EFFECT OF MINERALOGICAL COMPOSITION OF CLAY AS A DEFLUORIDATING MEDIA FOR DRINKING WATER

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ABSTRACT

A number of studies have been made to assess excessive Fluoride (F) removal from drinking water. Recent findings indicate that natural clays have the ability of reducing Fluoride from water. In this paper, findings on studies on F- binding potentiality of locally available clay are discussed. The results indicate that clays burnt at temperatures below 200 ºC are best suitable for defluoridation of potable water. Batch experiments into natural water of different initial concentrations between 13 mg/l and 9.6 mg/l have shown a reduction of up to 3 mg/l depending on the contact time. A steady state was reached in most cases after 60 minutes. The pH and residual fluoride were monitored at intervals. A substantial increase in pH was observed as more and more F- ions were removed from the water.

OCCURRENCE AND EFFECTS OF EXCESSIVE FLUORIDE

Fluoride as a natural constituent of some waters has been shown to be very essential in animal bone and teeth development if it is within the required amounts. If excessive, fluoride has detrimental effects which culminate in endemic fluorosis i.e. mottling of teeth stiffness of joints and crippling.

Comprehensive research has been carried out in different parts of the world to determine methods and media which could be used to reduce excessive fluoride in drinking water sources. Most of the methods known today can be categorised into two groups i.e.

- precipitation methods - where use is made of media such as alum, calcium chloride etc. Studies at the National Environmental

Engineering Research Institute (NEERI) in India recommended the Nalgonda Technique as low priced and ease to perform [1].

• The adsorption and iron-exchange methods which use media such as activated alumina, activated bauxite, bone char, clay pots etc.

Fluorine as a halogen is more reactive than the other halogens ie. chlorine, bromine, iodine and astatine. In its free state, it displaces the other halogens from their compounds and also displaces oxygen from most salts, oxides and acids. Fluorine acts as an electron acceptor resulting in the formation of fluorides.

Fluoride occurs in rocks in a compound form the most common being the compounds of phosphates and silicates. (Table 1).

Table 1: Fluoride bearing mineral Compounds

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)	(Ca La Dy) F_3	29.00	19.49 - 29.44
Cryolite	$Na_3 ALF_6$	54.29	53.55 - 54.88
B. Phosphates:			
Fluor-apatite	Ca5 $(PO_4)_3$ F	3.80	2.57 - 5.60
Wagnerite	Mg2 PO4F	11.68	5.06 - 11.48
Triplite	(Min. Fe, Mg(a)$_2$FPO4	-	6.02 - 9.09
Amblygonite	(F, OH)	12.85	0.57 - 11.26
C. Silicates:			
Topaz	Al (F, OH)$_2$ SiO$_4$	20.70	13.23 - 20.37
Humitegroup	Mg (OH, F)$_2$nMg$_2$SiO$_4$	-	Tr - 13.55
D. Mica groups		-	
Muscovite	Potash Mica	-	0.00 - 2.06
Phlogopite	Magnessium Mica	-	0.56 - 9.20
Biotite	Iron-Magnesium Mica	-	0.32 - 5.03
Lepidolite	Lithium Mica	-	4.39 - 8.09

Most of the above mentioned Fluoride minerals are nearly insoluble in water, but dissolution occurs both in ground and surface water only when conditions (especially pH) favour their solution. In Tanzania, these

conditions are mainly found along the Rift Valley and around the volcanic mountains of Kilimanjaro and Meru.

A number of studies have been made to assess the Fluoride binding potentiality of fired clay. Most researchers indicate that burnt clay has a good removal quality. Mjengera [2] reported a fluoride reduction of between 16% to 76% depending on the retention time, while Gitonga [3] reported reduction of 45% in 24 hours.

In general most researchers have concluded that the processes involved and the binding capacity of clays is slow.

CHARACTERISTICS OF CLAY MINERALS

Most soil classification systems arbitrarily define clay particles in terms of effective diameter i.e. less than two microns (0.002 mm). The most important grain property is the mineralogical composition. In small particles the electrical forces acting on the surface of the particle are greater than the gravitational forces. These colloidal particles which consist mainly of clay minerals; are built up of two dimensional sheets which are stacked one upon another. The layers are twofold:-

(i)   A silicon-oxygen sheet formed by linking tetrahedral $SiO4$ groups. The composition of this layer is a multiple of Si_2O_5 or with attached hydrogen $Si_2O_3(OH)_2$.

(ii)   An octahedral layer in which a metal ion (Al or Mg) lies within a group of six hydroxyls which are arranged at the corners of an octahedron. Adjoining octahedra are linked by sharing hydroxyls. Such an octahedral layer has the composition $Al_2(OH)_6$ or $Mg(OH)_6$. (the minerals gibbsite and brucite respectively) in addition substitution may take place for the metal ion for example Fe^{3+} Mg^{2+} or Al^{3+}.

The three most important clay minerals are montmorillonite, Illite and kaolinite which are crystalline hydrous aluminosilicates. Montmorillonite presents most of the expansive soil problems; due to absorption of water.

From the mineralogical standpoint, the magnitude of expansion depends

upon the kind and amount of minerals present, their exchangeable ions, electrolyte content of aqueous phase and the internal structure.

FORMATION OF CLAY MINERALS:

The clay minerals are formed through a complicated process from an assortment of parent materials. The parent materials include feldspar, mica and limestone. The alteration process includes disintegration, oxidation, hydration and leaching.

Tourtelot [4] pointed out the setting for montmorillonite formation as an extreme disintegration, strong hydration and restricted leaching. The leaching is restricted to allow magnesium, calcium and iron cations to accumulate in the system. Thus formation of montmorillonitic minerals is aided by an alkaline environment; pressure of magnesium ions and lack of leaching.

Such favourable conditions are found in semi-arid regions with relatively low rainfall ie where evaporation exceeds precipitation. Bentonite is a clay composed primarily of montimorillonite which is formed through a chemical weathering of volcanic ash. Swelling clays are referred to as bentonitic soils. Since commercial bentonite is white, the white calcium streaks present in stiff clays are mistaken for bentonite. Clay with abundance of calcium seldom exhibit swelling characteristics.

DEFLUORIDATION OF DRINKING WATER

Fluoride may be found in all natural waters even in precipitation. In most inland lakes and rivers, fluoride concentration may be less than 0.3 ppm. High values in surface water have been recorded in Nakuru, Kenya (2800 mg/l. F) [5] and Nanyaro et al [6] reported values as high as 600 mg/l in Arusha - Tanzania.

Prolonged intake of high-fluoride water may create problems such as dental, and skeletal fluorosis in human and animal population.

According to WHO, drinking water of adequate quality should not contain more than 1.5 mg/l Fluoride (WHO, 1984) and for the tropics where the rate of water intake is high the recommended fluoride concentration of

drinking water should be substantially reduced. A general formula was proposed by Galagan [7] where the "optimum" Fluoride concentration is given as:

$$Optimum \ F^- \ level = \left(\frac{0.34}{-0.038 + (0.0062 \ x \ mean \ max. \ temp.)(^oF)} \right)$$

High fluoride containing water should be defluoridated to render it potable. High technology water treatment is not affordable in rural areas of Africa where priority should be given to development of simple devices using locally available media for defluoridation, and preferably household based. Table 2 shows requirements for homebased defluoridation methods.

Table 2: Qualities of household defluoridation methods.

-	low cost
-	low maintenance and level of technology simple design
-	capable to reduce fluoride to low levels
-	resulting water at acceptable quality

CLAY AS A DEFLUORIDATING MEDIA

Clay was used as a defluoridating media. Experiments were carried out in a laboratory using jar tests which included a multiple stirrer in one litre beakers, a shaker and a column for filtration experiments.

Clay samples from two sources were used. One sample was from Mbambabay near lake Nyasa (Referred to as sample A) and the second sample was from Kisarawe along the coast near Dar es Salaam (Sample B). Mineralogical analysis of the samples from the two sources were as shown in table 3:

Table 3: Mineralogical Composition of Clay samples.

Sample A	Sample B
Quarzt fractured 3%	Iron oxide 95%
Calcite ($CaCO_3$) - 7%	oolitic crystals:
Hydrated iron oxide Fe(OH) and Limonite	Reddish brown.
$2Fe_2O_3.3H_2O$ - 89%	Quarzt and
Accessory minerals 1%	Accessory Minerals 5%

EXPERIMENTAL PROCEDURE AND SET-UP

Samples were collected from the two sources, and cast into small cubes of 50mm by 50mm. The samples were air dried for 48 hours. Some of the cubes were then oven dried and burnt (fired) for different durations ranging from 5 to 60 minutes at temperatures ranging from 50°C to 300°C. The burnt cubes were crushed and sieved. Different sizes were used in batch experiments at different dosages ranging from 25g/l to 200 g/l for different contact times.

The water used was natural from a stream nearArusha. It had initial fluoride concentration of 9.6 mg/l. Samples of 5 ml were extracted from the beaker using a pipette at different time intervals. After the addition of 5 ml TISAB (Total Ionic Strength Adjusting Buffer) the residual fluoride was measured using the selective combined electrode (orion) and the millivolts read according to standard procedure. During the extraction, the pH of the solution was also checked.

RESULTS AND DISCUSSIONS

Effect of Contact time and Clay burning temperature

A summary of the results of the experiments performed is given in graphical form fig.1. Clay particles were of diameter 2mm < d < 2.8mm and observed for a max. of 60 minutes.
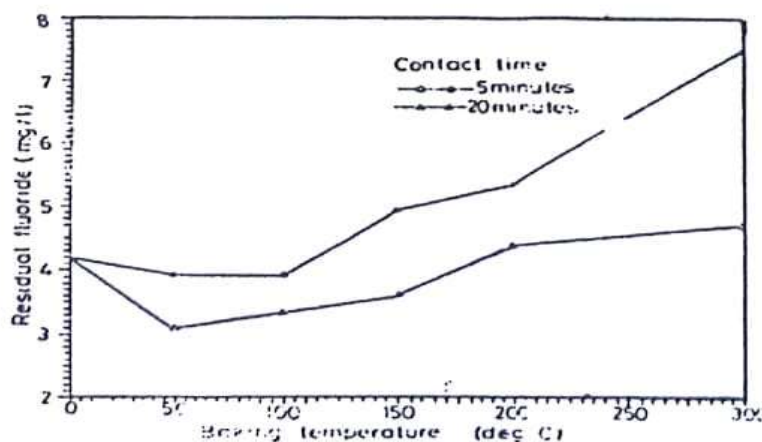

Fig.1: Residual Fluoride versus burning temperature for different contact times

The removal capacity of the clay improves with increased contact time but rising the burning temperature above 100ᵒC reduces the clays ability to reduce Fluoride from water.

However, contact times above 20 minutes show no appreciable increase in removal of Fluoride in the tested samples. The reaction is an adsorption case and such reactions are very fast; completed within the initial few minutes. Retention time longer than 20 minutes will not result in any appreciable Fluoride removal. In practice it is worth noting that a treatment process will not take longer than 20 minutes.
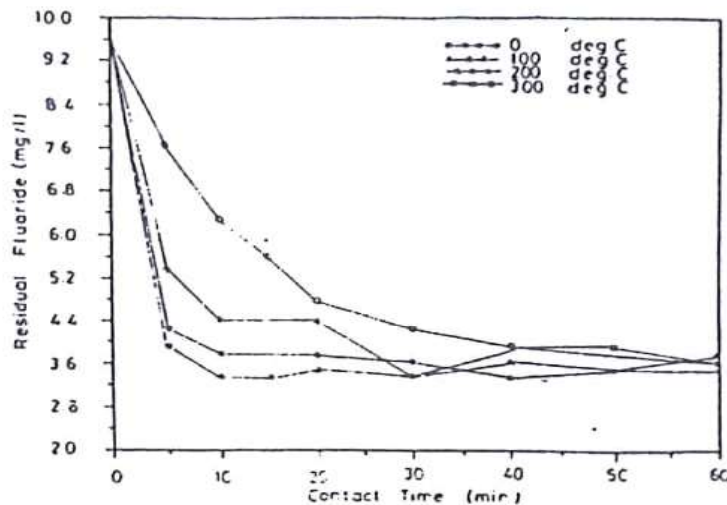

Fig.2: **Residual Fluoride for different contact times and burning temperatures.**

Effect of clay dosage on removal of fluoride.

Residual fluoride was measured for different dosages of clay in a litre of water for a retention time of 30 minutes.

The fluoride uptake by unit weight of clay (mg/g) was calculated after 20 minutes contact time and plotted versus residual fluoride in logarithmic form in fig. 4 From the plot the Freundlich adsorption isotherm relation holds and the equation is $Y = 0.5F^{-k} - 1.4$. Where Y is the logarithm of fluoride uptake per unit weight and F is the logarithm of the optimum residual Fluoride in mg/L. The capacity constant $k = 0.04$ and intensity constant $n = 2$.
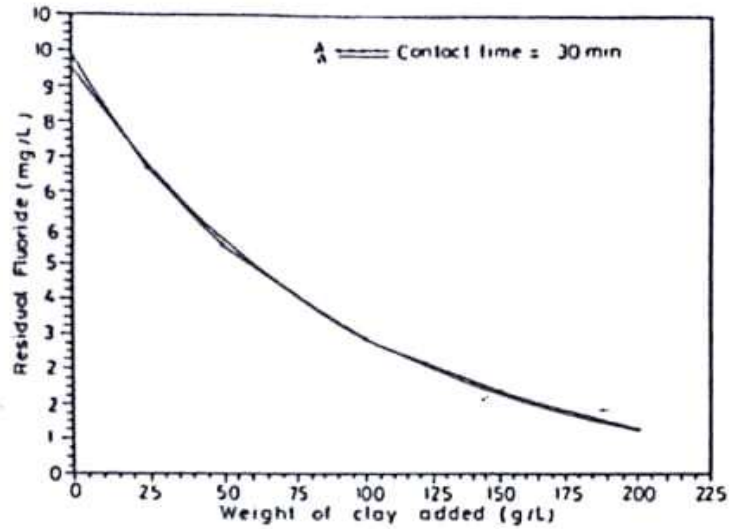
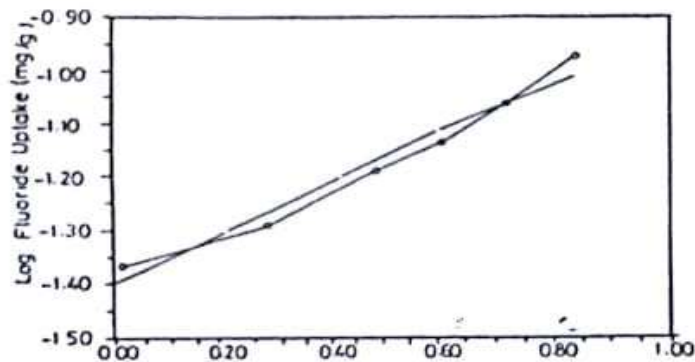Fig.3:Residual fluoride versus clay dosage

Fig.4: Freundlich adsorption isotherm

Effect of the mineralogical composition

Results from the samples backed at 100 °C from the two clays show that sample B which composed of mainly Iron Oxide (95% by volume) and oolitic crystals had better fluoride removal ability

Sample A was composed mainly of angular grains of quartz and feldspar (k-feldspar and plagioclase). Feldspar and quartz grains are floating in a matrix of clay minerals mainly kaolinitic.

The binding capacity of the rehydrated iron oxide in sample B is higher compared to that in sample A where the oxide is hydrated and mixed up

with calcite. Similar observations have been made in Cameroon where high iron containing lateritic clays were used [8].
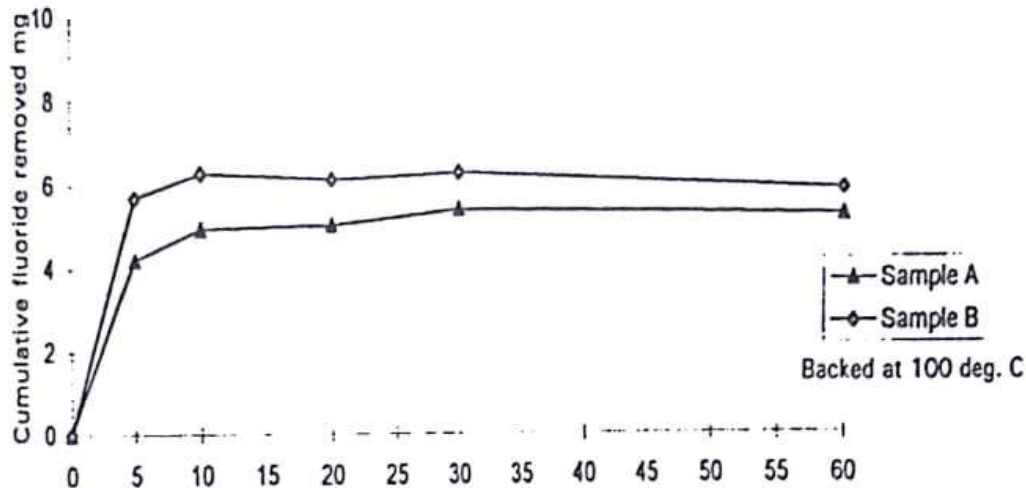

Fig. 5: Cumulative Fluoride removal for samples A and B

Effect of Initial pH of Raw water

Significant higher removals were observed when the pH values were in the acidic range ie low pH values. Initial pH values were lowered by using sulphuric acid (H_2SO_4) and higher values were obtained by using potassium hydroxide. At unadjusted pH of 8.6 the clay reduced the fluoride concentration in water from 22.5 mg/L to 13.6 mg/L ie 39% removal. When the pH was lowered to 1.3 the fluoride removal was 75% The effect of initial pH of raw water on the fluoride removal is shown in fig. 6. During the fluoride removal, the water pH changed from 5.0 to about 7.5 in 4 hours.

It was also noted that during the fluoride removal, the pH of the water increased with retention time. An initial pH value of 5 was raised to 7.5 after 4 hours retention time. It has been reported that fluoride containing minerals eg. apatite or mica can replace hydroxyl groups (reversibly). Fluoride and hydroxyl groups have almost identical valence and radius 1.3Aº for F- and 1.4Aº for (OH)- [9]. It is possible the decrease in amount of fluoride removed with high pH values is a result of the substitution of F and OH or vice versa and will compete for available sites on the adsorbent.
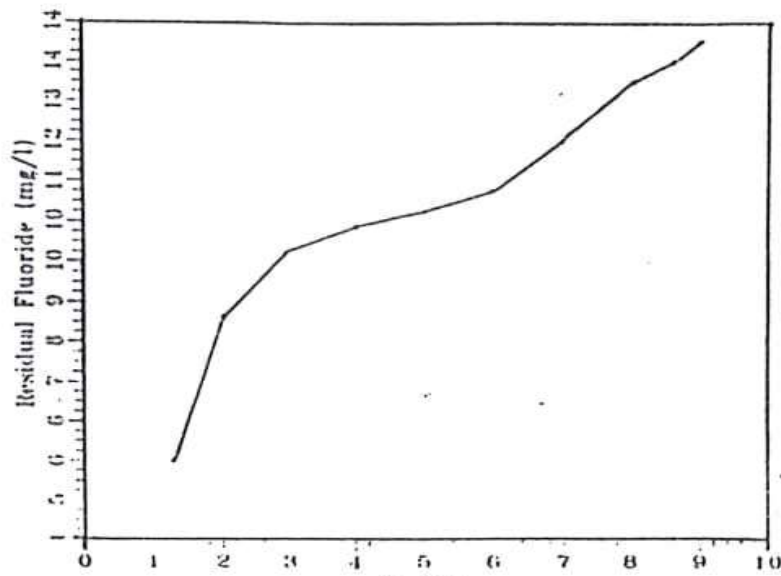
Fig. 6: Residual Fluoride versus initial pH values.

CONCLUSIONS AND DISCUSSIONS

The results show that red clay can be used as a defluoridating media. To reduce the problems of turbidity in the treated water, the clay can be baked at temperatures up to 100ͻC. Increase in the baking temperature of the clay reduces the fluoride removal efficiency of the media due to clay losing its structure. The fluoride removal process tends to be a physical adsorption where molecules are held on the adsorbent's surface on backing, the porosity is destroyed affecting the sites for fluoride adsorption. There exists an exponential relationship between the residual fluoride in the water and the weight of clay media used.

The clay samples used were collected from the surface (top soil) and consists of Iron oxide as the major constituent. Lateritic clays are rampant in many parts of the tropics where they are mainly used in the building industry as burnt bricks and in making pottery. However, since unburnt clay can also adsorb fluoride from water, it would be expected that clays collected from fluoride infected areas will consequently have low removal capabilities.

Phantumvanit et al [10] recommend that household defluoridators should be capable of lowering the fluoride content to about 0.5 mg/l. The results obtained from the use of the burnt clay media on water with 9.6 mg/l show

that the fluoride level can be reduced to about 3.5 mg/l in one hour which is below the Tanzania Temporary standard for drinking water. When the contact time was longer than 60 minutes, the residual fluoride in water started increasing indicating a negative fluoride uptake by the media.

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