluoride residual was within the WHO standards. PAC solution used in the experiments had pH value of 2.8.

Table 23. Dosage of polyaluminium chloride (PAC) in 500 ml of raw water.
Raw water: fluoride content 22 mg/l
pH 8.7

Sample no.	Dosage of PAC	pH	Fluoride content		Removed	Remarks
			Residual	Removed		
	ml/500 ml		mg/l	mg/l	%	
180	1.0	7.0	3.2	18.8	85	dense flocs
181	2.5	5.1	2.0	20.0	91	very light flocs
182	3.0	4.9	1.5	20.5	93	very light flocs
183	4.5	4.7	1.2	20.8	95	no flocs
184	6.0	4.6	0.3	21.7	99	no flocs
185	8.0	4.5	0.2	21.8	99	no flocs

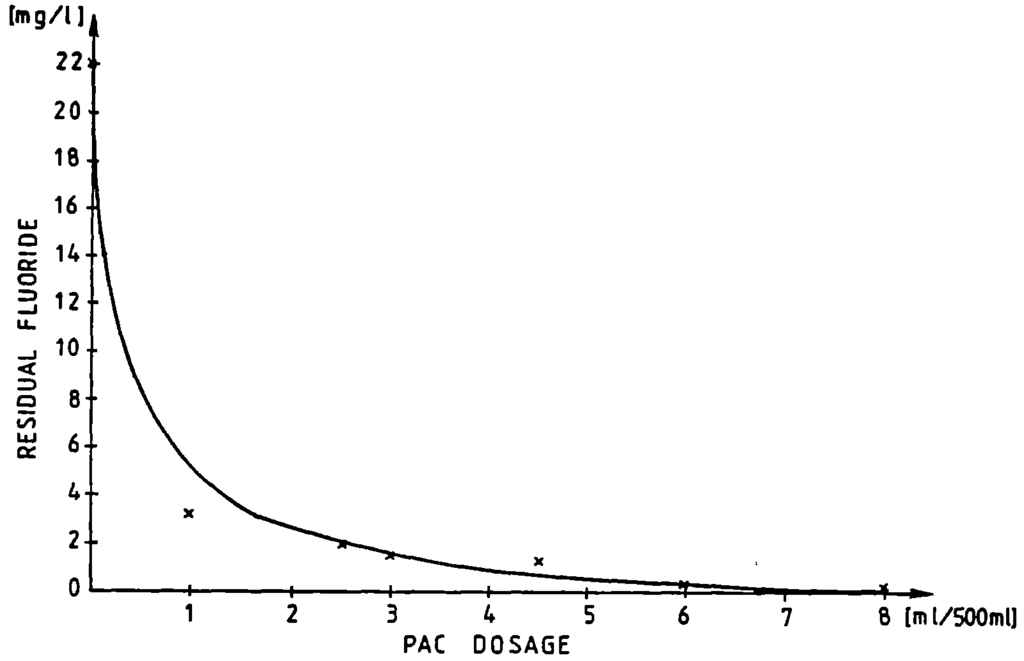


Figure 10. Fluoride removal using polyaluminium chloride (PAC).

According to Table 23 flocs were formed within 30 s in samples no. 180, 181 and 182. It took 3 min for complete settlement of flocs in sample no. 180, while in samples no. 181 and 182 the complete settlement was achieved within 2 h.

Dosage of PAC in 800 ml of raw water with fluoride concentration of 22 mg/l was attempted (Table 24). Flocs were formed within 30 s in all 6 samples. Settlement of flocs was very fast, within 2 min in samples no. 186, 187, 188, 189 and 190, while in sample no. 191 settlement took 30 min. This was because the flocs were by light.

Table 24. Results of dosage of polyaluminium chloride (PAC) in 800 ml of raw water.
Raw water: fluoride residual 22 mg/l
ph 8.7

Sample no.	Dosage of PAC ml/800 ml	pH	Fluoride content Residual mg/l	 Removed mg/l	Removed %	Remarks
186	1.0	8.0	7.5	14.5	66	dense flocs
187	2.0	6.9	6.0	16.0	73	dense flocs
188	2.5	6.1	3.4	18.6	85	dense flocs
189	3.0	5.8	1.8	20.2	92	very dense flocs
190	3.5	5.5	1.2	20.8	95	very dense flocs
191	4.0	5.0	1.0	21.0	96	very dense flocs

Fluoride removal by using PAC in Arusha urban water supply with fluoride content of 2.8 mg/l was experimented. The results in Table 25 show that less dosage of PAC is required for raw water with low fluoride content. It shows that fluoride can be reduced to a level of less than 0.1 mg/l. However, the pH values are very low for domestic use. There were no flocs in all 6 samples in spite of low fluoride residual. In order to improve flocs formation use of locally available clay bentonite was tested.

Table 25. Results of defluoridation by using polyaluminium chloride (PAC) for water with relatively fluoride content.
Raw water: fluoride content 2.8 mg/l
pH 8.0

Sample no.	Dosage of PAC ml/500 ml	pH	Fluoride content Residual mg/l	 Removed mg/l	Removed %	Remarks
192	0.3	4.6	0.4	2.4	86	no flocs
193	0.5	4.4	0.3	2.5	89	no flocs
194	0.8	4.4	0.3	2.5	89	no flocs
195	1.0	4.3	0.3	2.5	89	no flocs
196	1.5	4.3	0.2	2.6	93	no flocs
197	3.0	4.2	<0.1	2.7	96	no flocs

The experiments of PAC dosage were also made at the site (Table 26). When the discharge of raw water was 0.187 m^3/h and PAC dosage of 0.77 l/h, very light flocs were formed. Flotation methods could be used to remove light flocs instead of sedimentation.

Table 26. Dosage of polyaluminium chloride (PAC) at the treatment model.
Raw water: fluoride content 18 mg/l
pH 8.9

Sample no.	Flow of water	Dosage of PAC	pH	Fluoride content		Removed	Remarks
				Residual	Removed		
	l/h	l/h		mg/l	mg/l	%	
198	202	1.48	6.5	1.6	16.4	91	very dense flocs
199	198	0.78	6.5	1.7	16.3	90	dense flocs
200	187	0.77	6.6	1.6	16.4	91	light flocs

6.2.2 Use of clay bentonite as coagulant aid

Clay bentonite powder was experimented at the laboratory for improving flocs formation and settlement. According to results (Table 27, samples no. 201-203) good flocs were formed within 2 s and settlement was within 5 min.

The results in Table 27, samples 204-215 show that flocs were formed in samples no. 204, 205, 206, 207 and 208 within 2 s. Settlement in sample no. 204 happened in 2 min, while in samples no. 205, 206 and 207 it happened within 6 h and in sample no. 208 settlement was finished within 12 h. Bentonite raises the pH value of treated water to the acceptable level. The permissible pH level for domestic use is between 6.5 - 9.2 (Cairncross and Feachem 1983).

The use of bentonite as coagulant aid also increased the efficiency of PAC in fluoride reduction. However, bentonite clay alone has very little effect in fluoride reduction. It removed fluoride from 9 mg/l to 8 mg/l only (sample no. 215).

Although bentonite improved flocs formation, after 30 min there was a thin layer formed on the top of the supernatant. This layer speeds up the clogging rate of the filter.

Table 27. Effect of using clay bentonite as coagulant aid in defluoridation when using polyaluminium chloride (PAC).

Sample no.	Time after mixing min	Bento-nite added g/500 ml	PAC added ml/500 ml	pH	Fluoride content Residual mg/l	Fluoride content Removed mg/l	Removed %	Remarks
201		5	0.35	7.0	1.3	1.5	54	good flocs *)
202		5	0.45	6.8	1.1	1.7	61	good flocs
203		5	0.55	6.8	0.9	1.9	68	good flocs
204	30	20	1.0	6.5	1.4	7.6	84	dense flocs **)
205	30	20	1.5	6.5	0.7	8.3	92	light flocs
206	30	20	2.0	6.3	0.5	8.5	94	light flocs
207	30	20	2.5	5.8	0.6	8.4	93	light flocs
208	30	20	3.0	4.7	0.8	8.2	91	very light flocs
209	30	20	0.0	9.0	8.2	0.8	9	no flocs
210	60	20	1.0	6.5	1.4	7.6	84	good settlement
211	60	20	1.5	6.5	0.5	8.5	94	no settlement
212	60	20	2.0	6.3	0.2	8.8	98	no settlement
213	60	20	2.5	5.8	0.2	8.8	98	no settlement
214	60	20	3.0	4.7	0.4	8.6	96	no settlement
215	60	20	0.0	9.0	8.0	1.0	11	no flocs
216	20		1.0	6.7	6.4	16.6	72	dense flocs ***)
217		20	1.5	6.3	2.6	20.4	89	dense flocs
218		20	2.0	5.9	1.6	21.4	93	dense flocs
219		20	2.5	5.1	1.2	21.8	95	light flocs
220		20	3.0	4.7	1.7	21.3	93	light flocs
221		20	3.5	4.6	1.5	21.5	93	light flocs

*) Fluoride content in raw water 2.8 mg/l, pH 8.0

**) Fluoride content in pretreated water 9 mg/l, pH 9.0

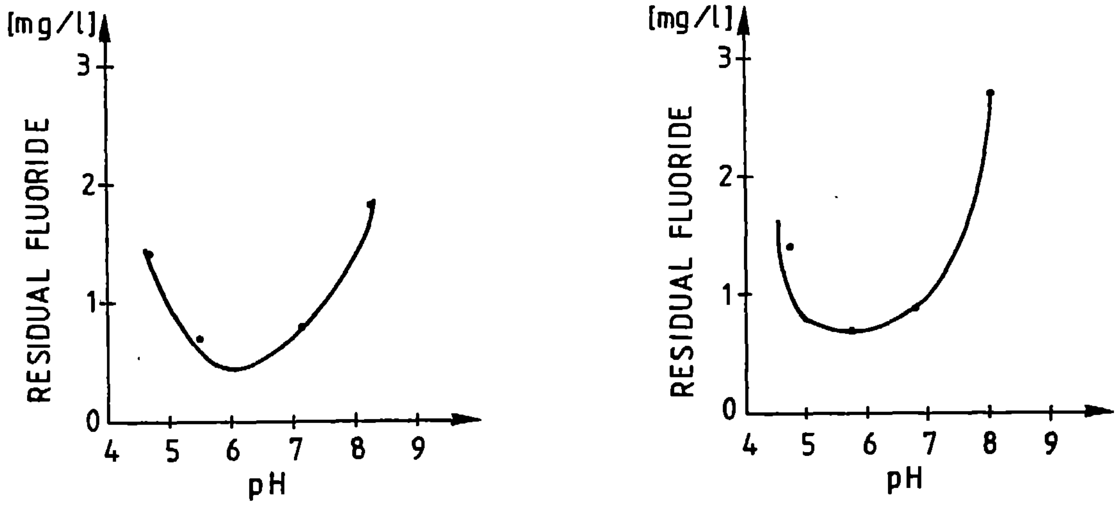
***) Fluoride content in raw water 23 mg/l, pH 9.0

6.2.3 Effect of pH in defluoridation and flocs formation

Normal solution of sodium hydroxide (NaOH) was used to raise the pH level of raw water. Results in Table 28 and Figure 11 show the effect of pH when PAC was used in defluoridation. The pH regulation was made by using hydrochloric acid (HCl) and sodium hydroxide, and the results are in Table 29 and graphically represented in Figure 12.

Table 28. Effect of pH on fluoride reduction when using polyaluminium chloride (PAC).
Raw water: fluoride content 19 mg/l
pH 8.7
Sodium hydroxide used: normal solution

Sample no.	NaOH added ml/ 500 ml	pH value	PAC added ml/ 500 ml	Final pH value	Fluoride content		Removed	Remarks
					Residual mg/l	Removed mg/l	%	
222	0	8.7	3	4.7	1.4	17.6	93	no flocs
223	2	10.3	3	4.8	1.2	17.8	94	very light flocs
224	4	10.9	3	5.5	0.7	18.3	96	light flocs
225	6	11.5	3	5.8	0.5	18.5	97	light flocs
226	8	11.9	3	7.2	0.8	18.2	96	dense flocs
227	10	12.0	3	8.3	1.8	17.2	91	dense flocs
228	0	8.7	2	4.6	1.5	17.5	92	no flocs
229	2	10.2	2	4.8	1.4	17.6	93	very light flocs
230	4	10.8	2	5.0	0.8	18.2	96	light flocs
231	6	11.5	2	5.8	0.7	18.3	96	light flocs
232	8	11.8	2	6.8	0.9	18.1	95	dense flocs
233	10	12.0	2	8.1	2.7	16.3	86	dense flocs



a) PAC dosage 3 ml in 500 ml raw water

b) PAC dosage 2 ml in 500 ml raw water

Figure 11. Effect of pH in fluoride reduction when using polyaluminium chloride (PAC). Initial fluoride content was 19 mg/l.

Table 29. Effect of pH in defluoridation when using polyaluminium chloride (PAC).
Raw water: pH 8.7

Sample no.	pH before PAC dosage	PAC added	Final pH value	Fluoride content			Removed	Remarks
				Raw water	Residual	Removed		
		ml/ 500 ml		mg/l	mg/l	mg/l	%	
234	1.9	3	2.4	23.0	3.7	19.3	84	no flocs
235	4.2	3	4.1	23.0	3.7	19.3	84	no flocs
236	5.5	3	4.1	23.0	3.4	19.6	85	no flocs
237	6.5	3	5.2	23.0	2.8	20.2	88	dense flocs
238	10.2	3	6.2	23.0	2.0	21.0	91	very dense flocs
239	11.6	3	10.0	23.0	6.0	17.0	74	dense flocs
240	8.7	3	4.7	19.0	1.6	17.4	92	no flocs
241	10.8	3	6.2	19.0	0.8	18.2	96	very dense flocs
242	11.8	3	8.2	19.0	1.4	17.6	93	dense flocs
243	12.0	3	9.0	19.0	3.5	15.5	82	dense flocs
244	12.2	3	9.8	19.0	5.5	13.5	71	dense flocs
245	12.4	3	10.2	19.0	5.7	13.3	70	dense flocs

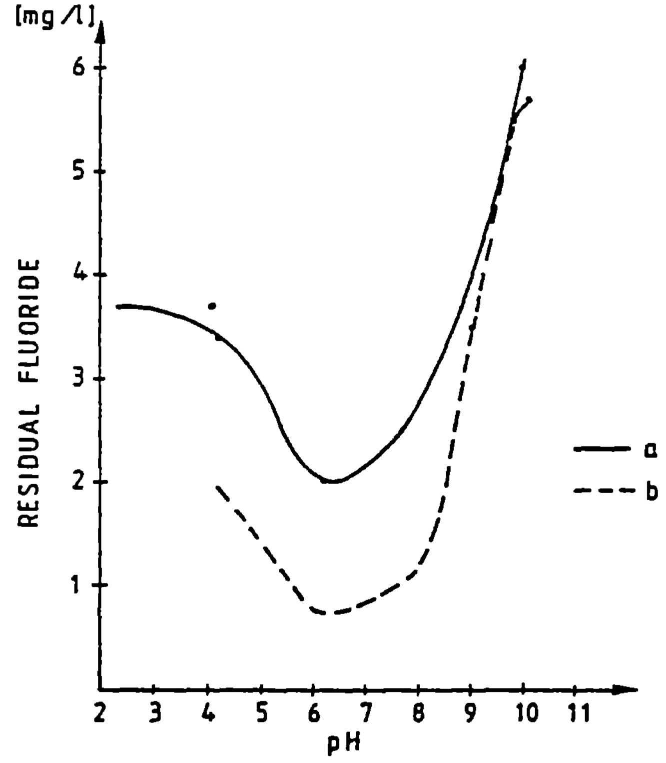


Figure 12. Effect of pH on fluoride reduction when using polyaluminium chloride (PAC). Initial fluoride content on raw water a) 23 mg/l, b) 19 mg/l.

The results show that the optimum pH values in defluoridation when using PAC are 5 and 7. However, PAC can work both in highly acidic and alkaline pH values. Fluoride was removed from 23 mg/l to 3.7 mg/l (84 %) when initial pH of the sample was 2.4 and from 19 mg/l to 5.7 mg/l (70 %) when initial pH of the sample was 10.2.

Magnesia was also used in pH adjustment. Two litres of water pretreated with magnesia was treated with PAC. The results are presented in Table 30.

Table 30. Defluoridation with polyaluminium chloride (PAC) when adjusting pH by using magnesia.
Water pretreated
with magnesia: fluoride content 4.2 mg/l
pH 10.3

Sample no.	PAC added ml/500 ml	pH	Fluoride content Residual mg/l	Removed mg/l	Removed %	Remarks
246	1	9.5	0.8	3.4	82	light flocs
247	2	8.1	0.6	3.6	86	dense flocs
248	3	7.1	0.5	3.7	88	dense flocs
249	4	4.9	0.4	3.8	90	no flocs

Addition of magnesia powder when PAC was used increases the density of flocs. The results are presented in Tables 31 and 32.

Table 31. Defluoridation with polyaluminium chloride (PAC) when adjusting pH by using magnesia.
Raw water: fluoride content 22 mg/l
pH 8.7
Magnesia powder: particles less than 0.2 mm

Sample no.	MgO added 800 ml ml/800 ml	PAC added 800 ml ml/800 ml	Final pH	Fluoride content Residual mg/l	Removed mg/l	Removed %	Remarks
250	6	1.0	7.6	8.0	14.0	64	dense flocs
251	6	1.5	7.3	3.2	18.8	86	dense flocs
252	6	2.0	7.1	2.2	19.8	90	dense flocs
253	6	3.0	6.3	1.4	20.6	94	dense flocs
254	6	3.5	6.1	2.0	20.0	91	dense flocs
255	0	1.0	7.1	4.6	17.4	79	light flocs
256	0	1.5	6.0	3.4	18.6	85	light flocs
257	0	2.0	6.8	2.2	19.8	90	dense flocs
258	0	3.0	6.1	3.5	18.5	84	dense flocs
259	0	3.5	4.9	3.9	18.1	82	no flocs

Table 32. Defluoridation with polyaluminium chloride (PAC) when adjusting pH by using magnesia powder.
Raw water: fluoride content 22 mg/l
pH 8.5

Sample no.	MgO added ml/ 1000 ml	pH value	PAC added ml/ 1000 ml	pH value	Fluoride content Residual mg/l	Fluoride content Removed mg/l	Removed %	Remarks
260	0	8.7	6	4.6	2.4	19.6	89	no flocs
261	10	10.3	6	5.6	2.6	19.4	88	light flocs
262	15	10.4	6	5.8	1.7	20.3	92	light flocs
263	20	10.4	6	6.2	1.6	20.4	93	dense flocs
264	25	10.4	6	6.2	1.6	20.4	93	dense flocs
265	30	10.4	6	6.3	1.4	20.6	94	dense flocs

Tables 23 to 32 show that in order to have flocs when using PAC as a coagulant the pH value should be above 4.8. Dense flocs were formed when the pH level was between 6 and 8. Figure 13 represents graphically the effect of pH in flocs formation.

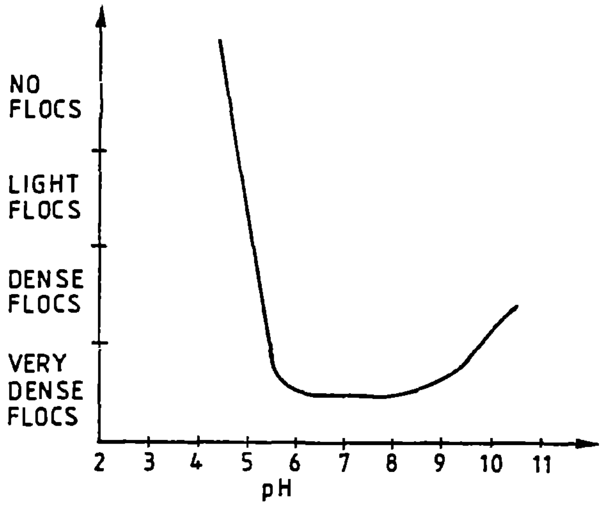


Figure 13. Effect of pH on flocs formation.

Figure 13 shows that PAC as a normal coagulant allows not only good flocculation of suspended solids, but it also removes fluoride during flocculation. The flocs can be removed successfully by sedimentation and filtration process. PAC reacts with alkalinity in water to form jelly like flocs. This occurs within a very short time and that is why it needs rapid mixing within the first 30 s. After neutralization of electrical charges of particles like positively charged turbidity particles and negatively charged fluoride ions, the particles come together to form larger settleable flocs (particles). Bentonite or magnesia powder added increases the density of flocs, hence improving flocs formation.

When using dosage of PAC there were no flocs but the fluoride removal was high. There were no flocs probably due to formation of aluminium complexes with fluoride which do not form flocs at low pH.

6.3 Defluoridation by using magnesia and polyaluminium chloride

Magnesia and PAC were used in a pretreatment tank and hydraulic rapid mixing chamber respectively for fluoride removal and pH adjustment. Table 33 shows that magnesia was exhausted when only 1.3 m^3 of water with 20 mg/l fluoride was filtered through it.

Good and dense flocs were formed. The rate of sludge settlement in the sedimentation tank was high: 0.04 m^3 sludge was collected when only 1 m^3 of water was treated.

Table 33. Fluoride reduction by using combined magnesia and polyaluminium chloride (PAC).
Raw water: fluoride content 20 mg/l
pH 8.6
Magnesia: particles greater than 2.00 mm,
0.009 m^3
particles 0.20 - 0.63 mm,
0.025 m^3
Flow rate: 202 l/h
PAC dosage: 0.4 l/h

Sample no.	Water treated with	Cumulative amount of water treated	pH	Fluoride content		Removed
				Residual	Removed	
		l		mg/l	mg/l	%
266	MgO	45	10.2	6.5	13.5	68
267	MgO+PAC	45	8.4	2.1	17.9	90
268	MgO	300	10.1	12.0	8.0	40
269	MgO+PAC	300	8.6	6.5	13.5	68
270	MgO	1 280	10.1	18.0	2.0	10
271	MgO+PAC	1 280	8.8	8.0	12.0	60
272	MgO	4 733	10.0	18.5	1.5	8
273	MgO+PAC	4 733	8.0	10.0	10.0	50
274	MgO	7 011	10.0	18.5	1.5	8
275	MgO+PAC	7 011	7.5	14.0	6.0	30
276	MgO	7 574	10.1	18.5	1.5	8
277	MgO+PAC	7 574	8.8	14.0	6.0	30
278	MgO	10 521	10.1	20.0	0.0	0
279	MgO+PAC	10 521	7.5	14.0	6.0	30

Another dosage of PAC and fresh magnesia in the pretreatment and filter tank gave the results represented in Table 34. Although magnesia reduces fluoride in the filter tank, it raises the pH of treated water. Magnesia in the filter media was exhausted after filtering about 0.9 m^3 of water, i.e. in samples no. 287 and 288 the fluoride residual is the same. Agitating the filter media was made in order to increase the efficiency.

Table 34. Defluoridation by using combined magnesia and polyaluminium chloride (PAC). The use of magnesia as filter media.
Raw water: fluoride content 18 mg/l
pH 8.6
Filter media: 1.00 - 2.00 mm, 0.04 m^3
0.63 - 1.00 mm, 0.01 m^3
Flow rate: 257 l/h
PAC dosage: 1.3 l/h

Sample no.	Water treated with	Cumulative amount of water treated l	pH	Fluoride content Residual mg/l	Fluoride content Removed mg/l	Removed %	
280	MgO	100	9.8	7.0	11.0	61	*)
281	MgO+PAC	100	8.8	1.9	16.1	89	
282	MgO+PAC+MgO_F	100	9.7	0.9	17.1	95	**)
283	MgO	240	9.8	10.0	8.0	44	
284	MgO+PAC	240	7.6	2.1	15.9	88	
285	MgO+PAC+MgO_F	240	9.7	1.8	16.2	90	
286	MgO	896	10.2	12.0	6.0	33	
287	MgO+PAC	896	6.7	2.3	15.7	87	
288	MgO+PAC+MgO_F	896	9.0	2.3	15.7	87	
289	MgO	3 000	10.2	16.0	6.0	13	
290	MgO+PAC	3 000	6.7	6.5	11.5	64	
290	MgO+PAC+MgO_F	3 000	9.0	6.5	11.5	64	***)
291	MgO	5 250	10.2	18.0	0.0	0	
292	MgO	5 270	10.2	11.5	6.5	36	
293	MgO+PAC	5 270	7.0	2.1	15.9	88	
294	MgO+PAC+MgO_F	5 270	9.1	2.1	15.9	88	
295	MgO	7 010	10.3	16.0	2.0	13	
296	MgO	7 390	10.3	18.0	0.0	0	***)
297	MgO	7 500	10.1	14.0	4.0	22	
298	MgO	7 723	10.1	15.0	3.0	17	
299	MgO	11 262	10.1	18.0	0.0	0	

*) MgO = in the pretreatment tank
**) MgO_F = magnesia in the filter
***) agitating for 10 min

Attempt to obtain water which is within the limits of WHO standards in fluoride content (1.5 mg/l) was made with fresh magnesia in the pretreatment tank and different PAC dosage rate. The results in Table 35 show that when using PAC dosage of 0.86 l/h, fluoride was reduced from 22 mg/l to 2.4 mg/l when the flow of raw water was 214 l/h. At this rate fluoride was reduced to 3.2 mg/l when magnesia was exhausted. At this dosage fluoride residual was above WHO standards but within Tanzanian temporary standards. Water was allowed to flow through the pretreatment media after sample no. 303 for 50 h. Sample no. 305 shows that there was no effect on fluoride reduction, however pH of treated water with exhausted magnesia was 9.7.

Table 35. Defluoridation by using combined magnesia and polyaluminium chloride (PAC).
Raw water: fluoride content 22 mg/l
pH 8.6
Filter media: coarse material > 2.00 mm, 0.02 m^3
particle sizes 1.00 - 2.00 mm, 0.02 m^3
Flow rate: 214 l/h

Sample no.	Water treated with	PAC dosage	Cumulative amount of water treated	pH	Fluoride content		Removed
					Residual	Removed	
		l/h	l		mg/l	mg/l	%
300	MgO	0	20	10.3	7.5	14.5	66
301	MgO	0	235	10.0	12.0	10.0	45
302	MgO+PAC	0.86	235	6.6	2.4	19.6	89
303	MgO	0	1 232	10.0	22.0	0	0
304	MgO+PAC	0.86	1 232	6.6	3.2	18.8	85
305	MgO	0	11 925	9.7	22.0	0	0
306	MgO+PAC	2.00	11 295	6.2	1.2	20.8	95
307	MgO		11 985	9.7	22.0	0	0
308	MgO+PAC	2.00	11 985	6.1	0.4	21.6	98

Dosage of PAC was changed to 2 l/h. Fluoride was reduced from 22 mg/l to 0.4 mg/l and the pH value was 6.2 which was low for domestic use.

Using of magnesia powder in the rapid hydraulic mixing chamber instead of using magnesia in the pretreatment tank was also attempted. The results in Table 36 show that fluoride was reduced from 18 mg/l to 1.6 mg/l. Flocs were dense, hence coagulation and flocculation were successful.

Table 36. Fluoride removal by using combined polyaluminium chloride (PAC) and magnesia powder in the hydraulic mixing chamber.

Initial fluoride in raw water	18	mg/l
Flow rate of raw water	202	l/h
PAC dosage rate	0.9	l/h
Dosage of MgO powder	1.8	l/h
pH of raw water	8.6	
pH of treated water	9.7	
Fluoride residual of treated water	1.6	mg/l

The disadvantage of this method was the settlement of some heavy flocs in the hydraulic baffled channels flocculator. Flocs were formed within 30 s.

Magnesia powder was mixed with tap water with fluoride content of 8 mg/l. One litre of magnesia powder was mixed with 2 l of tap water. The solution was used with PAC in the hydraulic mixing chamber for defluoridation. Table 37 shows the results. Fluoride was reduced from 22 mg/l to 1.5 mg/l with dense flocs in the settling tank. pH of water was reduced from 8.6 to 6.9 which is within the acceptable pH values for domestic use. Ten litres of magnesia powder was mixed with 20 l of tap water.

Table 37. Defluoridation by using combined polyaluminium chloride (PAC) and magnesia powder solution.

Fluoride content in raw water	22	mg/l
Flow rate of water	202	l/h
Dosage rate of PAC	0.8	l/h
Dosage of MgO in solution	18	l/h
(Dosage of MgO	6	l/h)
pH of raw water	8.6	
pH of treated water	6.9	
Fluoride residual in treated water	1.5	mg/l

There were very few flocs settling in the flocculator. The use of magnesia powder in the solution was much better for controlling the continuous fluoride reduction in water than using magnesia as pretreatment or filter media. It also avoids the labour of removing the exhausted magnesia and washing the media for regeneration. The disadvantage of this method is that it is not possible to regenerate the used magnesia powder solution.

6.4 Physical and chemical analyses of raw and treated water

Some physical and chemical properties were analysed in

a) raw water
b) treated water when magnesia was fresh
c) treated water when magnesia was exhausted
d) treated water with combined fresh magnesia and PAC.

Table 38 shows the results of physical and chemical analyses of both raw and treated water. Appendix 3 shows the WHO and Tanzanian temporary drinking water standards. The results show that some parameters are within the WHO standards or within Tanzanian temporary standards while some are above the limits. Some few parameters have been discussed briefly:

i) Calcium

There is no health objection to a high calcium content in water. The main limitations were made on the grounds of excessive scale formation. The calcium content in raw water and treated water was low. The treatment of water with magnesia or with PAC had little effect on calcium content. The results are contrary to Viswanadham et al (1974) findings of calcium removal when using magnesia in defluoridation. This contradiction might be due to difference in physical and chemical properties of both raw water and magnesia used in the experiments. However, more researches using different type of magnesia and different raw water sources are required to justify the removal of calcium when using magnesia since both magnesium and calcium are cations.

ii) Hardness

The level of hardness in drinking water can be categorized as follows (Twort et al 1985):

Range mg/l	Hardness level
0 - 50	soft
50 - 100	moderately soft
100 - 150	slightly hard
150 - 200	moderately hard
200 - 300	hard
over 300	very hard

Excessive hardness causes scale formation in boilers and hot water systems. Conversely water softer than 30 mg/l tends to be corrosive. It can corrode lead into solution. The softer the water the higher the incidence of cardiovascular diseases.

The raw water can be corrosive since it is soft (13 mg/l). The hardness of 132 mg/l for sample treated with exhausted magnesia was within acceptable hardness limits for domestic uses. Samples from fresh magnesia and magnesia with PAC have higher total hardness values of 719 mg/l and 743 mg/l respectively, than the required limits in Appendix 3. The hardness of water treated with fresh magnesia and the one treated with combined magnesia and PAC are susceptible in scale formation in boilers and hot water systems. Thus softening of the treated water with soda ash or lime will be required.

iii) Magnesium and bicarbonate

The results in Table 38 show that defluoridation of drinking water with magnesia increases the magnesia content in water and reduces the bicarbonates. It also shows that the raw water has bicarbonate alkalinity but after treating it with fresh magnesia the alkalinity of sample B was changed to carbonates. The exhausted magnesia of sample C has more carbonates than bicarbonates. The bicarbonate in water is probably reacting with magnesium oxide to form carbonate and dissolution of magnesium. It can also form magnesium carbonates. Samples B and D have higher magnesium contents, 172 mg/l and 179 mg/l, which are above the limit of 150 mg/l given in the WHO standards. Higher magnesium content in the treated water with fresh magnesia increases the hardness of water. This justifies the conclusion made by Viswanadham et al (1974) that using of magnesia in defluoridation reduces bicarbonates and raises the magnesium content in treated water.

The results show that raw water has low calcium and magnesium residuals which make high fluoride concentration possible. The presence of calcium, magnesium and aluminium in large amounts reduces the absorption of fluoride due to the formation of less soluble complex fluorides (WHO 1984 b and Lahermo 1983). That is why people living at Maji ya Chai, Kitefu and Ngurdoto areas are highly affected with fluorosis, mottling of teeth and skeletal damage. Thus people around these areas should be encouraged to take diet rich in calcium and magnesium minerals since the domestic water contains too small quantities of these essential minerals.

iv) Chloride

Chloride content of raw water was raised from 24 mg/l to 638 mg/l when PAC was used in sample D. The dosage rate of PAC was 0.86 l/h when the flow rate of raw water was 214 l/h. The chloride content in the treated water was above the maximum allowable WHO standard of 600 mg/l. The chloride content was within the limits of Tanzanian temporary standard of 800 mg/l (Appendix 3). Fresh magnesia raised chloride content from 24 mg/l to 32 mg/l. Thus the use of PAC in defluoridation raises the chloride content in treated water.

v) Other parameters

Sulphate was raised from 29 mg/l to 145 mg/l when water was treated with fresh magnesia. Iodine was raised from 0.27 mg/l to 1.29 mg/l when PAC and magnesia were used. The increase of both sulphates and iodine is probably due to the content of these minerals in the magnesia.

Nitrate in sample B was raised from 4.4 mg/l to 17.6 mg/l. Turbidity in samples B and C was also raised from 1 NTU to 25 and 15 NTU respectively. Potassium permanganate which indicates the presence of organic matter was higher in treated water than in raw water. These results show that magnesia contains organic matters which cause the raises of both nitrate, turbidity and potassium permanganates. However, the presence of these minerals is within the WHO standards.

The presence of phosphate in raw water which contributes to the presence of algae in the water was probably due to agricultural activities around the source. These activities contribute inorganic fertilizers to the water through runoff.

Conductivity was also raised from 848 s/cm to 1 926 s/cm when fresh magnesia was used in defluoridation, while alkalinity which was raised when fresh magnesia used, was reduced when PAC was added during defluoridation.

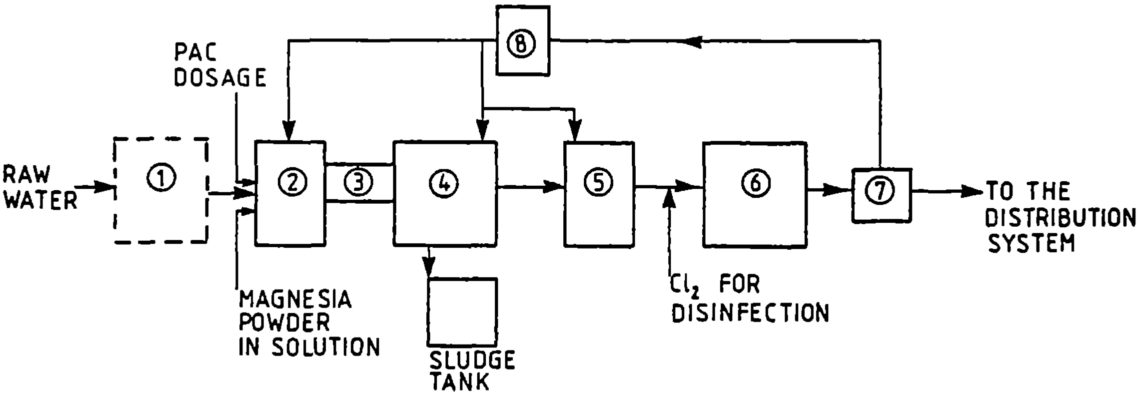
Table 38. Physical and chemical characteristics of the
A. Raw water from Ngurdoto
B. Treated water with fresh magnesia
C. Treated water with exhausted magnesia
D. Treated water with combined fresh magnesia and polyaluminium chloride (PAC).

Description of parameter	Unit	Values obtained			
		A	B	C	D
pH		8.5	10.3	10.0	6.2
Electrical conductivity at 25^{o}C	s/cm	848	1 926	958	1 525
Total dissolved solids	mg/l	425	964	480	765
Temperature	^{o}C	25.3	24.1	24.0	23.9
Turbidity	NTU	1	23	15	1
Total hardness as CaCO$_3$	mg/l	13	719	132	743
Total alkalinity as CaCO$_3$	mg/l	338	688	340	60
Bicarbonate	mg/l	338	0	160	60
Carbonate	mg/l	0	576	180	0
Phenophlene alkalinity as CaCO$_3$	mg/l	0	400	90	0
Magnesium	mg/l	1	172	39	170
Iron	mg/l	0.04	0.07	0.29	0.02
Manganese	mg/l	0.1	0.3	0.1	0.3
Nitrate	mg/l	4.4	17.6	4.8	1.3
Nitrite	mg/l	0	0.68	0	0
Sulphate	mg/l	29	145	25	63
Chloride	mg/l	24	32	24	638
Fluoride	mg/l	18.0	1.1	17.0	1.0
Permanganate value as KMnO$_4$	mg/l	0.23	8.64	2.88	5.12
Iodine	mg/l	0.27	0.22	0.13	1.29
Phosphate	mg/l	0.65	not determined	not determined	not determined

s/cm = microsiemens per centimetre
NTU = Nephthelometric Turbidity Unit

6.5 Design guidelines of defluoridation plant by using magnesia and polyaluminium chloride

The most appropriate defluoridation method when using combined magnesia and PAC is using magnesia powder in solution instead of filtration through magnesia. It is easy to control the constant dosage of both magnesia powder solution and PAC. There is no regeneration of the magnesia involved. With this method good and dense flocs are formed in the settling tank. However, it is very difficult to crush the magnesia to the powder form (particle sizes of less than 0.2 mm diameter). The defluoridation schematic flow diagram of this method is shown in Figure 14.



1) Pretreatment tank whenever necessary
2) Hydraulic rapid mixing chamber
3) Hydraulic baffle channel flocculation
4) Settling tank
5) Rapid sand filter
6) Treated clear water tank
7) Pump
8) Storage tank on raiser for backwashing

Figure 14. Defluoridation schematic flow diagram when using combined magnesia powder solution and polyaluminium chloride (PAC).

The dosage rate of magnesia powder solution and PAC will depend on physical, chemical and biological characteristic, the initial content of fluoride and pH value of the raw water.

The plant should have sludge tank to avoid contamination of the ground water around the defluoridation plant. More research should be carried on how to treat the sludge before discarding it.

The detention time in the hydraulic rapid mixing chamber should be less than 45 s. The detention time in the settling tank should not be less than 30 min. It is better to use hydraulic baffled channel 45° flocculation in order to avoid flocs settlement in the flocculator. The slope of the flocculator will depend on the velocity of the water. However, it should be in such way that there is no flocs settlement in the flocculator.

Whenever possible the settling tank should be covered to avoid wind disturbance. The use of magnesia as a filter media in the rapid sand filter reduces fluoride but it raises the pH value to unacceptable level for domestic use.

To avoid having a big pump with high discharge for pumping water for a short period during backwashing it is better to have a storage tank on raiser for the purpose. The tank can be filled slowly, hence a smaller pump with less initial cost and less power cost is required. However, if a larger pump will be required for distribution system, having the storage tank will avoid disturbance of water to the consumer during backwashing since large quantity of water will be required.

All other designing parameters for hydraulic rapid mixing chamber, hydraulic flocculator, sedimentation tank and rapid sand filter are as per normal specifications for conventional treatment plant.

7 COSTS OF DEFLUORIDATION BY USING MAGNESIA AND POLYALUMINIUM CHLORIDE

Factors which affect the costs are the water quality and quantity, the dosage of chemicals at the treatment plant, cost of magnesia including crushing and sieving, and cost of PAC from Finland to the treatment plant. Other factors are transportation cost, labour cost, initial construction cost, equipment, operation and maintenance cost, etc.

Training whenever necessary should also be considered because a qualified operator for the defluoridation plant will be required. The operator should be able to run routine water chemical analysis.

Briefly the costs of defluoridation by magnesia, PAC and combined magnesia and PAC have been analysed as follows:

7.1 Costs when using magnesia alone

(All costs are in Tanzanian shilling value on February 1990, when 1 USD = 195 TZS.)

The cost of raw magnesite at Chambogo is about 18 000 TZS/t. The cost of calcinated magnesia at Chambogo is 40 000 TZS/t. There are two alternatives of obtaining magnesia. The first alternative is to collect raw magnesite from Chambogo and calcinate it at Arusha. The second alternative is to send fire wood from Vumari forest 20 km away to Chambogo and then collect the calcinated magnesite from Chambogo to Arusha.

i) Cost of the first alternative:

Initial cost of constructing furnace	2 000 000 TZS
Cost of magnesite per ton	18 000 TZS
Cost of transporting 1 t from Chambogo to Arusha = 230 km (Transport cost = TZS 30/km/t)	6 900 TZS
Fire wood 1 m^3 for calcinating 1 t	1 300 TZS
Transport of 1 m^3 of fire wood 30 TZS/km x 40 km	1 200 TZS
Labour for calcinating 1 t	2 000 TZS
Supervision of 1 t	500 TZS
Total cost of calcinating 1 t of magnesite	29 000 TZS 30 000 TZS

Note: The initial construction cost was not included in the total cost of calcinating 1 t.

From 1 t of magnesite 0.42 t of magnesia will be obtained. Hence in order to have 1 t of magnesia 2.4 t of magnesite should be calcinated which will cost 72 000 TZS.

ii) Cost of the second alternative:

Cost of 2.4 m^3 of fire wood for 1 t of MgO	3 120 TZS
Transport of fire wood from Vumari to Chambogo	1 140 TZS
Cost of 1 t of magnesia	40 000 TZS
Transport of magnesia to Arusha	6 900 TZS
Total cost of 1 t of magnesia	51 160 TZS 51 000 TZS

The second alternative is the more economical solution.

Thus the cost of 1 t of magnesia is	51 000 TZS
Cost of crushing and sieving 1 t of magnesia to the powder form or particles less than 2 mm diameter	10 000 TZS
	61 000 TZS

Therefore the cost of 1 kg of magnesia powder or particles less than 2 mm is 61 TZS.

7.1.1 Costs when boiling water with magnesia powder in household unit

In order to reduce fluoride from 22 mg/l to 1.5 mg/l the costs will be as follows:

a) When using charcoal:

Charcoal for boiling 20 l of water	35.0 TZS
Magnesia 1 kg for 20 l	61.0 TZS
Sub total	96.0 TZS

Therefore the cost of defluoridation of 1 l from 22 mg/l to 1.5 mg/l is 4.8 TZS.

b) When using fire wood:

0.02 m^3 for boiling 20 l	26.0 TZS
Magnesia 1 kg for 20 l	61.0 TZS
	87.0 TZS

Hence cost of defluoridation of 1 l from 22 mg/l to 1.5 mg/l is 4.4 TZS.

In order to reduce fluoride from 22 mg/l to 8 mg/l the cost will be as follows:

c) When using charcoal:

Charcoal for boiling 20 l	35.0 TZS
Magnesia 0.5 kg for 20 l	30.5 TZS
	65.5 TZS

Cost of reducing fluoride from 22 mg/l to 8 mg/l is 3.3 TZS/l.

d) When using fire wood:

0.02 m3 of fire wood for 20 l	26.0 TZS
Magnesia 0.5 kg for 20 l	30.5 TZS
	56.5 TZS

Cost of reducing fluoride from 22 mg/l to 8 mg/l is 2.8 TZS/l.

All the costs are without adjusting pH value.

On the average it costs 23.5 Tcent to remove 1 mg of fluoride when using charcoal, while when using fire wood it costs 20.7 Tcent on the average.

7.1.2 Costs when filtrating through magnesia

Fluoride was reduced from 22 mg/l to 8 mg/l when 960 l of water was filtered through magnesia particles of 0.20 - 0.63 mm with the quantity of 0.06 m^3.

When 68 kg of magnesia were used to treat 960 l of water, 1 kg treated 14 l. The cost of 1 kg of magnesia is 61 TZS. Therefore the cost of reducing fluoride form 22 mg/l to 8 mg/l will be 4.4 TZS/l, which means 31.4 Tcent for removing 1 mg of fluoride.

This technology seems to be feasible for household only or for small scale project. That is why the cost of operator, and operation and maintenance was not included in the cost analysis. The cost of pH adjustment was also not included.

7.2 Costs when using polyaluminium chloride alone

In the pilot plant the most appropriate dosage of PAC for good and dense flocs in fluoride reduction was 1.48 l/h. Fluoride was removed from 18 mg/l to 1.6 mg/l when the water flow was 202 l/h. This rate implies that the dosage of PAC was 7 ml/l of water.

Cost of PAC is about 120 000 TZS/t CIF Dar-es-Salaam.
Cost of transport from Dar-es-Salaam to Arusha is 30 TZS/km = 20 880 TZS/t.
Cost of PAC at the site 141 000 TZS
Density of PAC = 1 200 kg/m^3
1 t = 800 l
800 l = 141 000 TZS
1 l = 176.25 TZS
0.007 l = 1.23 TZS

Cost of PAC for reducing fluoride from 18 mg/l to 1.6 mg/l is 1.23 TZS/l. The cost is equivalent to 7.5 Tcent for removing 1 mg of fluoride in 1 l of water.

7.3 Costs when using both magnesia and polyaluminium chloride during defluoridation

When magnesia powder solution was used with PAC at the hydraulic rapid mixing chamber, fluoride was reduced from 22 mg/l to 1.5 mg/l. The dosage of PAC was 0.8 mg/l while that of magnesia powder solution was 18 l/h. The flow rate of water was 202 l/h. The concentration of magnesia was 1 l of magnesia powder into 3 l of solution. Hence the dosage of magnesia powder was 6.84 kg/h.

Dosage of magnesia was 6.8 kg/h for 202 l/h raw water, 1 kg for 29.7 l raw water.
Cost of magnesia powder was 11.2 TZS/kg, 2.1 TZS for fluoride removal from 22 mg/l to 1.5 mg/l in 1 l which is equivalent to 10.2 Tcent for removing 1 mg of fluoride in 1 l.
Dosage of PAC was 0.8 l/h in 202 l/h raw water which was 4 ml in 1 l of raw water.
Cost of PAC is 176.25 TZS/l, 4 ml will cost 0.7 TZS.
Cost of combined PAC and magnesia for fluoride removal from 22 mg/l to 1.6 mg/l is 2.8 TZS/l of raw water.

The cost is equivalent to 13.7 Tcent for removing 1 mg of fluoride in 1 l of water. When using combined magnesia and PAC during defluoridation there is no need of using another chemical or compound for adjusting pH, since the pH of treated water was within the acceptable range for domestic use.

The cost of this method could be less if PAC could be manufactured in the country by using sulphuric acid and locally available bauxite or zeolite.

Defluoridation by using PAC alone is cheaper than using magnesia alone. However, magnesia is locally available. The cost of defluoridation by using magnesia could probably be less if electricity could be used in calcination instead of fire wood. There is electricity available at the mining site.

8 CONCLUSIONS AND RECOMMENDATIONS

a) Conclusions

Fluoride removal by filtration through magnesia is more favourable when the raw water is in acidic condition. Magnesia raises the pH value of treated water, thus apart from defluoridation magnesia can be used for raising the pH in water treatment plants.

Disinfection of water by boiling in a household can also be used for defluoridation when boiling it with magnesia powder. Fluoride in raw water is removed from 22 mg/l to 1.1 mg/l (95 %) when boiled with magnesia powder.

The most economical contact time during defluoridation by filtrating through magnesia is 4 - 6 h. Agitation of the filter media increases the efficiency of fluoride reduction.

The most appropriate magnesia particle sizes for defluoridation by filtration are 0.20 - 0.63 mm, at the filtration rate of 0.3 m/h. With these particle sizes and filtration rate, fluoride can be reduced from 22 mg/l to 0.3 mg/l. However, this method is most appropriate for small scale units rather than in large scale projects due to problems of regenerating the media.

PAC as a coagulant forms flocs very fast within 10 - 30 s during defluoridation. The use of local available clay bentonite powder as a coagulant aid improves the flocs settlement in the settling tank. For more efficient fluoride removal and good and dense flocs, the use of magnesia powder is more appropriate.

PAC can reduce fluoride from 22 mg/l to 0.2 mg/l (99 %) but it lowers the pH value to 4.5 which is unacceptable for domestic use. PAC removes fluoride in wide pH range of 2 - 10. The optimum pH value of defluoridation with this chemical is between 5 and 8. Flocs are formed when the pH value is 4.8 and above. However, good and dense flocs are formed when the pH value is between 6 and 8.

The use of combined magnesia and PAC reduces the needed dosage rate of PAC and the quantity of magnesia and it adjusts the pH value of treated water to the acceptable limits. The use of magnesia powder solution with PAC in the hydraulic mixing chamber is the more convenient technique than filtering the raw water through magnesia and then adding PAC. Fluoride is reduced from 22 mg/l to 1.5 mg/l (93 %) and the pH value of about 7 is gained by the former method.

The use of magnesia in defluoridation raises magnesium and sulphate contents in the treated water. It also increases the total hardness as $CaCO_3$ and conductivity. However, it reduces the bicarbonates content. The use of PAC in defluoridation raises chloride content of treated water.

Defluoridation by using magnesia and PAC is very expensive. It costs 30 Tcent, 8 Tcent and 15 Tcent when using magnesia alone, PAC alone and combined magnesia and PAC respectively. Fluoride removal by using magnesia alone is more expensive than defluoridation by using PAC alone. However, magnesia is locally available.

Defluoridation by using combined magnesia and PAC is very encouraging and promising for future use.

b) Recommendations

1. More research on the chemistry of fluoride, on how it reacts and behaves with other elements is essential for obtaining the appropriate fluoride removal technology.

2. People in highly fluoride polluted areas should be educated on the health hazards of fluoride, importance of taking balanced diet and the use of fluoride free tooth paste.

3. Raw water from Ngurdoto is very soft. It has low calcium magnesium content which makes high fluoride concentration possible. Hence people living in this area should be encouraged to take diet rich in calcium and magnesium minerals. These minerals are essential in reducing the absorption of fluoride in the body due to the formation of less soluble complex fluorides.

4. More research is needed to determine the quantity of water required to be boiled with a given quantity of magnesia before it expires for defluoridation.

5. More research should be carried out to find out the best method of regenerating the filter media in order to reduce the cost of defluoridation.

6. The costs of defluoridation by using PAC could be less if PAC could be manufactured in the country by using sulphuric acid and locally available bauxite. The costs of magnesia could also be reduced if calcination of magnesite could be done by using electricity which is available in the mining area instead of fire wood.

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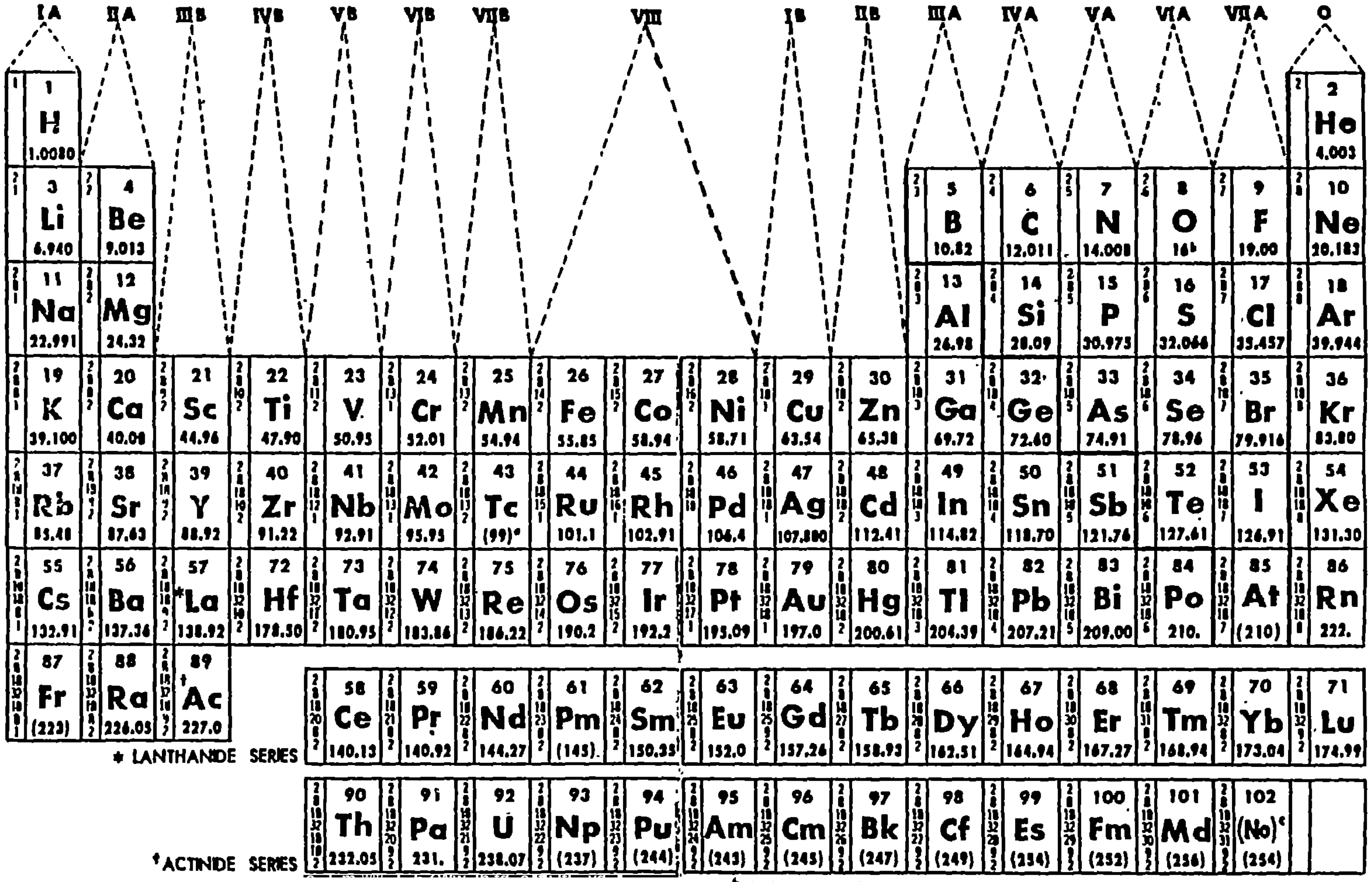

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1 H 1.0080																	2 He 4.003
3 Li 6.940	4 Be 9.013											5 B 10.82	6 C 12.011	7 N 14.008	8 O 16[b]	9 F 19.00	10 Ne 20.183
11 Na 22.991	12 Mg 24.32											13 Al 26.98	14 Si 28.09	15 P 30.975	16 S 32.066	17 Cl 35.457	18 Ar 39.944
19 K 39.100	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.94	26 Fe 55.85	27 Co 58.94	28 Ni 58.71	29 Cu 63.54	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.916	36 Kr 83.80
37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc (99)[a]	44 Ru 101.1	45 Rh 102.91	46 Pd 106.4	47 Ag 107.880	48 Cd 112.41	49 In 114.82	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.91	54 Xe 131.30
55 Cs 132.91	56 Ba 137.36	57 *La 138.92	72 Hf 178.50	73 Ta 180.95	74 W 183.86	75 Re 186.22	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 197.0	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 209.00	84 Po 210.	85 At (210)	86 Rn 222.
87 Fr (223)	88 Ra 226.05	89 †Ac 227.0															
* LANTHANIDE SERIES				58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Pm (145)	62 Sm 150.35	63 Eu 152.0	64 Gd 157.26	65 Tb 158.93	66 Dy 162.51	67 Ho 164.94	68 Er 167.27	69 Tm 168.94	70 Yb 173.04	71 Lu 174.99
†ACTINIDE SERIES				90 Th 232.05	91 Pa 231.	92 U 238.07	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (245)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (252)	101 Md (256)	102 (No)[c] (254)	

Atomic weights corrected to conform with 1957 International committee values.

[a] ( )Numbers in parentheses indicate mass number of most stable known isotope.

[b] The long-accepted standard of atomic weights, O = 16, is in the process of being changed. See page 403.

[c] Name and symbol are not officially accepted. See footnote to Table 3.1.

Periodic table of the elements (Keenan et al 1963).

APPENDIX 2

Atomic weights of the elements (Keenan et al 1963).

	Symbol	Atomic Number	Atomic Weight		Symbol	Atomic Number	Atomic Weight[a]
Actinium	Ac	89	227	Mercury	Hg	80	200.61
Aluminum	Al	13	26.98	Molybdenum	Mo	42	95.95
Americium	Am	95	[243]	Neodymium	Nd	60	144.27
Antimony	Sb	51	121.76	Neon	Ne	10	20.183
Argon	Ar	18	39.944	Neptunium	Np	93	[237]
Arsenic	As	33	74.91	Nickel	Ni	28	58.71
Astatine	At	85	[210]	Niobium	Nb	41	92.91
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Berkelium	Bk	97	[247]	Nobelium	(No)[b]	102	[254]
Beryllium	Be	4	9.013	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16[c]
Boron	B	5	10.82	Palladium	Pd	46	106.4
Bromine	Br	35	79.916	Phosphorus	P	15	30.975
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.09
Calcium	Ca	20	40.08	Plutonium	Pu	94	[244]
Californium	Cf	98	[249]	Polonium	Po	84	210
Carbon	C	6	12.011	Potassium	K	19	39.100
Cerium	Ce	58	140.13	Praseodymium	Pr	59	140.92
Cesium	Cs	55	132.91	Promethium	Pm	61	[145]
Chlorine	Cl	17	35.457	Protactinium	Pa	91	231
Chromium	Cr	24	52.01	Radium	Ra	88	226.05
Cobalt	Co	27	58.94	Radon	Rn	86	222
Copper	Cu	29	63.54	Rhenium	Re	75	186.22
Curium	Cm	96	[245]	Rhodium	Rh	45	102.91
Dysprosium	Dy	66	162.51	Rubidium	Rb	37	85.48
Einsteinium	Es	99	[254]	Ruthenium	Ru	44	101.1
Erbium	Er	68	167.27	Samarium	Sm	62	150.35
Europium	Eu	63	152.0	Scandium	Sc	21	44.96
Fermium	Fm	100	[252]	Selenium	Se	34	78 96
Fluorine	F	9	19.00	Silicon	Si	14	28.09
Francium	Fr	87	[223]	Silver	Ag	47	107.880
Gadolinium	Gd	64	157.26	Sodium	Na	11	22.991
Gallium	Ga	31	69.72	Strontium	Sr	38	87.63
Germanium	Ge	32	72.60	Sulfur	S	16	32.066[d]
Gold	Au	79	197.0	Tantalum	Ta	73	180.95
Hafnium	Hf	72	178.50	Technetium	Tc	43	[99]
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	164.94	Terbium	Tb	65	158.93
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.39
Indium	In	49	114.82	Thorium	Th	90	232.05
Iodine	I	53	126.91	Thulium	Tm	69	168.94
Indium	Ir	77	192.2	Tin	Sn	50	118 70
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.80	Tungsten	W	74	183.86
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.30
Lutetium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54 94	Zinc	Zn	30	65.38
Mendelevium	Md	101	[256]	Zirconium	Zr	40	91 22

APPENDIX 3

Drinking Water Standards

(Cairncross and Feachem 1983, Twort et al 1987 and Tanzania Water Utilization 1981)

Description of parameter	Undesirable effect that may be produced	Units	WHO standards		Tanzanian temporary standards
			Highest desirable level	Maximum permissible level	
pH	Taste, corrosion		6.5 - 8.5	6.5 - 9.2	6.5 - 9.2
Colour	Discolouration	^{o}Hazen	5	50	5
Odour	Odour		*)	*)	*)
Taste	Taste		*)	*)	*)
Suspended matter	Turbidity, possibly gastrointestinal irritation	NTU	5	25	30
Total dissolved solids	Taste, gastrointestinal irritation	mg/l	500	1 500	2 000
Phenolic compounds (as phenol)	Taste	mg/l	0.001	0.002	0.002
Total hardness as $CaCO_3$	Excessive scale formation	mg/l	100	500	600
Calcium (as Ca)	Excessive scale formation	mg/l	75	200	300
Chloride (as Cl)	Taste, corrosion in hot water system	mg/l	200	600	800
Copper (as Cu)	Bitter taste, discolouration and corrosion of pipes, fittings and utensils	mg/l	0.05	1.5	3.0
Iron (total as Fe)	Taste, discolouration, deposits and growth of iron bacteria turbidity	mg/l	0.1	1.0	1.0
Magnesium (as Mg)	Hardness, taste, gastrointestinal irritation in the presence of sulphate	mg/l	≥ 30 if there 250 mg/l sulphate	150	
Manganese (as Mn)	Taste, discolouration deposits in pipes turbidity	mg/l	0.05	0.5	0.5
Sulphate (as SO_4)	Gastrointestinal irritation when magnesium for sodium	mg/l	200	400	600
Zinc (as Zn)	Bitter taste, opalscence and sand-like deposits	mg/l	5.0	15	15
Aluminium (as Al)	It can affect brain	mg/l	0.05	0.2	
Nitrate	Harmful to infants and young children	mg/l	10	30	100
Fluoride	Fluorosis, knottling of the teeth, skeletal damage	mg/l		1.5	8
Lead	Toxic	mg/l	0.05	0.1	0.1

*) = unobjectionable