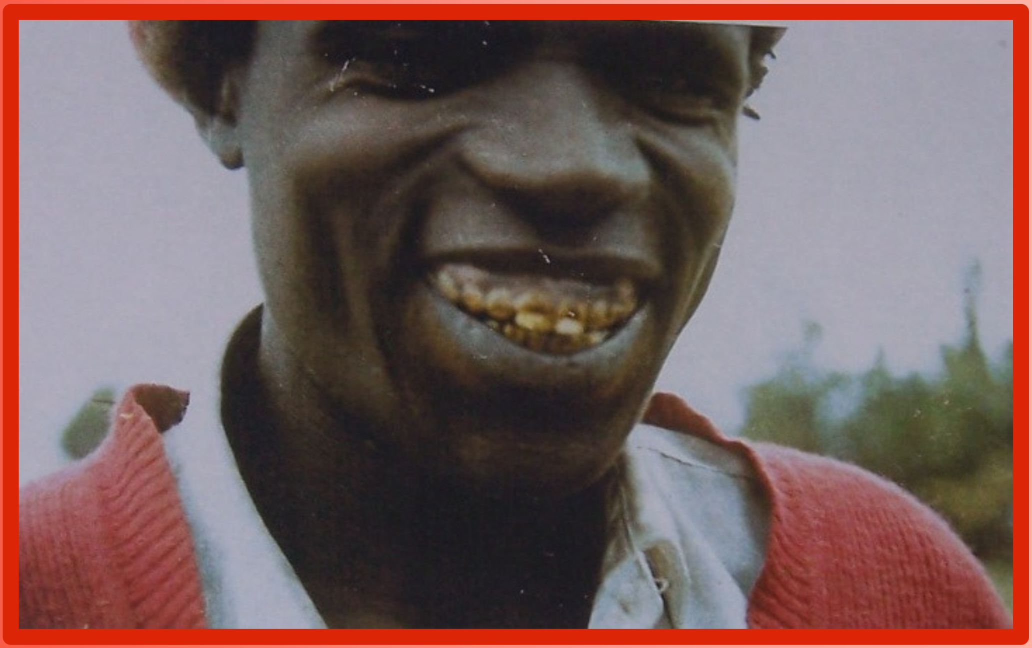
1st Workshop on Fluorosis & Defluoridation

ISFR

Proceedings of the 1st International Workshop on Fluorosis Prevention and Defluoridation of Water



Ngurdoto, Tanzania
October 18-21, 1995

Edited by:
Eli Dahi
&
Henrik Breghøj

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Dr Bruce Spittle,

727 Brighton Road, Ocean View,

Dunedin 9035, New Zealand.

Email: spittle@es.co.nzhttp://www.fluorideresearch.org/

PREFACE

During the years 1991-1995 The Centre for Developing Countries at the Technical University of Denmark carried out a Defluoridation Technology Research Project in collaboration with the University of Dar es Salaam and the Ministry of Water, Energy, and Minerals in Tanzania. The project was sponsored by the Danish International Development Agency DANIDA, under the so called Enhancement of Research Capacity programme, Enreca.

As a part of this collaboration annual seminars were arranged. However, in 1994 it was decided that the project should internationalise these seminars in order to facilitate professional interactions among researchers working within the field. Furthermore, that this interaction, through Enreca-Danida funds, should include professionals from other developing countries. Thus the 1st International Workshop on Fluorosis and Defluoridation of Water was held in Arusha, 18-22 October 1995, with participation from Denmark, Tanzania, Norway, The Netherlands, Ethiopia, Sudan, India, Thailand and China. During this Workshop it was decided to publish the proceedings in collaboration with the International Society for Fluoride Research, ISFR. Furthermore, to establish an International Committee for the 2nd International Workshop which will be held in Addis Ababa, 19-22 November 1997.

On behalf of the Workshop Committee I would like to address a thank to Danida for sponsoring the workshop, to the University of Dar es Salaam and the Ministry of Water, Energy, and Minerals in Tanzania for provision of the logistic on site, and to the International Society for Fluoride Research for support on the dissemination of the Workshop Proceeding. It is our hope that this workshop will be followed by others, until appropriate solutions to the fluoride problems in the affected regions are identified, optimised and implemented.

Eli Dahi

Chairman of the International Committee.

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SUITABILITY OF THE TF-DENTAL FLUOROSIS INDEX FOR DETECTION OF FLUORIDE SOURCES

L Mabelya* , MA van't Hof**, WH van Palenstein Helderman* and KG König**

SUMMARY: A study was conducted in three Tanzanian populations to investigate the prevalence and severity of dental fluorosis using the Thylstrup-Fejerskov Index (TFI). The study also aimed at establishing to which extent the TFI score follows an interval scale. The distribution of TFI scores for the 3 sub-samples was analyzed as one population. A bimodal distribution of the TFI scores was observed. When the analysis was done separately for each of the sub-samples, the distribution in the low fluorosis sub-sample (Tanga) was skewed, in the high fluorosis (Iramba) it was normal while the moderate fluorosis sub-sample (Singida) demonstrated a bimodal distribution similar to that observed in the overall sample. The bimodal distribution in the moderate fluorosis area was considered to be indicative of possible sub-samples with different fluoride exposures. In the present study the sub-sample from the moderate fluorosis area was sub-divided further into 4 groups according to the geographical locations. Among children in Sepuka 54% had fluorosis and the mean TFI score was 1.9, while 81% of the children in Kinyeto had fluorosis and the mean TFI score was 3.3. Samples of "Magadi" (a salt commonly used) were collected from Sepuka and Kinyeto. The fluoride content of the salt collected from the two locations differed greatly explaining the difference in fluoride exposure for the two groups. Application of the TFI was found to allow detection of possible variations in fluoride exposure therefore allowing to track other sources of fluoride in addition to water-borne fluoride.

Key words: Thylstrup-Fejerskov Index, fluorosis, fluoride, magadi.

INTRODUCTION

When an Index with an interval scale is used to detect exposure to a variable which is rather on a uniform level, two clear cut situations can occur: (a) if the exposure is generally high, a symmetric distribution should be observed; (b), in the case of very low exposure a skewed distribution should be found.

The Thylstrup and Fejerskov Index[1] of dental fluorosis was applied in three populations in Tanzania. The combined data demonstrated a bimodal distribution of dental fluorosis. When the data were separately analyzed for each population, the population with low dental fluorosis (Tanga) demonstrated a skewed distribution, the population with high dental fluorosis (Iramba) demonstrated a symmetric distribution, while the population with moderate dental fluorosis (Singida) demonstrated a bimodal distribution similar to that observed for the 3 mixed populations. The bimodal distribution in the moderate fluorosis population was considered to be indicative of a mixed sub-group with different fluoride exposure. To detect whether there was difference in exposure to fluoride, the population with moderate fluorosis was divided into 4 sub-groups corresponding to the location of the schools.

* Faculty of Dentistry, University of Dar es Salaam, PO Box 64014, Dar es Salaam, Tanzania.
** Faculty of Medical Sciences, University of Nijmegen, The Netherlands.

The purpose of this study was to examine to which extent the TFI was close to an interval scale and to test the suability of the TFI to detect groups with different exposure to fluoride.

MATERIALS AND METHODS

Three areas in Tanzania which had low fluoride concentrations in drinking water were identified and were investigated for dental fluorosis. The number of children who participated in this study was 1556, of which 520 were from Tanga, 586 were from Singida and 450 were from Iramba. All 11 to 18 years old children in the study population were interrogated about their intake of fluoride containing foods and drinks which was measured using a one week recall questionnaire. The fluoride intake was estimated on the basis of reported frequencies of intake of certain foods and drinks mainly fish, tea, magadi, fluoridated tooth pastes and fluoride tablets. The frequency of milk intake was asked as it is known to slow and reduce the rate of fluoride uptake.

The fluoride content of the drinking water was measured from water samples collected over a period of about one year from most drinking water sources. Magadi samples were collected from two villages out of five in Singida and in Iramba from three out of four villages. Samples of magadi were collected from the household stocks and from village markets which served the study population. A total of 35 samples were collected from Singida and 9 samples from Iramba. Fluoride concentrations in magadi were determined by laboratory analysis. Detailed information on dietary fluoride sources which was later compared to dental fluorosis conditions was collected from Sepuka and Kinyeto in Singida District and in Kiomobi in Iramba District.

RESULTS

Reproducibility of the TFI is reported in another publication using the same data[2]. The prevalence of dental fluorosis for the studied population was 72% and the mean TFI score was 2.7. The prevalence of dental fluorosis and the mean TFI score varied between the sub-groups (Table 1).

TABLE 1. Prevalence of dental fluorosis and fluoride in food additive (salt - magadi).

Location	Prevalence of dental fluorosis (%)	Mean TFI	Fluoride in magadi (μg-F/g)
Sepuka	53.8	1.9	111
Kinyeto	80.6	3.3	1160

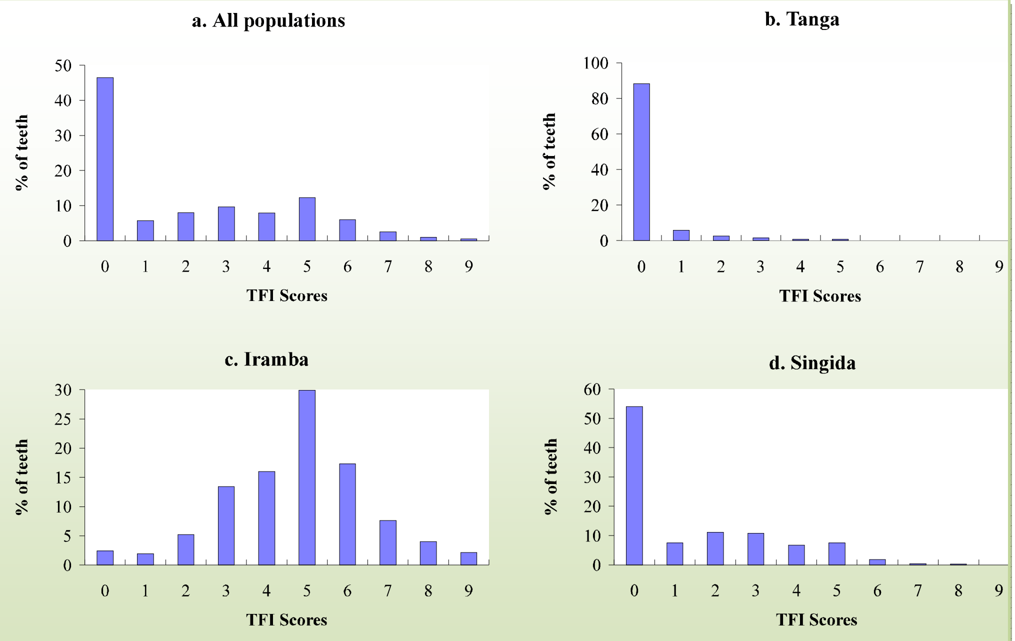

FIGURE 1. Distribution of TFI Scores. a: For all the three populations. b: In Tanga at sea level. c: In Iramba at 1,500 m altitude. d: In Singida at 1,500 m altitude.

The initial stage in analyzing and interpreting the data in this study was to establish the distribution of the TFI scores for all three populations. A bimodal distribution was observed (Figure 1a). The second stage was again to establish the distribution of TFI scores for each community separately. A skewed distribution was seen for the population from Tanga (Figure 1b), and a normal distribution for the population from Iramba (Figure 1c) whereas a bimodal distribution was observed for the population from Singida (Figure 1d). It was decided to further analyze the data from Singida. To determine whether the TFI was closer to an interval scale, two places in Singida (Sepuka and Kinyeto) were separated from the overall Singida population because variation of fluoride ingested through the volcanic salt (magadi) was known (Table 1).

The prevalence of dental fluorosis was 53.8% in Sepuka and 80.6% in Kinyeto with mean mouth scores of TFI 1.9 (st.dev. 2.1) and 3.3 (st.dev. 2.2) for Sepuka and Kinyeto respectively (Table 1).

In Sepuka most of the teeth were not affected by dental fluorosis and the majority of the teeth which were affected had TFI scores between 1 and 2. In Kinyeto the majority of the teeth were affected with fluorosis and the predominant TFI scores were between 1 and 5. Figure 2 shows the distribution of TFI scores in Kinyeto and Sepuka.

DISCUSSION

More teeth were affected by dental fluorosis in Kinyeto than in Sepuka and higher TFI scores were observed in Kinyeto (Figure 2). Since teeth are not equally exposed to the effect of fluoride an analysis of the prevalence of dental fluorosis was carried out and found different in Sepuka and Kinyeto. Sepuka had lower prevalence of dental fluorosis as compared to Kinyeto. The severity of the condition of mouth TFI scores for each sup-group corresponded to the increasing prevalence of dental fluorosis. The number of subjects with TFI ≥5 was found to be high in Kinyeto lower in Sepuka.

In an attempt to explain the within population variation, which was detected after splitting the population, dietary history and fluoride concentration in magadi samples were used.

The mean weekly frequency of magadi consumption as reported by mothers from this population was 4.5 times (st.dev. 1.4). Fluoride concentration in magadi varied, the median was 112 mg-F/L and 174 mg-F/L, while the mean was 111 mg-F/L and 1160 mg-F/L for magadi collected from Sepuka and Kinyeto respectively. The similar mean and median fluoride concentration in samples obtained from Sepuka indicated that there was little variation in fluoride concentration in the magadi, whereas the mean and median fluoride content in magadi samples from Kinyeto varied markedly.

Thus the results indicate that the relatively low prevalence of dental fluorosis in Sepuka is attributed to the low exposure to fluoride from both water and magadi, while the high prevalence and more severe dental fluorosis observed in Kinyeto is attributed to exposure to magadi with relatively high fluoride concentration.

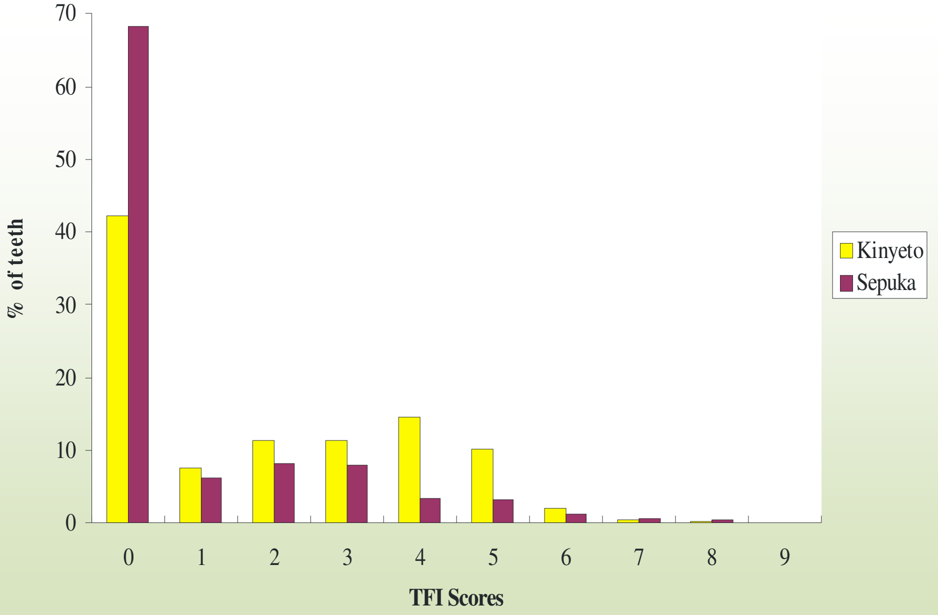

FIGURE 2. Distribution of teeth according to TFI scores in Kinyeto and Sepuka districts of Singida.

The prevalence and severity of dental fluorosis was found to vary between two locations, Sepuka demonstrated low prevalence and severity and Kinyeto was found to have more dental fluorosis both reported by prevalence and severity. The severity correspondingly increased with increase of the prevalence of dental fluorosis.

In conclusion, the TFI has demonstrated the ability to detect variation in fluoride exposure between populations due to its ability to categorize clinical changes of dental fluorosis logically and precisely. By utilizing the TFI it is considered possible to identity variations to fluoride exposure.

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FLUORIDE LEVELS IN WATER AND ENDEMIC FLUOROSIS IN ETHIOPIAN RIFT VALLEY

R Tekle-Haimanot*, A Fekadu, B Bushera and Y Mekonnen

SUMMARY: The fluoride content of drinking water and the prevalence of endemic fluorosis were assessed and correlated in large farms, villages and towns of the Ethiopian Rift Valley. The fluoride level of drinking water collected from deep wells ranged from 1.5 mg-F/L to 36 mg-F/L (mean 10.0 mg-F/L). Dental fluorosis was found to be widespread among children, mainly in the age group of 10 to 14 years. Skeletal and crippling fluorosis were found predominantly among male workers of the sugar estates within the Rift Valley. Skeletal fluorosis invariably occurred in those that were consuming water with fluoride levels of more than 4 mg-F/L for over 10 years. The most common incapacitating neurological complication of crippling skeletal fluorosis was cervical radiculo-myelopathy.

Key Words: Fluoride, Ethiopia, Rift Valley, fluorosis, crippling skeletal fluorosis.

INTRODUCTION

More than 260 million people all over the world consume drinking water with a fluoride concentration higher than 1.0 mg-F/L. The majority of these people live in tropical countries1. Fourteen countries in Africa, eight in Asia and the Middle East and six in the Americas face the problem of fluoride concentration above 1.5 mg-F/L in drinking water2. Many of these countries are confronted with the problems of endemic dental and osteofluorosis.

Osteofluorosis and its complications, related to high-fluoride water consumption, have particularly gained attention in India3-5. Similar reports, but mainly on endemic dental fluorosis, have appeared from the African continent, the majority from African Rift Valley regions[6–10].

The East African Rift Valley which cuts through Ethiopia is geomorphologically still an active volcanic region. The volcanic rocks particularly in the young basalt contain high concentrations of fluoride and fluorapatite. Large fault systems in the Valley create conditions that allow very deep percolation of infiltrating surface water. The floor of the Rift Valley which is characterized by high hydrothermal activity accelerates the solubility of fluorite. The hot climate and high fluoride water bed of the Rift Valley therefore favour the development of endemic fluorosis.

The water supplies in the Ethiopian Rift Valley come mainly from boreholes with depths from 10 to 100 meters; the majority are deep boreholes. This study was carried out to determine the fluoride content of the water supply systems in the Ethiopia part of the Rift Valley and the prevalence of the dental and skeletal fluorosis among the inhabitants of the region.

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* *Faculty of Medicine, Addis Ababa University, P.O.Box 4147, Addis Ababa, Ethiopia*

MATERIAL AND METHODS

Samples of drinking water from representative sites in the Rift Valley were analyzed for fluoride content at the laboratory of the Wonji Sugar Estate laboratory, using ion analyzer Orion Research Specific Ion meter. Since 1985 clinical surveys have been regularly undertaken to examine the prevalence of endemic fluorosis in the Rift Valley at large and the sugar estates in particular. The prevalence of dental fluorosis was performed on randomly selected children between the ages of 7 and 20 years at schools in areas of large populations. The classification of dental fluorosis was according to Siddiqui[3].

Skeletal fluorosis was detected by examining all persons with abnormal postures, deformities and other physical disabilities, including those who were bedridden. Persons so identified in the selected villages and towns were examined neurologically, using a special protocol X-rays.

TABLE 1. Fluoride Content of Water in Various Areas of the Ethiopian Rift Valley

Samples sites:	Fluoride (mg/L)	Source of water	Years in service
Dubti (village)	1.2	Borehole	9
Logiya (town)	1.0	Borehole	10
Mille (town)	0.4	Borehole	10
Gewane (town)	0.7-2.5	Borehole	16
Amibara (farm)	2.4-3.0	Borehole	5
Melka Warer (farm)	3.5	borehole	9
Melka sedi (farm)	1.5-4.3	borehole	13
Awash (station)	1.4-1.6	treated river	20
Meterhara (estate)	2.5-6.2	borehole	20
Abadir (farm)	4.0	borehole	12
Wolenchiti (town)	2.5	borehole	15
Nazareth (town)	0.8-3-3	borehole	20
Wonji-Shoe (estate)	2.5-14.0	borehole	30
Koka (town)	26.0	borehole	20
Alem Tena (town)	9.0	borehole	17
Sami berta (village)	9.0	borehole	23
Meki (town)	0.7-1.0	borehole	6
Zeway (town)	1.0-1.6	borehole	10
Waig (village)	3.5	borehole	8
Koshe (village)	3.0	borehole	15
Adami tulu (town)	5.1	borehole	10
Abernosa (village)	36.0	borehole	7
Jido (village)	33.6	borehole	12
Bulbula (town)	14.6	borehole	7
Alaba (village)	1.1	borehole	18
Togo (village)	4.9	borehole	4

RESULTS

Table 1 shows the fluoride levels of water samples in the different sites of the Rift Valley. This ranged from 1.0 mg-F/L to 36 mg-F/L. The sugar estates that had the highest population densities recorded high fluoride levels: Wonji-Shoa 2.5 to 14 mg-F/L, and Metahara 2.5 to 6.2 mg-F/L.

TABLE 2. Children with Fluorotic Mottling of Teeth in the Ethiopian Rift Valley: Age and Sex Distribution.

Age group	Males			Females			Total		
	Exa-mined	Dental Fluorosis		Exa mined	Dental Fluorosis		Exa-mined	Dental Fluorosis	
(years)	No	No.	%	No	No.	%	No	No.	%
5 - 9	190	158	83.2	240	172	84.3	394	330	83.8
10-14	517	470	90.9	301	258	85.7	818	728	90.0
15-19	149	113	75.8	53	30	56.6	202	143	70.8
20+	25	10	40.0	17	10	58.8	42	20	47.6
Total	881	751	85.2	575	470	81.7	1456	1221	83.9

Dental Fluorosis. Table 2 demonstrates the extent of dental fluorosis among the children in the surveyed sites. The prevalence ranged from 70 to 100%, with 35% having the severe form of the complication. The condition was found to be statistically worse in males and the age group 10 to 14 years.

Skeletal Fluorosis. In the Rift Valley skeletal fluorosis was identified to be a serious problem in the long established sugar estates and two towns along the Ethiopian-Kenyan highway, Alem Tena and Sami Berta.

The subjective symptomatology in persons with skeletal fluorosis is variable depending on the degree of affection. It may be asymptomatic osteofluorosis where the changes are apparent only on X-rays. The majority of the more advances cases develops progressive bone pains and stiffness of the whole body. Squatting, particularly when defecating, becomes very troublesome. Standing up from a sitting position, and sitting up in bed, become increasingly difficult. Progressive kyphosis and limitation of movements become apparent. This clinical condition progressively worsens to the more severe debilitating state of crippling fluorosis.

DISCUSSION

The Ethiopian Rift Valley groundwater have very high fluoride levels, ranging from 0.4 to 36 mg-F/L. The water sources used in areas with the highest population densities have fluoride contents of 3.5 to 13.0 mg-F/L. Studies from other countries[11,12] and our own experience in Ethiopia[10] have shown that these levels cause dental fluorosis in children and over a prolonged period skeletal and crippling fluorosis.

In the Ethiopian Rift Valley dental mottling has been recognized in areas with fluoride concentrations in water as low as 2 mg-F/L. Higher levels, above 4 mg-F/L cause severe disfiguring dental fluorosis with enamel hypoplasia.

Under the hot and dry conditions in the tropics, fluoride concentrations of 4 to 6 mg-F/L in the drinking water (or a daily fluoride absorption of more than 10 mg-F) may cause skeletal fluorosis with serious complaints in a substantial part of the population over the age of 45 years[13]. In our experience, high fluoride content in drinking water appears to play the determining role, as was observed by Reddy[14]. However, men doing manual labor in hot environments appear to be more susceptible to advanced osteosclerosis with neurological complications. Similar observations have been recorded by Siddiqui[3]. In hot climates the values for the maximum fluoride concentration in drinking water may have to be lower than the WHO recommended 1.5 mg-F/L.

In the Ethiopian Rift Valley, with fluoride levels above 4 mg-F/L, most of our patients developed neurological complications after 15 years of exposure. In the progressive cervical radiculo-myelopathy that develops insidiously, the common predominant neurological picture usually consists of marked wasting and atrophy of the small muscles of the hands, in addition to spastic paraparesis or quadriparesis, often in flexion. In advanced stages of neurofluorosis, the clinical picture is rather uniform, with complete incapacitation and the bedridden state of severe spastic paraparesis, or quadriparesis with incontinence of urine and flexor spasms. Hyperreflexia, with absent abdominal reflexes and extensor plantar responses with or without patellar and ankle clonus confirm long tract involvement.

The World Health Organization had set guidelines limits on fluoride. The guidelines, with 1.5 mg-F/L as the upper limit of safe level are based on an average per capita daily water consumption of 2 liters. However, it is abundantly clear that the daily consumption of water in hot tropical environments is much higher that the WHO propose average and can be as high as 10 l/day.

Based on their studies in Senegal Brouwer et al. suggest that other guiding values would be more appropriate in tropical regions. They proposed that dental fluorosis will occur at fluoride levels above 0.6 mg-F/L and crippling fluorosis above 7.0 mg-F/L[15]. Other countries, notably Argentina[16] and Tanzania[17] have other types of standards operational on basis of economical, practical and technical considerations. Such controversial decisions are also confronting Ethiopia when deep bore holes are being dug in the hot dry areas of the fluoride endemic Rift Valley. When alternatives are not available the Ethiopian Water Resource Commission has chosen the better of two evils: to make water with inevitably high fluoride available to the thirsty populations.

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THE OCCURRENCE OF FLUORIDE CONTAMINATED MAGADI (TRONA) IN KENYA AND TANZANIA

J M Nielsen* and E Dahi*

SUMMARY: The concentration of fluoride is measured in crystalline and scooped magadi originating from 5 alkaline lakes in Tanzania and Kenya and in scooped magadi from Northern Tanzania. The fluoride concentration is found to be comparable to what has been reported so far. The fluoride concentration varies from 0.12-17.9 mg/g magadi for crystalline magadi and from 0.10-5.09 mg/g for scooped magadi. The concentration is subject to considerable variation even for magadi originating from a given lake. The alkaline lakes, Lake Balangida, Lake Eyasi, Lake Magadi, Lake Manyara, and Lake Natron show fluoride concentrations of 0.13-17.9, 0.29-7.4, 0.12-8.7, 0.16-4.4, and 0.71-9.66 mg/g magadi respectively.

Key words: Magadi, food, alkaline lakes, fluoride, fluorosis

INTRODUCTION

The mineral trona, $Na_2CO_3{\cdot}NaHCO_3{\cdot}2H_2O$, is an evaporite mineral which can be found at the alkaline lakes (crystalline) or as an efflorescent crust (scooped) on the earth's surface in the Rift Valley of East Africa. Trona, locally called magadi, is often contaminated with fluoride which is caused by the high fluoride content of the volcanic rocks enriched in alkalis in the rift zone.[1]

In East, West, and Central Africa magadi is used in food preparation as a tenderiser to speed up the cooking process for food such as beans, maize, and meat, as a flavouring agent, and as food preservative.[2-11]

It has been reported that in trona, fluoride is occurring as villiaumite, NaF, and as kogarkoïte, $Na_2SO_4{\cdot}NaF$[12,13], and that the fluoride concentration in magadi varies between 0.2 and 14.9 mg F^-/g magadi.[5,8,12,14] Studies have shown that the use of magadi heavily contaminated with fluoride contributes to the high fluoride intake in fluorosis areas of East Africa. In fact, in some cases the fluoride uptake from magadi may be higher than that from water.[5]

This paper presents results of measurements of fluoride concentration in magadi originating from Tanzania and Kenya and the concentration's dependence on the form and origin of the magadi is elucidated.

MATERIALS AND METHODS

Magadi Samples, both scooped and crystalline, have been collected from Lake Balangida, Lake Eyasi, Lake Manyara, and Lake Natron in Tanzania (see location in Figure 1) and bought at different markets in Kenya and Tanzania. The origin of the magadi samples were determined according to the information given by the dealers. The amounts of magadi collected and bought were very different, therefore an available amount of magadi was crushed and homogenised in a mortar and 2.00 g was dissolved in 100.0 ml distilled water. Thereafter the fluoride concentration was measured in the solution.

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* Center for Developing Countries, Technical University of Denmark, 2800 Lyngby Denmark.

Fluoride measurements: The fluoride concentrations were measured using a Radiometer F1052 fluoride electrode and a Metrohm Ag/AgCl reference electrode with a sleeve type diaphragm connected to a Metrohm potentiometer (692 pH/Ion Meter). A 10-ml sample of the solution was mixed with 10 ml CDTA-tisab and the fluoride concentration was measured using the calibration method, according to Standard Methods.[15]

RESULTS

The crystalline and scooped magadi from Kenya and Tanzania are very different in colour and form, ranging from crispy flakes mixed with light brown soil to long grey crystals shaped like needles of a length of 30 mm.

The fluoride concentration in the magadi reported by other researchers can be seen in Table 1.

In Figure 2 the fluoride concentration in magadi samples from this study, 94 in total, is plotted on logarithmic probability paper.

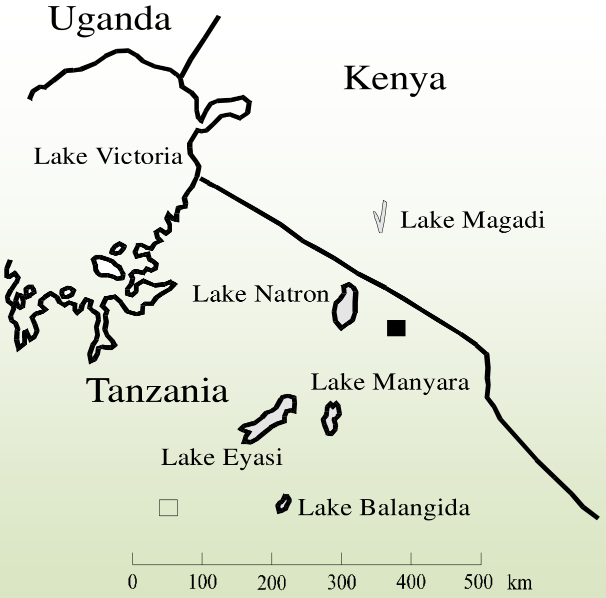

FIGURE 1. Map of the alkaline lakes in Northern Tanzania and Southern Kenya. See Table 1 for explanation of ■ and □.

TABLE 1. The fluoride concentration in magadi samples from Northern Tanzania and Lake Magadi, Kenya. For location see Figure 1.

Source (village/river/lake)	Fluoride (mg/g)	n	Reference	Location
Sepuka	0.036-0.18	22	Mabelya et al.[5]	□
Kiomboi	0.69-6.8	9	Mabelya et al.[5]	□
Engare Nanyuki River	0.20-6.0	11	Nanyaro et al.[14]	■
Kitefu	0.9-14.9	3	Mungure[8]	■
Kimandafu	2.80-7.4	3	Mungure[8]	■
Lerai	6.5-7.4	2	Mungure[8]	■
Kikatiti, near spring	0.80	1	Mungure[8]	■
Lake Natron	6.2	1	Adhia[16]	
Lake Magadi	4.0	1	Baker[12]	

In Figure 3 box plots of the fluoride concentration in crystalline and scooped magadi samples can be seen. The number of crystalline and scooped samples are 79 and 15 respectively. The ends of the box are the 25th and 75th percentiles, so that the length of the box is a measure of the spread; that gives the range covered by the middle half of the data. The line within the box is indicating the median value and the two lines (whiskers) outside the box extend to the smallest and the largest observation.

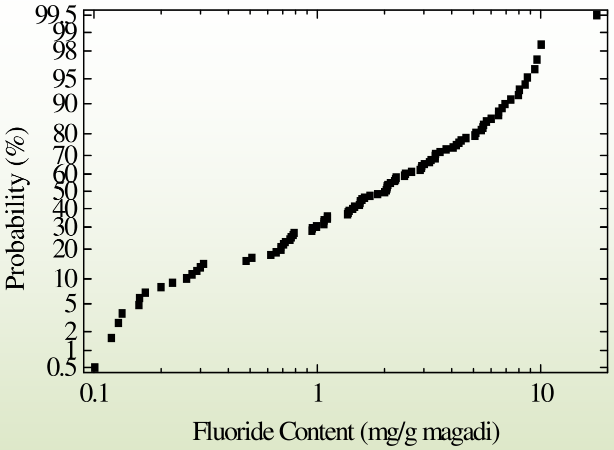

FIGURE 2. The fluoride concentration in magadi samples from this study plotted on logarithmic probability paper.

In Figure 4 box plots of the fluoride concentration in lake samples can be seen. The samples originate from Lake Balangida, Lake Eyasi, Lake Manyara, and Lake Natron, Tanzania and from Lake Magadi, Kenya and the number of samples from each lake are 18, 8, 11, 20, and 17 respectively.

this study plotted on logarithmic probability paper.

The box plots are worked out like in Figure 3, e.g. the ends of the whiskers are the smallest and the largest observation, the ends of the box represent the 25th and 75th percentile and the line within the box is the median value.

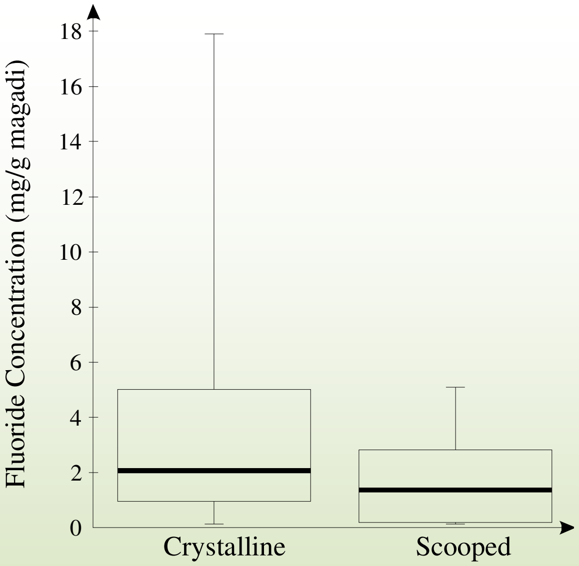

FIGURE 3. Box plot of the fluoride concentration in crystalline and scooped magadi samples. The box illustrates the 25th, 50th, and 75th percentiles, while the lines illustrate the lowest and highest measurements. results from this study and from Baker12 and Adhia16.

DISCUSSION

Looking at Figure 2 it can be observed that the fluoride concentration in the magadi samples is subject to considerable variation. The same tendency is observed from results reported by other researchers (see Table 1). The fluoride concentration in samples from Kitefu reported by Mungure[8] ranges from 0.9 mg/g to 14.9 mg/g and Nanyaro and coworkers[14] report fluoride concentrations between 0.2 and 6.0 mg/g in 11 different samples from the Engare Nanyuki River system.

In Figure 2 where all samples from this study are shown it can be seen that 50% of the samples have a fluoride concentration equal to or lower than 2.0 mg/g, and the 25th and 75th percentiles are 38% and 208% of the median respectively.

The cumulative frequency curve is not a straight line, thus the logarithmic fluoride concentration in the magadi samples is not normal distributed.

Some differences are observed when the samples are divided into 2 different groups representing their form, e.g. crystalline and scooped like seen in Figure 3. The variation, the length of the box, is bigger for crystalline samples than for scooped samples, even though the number of samples is higher, 79 compared to 15. The fluoride concentration is in general lower in scooped magadi than in crystalline, all scooped magadi samples have a fluoride concentration lower than 5.1 mg/g, whereas it is only 75% of the crystalline magadi samples.

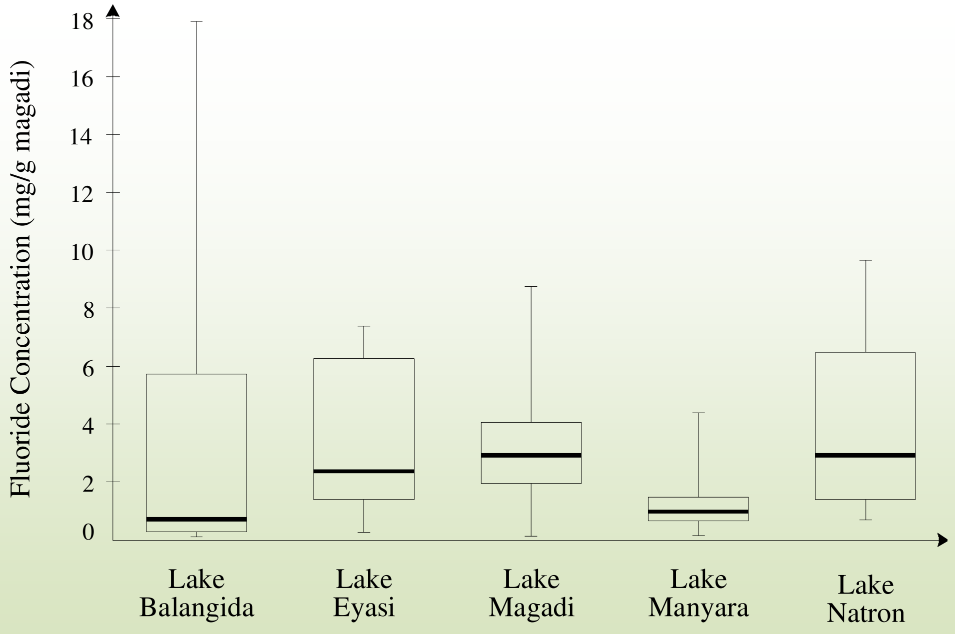

FIGURE 4. Box plot similar to Figure 3, for magadi samples divided into 5 groups representing the individual lakes. results from this study and from Baker[12] and Adhia[16].

The samples have also been divided into 5 groups representing their origin, Lake Balangida, Lake Eyasi, Lake Manyara, and Lake Natron from Tanzania and Lake

Magadi from Kenya (see Figure 4). The median fluoride concentrations in magadi from Lake Balangida, Lake Eyasi, Lake Magadi, Lake Manyara, and Lake Natron are 0.73. 2.39, 3.19, 0.99, and 2.94 mg/g respectively, and the variations, the length of the boxes are high, especially for Lake Balangida, Lake Eyasi, and Lake Natron. The upper quartile of the fluoride concentration for these three lakes are equal to 5.7-6.5 mg/g compared to 4.1 mg/g for Lake Magadi and 1.5 mg/g for Lake Manyara. The fluoride concentration in magadi from Lake Manyara is in general lower than in magadi from the other lakes.

ACKNOWLEDGEMENTS

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SEVERE FLUOROSIS IN CHILDREN CONSUMING FLUORIDE CONTAINING MAGADI

W H van Palenstein Helderman*, E Mkasabuni**, H J Mjengera*** and L Mabelya*

SUMMARY: The Prevalence and severity of dental fluorosis among children in East Africa has in several areas been reported higher than would be expected from the fluoride content in the water supplies. This study aimed to measure dental fluorosis in 50 randomly selected 12 to 15-year-old children who were born and raised in an endemic fluorosis area in the northern Tanzania, and aimed to relate the prevalence and severity of their dental fluorosis to fluoride exposure. Buccal surfaces of all permanent teeth were scored for fluorosis according to the Thylstrup Fejerskov Index (TFI). Children and their mothers were interviewed with aid of a questionnaire about dietary habits and methods of food preparation. 96% of the examined children exhibited dental fluorosis of TFI 4 on more than 2 teeth. The water sources used since birth had a fluoride content of less than 0.4 mg-F/l. results of the interviews revealed a frequent use of "magadi", a potash (trona) salt, which is added to food as a tenderizer. The magadi samples collected from 25 different households showed a fluoride concentration of 760 - 6800 µg-F/g (mean 2776 µg-F/g). It was calculated that adults in this community consumed approximately 34 mg-F per week through magadi containing meals. Infants started to ingest fluoride through magadi in the first year after birth. However, an accurate estimate of fluoride consumption during period of tooth formation was not possible on the basis of the present data. The lack of an association between dental fluorosis and fluoride exposure through drinking water in some of the previous reports from African communities may be explained by inadequate identification of available fluoride sources. It is suggested that in many areas in Tanzania endemic fluorosis may occur as a result of fluoride supplementation to food through magadi rather than exposure to fluoride in drinking water. This urges further research.

Key words: Fluorosis, fluoride exposure, Thylstrup Fejerskov Index, magadi.

INTRODUCTION

Dental fluorosis is a disorder of tooth mineralization caused by excessive intake of fluoride during tooth development. The severity of dental fluorosis increases with the amount of fluoride ingested during the period of tooth formation[1]. The mild form is characterized by opaque white lines along the perikymate which may fuse to form opaque white patches, mottled enamel. It may be stained yellow to dark brown by uptake of pigments from food and drinks after the teeth have erupted. In more severe cases discrete pits and larger areas of hypoplasia of enamel may occur to the extent that the normal morphology of the tooth is lost. Endemic dental fluorosis is most prevalent in areas where the drinking water contains elevated levels of fluoride. The dental fluorosis prevalence in some regions in East Africa is believed to be caused by fluoride in drinking water[2-5]. However an increasing number of reports have appeared from East African countries indicating a high prevalence and severity of dental fluorosis that can not be explained by the fluoride content of the drinking water[6-10].

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* Faculty of Dentistry, University of Dar es Salaam, PO Box 64014, Dar es Salaam, Tanzania

** Peramiho Hospital Songea, Tanzania.

*** Ministry of Water, Tanzania.

Recently, a low fluoride community which used drinking water with 0.4 mg-F/l but still was affected with severe dental fluorosis was identified in the central region of Tanzania. An additional fluoride source was discovered in the form of "magadi" $Na_2CO_3 \cdot NaHCO_3 \cdot H_2O$. Magadi are used as a tenderiser to speed up the cooking time of certain foods. Magadi is found in numerous places in Tanzania. Not all magadi contains high levels of fluoride but the type used in this community appeared to be heavily contaminated with soluble fluoride salts. The exposure to magadi with a high fluoride content was considered to explain the severity of dental fluorosis in the observed community[11].

The present study aimed to determine the prevalence and severity of dental fluorosis in association with fluoride levels in drinking water and magadi in a community in the northern region of Tanzania. This region has for decades been known for endemic fluorosis[12] and for numerous places with high fluoride in water supplies[3].

MATERIALS AND METHODS

The study was carried out in Kibosho at 1,300 m altitude near Moshi in the Kilimanjaro region. School-children aged between 13 and 15 year, who were born and brought up in that community, were identified. All children who met the selection criteria in classes 3 and 4 and some children according to the alphabetical order of their surname in class 5 were selected to form a sample of 50 (mean age 13.9 years).

The children had used several water sources in that area since birth. Water samples from these sources (n = 9) were collected in August 1991 in a period of long rains, in January 1992 during a long dry period and again in October 1992 in a period with occasional rains. The water samples were collected in plastic containers. Analysis of the fluoride ion concentration was done using the fluoride ion specific electrode.

The children were examined in natural daylight in a shaded area by one examiner. Buccal surfaces of erupted permanent teeth were wiped with a gauze and were left to dry before they were scored for fluorosis according to the TFI. Colour photographs of teeth with different TFI scores were available as an aid to reliability[14]. The examiner was not aware of the prevailing fluoride content in the water sources.

The children were interviewed about their dietary habits with the aid of a 24-hour-recall questionnaire. In addition they were asked how frequently they consumed tea, fish and magadi on a weekly basis at the time of the interview. Every second mother (n = 25) was interviewed about the frequency of magadi use for food preparation. They were also asked how long they were using magadi and at which age their children were introduced to foods which contained magadi. Each interviewed mother provided the interviewer with a sample of magadi equal to the amount they normally used for cooking meals. Magadi in this community has been supplied through local market traders who, bring it from salt lakes in the northern part of Tanzania, implying that there are several sources of magadi. The samples of magadi were weighed and subsequently 5 grams were dissolved in 20 ml of distilled water prior to the analysis with the fluoride ion specific electrode.

RESULTS

The fluoride content in the water sources in Kibosho varied over time but the variation was very low (Table 1). These sources have been used by the studied community for the at least 15 years.

The prevalence and severity of fluorosis among the 50 children is illustrated in Figure 1. Forty six percent of the children exhibited TFI higher than 3 on all their teeth whereas 96% of the children exhibited TFI higher than 4 in more than 2 teeth and 63% showed at least 50% of their teeth with TFI higher than 4. A TFI score higher than 4 represents severe fluorosis as it manifests hypoplasia and deformations of the normal morphology of the teeth. Due to the porosity of the enamel, dark discoloration may occur.

TABLE 1. Average and range of fluoride concentrations in 9 water sources at different times of the year.

Sampling time	Average (mg-F/l)	Range (mg-F/l)
August 1991	0.04	<0.05 - 0.12
January 1992	0.35	0.26 - 0.43
October 1992	0.28	0.21 - 0.56

Information from the children revealed that tea was not drank excessively (average 5.7 times per week), neither was fish consumed frequently (average 0.7 times per week). Mothers reported that "magadi" was added to the boiling pot for taste and to reduce the cooking time particularly for beans. Mothers reported that they cooked beans with magadi in average 4.1 times per week (the children reported nearly the same frequency of 4.3 meals per week). The amount of magadi addition for preparation of beans for 6 - 8 persons were on average 21 grams. The usual meal containing beans and cooked bananas were served as a juicy dish. No water was discarded after the cooking process. Consequently all fluoride added through magadi was consumed. Only when the cooking pot did not contain bananas some remaining water was discarded before the meal was served.

The average fluoride concentration in the magadi samples was 2776 µg-F/g with a range of 760 - 6800 µg-F/g.

All mothers reported to have introduced magadi to their infants meal in the weaning period between 4 - 9 months (mean 6.9) after birth. The mothers stated that they had always used magadi and that small children shared the meal with adults.

DISCUSSION

The fluoride content of the water sources in the examined community varied with time but was always found low. This finding corroborates previous reports on the fluctuating fluoride concentrations in drinking water in several countries[15]. The low fluoride content on the drinking water of the present community (on average < 0.4 mg-F/l) could not explain the high prevalence (96%) of the children with TFI higher than 4 which is severe according to Dean's score[16]. The severity of dental fluorosis in the present community, if caused solely by fluoride in drinking water, would be accounted for by a fluoride concentration of at least 7 mg-F/l in the water[1].

Other usual sources of fluoride prevailing in developed countries e.g. infant formulae, fluoride in toothpaste, fluoride tablets fluoride rinsing and other fluoride applications do not exist. However, an additional source of fluoride was identified in the form of magadi. The magadi used in this community contained on an average 2800 μg-F/g magadi. The average amount of fluoride ingested from this source in the Kibosho community for adults was approximately 34 mg-F per person per week. It is precarious on the basis of the present data to calculate the amount of fluoride ingested by infants and young children in this community. According to the information of mothers, their infants ingested magadi in the first year of their life through weaning foods but the quantity is not known. Fifty percent of the children in Tanzania are breast-fed up till age of 23 months[17] and although they share their meals with other members of the family, the amount of fluoride consumed through magadi during weaning and later up till the age of 12 years is unknown.

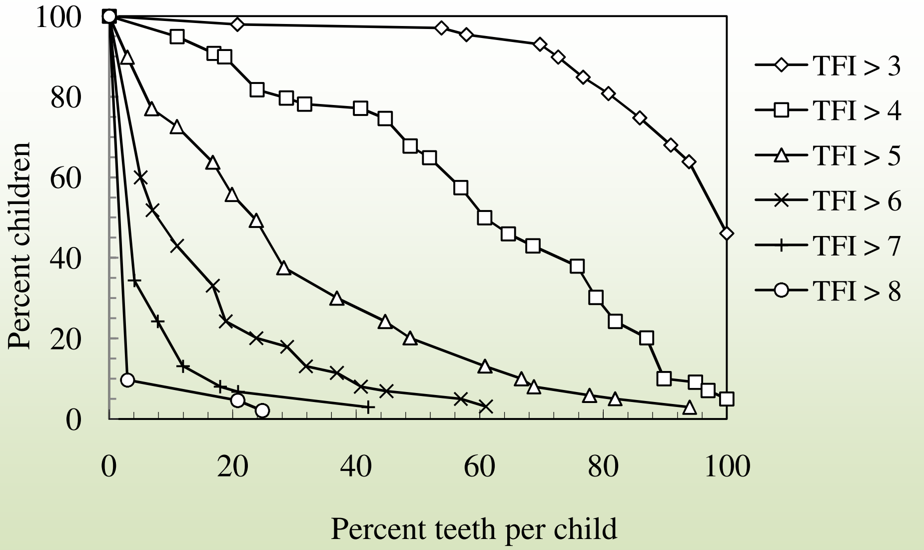

FIGURE 1. Prevalence and severity of fluorosis among 50 selected children.

Besides the fluoride exposure during the period of tooth formation up till the age of 12 years, other factors have been suggested to exert effects on the severity of dental fluorosis[18]. Several reports from Tanzania, South Africa, Kenya, and Senegal have shown a higher severity of dental fluorosis than would be expected from the fluoride content in their drinking water supplies[6-10,13,19]. In an attempt to explain the high prevalence and severity of dental fluorosis in those communities, climate[8-10], altitude[19], diet and malnutrition[20] have been suggested as possible factors.

The present community did not exhibit malnutrition among its infants and young children. The climate in Kibosho is not very hot and dry, since Kibosho is located at the foothills of the Kilimanjaro at 1300 meters altitude.

The prevalence and severity of dental fluorosis found in this study were in agreement with a report from another Tanzania community in the central region on the country at a comparable altitude, but in disagreement with data from a community in the coastal region at sea level which exhibited low levels of dental fluorosis[11]. Both these communities consumed drinking water with a low fluoride content of 0.4 - 0.6 mg-F/l. The main difference in fluoride exposure between the two communities appeared to be the use of magadi in the community at high altitude[11]. This correlation to magadi consumption raise doubts about the explanation given for a Kenyan community, that altitude related hypobaric conditions may have modified the susceptibility of individuals of fluoride[18]. It seems more likely that unidentified dietary fluoride source in those people may have caused the observed severe dental fluorosis. It is suggested that in studies on dental fluorosis careful attention should be paid to dietary habits and local customs in the preparation of food in order to identify possible additional fluoride sources.

Tanzania has several endemic dental fluorosis areas and the possibility is suggested that many of these areas may exist as a results of high fluoride supplements to food rather than the fluoride content of water supplies. This urges further investigation.

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FLUORIDE AND FLUOROSIS IN THE SUDAN

Y Ibrahim*, AA Affan* and K Bjorvatn**
Sudan and Norway

SUMMARY: In Sudan the Nile River provide water for agriculture and industry, and for the majority of Sudanese households. Where Nile water is unavailable, sub-surface water reservoirs are tapped. No comprehensive study has ever been made on the fluoride contents of Sudanese ground water. Dental fluorosis is, however, found in certain areas of the country, especially in the Northern and Western provinces. In the present study water samples were collected from 55 wells in various provinces in the northern part of Sudan. The fluoride concentration of the waters ranged from 0.08 to 3.55 mg-F/L. The overall average fluoride concentration was 0.34 mg-F/L. Dental fluorosis was studied in two villages in the Khartoum area, Treit el Biga (TeB) and Abu Groon (AG). The fluoride contents of the village wells were 0.25 and 2.5 mg-F/L, respectively. All the examined children in AG had dental fluorosis, with Dean's scores ranging from 1 to 4. The Community index was 2.44. The prevalence and degree of dental fluorosis in high-fluoride AG was comparable to what has previously been reported from areas with a similar fluoride concentration. Dental fluorosis was seen in 91 percent of the children in low-fluoride TeB. The TeB community index was 1.40. The fact that 91 percent of the examined children developed dental fluorosis in TeB; an area with lower than average fluoride concentration in the drinking water, is alarming, and requires further studies.

Key words: Fluorosis, fluoride, Sudan, Dean's Index.

INTRODUCTION

As the local yearly precipitation is low, the Nile rivers are the main source of water in the Sudan. According to recent reports[1], the fluoride contents of Nile waters fluctuate between 0.2 and 0.4 mg-F/L. Emslie (1966), however, indicated that fluoride values as high as 1.0 mg-F/L may be recorded, especially when the Nile water is low[2].

Most Sudanese communities outside the Nile valley depend on ground water. As compared with the local surface water, ground water is, on an average, richer in fluoride[3]. Anecdotal information on fluoride containing ground water is available, but no comprehensive study of the fluoride contents of Sudanese ground water has ever been made. Dental fluorosis was reported already 30-40 years ago among children in certain areas, especially in Northern and Western Sudan[2]. To our knowledge, skeletal fluorosis has not been reported in the Sudan.

The aim of the present study was twofold:

- To assess the fluoride contents of water from selected groups of deep wells in Central, Northern and Eastern Sudan, and
- To study the prevalence of dental fluorosis in a low-fluoride and a high-fluoride village in the Khartoum area.

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* *Faculty of Dentistry, University of Khartoum, Sudan*
** *Faculty of Dentistry, University of Bergen, Norway*

MATERIAL AND METHODS

Fifty five individual water samples were collected from deep wells in the Gezira area (21 wells); Kordufan area (13 wells); Northern area (4 wells); Red Sea area (5 wells); and Khartoum area (12 wells).

Water samples were taken directly from faucets/pumps and filled into 30 ml Sarstedt polypropylene bottles, fitted with tight lids. The samples were brought to Norway by courier, and the water was analysed for fluoride at the Inst. of dental research, University of Bergen. Fluoride selective electrodes were used for the analysis, according to standard procedures[4].

Dental fluorosis was studied in two villages, Treit el Biga (TeB) and Abu Groon (AG). The villages, situated within a distance of 50 km from Khartoum, were of similar size and had comparable socio-economic conditions. Both communities were supplied with water from boreholes drilled into the bedrock (Nubian sandstone) 15-20 years ago. The Treit el Biga water contained 0.25 mg-F/L while the fluoride contents of the Abu Groon well were ten times higher; 2.54 mg-F/L.

Permission to examine school children in the villages was obtained through the teachers. The examination was carried out by one person (YI) according to WHO's criteria for field studies[5]. One hundred and thirteen children (55 in TeB and 58 in AG), 6 to 16 years old, were available for examination. Fluorosis was scored according to Deans Index[6], based on inspection of the upper central incisors.

RESULTS

The fluoride contents of water samples from fiftyfive different villages ranged from 0.08 to 3.55 mg-F/L. The average value was 0.34 mg-F/L. Regional differences were moderate, as appears from Table 1.

Dental fluorosis was found in all the AG children. As demonstrated by Figure 1, the fluorosis scores varied from 1 (very mild) to 4 (severe). The "community fluorosis index" (Fci) of AG was 2.44. Dental fluorosis was observed in 91% of the children in TeB. The fluorosis scores covered the whole spectre, from 0 to 4. Fci of TeB was 1.40.

TABLE 1. Fluoride concentration of ground water in mg-F/L, according to region.

Region	Mean	s.d.	Range	n
Kordufan	0.27	0.16	0.12-0.63	13
Red Sea area	0.28		0.18-0.38	5
Gezira	0,34	0.43	0.09-1.96	21
Northern area	0.40	0.29	0.13-0.81	4
Khartoum area	0.46	0.99	0.08-3.55	12
Overall average	0.36	0.55	0.08-3.55	55

DISCUSSION

The wells examined were all placed within areas dominated by Nubian sandstone. Fluoride containing aquifers may be found in sandstone, but high-F water is less prevalent in the Sudan than e.g. in the Rift Valley areas of East Africa. The highest value found in the present investigation was 3.55 mg-F/L. Previous reports have recorded fluoride containing ground water, e.g. in the Western provinces of Kordofan and Darfur[1]. In these areas pockets of volcanic basalt may be found.

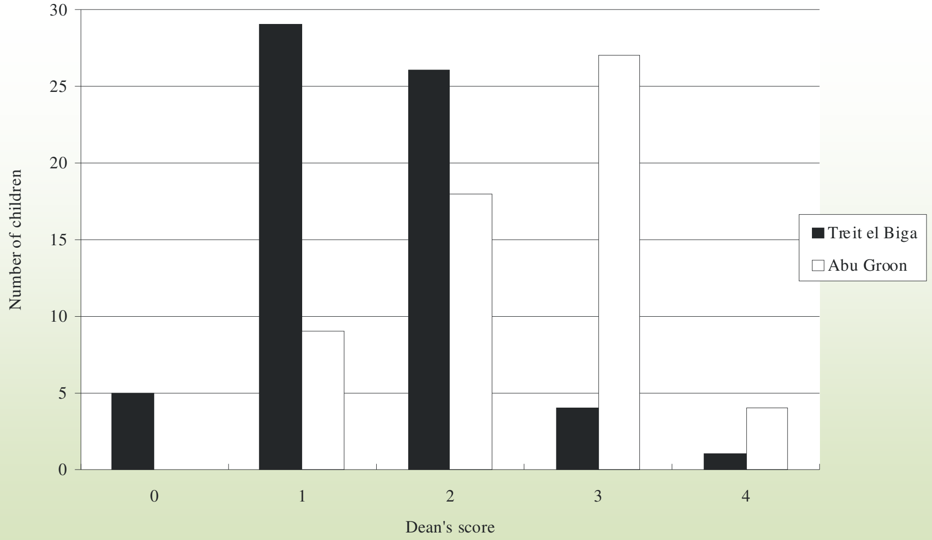

FIGURE 1: Dean's score for dental fluorosis among children in the cities Treit el Biga and Abu Groon.

Dental fluorosis in the Sudan was first reported in 1953, when Smith, Harris and Kirk examined schoolboys in the Butana desert[7]. The prevalence of fluorosis was 60.6 per cent. The relevant water sources contained fluoride in the range of 1.1 to 4.0 mg-F/L. According to the generally held opinion, Smith and co-workers regarded fluoride concentrations of less than 0.8 mg-F/L as harmless, and consequently had problems in explaining the fact that five (out of eight) boys living in a village with only 0.65 mg-F/L in the drinking water developed dental fluorosis. Emslie (1966) found fluoride concentrations in Sudanese drinking water of up to 5 mg-F/L and reported a prevalence of 90 per cent fluorosis in one area[2]. Conflicting information on the prevalence of dental fluorosis in the Sudan has appeared recently: Ghandour, Ibrahim and Shehata found a fluorosis-prevalence of 64 per cent in boys and 50 per cent in girls from Omdurman[8], while Elhassan found dental fluorosis only in 4.5 percent of the children in neighbouring Khartoum[9]. The fluoride concentration of the relevant drinking water is not mentioned, but the two cities would be expected to take water from the same source; the river Nile.

The prevalence of dental fluorosis presently found in Abu Groon is high, but comparable to results from other African villages with similar fluoride concentrations in the water[10]. The results from low-fluoride Treit el Biga are unexpected. Equally high prevalence of dental fluorosis has not previously been reported in areas with only 0.25 mg-F/L in the drinking water.

CONCLUSION

Based on the present material, the average fluoride contents in Sudanese ground water is relatively low (~ 0.3 mg-F/L), but pockets of high-fluoride water may exist, even in low-fluoride areas. Water sources used for household purposes should, consequently, be analysed for fluoride.

It is important to bear in mind that the development of dental and skeletal fluorosis depends on the total daily intake of fluoride. The Treit el Biga findings (more than 90 percent prevalence of dental fluorosis in a community using water with 0.25 mg-F/L), may therefore indicate that drinking water is not the only fluoride source to be taken into consideration. Until all relevant sources are known, no safe limit can be defined for fluoride in water.

Follow-up studies are needed in order to assess total daily water intake, scrutinise feeding habits during the critical weaning period, and identify possible additional fluoride sources, such as tea, fish and - maybe - fluoride containing trona.

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MECHANISMS OF DEFLUORIDATION OF DRINKING WATER BY TRICALCIUM PHOSPHATE

GL He*, Y Chang* and RD Ji*

SUMMARY: Hydroxyapatite (HAP) is a natural material that is strong in fixing fluoride. An X-ray diffraction analysis proved that the densitometric tracings of tricalcium phosphate (TCP) are similar to those of HAP. The present work examines and compares the efficiency of defluoridation from drinking water by TCP under various pH level, temperature and contact time conditions. Its defluoridation mechanisms are discussed in detail. The results showed that there was a close negative correlation between the defluoridation efficiency of TCP and the pH levels of raw water, $r^2 \in [-0.8934 ; -0.9915]$, as well as evident positive correlation between defluoridation efficiency and both the temperature and the contact time, $r^2 \in [0.6420 ; 0.9207]$ and $r^2 \in [0.1956 ; 0.9839]$, respectively. This suggested that the defluoridation mechanism of TCP could be a complex chemical reaction needing energy.

Key words: defluoridation, mechanism, tricalcium phosphate, endemic fluorosis

INTRODUCTION

China is severely affected by endemic fluorosis. Excess fluoride intake has recently been estimated to affect some 100 million people. Fluorosis districts, where fluoride occurs in drinking water in concentrations higher than 4 mg-F/L, account for about 20 % of the affected population, and maximum fluoride concentrations in drinking water reach 40 mg-F/L. Most of endemic fluorosis are found in the arid or semi-arid regions where it is difficult to find drinking water with low fluoride concentrations, and there is no piped supply. Therefore, physical or chemical methods of removing fluoride from drinking water are important measures to prevent endemic fluorosis.

In recent years, considerable attention has been paid to develop effective defluoridation materials with steady qualities and a wide range of applications as well as development of new techniques. Extensive studies on different sorts of calcium phosphate have been performed. Simple methods have been reported for home water treatment based on co-precipitation of fluoride with calcium and phosphate, forming fluorapatite and fluorhydroxyapatite[1-4]. However, no quantitative data for practical application were given. Tricalcium phosphate has been used to remove fluoride from drinking water since the 1930's. Nevertheless, limited information exists on the fluoride removal efficiency from different water qualities and under different conditions. The mechanism of defluoridation is not yet clear.

This present study examines in detail the effects of various water quality parameters: different pH levels, temperatures and contact periods, on the fluoride removal efficiency of TCP, and discusses the possible mechanism of its defluoridation. Finally, a home-based defluoridation method is established.

Institute of Environmental Health and Engineering, Chinese Academy of Preventive Medicine, Beijing 100050, People's Republic of China.

TABLE 1. Effects of pH, temperature and contact time on defluoridation efficiency of $Ca_3(PO_4)_2$.

Raw Water			Treated Water					
pH	Fluoride	Temp	Fluoride, mg/L				Phosphate	pH
	mg/L	°C	9 h	23 h	30 h	46 h	mg P/L	
5.52	10.23	6	1.63	0.97	0.85	0.62	0.88	6.64
		15	1.04	0.6	0.52	0.46	0.49	6.7
		25	0.86	0.46	0.42	0.35	0.56	7.4
		35	0.75	0.5	0.39	0.3	0.53	7.13
6.51	10.33	6	2.17	1.6	1.42	1.18	0.6	7.4
		15	1.58	0.8	1.24	1.19	0.49	7.47
		25	1.37	1	0.98	0.87	0.34	8.06
		35	1.34	0.98	0.96	0.9	0.45	7.85
7.6	10.31	6	2.47	1.9	1.78	1.6	0.6	7.88
		15	1.89	1.45	1.49	1.27	0	8.31
		25	1.8	1.34	1.4	1.21	0.49	7.89
		35	1.66	1.41	1.46	1.47	0.67	8.35
8.49	10.29	6	½	2.25	2.17	1.9	1.53	7.97
		15	1.85	1.46	1.43	1.26	2.07	8.05
		25	1.84	1.39	1.34	1.26	0	8.36
		35	1.6	1.39	1.5	1.43	1.46	8.32
9.42	9.4	6	3.42	2.88	2.6	2.53	1.24	8.28
		15	2.94	2.41	2.44	2.15	0.41	8.75
		25	2.93	2.35	2.36	2.19	0	8.66
		35	2.69	2.4	2.42	2.37	0.45	8.53

pH levels and phosphate concentrations in treated water were determined after 23 h.

MATERIALS AND METHODS

All chemicals used for analysis were of analytical grade. Fluoride water of various concentrations was prepared from distilled- and tap water. The experiments were performed in 250 ml cone glass bottles containing 100 ml of fluoride solution at five pH levels and four ranges of temperature by static coagulation.

300 mg of TCP, 40 meshs, was suspended in 100 ml of fluoride-containing water under magnetic stirring. After continuous mixing for 1-2 minutes, the glass bottles were left for static reaction at different temperatures, and supernatant was sampled after different contact times for determination of pH, fluoride, phosphate and calcium using standard methods. For the adsorption equilibrium experiments, the added amounts of TCP were varied. Batch experiments with 2 and 30 litres of fluoride-containing water respectively were carried out at neutral pH level (pH = 7-8) and at room temperature (T = 20-25 °C). 3 g of TCP was added per litre in order to examine the feasibility of the method.

RESULTS AND DISCUSSION

The results of defluoridation using TCP at different pH, temperatures and contact times are presented in Table 1. Within the ranges of temperature and contact time tested in this study, there are close negative correlations between the removal efficiency and the pH of raw water. The removal efficiency at pH 5.52 is 19.7-21.4 %

higher than at pH 9.42. The removal efficiency decreased by approximately 3-7 % per pH unit in the pH range 5.5-7.6; 0-3 % in the pH range 7.6-8.5 and 11-13 % at pH range 8.5-9.5. This indicates that the removal efficiency of fluoride by TCP decreases considerably when pH exceeds 8.5. The pH levels of the treated water in all experiments ranged from 6.64 to 8.35, which proved that there is a phenomenon of pH neutralisation.

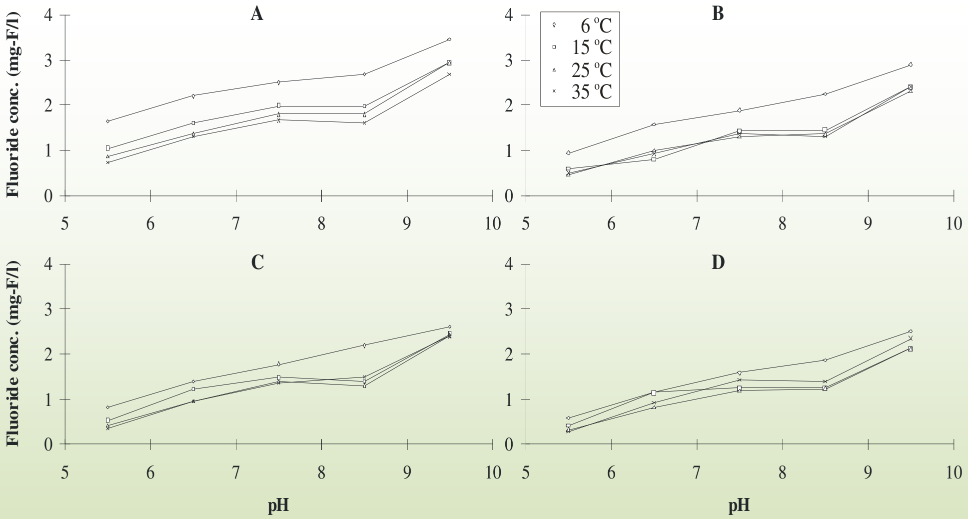

FIGURE 1 Effects of pH, temperature and contact time on the defluoridation efficiency of TCP. Initial fluoride concentration: 10 mg-F/L, volume: 100 ml, TCP: 300 mg.

A: 9 h, B: 23 h, C: 30 h, D: 46 h.

TABLE 2. Relationship between coagulant and defluoridation amount and contact time.

Raw water Fluoride (mg-F/L)	Time of adding coagulant (min)	Total experimental time (min)	Treated water fluoride (mg-F/L)
4.0	0	30	1.25
	30	60	1.08
	60	90	0.95
	120	150	0.94
3.33 (Natural water sample)	Not added	14 hr	1.02
	4 hr	5 hr	0.71

Conditions: 2 litres of fluoride-containing water at neutral pH (pH = 7-8) and at room temperature

(T = 20-25 °C); 3 g/L TCP is added at t=0; polyacrylamide concentration 0.2 mg/L.

The effects of the water temperature on the defluoridation efficiency of TCP generally show positive correlation. However, the positive correlation became less significant with longer contact times.

At given pH and temperature, a close positive correlation existed between the contact time and the defluoridation efficiency, $r^2 \in [0.6201 ; 0.9839]$. The effects of pH, temperature and contact time on the defluoridation efficiency of TCP are presented in Figure 1. Most defluoridation takes place during the first 10 hours (64 - 92 % removal of fluoride), whereas lesser defluoridation occurs after this time. When polyacrylamide was used as coagulant, the fluoride concentration was e.g. reduced to 0.95 mg/L from 4.0 mg/L in 1.5 hours (Table 2). The defluoridation capacity of TCP is presented in Figure 2. The adsorption isotherm indicates the defluoridation capacity as a function of the TCP amount.

Many methods of defluoridation are based on one of two principles; ion adsorption and ion exchange. In case of ion adsorption, fluoride is attracted to the surface of an inert substance, usually an insoluble aluminium salt, while ion exchange involves the uptake of fluoride in exchange for some other anion. Maier (1947) reported that synthetic calcium phosphate most often has been used in ion exchange[5]. However, TCP has no anion group which can be exchanged by fluoride.

Our results show that the fluoride removal efficiency of TCP increased with decreasing pH levels of the raw water under given temperature and contact time conditions.

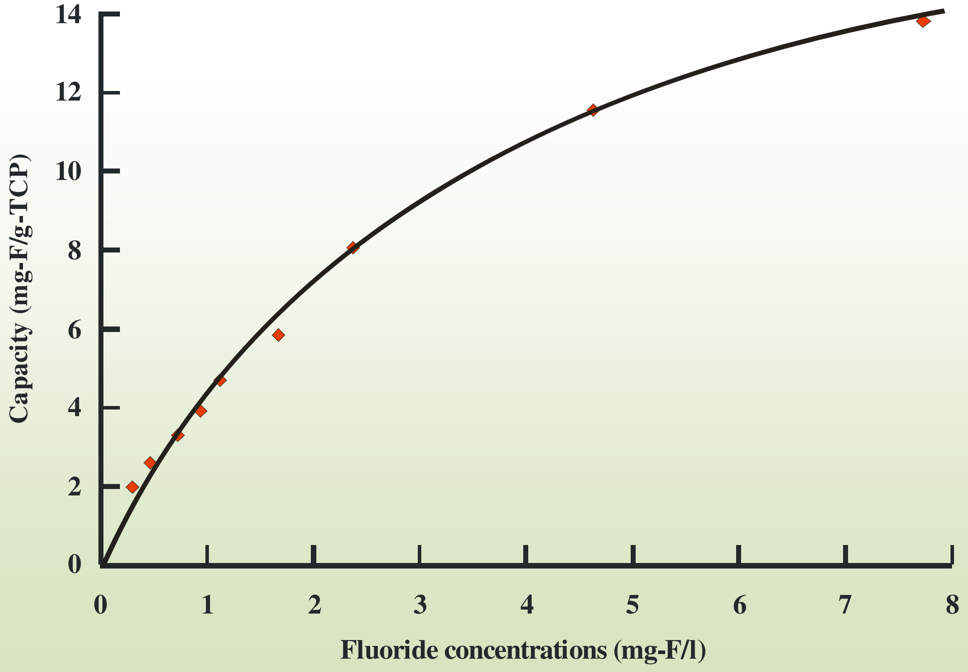

FIGURE 2. TCP absorption isotherms at pH 7.5. The continuous line represents

The concentration of phosphate in the treated water in all experiments increased by 0.5-1.5 mg-P/L, independent of initial pH levels. This indicates that the higher defluoridation activity of TCP at lower pH is not due to a higher degree of dissolution of TCP at lower pH. The results from experiments with distilled water and tap water (containing 85 mg-Ca^{2+}/L), showed that the defluoridation efficiency of TCP was not affected by the existence of Ca^{2+} in the raw water. Therefore, precipitation of CaF_2 is not likely to play any major role in this defluoridation system. During the process of defluoridation, the results were obviously affected by water temperature. Under given pH levels and contact time conditions, the higher the water temperature, the higher removal. This phenomenon indicates that defluoridation using TCP can be a chemical reaction needing energy rather than a physical surface adsorption. Physical adsorption usually declines with higher temperatures. Furthermore, there is a positive correlation between the defluoridation rate and the contact time, and equilibrium does not appear within 46 hours. Therefore, the defluoridation process of TCP expresses typical characteristics of a chemical reaction: Higher reaction rate with higher temperature and higher H^+ ion concentration.

One of the defluoridation mechanisms may be: H^+ ion concentration is higher than OH^- ion under weak acidic conditions (pH = 5.5-6.5). H^+ combines with fluoride to form HF_2^-. TCP ($K_{sp}* = 10^{-23}$) can be partially dissociated in water, forming the positive ion $Ca_3PO_4^{3+}$, which can combine with HF_2^- to produce $Ca_3PO_4{\cdot}(HF_2)_3$. Thus six fluoride ions and three hydrogen ions are fixed in this reaction. This is in accordance with our experiments where pH increased with 0.66-1.64 units during the defluoridation process when the raw water was acidic (Table 1). At neutral pH range (pH = 7.6-8.5), the concentration of H^+ ions in the solution is approximately equal to the concentration of OH^- ions. In this case, OH^- can compete with HF_2^- in the reaction with $Ca_3PO_4^{3+}$, to form $Ca_3PO_4{\cdot}(HF_2)_2(OH)$. At neutral pH, the rate of defluoridation was lower than at acidic pH. Also the consumption of H^+ ions decreases so that the pH levels are only increased by 0.07-0.52 during the process (Table 1). In a weak alkalinity solution (pH = 8.5-9.5), the concentration of OH^- ions is higher than the concentration of H^+ ions, and thus, higher than the concentration of HF_2^-. In this case $Ca_3PO_4{\cdot}(HF_2)(OH)_2$ may be formed, in which less fluoride is fixed and OH^- is consumed so that the pH levels of treated water decrease. This is in accordance with our experiments where pH decreased by 0.32-1.24 units, based on the raw water.

The possible reactions are:

Acidic pH:

$$Ca_3(PO_4)_2 + 3\ H_2O + 6\ F^- \rightarrow Ca_3PO_4{\cdot}(HF_2)_3 + PO_4^{3-} + 3\ OH^-$$

Neutral pH:

$$Ca_3(PO_4)_2 + 2\ H_2O + 4\ F^- \rightarrow Ca_3PO_4{\cdot}(HF_2)_2(OH) + PO_4^{3-} + OH^-$$

Alkaline pH:

$$Ca_3(PO_4)_2 + 2\ H_2O + 2\ F^- \rightarrow Ca_3PO_4{\cdot}(HF_2)(OH)_2 + PO_4^{3-} + H^+$$

These chemical reactions will predict that the removal activity of TCP will decrease with increasing pH, that the concentration of phosphate in the treated water is independent of pH, and that pH will move towards neutral pH. These predictions are identical with our findings.

Wang Liangfang et al. (1993)[6] reported that defluoridation of water using TCP can be a mechanism which needs Ca^{2+}. That fluoride combines with Ca^{2+} forming CaF_2 which then links with $[Ca_3(PO_4)_2]_n$ forming $[Ca_3(PO_4)_2]_n{\cdot}CaF_2$. However, this reaction mechanism cannot explain such phenomenon as the pH movement towards neutral pH. Further studies and demonstrations are required on the effects of Ca^{2+} containing raw water on the defluoridation mechanism of TCP and interaction conditions.

CONCLUSIONS

Based on the results presented above, the following conclusions can be drawn:

There is a negative correlation between the defluoridation efficiency of TCP and the pH levels of raw water, and a positive correlation between the defluoridation efficiency and the temperature as well as the contact time.

The defluoridation contact time is practically cut down when polyacrylamide is used as coagulant.

The defluoridation of TCP may be a complex chemical reaction mechanism which needs energy.

ACKNOWLEDGEMENTS

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EFFECT OF pH ON DEFLUORIDATION OF WATER BY MAGNESITE

JJ Singano*, DA Mashauri[**] E Dahi[***] and FW Mtalo[**]

SUMMARY: The dissolution of fluoride in water as well as its adsorption on defluoridation agents is very much influenced by the pH of the solution. Studies carried out showed that magnesite calcined into magnesia has an optimum fluoride removal capacity at pH levels between 10.0 and 11.0. For cases where the initial pH was lower than the optimum range, the reaction increased the pH to the optimum range. For drinking water quality purposes, it is recommended to have pH adjusted after treatment.

Key words: Calcined magnesite, magnesia, fluoride, defluoridation, pH.

INTRODUCTION

In Tanzania magnesite is locally available in the northern part at Chambogo in Same District, Loborosite in Kiteto District and Longido in Monduli District. At present magnesite is being exploited at Chambogo mines[1].

In defluoridation of drinking water by using magnesite, fluoride is removed by ion exchange or by chemical reaction with the adsorbent. Removal in this paper refers to total mechanism of adsorption and ion exchange.

The general principles of the surface chemistry of oxides in contact with an aqueous solution are as follows: The hydroxyl groups behave amphoterically. The hydroxide ion association reaction are as shown in equation 1 for positively changed surfaces, in equation 2 or 3 for neutral surfaces and in equation 4 for negatively charged surfaces.

$$\text{-M-OH}_2^+ \rightleftarrows \text{-M-OH} + H^+ \qquad \text{Eq. 1}$$

$$\text{-M-OH}_2^+ + OH^- \rightleftarrows \text{-M-OH} + H_2O \qquad \text{Eq. 2}$$

$$\text{-M-OH} \rightleftarrows \text{-M-O}^- + H^+ \qquad \text{Eq. 3}$$

$$\text{-M-OH} + OH^- \rightleftarrows \text{-M-O}^- + H_2O \qquad \text{Eq. 4}$$

Equation 1 is favoured at low pH, while equation 4 is favoured at high pH.[2]

Despite the high affinity of fluoride for the metal on the surface of adsorbents, fluoride ions are adsorbed mainly by the positively changed surface as shown in equation 5 and 6. However, to some extent it can also be adsorbed by an ion exchange mechanism even when the surface is neutral as shown in equation 7.[2]

At positive surfaces:

$$\text{-M-OH} + HX \rightleftarrows \text{-M-OH}_2^+ \text{---} X^- \qquad \text{Eq. 5}$$

$$\text{-M-OH}_2^+ \text{---} X^- + F^- \rightleftarrows \text{-M-F} + X^- + H_2O \qquad \text{Eq. 6}$$

At neutral surfaces:

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[*] * Ministry of Water, Energy and Minerals, PO Box *, Dar es Salaam Tanzania.
[**] Faculty of Engineering, University of Dar es Salaam, PO Box , Dar es Salaam Tanzania.
[***] Center for Developing Countries, Technical University of Denmark, DK-2800 Lyngby.

$$-M\text{-}OH + F^- \qquad + F^- \quad \rightleftarrows \quad -M\text{-}F \qquad + OH^- \qquad \text{Eq. 7}$$

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 charges complex and the positively charged surface. At the same time, when the pH increase beyond an optimum value, the hydroxyl groups (-M-OH) will gradually disappear forming more negatively charged surfaces as shown in equation 3. In addition OH^- will compete with fluoride ions for available sites left on the surface[1,2].

Hence effect of pH plays a big role in defluoridation by magnesia (MgO). In order to examine the effect of pH on defluoridation by using magnesia, chemo-stat experiments were carried out.

MATERIALS AND METHODS

Preparation of Magnesia: Pieces of magnesite from Chambogo were calcined at 700°C for 4.5 hours.

Chemo-stat Experiments. The different experiments were carried out in series under different conditions, namely: (a) fluoride and pH were kept constant. (b) fluoride was constant and pH was not controlled. (c) pH was constant and fluoride was not controlled.

The chemo-stat consisted of three units from Metrohm: 715 Dosimat, 614 Impulsomat and a 691 pH Meter. In experiments (a) and (b) fluoride was added automatically to the reaction beaker from a stock fluoride solution on the dosimat of 2.00 g F/L. In experiment (a) acid or base was added manually from stock solutions in burettes of 0.25 M HNO_3 and 0.25 M KOH. In experiment (c) acid was added by the dosimat. The reaction beaker contained 1 L 10 mg F/L (NaF in distilled water). The beaker was placed in a Julabo 3U water bath at 25°C and the solution was stirred by a paddle stirrer. The fluoride concentrations were recorded directly in the reaction beaker using a Radiometer F1052 fluoride electrode and Metrohm Ag/AgCl reference electrode with sleeve type diaphragm connected to the Metrohm 691 pH-meter. pH were measured using a Metrohm combined glass electrode in connection with a Metrohm 691 pH-meter.

At time zero 0.5 g magnesia was added to the reaction beaker. All experiments were run for 5 hours. In (a) and (c) pH was kept constant at different values between 7 and 12. Recordings were made of fluoride added, pH, mV readings and acid added.

Batch experiment: In another experiment neither pH nor fluoride were kept constant. All other conditions as in the chemo-stat experiments.

RESULTS

Experiments with constant fluoride concentration. Figure 1 shows the fluoride uptake on magnesia, measured as the amount of fluoride added to keep a constant fluoride electrode potential in the solution, at the various constant pH-values together with the experiment with no control of pH. The 5 hours fluoride removal capacity is in this context defined as:

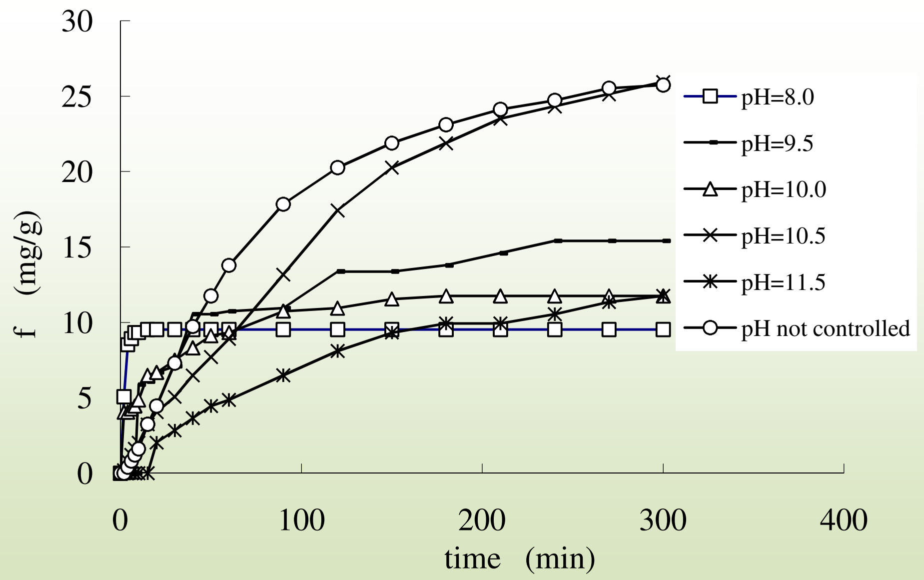

FIGURE 1. Fluoride uptake on 0.5 g/L magnesia in chemostat experiments with constant fluoride concentration S = 10 mg/L and constant pH as indicated.

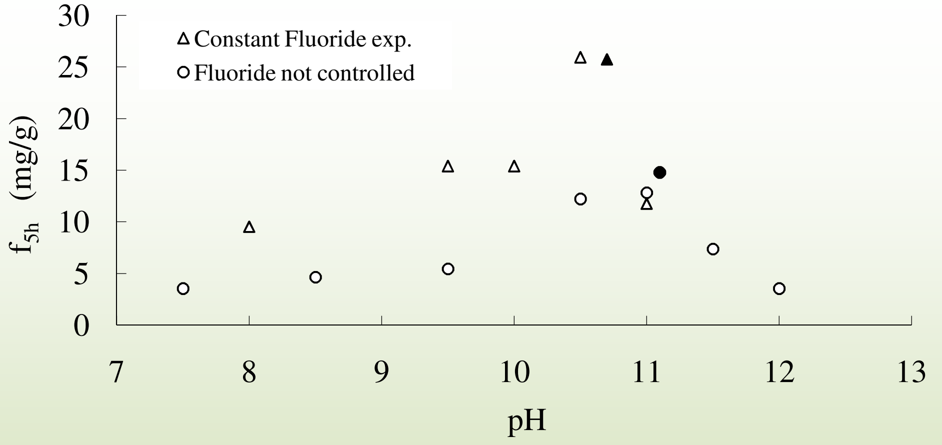

FIGURE 2. Five hours fluoride removal capacity as a function of pH. Fluoride concentration is held constant at S = 10 mg/L (triangles) or left uncontrolled from S_0 = 10 mg/L (circles). pH is held constant by a chemostat except in two experiments (filled in marks).

Suspended magnesia concentration X_M= 0.5 g/L.

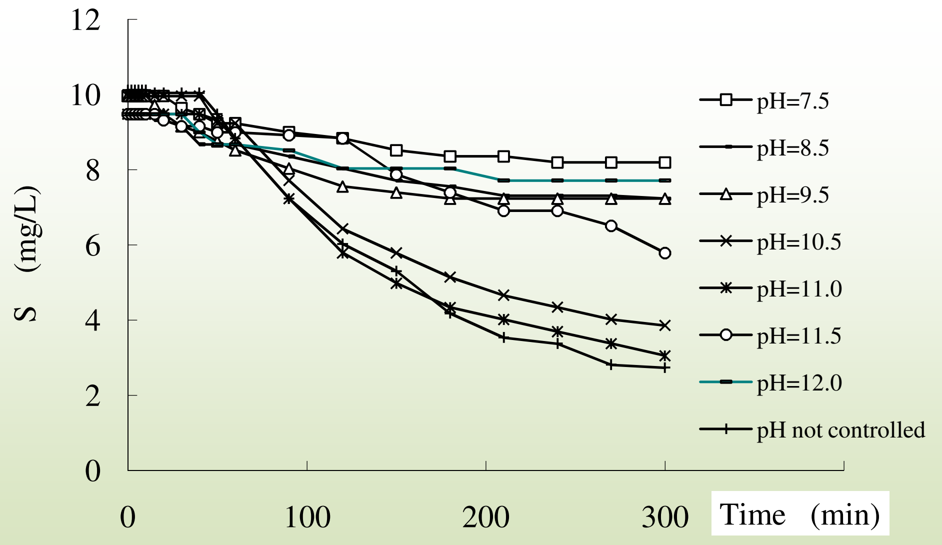

FIGURE 3. Fluoride concentration development in chemostat experiments with constant pH as indicated. Magnesia suspended concentration X_M= 0.5 g/L.

$$f_{5h} = \frac{V \cdot \sum m_{F^-}}{X_M} \qquad \text{Eq. 8}$$

Where:

f_{5h} is the specific fluoride removal capacity at 5 hours experiment (mg/g)

V is the volume of water (L)

$\sum m_{F^-}$is the amount of fluoride added after 5 hours (mg)

X_M is the suspended concentration of magnesia (g/L)

f_{5h} is shown as a function of pH in Figure 2. The results show that the optimum pH for fluoride removal is at about 10.5 to 11.0.

Experiments with no addition of fluoride. Figure 3 shows fluoride concentrations as a function of time in experiments with and without control of the pH. A 5 hours fluoride removal capacity is defined similar to the experiments with addition of fluoride:

$$f_{5h} = \frac{S_0 - S_{5h}}{X_M} \qquad \text{Eq. 9}$$

Where

$S_0$is the fluoride concentration at time zero (mg/L)

Sis the fluoride concentration after 5 hours experiment (mg/L)

f_{5h} is shown in Figure 2 as a function of pH, together with results of the constant fluoride concentration experiments. It also shows that the fluoride removal is highest when pH is about 11.0.

DISCUSSION

It is demonstrated through the present experiments that calcined magnesite from Chambogo in Tanzania is able to adsorb fluoride from water in batch systems. The uptake curves seems to differ from usual adsorption curves by a certain lag period or delay before adsorption starts, as seen in Figure 3. This has no influence on practical defluoridation as defluoridation using magnesia is thought to be carried out in columns.

The results clearly show that pH is extremely important for defluoridation by magnesia. Figure 2 demonstrates that adsorption has a maximum at pH 10.5-11.0. This result is obtained in two different types of experiments, in some experiments fluoride concentration was kept constant and in others it was falling during adsorption. The optimum is thought to be related to the surface chemistry of magnesia. At very high pH the surface will be negatively charged and fluoride will compete with OH^- for adsorption.

An important result of this study is also that the magnesia is by itself exactly adjusting the pH to the optimum pH = 10.5-11.0. Although the magnesia is very sensitive to pH, it is for practical applications therefore not necessary to adjust pH for optimization of treatment.

However it should be stressed that for practical applications pH needs to be adjusted *after* treatment. The resulting pH is far above the WHO guidelines of 6.5-8.5. More investigations are needed to find a way of regulating the pH, which is appropriate for use in Tanzania.

ACKNOLEGMENTS

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SORPTION ISOTHERMS OF FLUORIDE ON FLOCCULATED ALUMINA

E Dahi*, H Bregnhøj* and L Orio*
Copenhagen, Denmark

SUMMARY: A new model for the design of alum dosage in the flocculation-sedimentation process for defluoridation of water is developed. It is based on the finding that correlation between the fluoride residual in the water and the concentration of the uptaken fluoride in the flocculated alum follows a Freundlich isotherm for identical residual pH in the treated water. The sorption capacity constant α is estimated to be 6.5 $mg^{1-1/\beta} \cdot L^{1/\beta} \cdot g^{-1}$, and the sorption intensity constant β is estimated to be 1.4, valid for optimum pH in the treated water. This was found to be between 6.2 and 7.0. Deviation from this range may cause a significant decrease in the removal efficiency of the added alum. It is recommended that the addition of lime should no longer be 5% of the alum dosage, as given in the Indian Guidelines, rather adjusted in order to reach the optimum pH. In Tanzania waters this was found to account 20-50 % of the alum dosage.

Key words: Alumina, fluoride, sorption isotherms, Nalgonda technique, lime, defluoridation, pH-optimum.

INTRODUCTION

Defluoridation of water is mainly based on two categories of techniques. The first is the flocculation-sedimentation and the second is the filterbed sorption. Aluminum components are well known to be applicable in both categories, e.g. the use of alum in flocculation-sedimentation and the use of activated alumina in column sorption. Especially the use of alum, i.e. aluminum sulfate or potassium aluminum sulfate has been tested for defluoridation of water in many countries.

Since its discovery by Boruff in 1934[1], the defluoridation by means of alum has been studied and developed by many workers. Cheap and simple as it is, the alum process has been studied mainly for use in developing countries. The work carried out by the National Environmental Engineering Research Institute, NEERI, in India has been most significant and resulted in development of the technique at a small water works in the Nalgonda town in the Southern part of the country. Furthermore, detailed testing and dosage design criteria were developed.[2] The mechanisms of removal are not yet completely understood. While the activated alumina defluoridation has been understood as a sorption process, the Nalgonda technique has mainly been understood as a "co-precipitation". This is probably due to lack of a simple stoichiometric correlation between the added alum and the obtained fluoride removal.

The purpose of this study is to elaborate on the significance of pH on optimization of the dosage of alum and lime. Furthermore to develop a scientific tool for estimating of the required dosage of alum, as a function of the contents of fluoride in the raw water and the required residual concentration in the treated water.

* *Center for Developing Countries, Technical University of Denmark, DK-2800 Lyngby, Denmark.*

MATERIALS AND METHODS

Two types of experiments were carried out using a jar test apparatus (Phipps & Birds Stirrer 7790-402), as 6 batches in parallel. Each batch consisted of 1-L plastic beakers containing 1 L solutions of sodium fluoride, analytical grade, in distilled water at different given initial concentrations and pH-buffering. The temperatures were 20 ± 1 °C.

Dosage Determination Experiments. In the first type of experiments, pH was allowed to vary as a function of the dosage of alum and lime. Alum, technical grade normally used in water works, was added together with lime as powder. The chemicals were added at time nil to alle jars in parallel. The beakers were mixed vigorously using 100 RPM paddle stirring for ½ minute. Then slow mixing, 25 RPM, was carried out for 10 minutes. Hereafter 1 hour of settling before measurement of pH and fluoride concentrations. Alle experiments and measurements were carried out in 2-4 replicates. The Nil dosage was used as a control.

pH-controlled Experiments: In the other type of experiments pH = 6.8 was controlled by pre-addition of 0.025M buffer of KH_2PO_4 and Na_2HPO_4, both pro analysis. Each experiment was carried out in 2-4 replicates.

Fluoride and pH Measurements: The concentration of fluoride and pH in the water were both measured and monitored continuously using a Radiometer F1052 fluoride electrode and Metrohm Ag/AgCl reference electrode with sleeve type diaphragm connected to a Metrohm 691 pH-meter. Tisab[3] was added to 5 mL samples taken for fluoride measurements according to Standard Methods.[4]

RESULTS

By adding alum to water containing 12.2 ± 0.9 mg F/L at three different levels, different removal efficiencies are obtained. Figure 1 illustrates the obtained residual concentration as a function of residual pH. The different pHs are obtained because of different additions of lime, between 75 and 350 mg/L. It is seen that fluoride removal efficiency varies between 54 and 79 % for the same dosage level, 700 mg/L alum. Similar figures are obtained for the other dosage levels applied. Clearly, the removal has an optimum within the range pH 6.2 to 7.0. This phenomena is well-known for removal of silt by the same method and has also been reported for fluoride by Lagaude *et al.*[5]

Designating the amount of added alum as A (in g), the volume of treated water as V (in L), and the concentration of fluoride in the raw and treated water as F_r and F_t (in mg/L), the concentration of removed fluoride in the flocculated aluminum f (measured as mg F/g added alum) may be calculated as

$$f = \frac{(F_r - F_t) \cdot V}{A}$$

When this fluoride density in the "flocculated alum" is correlated to the residual concentration of fluoride in the water, a very scattered picture shows up, as long as pH is not controlled. However, when the same correlation is determined for a given residual pH, the correlation turns out to be a Freundlich type, figure 2.

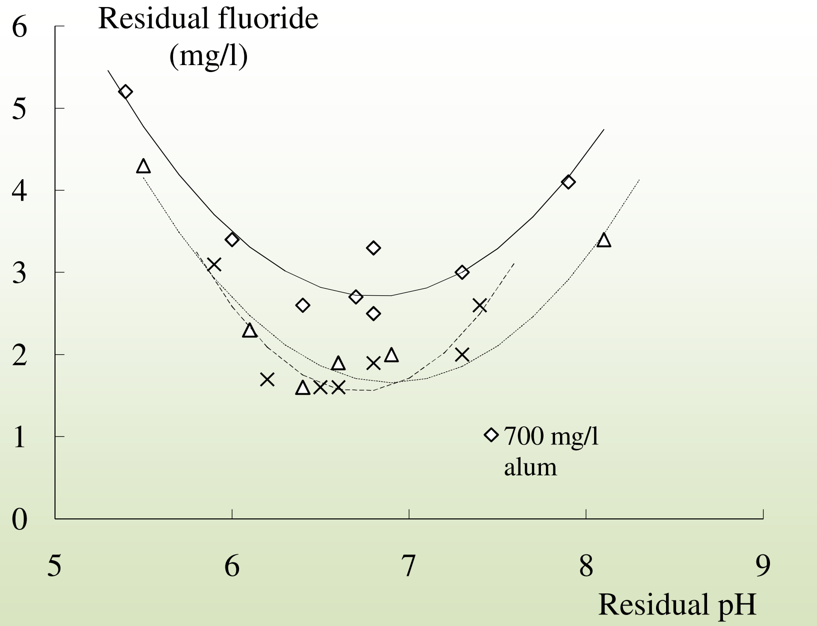

FIGURE 1. results of batch experiments with different amounts of alum and lime and start fluoride concentrations of F_r = 12.2 ± 0.9 mg/L.

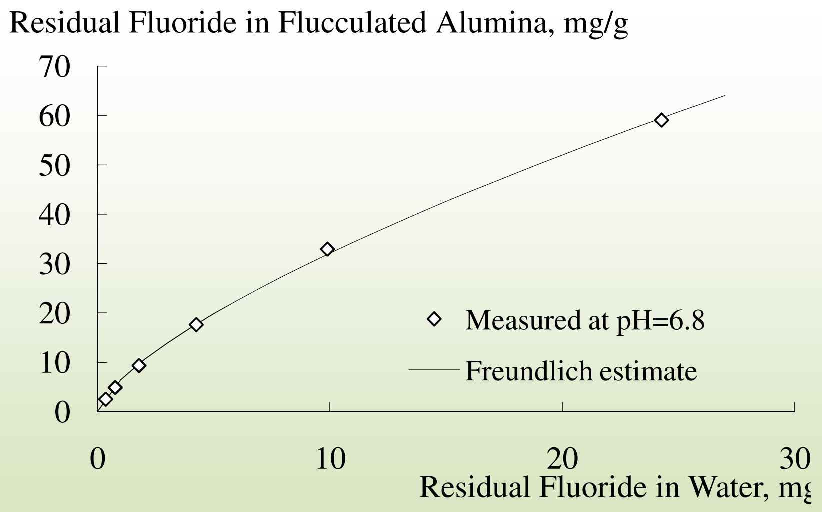

FIGURE 2. results of batch experiments with constantly held pH = 6.8, with Freundlich estimate.

$$A = \frac{(F_r - F_t)\cdot V}{\alpha \cdot F_t^{1/\beta}}$$

Where:

α is the sorption capacity constant, the unit being $mg^{1-1/\beta}\cdot L^{1/\beta}\cdot g^{-1}$

β is sorption intensity constant, dimensionless.

The results showed that, for residual pH = 6.8 and residual fluoride concentration F_t between 0.35 and 24 mg/L:

$\alpha = 6.5\ mg^{1-1/\beta}\cdot L^{1/\beta}\cdot g^{-1}$

$\beta = 1.4$

The results of this and other studies of ours show that the amount of lime required to obtain optimum pH may vary as much as 20-50 % of the added alum. Thus it has not been possible, if optimum pH are to be achieved, to develop valid guidelines about how much lime should be added. The amount of lime seems to be dependent on several factors, including the alkalinity of the water, the added amount of alum, the removed fluoride, and above all on the quality of the used lime.

DISCUSSION

Figure 1 confirms that larger amounts of alum can be used without gaining correspondingly more efficient removal of fluoride. Furthermore it is seen that high dosage of alum, i.e. more than 1,000 mg/L is required in order to treat water having fluoride contents about 10 mg/L, even when a residual concentration of 1.5 mg/L is accepted. Such high concentration of alum would result in too high concentrations of sulfate in the treated water. All sulfate, about 43% of the added alum, would reside in the water, along with waters original content of sulfate. Water containing more than 250 mg/L sulfate is taken by some consumer as a little bit "salty", and 500 mg/L sulfate may cause laxative effect among the consumers, first and foremost the children[6]. Thus there are good reasons to rationalize the design of defluoridation by alum. On one hand it may be difficult to obtain sufficient removal of fluoride, on the other hand it may be difficult to avoid impairing the water quality with respect to sulfate.

In the guidelines for defluoridation published by NEERI in 1987[7], later confirmed in guidelines of 1993[8], the alum required to reduce the fluoride contents of a water from 10, 8, 6, 5, 4, 3 and 5 mg/L down to 1 mg/L are presented in a table form. The table includes selected contents of alkalinity of the raw water, between 125 and 1,000 mg $CaCO_3$/L. Unfortunately, the experiences gained in Tanzania and in Denmark have shown that the usability of these design guidelines has two serious limitations.

Firstly many water sources have fluoride/alkalinity characteristics outside the ranges presented in the NEERI table. In such a situation, as found in the Arusha region in East Africa, the NEERI guidelines are of less use.

Secondly, addition of lime, as recommended by NEERI to be 5 % of the added alum, have shown to result in pH-values in the treated water, which are significantly different from what is optimum for the fluoride removal. This study has shown that any addition of lime which may result in pH values different from 6.2 - 7.0 would reduce the effectiveness of the treatment. Furthermore it may be seen from figure 1 that the reduction of effectiveness may be quite significant even for 1 unit deviation from the optimum range.

On this background it may be considered as an advantage to use the Freundlich correlation for design purposes. However, the Freundlich formula does not include the dependency of the sorption constants on pH. Thus it may give the false impression, that the same constants can be used for any residual pH. Probably this could be solved by deriving another formula for the dependency of the sorption constants on pH. From practical point of view however, only optimum pHs are of interest.

The results of this study indicate that α, on the contrary to β, is dependent on pH. For engineering design, β may be assumed to be constant, 1.4. This simplification may be utilized to estimate an appropriate α for any given treatment conditions. In this way one could take into consideration locally determined variations in water quality and alum characteristics.

CONCLUSION

The removal of fluoride in the alum flocculation-sedimentation process is highly dependent on the residual pH of the water, the optimum is estimated to be obtained at pH = 6.2 - 7.0. The addition of lime should then be adjusted to obtain the optimum pH in the treated water. In such a case the residual fluoride concentration shows a Freundlich type sorption isotherm, which may be used in the process design for estimation of the required alum dosage.

ACKNOLEGMENTS

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USE OF ACTIVATED CLAY FOR DEFLUORIDATION OF WATER

K Bjorvatn[*] and A Bårdsen[*]

SUMMARY: A number of studies have been made to assess the fluoride binding potential of fired clay. Most researchers have concluded that the processes involved are too slow, and the fluoride binding capacity is too low. Recently reported findings, however, indicate that clay calcined at temperatures < 800°C may be suited for practical defluoridation of potable water. The present study presents data obtained by the use of red soil (lateric clay), calcined at 570°C for three hours. Fluoride containing water, at concentrations from 5.50 and 7.75 mg-F/L (well water) to 12, 30 and 130 mg-F/L (NaF-solutions), were exposed to calcined laterite, w/v 1:10. Water samples were taken at 1, 2, 4, 12, 24, 48, 72 h and after one week and analysed for fluoride by the use of a fluoride selective electrode. Rapid reduction of the fluoride concentration in the water was observed during the first few hours. A steady state was in most cases reached in 48 hours. Best results were obtained by the use of laterite from Balang, Northern Cameroon: Here the fluoride concentration was reduced from 5.47 to 0.48 mg-F/L in two h, from 12.2 to 0.26 mg-F/L in 12 hours and from 31.2 to 0.76 mg-F/L in 12 h. Water with 132 mg-F/L had a fluoride concentration of only 4.58 mg-F/L after one week's exposure to calcined lateric clay. A "total" analysis (ICP/MS) of well water before and after defluoridation showed minor changes in most micro elements. No adverse changes in taste or smell were observed in defluoridated water.

Key words: Activated clay, defluoridation, fluoride, calcined clay.

INTRODUCTION

Fluoride may be found in all natural waters; even in precipitation. The fluoride content of creeks and rivers and most inland lakes is normally less than 0.3 mg-F/L1; subsurface water has, on an average, slightly more fluoride2, while wells and lakes in certain high-fluoride areas may contain very high fluoride concentrations. The maximum value reported for surface water seems to be 2.8 g-F/L, which was found in Lake Nakuru, Kenya3.

Fluoride in low-fluoride rivers and lakes may be derived from precipitation, while chemical weathering of fluoride-rich rocks in the drainage basin seem to provide fluoride for high-fluoride inland lakes[4]. The volcanic rocks of the rift zone of East Africa are richer in F than analogous rocks in other regions[5]. Consequently, rivers, lakes and boreholes in the African Rift Valley often provide water with exceptionally high fluoride content.

Fluoride in waters is of concern for public health officials as well as for hydrogeologists and geochemists. Prolonged intake of high-fluoride water may create problems such as dental and skeletal fluorosis in the human and also in the animal population. According to WHO, drinking water of adequate quality should contain max. 1.5 mg-F/L[6]. Where water intake is high, e.g. in tropical areas, the recommended fluoride concentration of drinking water should be substantially reduced. A formula has been proposed to calculate "optimum" fluoride concentration[7]:

Department of Dental Research, University of Bergen School of Dentistry, Aarstadveien 17, N-5009 Bergen, Norway.

$$Optimum\ level = \frac{0.34}{-0.038 + (0.0062 \cdot \text{mean max.temp.(°F)})}$$

To avoid health problems, high-fluoride water should not be used for household purposes. In arid or semiarid areas, however, alternative, low-fluoride water sources may not be available, and defluoridation is needed to render the water potable8. Excessive fluoride may easily be removed by modern water treatment. For practical and financial reasons, however, high-technology water treatment is unavailable in rural East Africa. Priority, therefore, should be given to the development of simple devices for defluoridation of drinking water at a (preferentially) home based level. A number of methods have been proposed, see e.g. Hendrickson and Vik.[9]

Defluoridation devices should meet a number of the following requirements[10]:

- Modest investment
- Low maintenance cost
- Simple design
- Operable by villagers
- Able to reduce fluoride content, e.g. from 5 to 0.5 mg/L
- Improve water quality in general
- Ingredients maintainable for acceptable period

No single method seems to meet with all the requirements, but some techniques are more widely used than others. The so-called Nalgonda technique, which comprises addition to high-fluoride water of, in sequence, Na-aluminate or lime, bleaching powder and filter alum, is in frequent use in India11. Likewise, the use of bone char has received much attention[12].

The aim of the present paper is to discuss a third possibility: the use of clay or soil for defluoridation of drinking water.

Clay consists of minute mineral particles which have precipitated under water. The main components of clay are *oxygen, silicon, and aluminium.* Smaller amounts of *iron, potassium, calcium, magnesium,* and other elements are also present. Most clays also contain *fluoride*; concentrations of 2 to 4 g-F/kg have been reported[13]. Also the physical composition of clay varies; several clay minerals, such as kaolinite, illite, bentonite, and montmorillionite, can be distinguished. The different clay minerals may have different fluoride-binding capacities[14]. Naturally occurring clays normally contain a mixture of clay minerals.

Simple, locally made pottery has been used for "water treatment" for thousands of years; especially for transportation and storage of water. Claypots have a cooling effect on the water, and may - possibly - also cause a reduction in the water's fluoride content[15].

Various researchers have assessed the fluoride binding effect of simple pottery. Thus Ndegwa[16] reported a fluoride binding capacity in clayware of 80 mg-F/kg, while Zewge & Moges[17] found that pot chips were able to bind as much as 560 mg-F/kg. Hendrickson & Vik[9], however, concluded that fluoride uptake in clayware is slow and of limited capacity.

In a more recent investigation Hauge et al (1994) assessed the effect of firing temperature on the fluoride binding capacity of clay[18]. They concluded that firing temperatures between 500 and 700ºC produced clayware with optimal fluoride binding properties, while the fluoride binding processes were greatly reduced by firing above 800 degrees. A certain increase in the fluoride content could sometimes be seen when water was exposed to high-fired ceramics.

During the last few years the fluoride binding capacity of a series of different clays have been tested at the Inst. of Dental Research, Univ. of Bergen School of Dentistry[19].

The aim of the present paper is to demonstrate defluoridation of water by the use of lateric red clay from Cameroon, West-Africa.

MATERIALS AND METHODS

Red top soil (laterite) was collected from two different sites, N'Gaoundéré and Balang, in the Adamoua province, North Cameroon. The material was dried, and subsequently fired at 570 °C for three hours. The fired clay was crunched, and 10 g samples were weighed up and placed in plastic bottles to which 100 ml aliquots of aqueous *fluoride solutions* were added, at concentrations ranging from 5.42 to 132 mg-F/L. All solutions above 10 mg-F/L were made by dissolving suitable amounts of NaF in de-ionized water, while solutions of less than 10 mg-F/L were taken from natural Norwegian ground water wells. Two parallel tests were performed for each of the laterite samples. Bottles were kept agitated during the test period.

At given time intervals (1h, 2h, 4h, 12h, 24h, 48h, 72h, 1 week) 5 ml liquid test samples were extracted. After the addition of TISAB III (1:10) the fluoride content of the samples was measured by the use of a fluoride selective combined electrode (Orion 96-09-00) connected to an Orion Ionalyzer 906 - according to standard procedure[20].

The elemental composition of the Balang clay was analysed by the use of a Philips SEM 515 scanning electron microscope combined with an EDAX PV 9900 energy dispersive x-ray analyser. KV = 20.0.

In order to assess possible changes in ionic composition of the waters, a total analysis of water from Well II was made by the use of ICP/MS - *before* and *after* defluoridation with lateric clay from Balang, Cameroon.

RESULTS

Upon exposure to fired clay a sharp reduction of fluoride concentration in the water was seen all solutions, especially during the first hour, see Table 1 and 2. The rapid initial fluoride binding process tapered off, in most cases reaching a plateau (steady state) in approximately 48 hours. During the agitation the fluoride containing water tended to become discoloured. The red soil, however, settled quickly when agitation stopped. The water tasted good, even after one week's defluoridation.

The main elements of the Balang-laterite were Al, Si and Fe. As compared to ordinary (grey) clay, the iron content of the red lateric clay was very high. The elemental set up, according to the EDAX analysis, is given in Table 3.

TABLE 1: Defluoridation of High-fluoride water by the use of (humus-containing)laterite from N'Gaoundéré, Cameroon. results in mg-F/L.

Water sample	Contact time: Start	1h	2h	4h	12h	24h	48h	72h	1w
Well I	5.42	2.52	2.22	1.34	0.73	0.59	0.50	0.48	0.42
Well II	7.76	4.73	3.76	2.41	1.19	0.81	0.71	0.69	0.58
NaF I	12.1	7.28	5.96	4.27	1.43	0.84	0.67	0.65	0.55
NaF II	29.7	17.9	15.9	12.5	6.15	4.48	3.33	2.89	2.17
NaF III	120	82.5	78.0	68.2	60.8	54.1	48.7	46.0	42.4

TABLE 2. Defluoridation of high-fluoride water by the use of laterite from Balang, Cameroon. results in mg-F/L.

Water sample	Contact time: Start	1h	2h	4h	12h	24h	48h	72h	1w
Well I	5.47	0.55	0.48	0.46	0.22	0.17	0.18	0.09	0.11
Well II	7.75	1.08	0.88	0.78	0.39	0.27	0.23	0.15	0.15
NaF I	12.2	2.44	1.94	1.36	0.26	0.17	0.13	0.11	0.11
NaF II	31.2	11.7	9.98	8.05	1.69	0.76	0.55	0.45	0.40
NaF III	132	73.2	64.1	55.4	27.5	18.5	11.4	8.62	4.58

The chemical profile of water from Well II, before and after defluoridation, is given in Table 4.

DISCUSSION

Fluoride is a natural constituency of soils. Most fluoride is firmly bound to minerals or other chemical compounds but may, over time, be washed out. Fluoride concentrations in soil tend to increase with depth. In high mountain areas, the fluoride content of the soil is usually low[3]. The clay samples used for the present experiments were taken from top soil in the savannah of Northern Cameroon, at approximately 1100 m above sea level. Laterite is a reddish ferruginous soil, which is formed in tropical regions by the decomposition of the underlying rocks.

As to the main components, laterite is similar to other clays. Table 3, however, demonstrates the high iron content of laterite. Lateric clays are widespread in Africa, and are frequently used for the production of bricks and simple clay ware. The fluoride content of the lateric clays used for the present experiments is not known. There seems to be, however, an inverse relationship between the soil's fluoride content, and its ability to absorb fluoride from water, and, consequently, low fluoride values in the relevant clays would be expected.

TABLE 3. Elemental composition of lateric clay from Balang, Cameroon according to EDAX analysis.

Element	Weight percent
Na	0.10
Mg	0.60
Al	30.50
Si	25.13
P	0.15
K	0.29
Ca	0.18
Ti	6.01
Fe	36.83
Ni	0.07
Cu	0.15

TABLE 4. Total analysis. Natural ground water before and after defluoridation with laterite from Balang, Cameroon.

Element	Before def. µg/g	After def. µg/g	Element	Before def. µg/g	After def. µg/g
F	7.76000	0.15000	Pr	0.00000	0.00004
Li	0.00111	0.00077	Nd	0.00000	0.00012
B	0.00643	0.00226	Sm	0.00000	0.00001
Na	18.00000	15.00000	Eu	0.00001	0.00002
Mg	0.88550	0.90000	Gd	0.00000	0.00002
Al	0.01328	0.03773	Ni	0.00000	0.00154
Si	1.34100	1.00200	Cu	0.00513	0.07573
Ca	9.70000	2.30000	Zn	0.00000	0.00987
Sc	0.00110	0.00075	Ga	0.00019	0.00005
Ti	0.00962	0.00451	As	0.00011	0.00019
V	0.00011	0.00526	Se	0.00086	0.00395
Cr	0.00500	3.50000	Br	0.10750	1.31100
Mn	0.00024	0.01681	Rb	0.00189	0.00078
Fe	0.00632	0.02452	Sr	0.20000	0.20000
Co	0.00001	0.00046	Y	0.00001	0.00005
Rh	0.00003	0.00004	Zr	0.00001	0.00016
Pd	0.00001	0.00000	Nb	0.00000	0.00004
Cd	0.00029	0.00745	Mo	0.00848	0.00518
Sn	0.00000	0.00004	W	0.00290	0.00004
Sb	0.00000	0.00003	Os	0.00000	0.00003
I	0.00049	0.00127	Au	0.00000	0.00003
Cs	0.00007	0.00002	Th	0.00000	0.00002
Ba	0.06042	0.10630	U	0.00029	0.00001
Ce	0.00002	0.00019			

The defluoridation kinetics in lateric clays seemed to be in accordance with the model established by Bregnhøj and Dahi[12,21], and the results obtained were safely within the requirements put forward by Phantumvanit et al: fluoride reduction from 12 to ~ 0.25 mg-F/L within 24 h[10]. Water with more than 12 mg-F/L is rarely used for consumption, even in the Rift Valley area.

It is of interest to note that the fluoride concentrations finally obtained in the present experiments, were slightly higher for *natural spring water* which originally contained 7.75 (7.76) mg-F/L than for laboratory-produced water with 12.5 mg-F/L. This may be due to interference of "competing" anions (other than F^-) in the well-water[21].

More research is needed in order to establish the chemical processes responsible for the defluoridation of the water. For practical purposes, however, the important thing is to remove excessive fluoride, without introducing other noxious agents. According to the pilot study (total analysis) of ground water before and after defluoridation, fired laterite caused a relatively great decrease in the calcium concentration and a similar increase in the concentration of chromium. The increase in chromium is unwanted. Apart from Cr, however, all elemental concentrations in defluoridated water were safely within the limits accepted for good drinking water quality[22]. Due to the high iron content of the laterite, one might have expected an increase in the Fe content of defluoridated water. No such change was observed.

Large scale defluoridation tests with lateric clays from various parts of the world should be carried out. Likewise, further studies should be performed to decide the total composition of water before and after defluoridation.

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FLUORIDE SORPTION ISOTHERM ON FIRED CLAY

A Bårdsen* and K Bjorvatn*

SUMMARY: The present study assesses the fluoride-binding capacity of ordinary potters clay, calcined at 600°C and subsequently crushed. Fluoride solutions at concentrations ranging from 12.5 to 1,600 mg-F/L were added to the clay, w/v ratio 1:10. Fluoride concentration was measured after 1 h, 6 h, 24 h, 5 days and 10 days of contact. Based on the registered maximum values for fluoride adsorption in the various solutions, fluoride-binding capacities were calculated. A linear relation was found between the fluoride uptake and the fluoride concentration in solution at equilibrium, in logarithmic values. This is according to Freundlich's formula: $\ln f = \ln \alpha + 1/\beta \ln S \Rightarrow \ln f = -1.12 + 0.589 \ln S$, where f is fluoride uptake (mg-F/g) and S is the fluoride concentration in solution at equilibrium (mg-F/L). Correlation coefficient (r^2) for this relation was 0.991, p-value < 0.001. This indicates that adsorption is a major factor in the fluoride-binding process.

Key words: Defluoridation, potters clay, activated clay, fluoride, adsorption, Freundlich

INTRODUCTION

Due to high fluoride content of drinking waters, fluorosis is endemic in many developing countries[1-4], and simple low cost methods for defluoridation of water are urgently needed[5]. World Health Organization has, for more than 20 years, given this purpose high priority. A number of methods have been developed[6], but so far the ideal method for home-based fluoride removal from drinking water has not been found.

TABLE 1. Composition of potter's clay #1106 given as oxides of elements

SiO_2	58,0 %
Al_2O_3	30,0 %
K_2O	1,2 %
Fe_2O_3	1,0 %
TiO_2	0,9 %
Na_2O	0,6 %
CaO	0,3 %
MgO	0,3 %
Igneous loss	8,0 %

Calcined clay, "ceramics", is frequently used for water purification[7]. Highly sophisticated ceramic water filters are available, but simple pottery may also be used, e.g. for the removal of fluoride in water. Various researchers have tested the fluoride-binding capacity of clay and have come up with rather different results[8,9]. The general conclusion has been, however, that the physico-chemical processes involved are too slow, and that the fluoride-binding capacity of clay is too low for practical water defluoridation purposes[10].

New research has aroused new interest in clayware as a defluoridating agent. Thus Hauge et al[11], have shown that the fluoride-binding capacity of clay decrease with increasing calcination temperatures. When temperatures, however, were maintained at 600-700 °C, encouraging results were obtained. The main components of clay are oxygen, silica, and aluminum. But clay is a very heterogeneous material, and various clay-types may have strikingly different physical and chemical properties. Also the fluoride binding capacities show great variations[8,9,12].

Department of Dental Research, University of Bergen School of Dentistry, Aarstadveien 17, N-5009 Bergen, Norway.

The aim of the present study was to assess the fluoride-binding capacity of ordinary potter’s clay, calcined at 600 °C, when exposed to fluoride solutions of different concentrations.

MATERIALS AND METHODS

Fluoride solutions. A fluoride solution of 1.6 g-F/L was made by dissolving NaF in de-ionized distilled water (3.537 g NaF/L). Solutions of 800, 400, 200, 100, 50, 25, 12.5 mg-F/L were subsequently made by sequential dilution with de-ionized distilled water.

Clay. Ordinary potter's clay (1106 White St Thomas body) was used for the experiments. The composition of the clay, according to the manufacturer (Pot Clay Ltd, Stoke-on-Trent, UK), is given in Table 1.

TABLE 2. Fluoride concentration* (mg-F/L) in different solutions after exposure to fired clay

	Concentration after				
0 h	**1 h**	**6 h**	**24 h**	**5 days**	**10 days**
1600	1327	1270	1270	1140	1150
800	700	635	581	471	460
400	356	327	287	234	230
200	166	144	115	90.7	87.6
100	78.6	65.6	49.2	38.2	36.7
50	34.7	30.9	24	18.1	16.9
25	17.7	16.7	10.6	6.5	5.7
12.5	9.1	8.2	5.1	2.1	17

* mean of three samples

Dry clay was calcined in an electrical furnace, at 600 °C, for 3 hours. The calcined clay was crushed and sieved. Particles <1.0 mm and >3.0 mm were discarded. Twenty-four ten-gram samples of crushed clay were prepared. The individual samples were placed in capped plastic bottles, and 100 ml fluoride solution (w/v ratio 1:10) was added to each bottle. Three parallel samples were prepared with each fluoride concentration. The experiment were carried out at room temperature (21 °C). Test-samples of 3 ml were taken from each bottle for fluoride analyses after 1 h, 6 h, 24 h, 5 days, and 10 days. The fluoride concentration was determined with a fluoride-ion specific electrode (model 96 09 00; Orion Research, Cambridge, Mass., USA), with total ionic strength adjustment buffer (TISAB III) added to the solution as recommended by the manufacturer[13]. The lower detection limit was 10^{-6} M, ~ 0.02 mg-F/L[13].

RESULTS AND DISCUSSION

The experiment showed that the fluoride adsorption in the different solutions increased with increasing time. For all concentrations the equilibrium seemed to be established within 10 days, as shown in Table 2.

The registered maximum values for fluoride adsorption in the various solutions (most often 10-day results) were used for calculating "fluoride binding capacities", as shown in Table 3.

TABLE 3. Fluoride uptake in fired clay (mg-F/g)* after exposure to solutions with different fluoride concentrations

Fluoride concentration in the water at equilibrium S* (mg-F/L)	Fluoride concentration on the clay at equilibrium f* (mg-F/g-clay)
1,140	4.60
460	3.40
230	1.70
87.6	1.12
36.7	0.62
16.9	0.34
5.7	0.20
1.7	0.12

* calculated by the mean of three samples

Adsorption is defined as a process in which molecules adhere to the surface of a solid. In ordinary physical adsorption, the molecules are held to the surface of the adsorbent by Van der Waal's forces. However, the physico-chemical reactions taking place between clay and fluoride in solution is not known in detail. According to Freundlich's adsorption isotherm[14], a linear relation exists between the fluoride uptake and fluoride concentration in a solution at equilibrium, in logarithmic values. This is in harmony with our findings, shown in Figure 1. The equation for Freundlich's adsorption isotherm is $\ln f = \ln \alpha + 1/\beta \ln S$, which when applied to potter's clay gives: $\ln f = -2.58 + 0.589 \ln S$, where f is fluoride uptake (mg-F/g) and S is the fluoride concentration in solution at equilibrium (mg-F/L). Correlation coefficient (r^2) for this relation was 0.991, p-value < 0.001. This indicates that adsorption is a major process in this reaction.

Our study was carried out at room temperature. The rate of chemical reactions normally increases when the temperature increases. Faster reactions might therefore be expected in a hot climate, such as the African Rift Valley, were the simple home-based defluoridation techniques are most urgently needed.

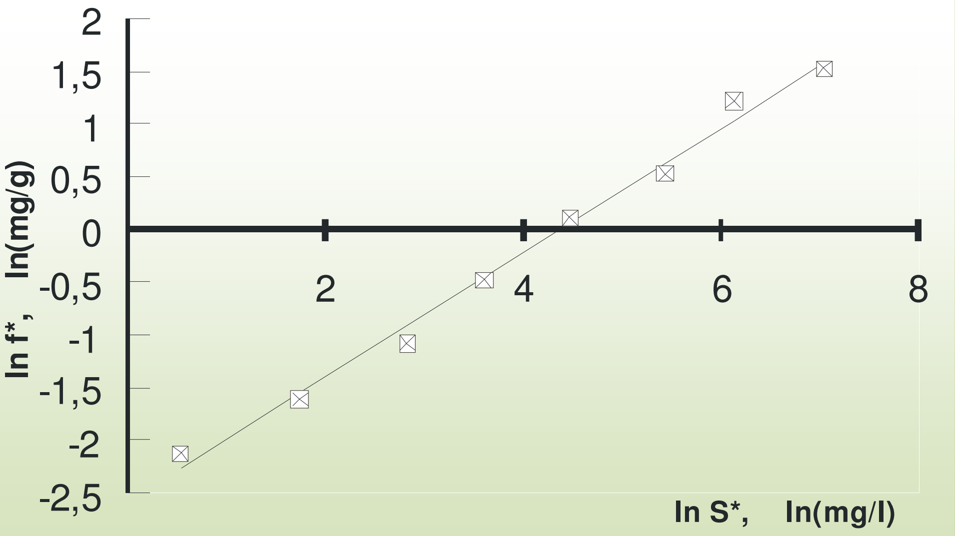

FIGURE 1. Adsorption of fluoride according to Freundlich's formula.

The fluoride binding capacity of clay depends on various factors, and can not be given as one quantity. In order to compare different types of clays, standard procedure for testing should be worked out.

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OPTIMUM OPERATION OF COUNTER-CURRENT WATER DEFLUORIDATION SYSTEM

DS Bhargava*

SUMMARY: In many regions of the world, the groundwater and the surface water have higher than permissible fluoride concentration. A system based on the counter-current movement of the sorbent and the sorbate has been discussed as an ideal, most efficient and economical method of water defluoridation. A technique based on experimental runs on a simple column type moving media adsorber is described for evaluating the optimal operating conditions for maximum advantage. The presented defluoridation methodology has vast scope for field application.

Key Word: Water defluoridation, optimal operation, moving medium reactor, fluoride, bone char.

INTRODUCTION

Fluoride may be present in surface or ground water in varying quantities. The sources of fluoride in water can be the Earth's crust, the ocean and industrial activities. The surface or ground waters contain low to medium fluorides. The manufactures of certain products such as glasses, metals, electroplating, manufacturing parts, pesticides, disinfectants, etc., contribute the fluoride bearing waste waters[1-3]. Such industrial effluents contain large quantities of fluoride. The fluoride content of ground waters in certain parts of India have been reported to vary from 1.5 to 6.3 mg-F/L and even as high as 18 mg-F/L[4]. Excessive fluoride in water, unless removed, cause dental or skeletal fluorosis[5,6]. Indian drinking water supply standards recommended an acceptable fluoride concentration of 1.0 mg-F/L and allowable fluoride concentration of 1.5 mg-F/L for potable waters[4].

Defluoridation methods included physico-chemical methods such as adsorption, ion exchange or chemical precipitation[7,8]. In adsorption, the sorbate from aqueous solution concentrates on sorbent surface. The efficiency depends on the mode of contact between the sorbent and sorbate.

The fixed bed continuously operating column reactor is more efficient than batch reactors[9]. Hassler[10] and Weber[9] suggested that a continuously operating expanded bed reactor increases the sorbent effectiveness.

The expanded bed reactor permits the use of small particle size without the associated problems of excessive head loss or air-binding etc., common to packed-bed operation with fine media[11].

In a continuous operation of the expanded bed reactor, the solid sorbent is added at the top of the column and the spent sorbent withdrawn from the bottom. The solution from which adsorption takes place, flows upwards through the regions of partially utilized sorbent to regions of freshly added sorbent material. Natural segregation of sorbent would allow greater sorbent capacity, because individual particles of the porous material became denser with increasing adsorption and therefore, tend to

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* Department of Civil Engineering, University of Roorkee, Roorkee - 247 667 (U.P.), India

concentrate near bottom of the column. The author developed a continuous operating moving media rector to facilitate the fullest utilization of the sorbent capacity.[12-15]

This paper presents a technique to optimize the operation of moving media reactors.

MATERIALS AND METHODS

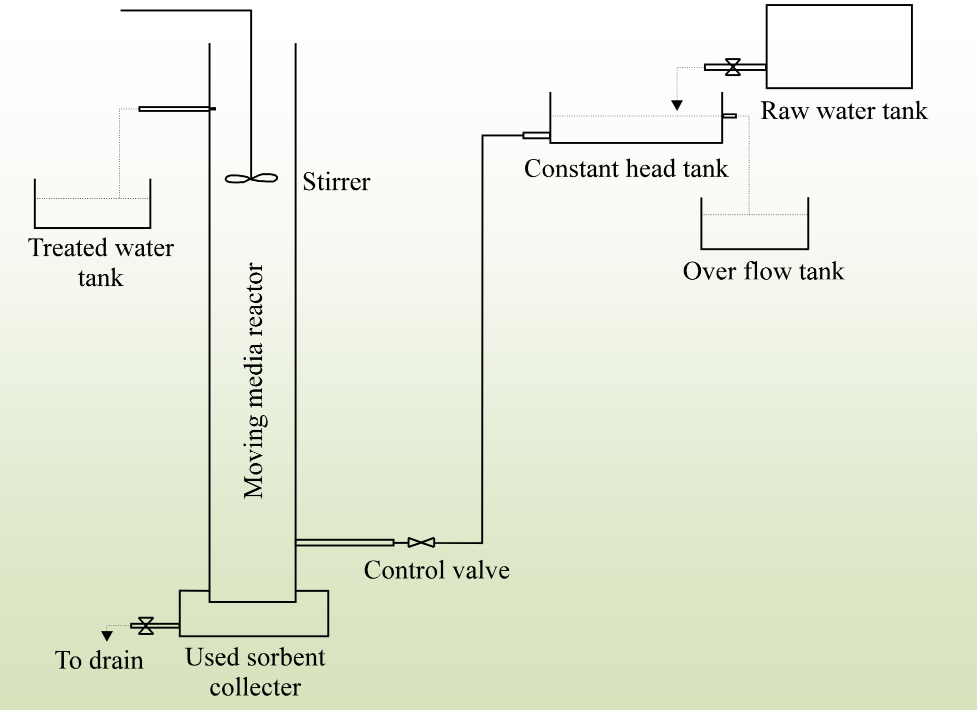

FIGURE1. Experimental setup

The experimental set-up for a moving media adsorber or reactor consisted of a 3.5 cm internal diameter PVC column of 2.0 m in length. The detailed arrangement of this set-up is shown in Figure 1 and consists of an overhead tank, a constant head tank, treated water tank, the adsorption column with necessary accessories, such as a stirrer, a plastic container at the bottom for collecting used adsorbent etc.

The sorbent, fishbone charcoal[14,15] was lead into the top of the column at a predetermined rate and the sorbate, the fluoride-containing water, was lead into the bottom of the column at a predetermined rate. The residual fluorides concentration in the effluent samples was determined by an Orion Ion Analyzer, Model 901. The counter-current movement of the sorbent and the sorbate provided ample opportunity for reaction, and the water with the highest concentration of fluoride is in contact with the most exhausted adsorbent while the water which is about to be discharged as effluent is in contact with fresh adsorbent. The set-up manifest a counter-current principle of operation and provides an efficient yet economical system.

RESULTS AND DISCUSSION

Comprehensive studies of water defluoridation using the fishbone charcoal in the dynamic system available in the moving media adsorber, yielded the following performance[12,14,15].

The ratio of the effluent concentration to the inlet concentration of fluoride decreased with an increase in the sorbent mass input flow rate due to larger surface area of the sorbent. This ratio however, increases with the increasing water flow rates due to the decreased reaction or liquid hydraulic residence time. Likewise, the ratio also increases with increasing initial sorbate concentration.

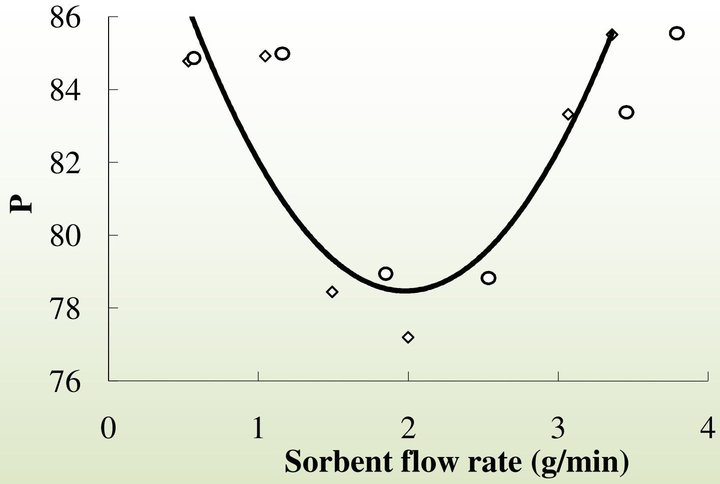

FIGURE 2. Relation between the sorbent flow rate in g/min and the arbitrary chosen parameter P, representing a summation of removal capacity of the sorbent and the percentage fluoride removal from the water. Data for inlet concentration 10 mg-F/L and liquid flow rate 10.0 ml/min.

The fluoride removal capacity of the sorbent expressed in μg-F/g-sorbent decreases with an increases in sorbent mass input rate (in g/min) probably due to an overcrowding and overlapping of sorbent particles reducing the effective surface area available for adsorption. The decrease in capacity is rapid at lower sorbent mass input rates. At greater fluoride removal rates, the fluoride removal per unit mass of sorbent decreases indicating an uneconomical utilization of sorbent. The optimum sorbent mass input rate is where maximum capacity of sorbent, and minimum ratio of effluent to influent fluoride concentration in the water is obtained. The sorbent capacity increases with increasing water flow due to a reduced overcrowding, reduced boundary layer and greater concentration gradient of sorbate. Likewise, the sorbent capacity increases with the initial fluoride concentration in the influent water due to an increased concentration gradient.

The isotherms in the dynamic system were investigated and specific modifications in a conventional isotherm were proposed[15]. Several approaches[13] were used to evolve models for predicting the ratio of effluent to initial sorbate concentration which increased with increasing influent flow rate and increasing initial sorbate concentration. The ratio, however, is decreasing with increasing sorbent input rate.

As the sorbent mass input rate increases, the fluoride removal increases but fluoride removal capacity per unit mass of sorbent decreases. This indicates that higher fluoride removal can be obtained at the cost of fluoride removal capacity of the sorbent. Thus it is critical to decide upon an optimal sorbent mass input rate value to obtain a balance between the percentage of fluoride removal and the fluoride removal capacity of the sorbent on the one hand, and the minimum sorbent mass input rate value on the other. Unitizing the data[14] a plot was prepared (Figure 2) between an arbitrarily chosen parameter P and the sorbent mass input rate. The P values represent a summation of fluoride removal capacity of the sorbent and the percentage fluoride removal. Both the terms summarized in the parameter P represent dimension-less parameters and are in some way (directly or indirectly) functions of the fluoride removal. Fluoride removal capacity of sorbent (q_e) dominate at lower sorbent mass input rates (W), and accounts for optimum utilization of the costly adsorbent, while the percentage sorbate removal (R) dominate at higher W values, and accounts for the systems removal efficiency. The summation of q_e and R thus, represents in some way, the overall removal effect against a W value. This plot of P versus W (Figure 2) indicates that the P value initially decreases with an increase in the W value, reaching a minimum at W = 1.75 to 2.0 g/min beyond which, the P value increases with further increases in the W value.

Thus, it is suggested that for actual operation of the reactor the sorbent mass input rate (W) and the corresponding P value may be taken as design values. The provision of a P value would strike a balance between the fluoride removal and the fluoride removal capacity of the sorbent for the observed test conditions, i.e. it will ensure a fairly high fluoride removal percentage with minimum sacrifice of fluoride removal capacity of the sorbent.

CONCLUSIONS

The methodology for an ideal and most efficient and economical system for water defluoridation has been described. Apart from a discussion of the effects of the various operating variables, a technique to determine the optimal operating conditions in a moving media adsorber has been presented. A few trial experimental runs on a simple column adsorber can establish the most desirable operational requirements for maximum advantage. This can be used for any sorbent-sorbate system. The method and the techniques presented can have immense field and practical applications.

ACKNOLEGMENTS

The data and some material forming a part of this paper has been abstracted from the various papers published in co-autorships of Dr. D.J. Bhatt and Shri D.J. Killedar both of whom worked for their Ph.D. under the author's guidance.

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KINETICS OF UPTAKE OF FLUORIDE ON BONE CHAR IN BATCH

H Bregnhøj* and E Dahi*

SUMMARY: A new series of data concerning the uptake of fluoride on bone char were obtained from experiments using both a chemostat, maintained at a constant temperature and pH and a jar test apparatus. A model for the sorption kinetics is developed, based on first order reaction with respect to the deficit towards saturation and first order reaction with respect to the concentration of the fluoride in solution and the inverse square root of time. The model fits the data collected during this study as well as data taken from the literature. The kinetic pattern can be described completely, for any given dosage and initial fluoride concentration, by means of a dynamic capacity parameter, $f_{m,b}$, and the reaction rate parameter, *k*. Both are subject to considerable variation, $f_{m,b}$ between 0.8 and 5.6 mg/g, and *k* between 0.002 and 0.12 L mg^{-1} $h^{-0.5}$. A high dynamic capacity parameter would probably reflect proper bone charring independent of the grain size, while higher reaction rates are observed for smaller grain sizes.

Key words: defluoridation, bone char, batch, mathematical model, capacity, reaction rate.

INTRODUCTION

In spite of the facts that charred bone has been proposed as an agent for defluoridation of water more than five decades ago[1], that it has been used as such in water works in USA[2], and that it is one of the most promising defluoridating agents for use in developing countries[3], the basic batch kinetics of the fluoride uptake on bone char are yet to be established. A literature survey has revealed that only a few batch experiments have been reported. Some are carried out in shaken containers[4,5], others in jar test apparatus where the paddle stirring is assumed to be more reproducible.[6,7] Whatever experimental setup, the results, which are often shown as fluoride concentration versus time, seem to have deviating patterns. Some show that the fluoride uptake is very fast in an initial phase, followed by a second phase of slow reaction.[4,6] Others show a relative continuous pattern.[4] In some cases the uptake is still going on even after one week of observation time[5], in others the curve is illustrated to be brought to an equilibrium within few hours.[6,7]

It is therefore not surprising that establishment of mathematical models to describe the uptake kinetics on bone char materials has been difficult. It is natural to consider similar studies of fluoride uptake on other hydroxyapatite (HAp) materials like bone meal[8], dental enamel[9] and synthetic Hap.[10-12] If such studies are considered, three different models may be distinguished:

- Larsen[9], using dental enamel, and Bhargava and Killedar[6], using bone char, describe the uptake as a simple first order process kinetics with respect to the fluoride concentration in water, that is:

Center for Developing Countries, Technical University of Denmark, Building 208, DK-2800 Lyngby, Denmark.

$$\frac{dS}{dt} = -k_1 \cdot S \qquad \text{Eq. 1}$$

- Christoffersen *et al.*[11], using synthetic HAp, describe the uptake as first order with respect to the fluoride concentration in water and first order with respect to the fluoride saturation deficit in HAp, that is:

$$\frac{dS}{dt} = -k_1 \cdot X_{BC} \cdot (f_{m,b} - f) \cdot S - k_2 \cdot X_{BC} \cdot f \qquad \text{Eq. 2}$$

- Bhargava and Killedar[6], without introducing the (differential) rate equation, describe the uptake on bone char as an (integrated) empirical equation dependent on two parameters a and b:

$$S = S_0 \cdot (1 - \frac{t}{a + b \cdot t}) \qquad \text{Eq. 3}$$

In this model a and b are derived as mathematical functions of the initial fluoride concentration, S_0, and the initial bone char dosage, X_{BC}, plus not less than six different rate constants, which have to be determined empirically.

In addition to the above mentioned models, the authors tested, among others, a "semi-infinite linear diffusion model" used by Stumm[13] for diffusion limited sorption in porous media in general, where the uptake is proportional with not only S and X_{BC} but also the reciprocal of square root of contact time:

$$\frac{dS}{dt} = -k_1 \cdot X_{BC} \cdot S \cdot t^{-0.5} \qquad \text{Eq. 4}$$

The tested models, fit some of the data collected as part of this study very well, but none of them seem to fit in general for all different experimental conditions and results obtained. This is in agreement with Gasser *et al.*[12], who concluded that the uptake of fluoride on HAp can not be described by a simple function if different series and experimental conditions are included.

The objectives of this paper is to present a new series of sorption data and to present a model for the kinetics of fluoride uptake on bone char as obtained in these experimental series as well as in series carried out by other workers.

MODEL DESCRIPTION

The idea of this model development is to describe the change of the fluoride concentration in water in batch as a function of time by means of an explicit mathematical equation, including as few as possible experimental variables and rate parameters. The model should be applicable for drinking water treatment, as it may take place in fluoride affected areas in developing countries, without any use of advanced characteristics of media like for example bulk density, bulk porosity, grain size, grain size uniformity, particle spherity, surface area and porosity. It was also set as a precondition that the model should fit the data collected in this study as well as data given in selected literature.

Using a trial and error approach considering many different models, both some reviewed in this paper and some not, the following differential equation was developed and adopted:

$$\frac{dS}{dt} = -k_1 \cdot X_{BC} \cdot (f_{m,b} - f) \cdot S \cdot t^{-0.5} \qquad \text{Eq. 5}$$

As f is the concentration of fluoride uptaken in the bone char and $f_{m,b}$ is a measure of the maximum concentration of possible uptake, $(f_{m,b} - f)$ would represent a deficit towards saturation of the bone char. $X_{BC} \cdot (f_{m,b} - f)$ is thus the total potential uptake per volume of batch. So far the equation may be accepted logically and considered as a modification of Fick´s law for diffusion quite similar to the normal uptake of gasses in liquid media.[14]

This part of the equation expresses that the rate of fluoride uptake is first order with respect to the fluoride concentration in the water, S, as well as first order with respect to the deficit of saturation of bone char, $X_{BC} \cdot (f_{m,b} - f)$. However, when testing the data it was found inevitable to attach the inverted square root time function $t^{-0.5}$. This term seems to be necessary to get an acceptable model fit to the data, not only to the fluoride uptake on bone char but also to its uptake on other media and in many other diffusion limited processes.[13]

Assuming that the initial concentration of fluoride in the bone char is negligible, that is $f_0 = 0$, f may at any time be given as $f = (S_0 - S)/X_{BC}$. By substitution into equation 5 and integration of the equation, the concentration of fluoride in the water is given as a simple function of time:

$$S = \frac{X_{BC} \cdot f_{m,b} - S_0}{\frac{X_{BC} \cdot f_{m,b}}{S_0} \cdot e^{2(X_{BC} \cdot f_{m,b} - S_0) \cdot k \cdot t^{0.5}} - 1} \qquad \text{Eq. 6}$$

Thus the S-t curve of uptake of fluoride is characterised for a given dosage of bone char, X_{BC}, and a given initial fluoride concentration, S_0, by the means of only two parameters $f_{m,b}$ and k, where $f_{m,b}$ is a dynamic capacity parameter and k is a reaction rate parameter.

MATERIALS AND METHODS

Two types of experiments were carried out, one using a chemostat regulated at constant temperature and pH and the other using a jar test apparatus.

pH-chemostat. Batch experiments were carried out in 1-L plastic beakers in a water bath thermostated at 25°C. The beakers contained 1 L of NaF-solutions in distilled water at different given initial concentrations. The solutions were kept stirred using a paddle rotating at 100-150 revolutions per minute (rpm). The speed was adjusted in order to keep the bone char particles evenly suspended in the solution. The bone char was added at time zero in different given dosages. The control for this set of experiments contained no bone char. The concentration of fluoride and pH in the water were monitored continuously by potentiometric measurements. Experiments were run for 5-10 hours. The pH were kept constant using a Metrohm system of pH-meter 691, Impulsomat 614 and Dosimat 715. The pH of these systems was adjusted using a 0.25 M HNO_3 solution. Each experiment was carried out in 2-4 replicates.

Jar test experiments. Experiments were carried out in 1-L glass beakers, using a Jar test apparatus (Phipps & Birds Stirrer 7790-402). Each of the six beakers was filled with 1 liter of naturally occurring spring water from the Ngurdoto National Park pumped directly to the Defluoridation Research Station in Arusha, Tanzania. The water had a pH of 8.2 and a fluoride concentration of 21 mg/L and total alkalinity of 6.7 meq/L. Stirring was carried out at 25 rpm, just enough to keep the water totally mixed without moving the bone char particles. The bone char was added at time zero in different given dosages. The control for this set of experiments contained no bone char. Five mL samples were taken at the different given times for filtration and fluoride measurement. These experiments were run for 4 hours.

Bone char preparation. In the *chemostat experiments* a mixture of various farm animals bones and teeth were used. The bone materials were delivered from the Danish bone meal and animal feed industry DAKA, after being boiled, washed, dried and crushed down to 2-3-cm particle size. Four kilogram bone material were charred in a programmable ceramic oven (Scandia-Ovnen AS SK 35 S). The temperature was gradually raised at a rate of 2°C/min from room temperature to 500°C, and then kept constant for 2 hours. The oven was then allowed to cool down during overnight to ambient temperature before opening. The bone char was ground further in a plate crusher and sorted out in a test sieve shaker (Endecotts LTD EFL2 mk3). The grain size, $d_h < 45 \mu m$, was used in the experiments. The specific surface was tested according to BET method and found to be 69±3 m^2/g, for particles of both $d < 0.053$ mm and $0.3 < d < 0.6$ mm, that is independent of the grain size.

In the *jar test experiments* rib bones from goats and sheep grown up in the fluoride affected areas of Arusha, Tanzania, were used. The bones were sun dried and crushed into pieces of 2-3-cm grain size. The bone materials were then calcined in a 1-L can open to atmospheric air on a kerosene pressure cooker. The temperature was controlled using a Viking 1000 thermometer with Viking type UHT3 bimetallic sensor. The temperatures were kept between 500 and 600°C for 10-15 minutes. The bone char which appeared grey on the surface and black in the interior was then ground and sorted out as mentioned above in 3 fractions to grain sizes of $d_h < 0.2$ mm, 1.2-2-mm and 3-4-mm.

Fluoride & pH-measurements. The fluoride concentrations were measured directly in the water using a Radiometer F1052 fluoride electrode and Metrohm Ag/AgCl reference electrode with sleeve type diaphragm connected to a Metrohm 691 pH-meter. Every one hour 5-ml samples were taken, filtered through 0.45 µm membrane filters (Schleider & Schuel) and measured for fluoride contents after addition of TISAB, according to Standard Methods.[15]

pH were measured according to Standard Methods[15] using a Metrohm combined glass electrode in connection with the above mentioned pH-meter.

RESULTS

Experimental results. The results from the pH-chemostat series of experiments are shown as discrete points in Figure 1a for initial fluoride concentrations of 10 mg/L and bone char dosage, X_{BC}, of 1-, 2-, 3- and 4-g/L, and in Figure 1b for initial fluoride concentrations of 20 mg/L and bone char dosage of 2-, 3- and 4-g/L.

The results from the jar test series of experiments are shown as discrete points in Figure 2a for bone char grain size < 0.2 mm, the dosage being 3.55, 7.0, 13.0 and 32.5 g/L.

Figure 2b shows the results from the similar experiments, where bone char of grain size 1.2 - 2 mm was used, the dosage being 5.6-, 11.2-, 20.8- and 32.5-g/L. Figure 2c show the results from the similar experiments, where bone char of grain size 3-4-mm was used, the dosage being 8.5-, 16.9-, 31.2- and 78-g/L. The initial fluoride concentration in all jar test experiments is 21.0 mg/L.

Model Simulations. The dynamic capacity parameter $f_{m,b}$ and the reaction rate parameter k may be estimated by means of non-linear regression. This is carried out by computer iteration, using a function which minimises the deviation between the measured data and the model calculated data (as sum of squares) by changing k and $f_{m,b}$. The parameters are listed in Table 1 for as well the series of this study as the series selected from reported studies.

Figures 1a-b & 2a-c, illustrate the model estimates of the uptake kinetics as curves, in comparison with the experimental data of this study. Similarly, Figure 3a-c illustrates the model estimates of the uptake kinetics as compared to the experimental data of selected reported studies. The kinetic parameters of these simulations are also presented in Table 1.

DISCUSSION

The two types of experiments represent different approaches. The pH-chemostat experiments being controlled in the laboratory, while the jar test experiments rather represent the field practise and the poor quality bone char. Yet, as seen in Figures 1a-b & 2a-c, the model seems to reproduce the trends of the experimental data very well.

Even when the literature data are taken into consideration, and thus including the broad variation of experimental conditions and charring techniques, the model seems to reproduce the trends of the experimental data surprisingly well. This is illustrated in Figure 3a-c.

Based on this it seems feasible to use $f_{m,b}$ quantitatively first and foremost as a parameter for characterization of the bone char capacity to uptake the fluoride. Moreover, to use k quantitatively first and foremost for characterization of the reactivity of the bone char as well as experimental setup, including the influence of grain size, the temperature, the intensity of mixing and of the water quality in the batch system.

From Table 1 it may be seen that $f_{m,b}$ is subject to considerable variation, between 0.8 and 5.6 mg/g. Especially the data of Larsen *et al.*[5] and Bhargava and Killedar[6] illustrate that $f_{m,b}$ is very much dependent on the heating procedure used for bone char preparation. The low sorption capacities encountered is probably a direct result of destructive charring. Also with the data of this study $f_{m,b}$ seem to vary between 2 mg/g for the jar test experiments, where pH is 8-9 and 5.6 mg/g for the chemostat experiments where pH is controlled to 7. Probably the bone char preparation is, at least in part, responsible for these discrepancies.

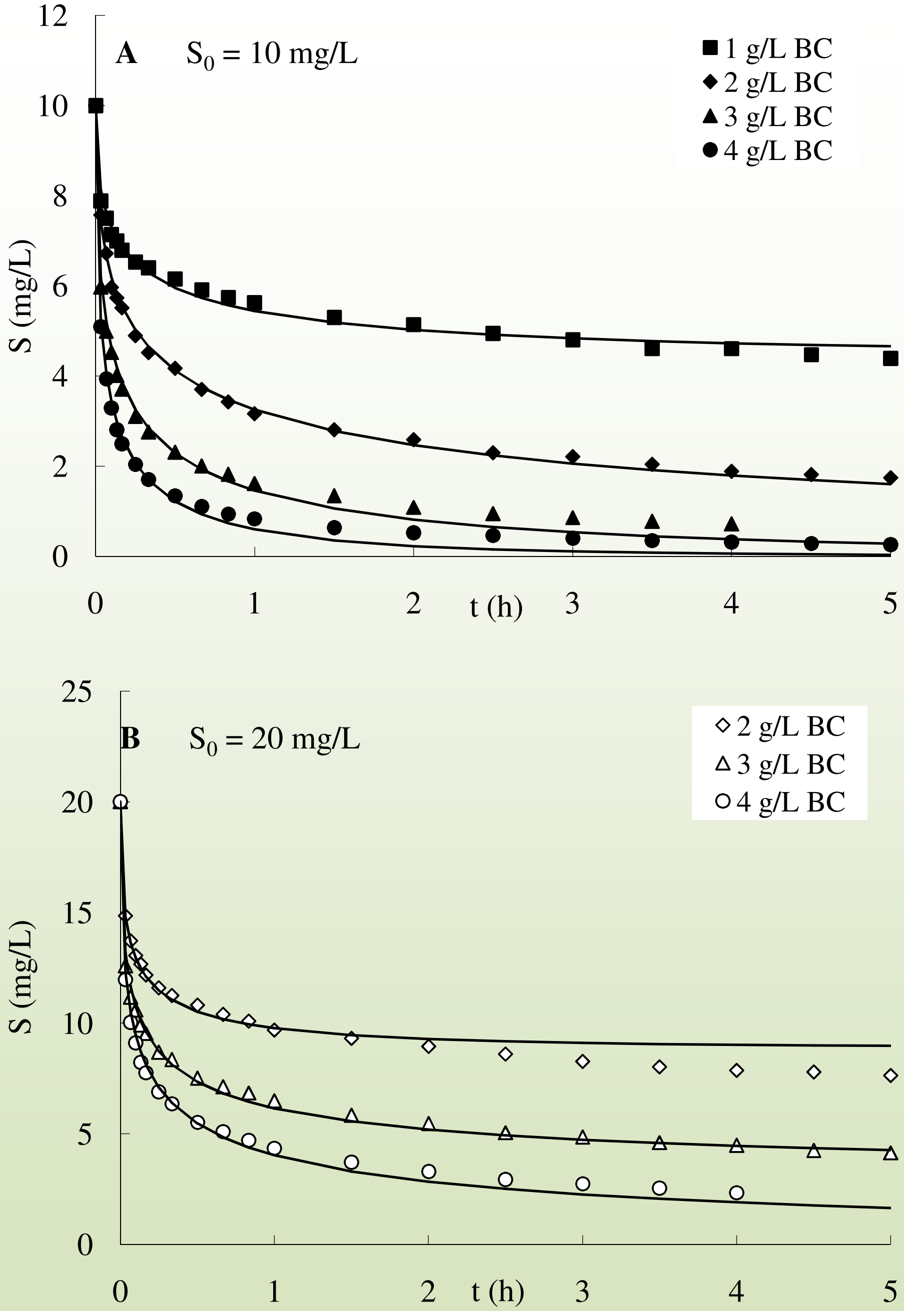

FIGURE 1A & 1B. Fluoride uptake on bone char in batch chemostat, pH is kept at 7.0. Initial fluoride concentrations and dosages are indicated. The experimental results are shown as discrete symbols, while the curves are generated by the model for best estimates of $f_{m,b}$ = 5.6 mg/g and individual k for the different series, see Table 1.

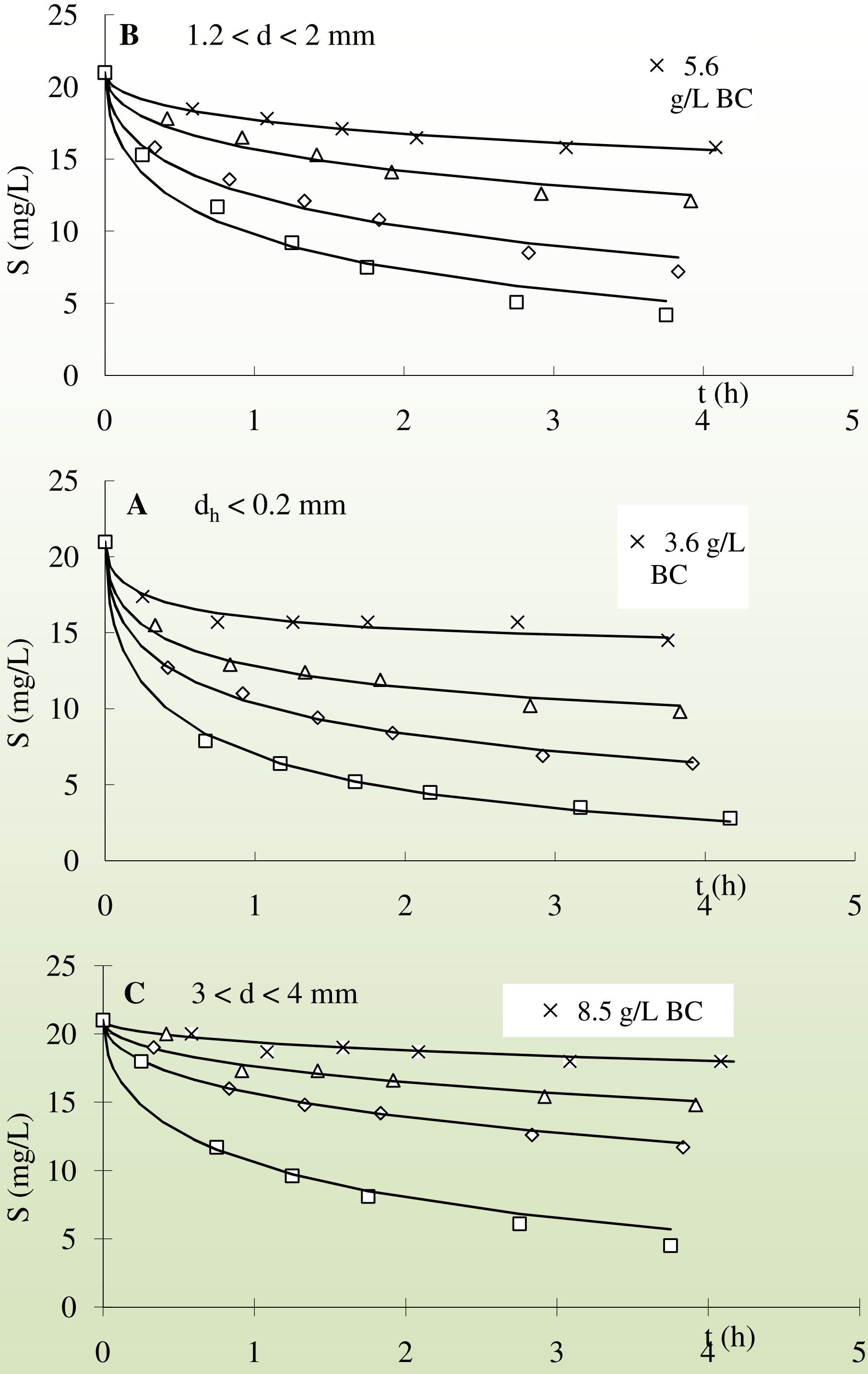

FIGURE 2A-C. Fluoride uptake on bone char in jar test experiments with gentle stirring (25 rpm) S_0= 21 mg/L. Dosages of bone char and the grain sizes are indicated. The experimental results are shown as discrete symbols, while the curves are generated by the model for best estimates of $f_{m,b}$= 2.0 mg/g for all series and individual k for the different series, see Table 1.

TABLE 1. Estimated k's and fm,b's in pH-chemostat and Jar test experiments of this study in comparison with selected data from the literature.

Experiment type	Charring	S_0 (mg/L)	X_{BC} (g/L)	d (mm)	Period (h)	$f_{m,b}$ (mg/g)	k $L \cdot mg^{-1} \cdot h^{-\frac{1}{2}}$	Ref
Chemostat 100-150 rpm	550 °C 2 h	10	1	<0.045	0-5	5.6	0.12	
			2				0.09	
			3				0.09	
			4				0.09	
		20	2				0.10	
			3				0.09	
			4				0.075	
Jar test 25 rpm	Ca. 600°C 0.5 h Kerosene cooker	21 Natural water source	3.55	< 0.2	0-4	2.0	0.036	
			7				0.028	
			13				0.018	
			32.5				0.010	
			5.6	1.2-2.0			0.0087	
			11.2				0.0076	
			20.8				0.0072	
			32.5				0.0067	
			8.5	3-4			0.0027	
			16.9				0.0028	
			31.2				0.0025	
			78				0.0023	
Gently shaken containers	400°C, 1 h	10	2.5	0.1-1.5	0-144	6.37	0.009	9
	400°C, 4 h					4.24	0.024	9
	550°C, ½ h					2.84	0.023	9
	550°C, 4 h					1.76	0.030	9
	550°C, 48h					0.81	0.018	9
Agitated containers	350 °C	200	50	< 0.42	0-8	3.98	0.008	4
				1.2 - 2.1			0.0012	4
				3 - 5			0.0009	4
Jar test 100 rpm	1000°C 2 h	10	4	0.09- 0.125	0-9	2.51	0.021	6
				0.125- 0.18			0.010	6
				0.18- 0.355			0.008	6
				0.355 - 0.6			0.007	6
				0.6 - 0.85			0.005	6

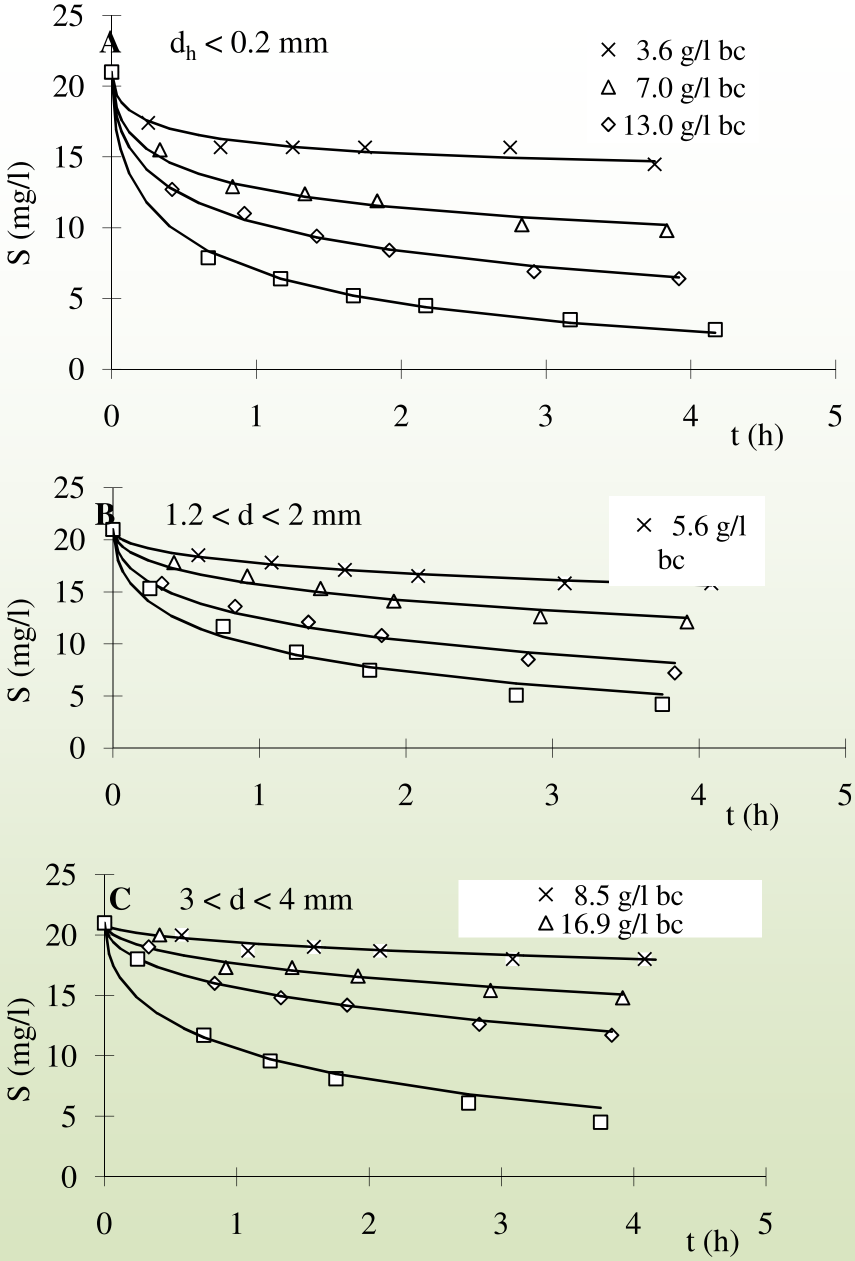

FIGURE 3A-C. Fluoride uptake on bone char as reported by A: Larsen et al.[5], B: Mwaniki[4], and C: Bhargava and Killedar[6]. Dosage of bone char are A: 2.5 g/L, B: 50 g/L and C: 4 g/L, and the utilized grain size A:0.1-1.5 mm, B & C: indicated. The experimental results are shown as discrete symbols, while the curves are generated by the model for best estimates of fm,b= A:0.8-6.4, B:4.0 and C:2.5 mg/g and individual k for the different series.

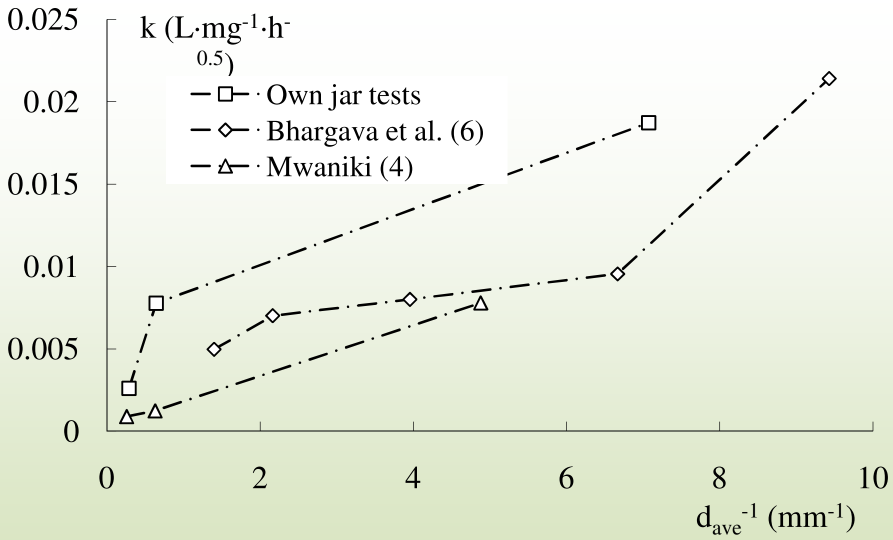

FIGURE 4. Variation of the reaction rate parameter k as a function of the reciprocal average grain size. Estimates are made from our own jar test experiments (average for each grain size) and results from the literature[4,6]. Values are from table 1.

It must be mentioned that experiences gained in our laboratory indicate very clearly that charring at 350°C may result in high or even highest possible fluoride removal capacity, but is not sufficient for the removal of bad taste and colour given by residuals in the bone char. Moreover, that the use of extremely high dosages of bone char and high concentration of fluoride may favour the precipitation of calcium fluoride in comparison with the fluoride sorption taking place in normal water treatment. It is worth noticing that the dynamic capacity parameter is almost totally independent of the grain size of the bone char.

This is in the line with the results given by Mwaniki[4], where the capacity of the bones are relatively preserved during the low temperature used for charring. Also that the capacity parameter is of the same order of magnitude, in spite of the fact that Mwaniki[4] utilises extremely high fluoride concentrations and correspondingly high dosage of bone char.

Reaction Rate Variation. From Table 1 it is seen that the rate parameter variation is subject to even wider variation than observed by $f_{m,b}$, the estimated k's are between 0.0009- to 0.12-L mg^{-1} h$^{-0.5}$. The rate parameter is low for bone char heated at too high temperature, cf. data of Bhargava and Killedar[6], and for bone char of gross grain size. In contrast to the dynamic capacity, the reaction rate parameter is observed to be very much dependent on the grain size, the smaller the grain size, the higher is the reaction rate parameter, Figure 4.

The grain size for a fraction of bone char is normally given as an interval between the size of the sieve opening which retain the smallest grains (d_l), and the size of the sieve opening which all the grains have passed (d_h). In some cases, for the finest fraction, the grain size is given as < d_h. From the assumption that the grain size in any sample is logarithmically normal-distributed, an average grain size in a fraction can be calculated as $d_{ave} = (d_l\, d_h)^{1/2}$.

When the grain size is given as < d_h this definition does not apply. However, in this case, for d_h < 0.2 mm, an arbitrary value of $d_{ave} = (0.1 \cdot 0.2)^{1/2} = 0.14$ mm has been applied. The data are seen in Figure 4. This Figure illustrates that the rate parameter varies almost directly proportional with the reciprocal of grain size. However, a mathematical relationship is not established as the grinding process, the grain fractioning and the determination of the grain size are all subject to high variation.

The reaction rate to grain size relationship is in agreement with the findings in the studies of Bhargava and Killedar[6] and Mwaniki.[4] Moreover, this study indicates that dynamic capacity parameter $f_{m,b}$ of the bone char can not be directly related to the reaction rate. Thus the capacity of the different grain size fractions of a given batch of bone char may be of the same order of magnitude in spite of the fact that the reaction rate for the different fraction is higher the smaller is the grain size.

In order to describe the kinetic properties of the bone char with respect to uptake of fluoride from water, it seem most appropriate to use the dynamic capacity and the rate reaction parameters as these would reflect the complete sorption pattern.

ACKNOWLEDGEMENTS

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LIST OF SYMBOLS

a,b	Reaction constants in eq. 3
d	Grain size of a bone char sample, (mm (interval))
d_{ave}	Average grain size of a bone char sample, (mm)
d_l	Size of sieve opening retaining a bone char sample, (mm)
d_h	Size of sieve open. just allowing the bone char sample to pass, (mm)
f	Fluoride concentration in the bone char, (mg/g)
f_0	Fluoride concentration in the bone char at t=0, (mg/g)
$f_{m,b}$	Capacity parameter for fluoride uptake on bone char, (mg/g)
k	Reaction rate parameter, ($L\ mg^{-1}\ h^{-0.5}$)
k_1,k_2	Reaction rate constants in eq. 1, 2, and 4
S	Fluoride concentration in the water phase, (mg/L)
S_0	Fluoride concentration in the water phase at t = 0, (mg/L)
t	Time, (h)
X_{BC}	Dosage of bone char, (g/L)

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KINETICS OF DEFLUORIDATION OF WATER BY CALCINED MAGNESIA AND CLAY

E Dahi*, J J Singano**, and J M Nielsen*

SUMMARY: Series of fluoride removal by means of calcined magnesite are obtained from Jar test experiments. The model developed by Bregnhøj and Dahi[1] is tested on these results and on experiments made by Bjorvatn and Bårdsen[2] using laterite. The model do not describe the results very well when using calcined magnesite, especially not for different grain sizes. The reaction rate parameter, *k*, varies between 0.00076 and 0.0029 L/(mg·h$^{0.5}$) for a capacity, f_m, as high as 56 mg/g. This variation is probably because other processes than defluoridation are determining the kinetics, like the change of MgO into $Mg(OH)_2$. The model describes the laterite kinetics well, though it has some limitations in estimating both parameters if there is a big variation in the raw water quality. The f_m is estimated to 0.77 mg/g and *k* varies between 0.0031 and 0.0049 L/(mg·h$^{0.5}$) for humus containing laterite.

Key words: Defluoridation, magnesia kinetics, laterite kinetics, drinking water treatment, sorption capacity

INTRODUCTION

A model for describing the sorption kinetics on bone char in batch has been developed by Bregnhøj and Dahi.[1] This model is based on a first order reaction with respect to the deficit towards saturation and a first order reaction with respect to the concentration of fluoride in the solution and the inverse square root of time. The fluoride concentration in the water, *C,* is given as a function of time:

$$C = \frac{X \cdot f_m - C_0}{\left[\frac{X \cdot f_m}{C_0} \cdot \exp\left(2(X \cdot f_m - C_0) \cdot k \cdot t^{0.5}\right)\right] - 1}$$

The C-t curve can be characterised for a given dosage of sorbent, *X*, and a given initial fluoride concentration, C_0, by means of only two parameters, the dynamic capacity parameter f_m, and the reaction rate parameter *k*.

The objective of this paper is to estimate the model parameters, f_m and *k*, for defluoridation agents such as calcined magnesite, this study, and laterite with and without humus[2] and to elucidate whether the model is suitable for these materials.

MATERIALS AND METHODS

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* *Center for Developing Countries, Technical University of Denmark, Building 208, DK-2800 Lyngby, Denmark.*

** *Department of Civil Engineering, University of Dar es Salaam, P.O. Box 35131, Dar es Salaam, Tanzania.*

The raw magnesite was crushed into small pieces and thereafter heated in an electrical oven. The temperature was raised with a gradient of 4°C per minute from room temperature to 750°C and kept constant for 4.5 hours.

he raw magnesite was crushed into small pieces and thereafter heated in an electrical oven. The temperature was raised with a gradient of 4°C per minute from room temperature to 750°C and kept constant for 4.5 hours.

The oven was allowed to cool to room temperature before opening. The calcined magnesite was sieved into different grain size fractions using an electrical shaker before the experiments were made.

The experiments were carried out in 1 L plastic beakers using a Jar test apparatus. Each beaker was filled with distilled water containing NaF equivalent to 10 and 20 mg/L F^-. Stirring was carried out at 45 rpm. The magnesia was added at time nil in different dosages and in different grain sizes. The experiments were run for 24 hours.

The fluoride concentration was measured using a Radiometer F1052 fluoride electrode and a Metrohm Ag/AgCl reference electrode with a sleeve type diaphragm connected to a Metrohm potentiometer. At given times 5 ml samples were taken and mixed with CDTA-Tisab before analysing for fluoride using the calibration method according to Standard Methods.[3]

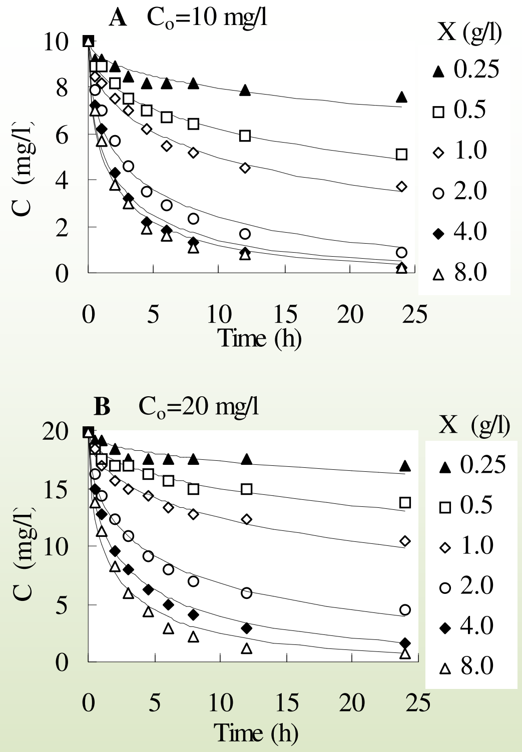

FIGURE 1. Fluoride concentration in water in Jar test experiments. Initial fluoride concentration and dosages of calcined magnesite are indicated and GS=0.25-0.5mm. The experimental results are shown as discrete symbols and the curves are best fit with f_m=56mg/g and individual *k* for each dosage, see Table 1.

RESULTS

The results from the Jar test experiment series are shown as discrete symbols in Figure 1a for an initial fluoride concentration of 10 mg/L using the grain size 0.25-0.50 mm, the dosages being 0.25, 0.50, 1.0, 2.0, 4.0, and 8.0 g/L. Figure 1b shows the results from a similar experiment where the initial fluoride concentration was 20 mg/L.

In Figure 2 the results of adding different grain sizes can be observed. The initial fluoride concentration was 19.6 mg/L and the dosage of calcined magnesite was 2.0 g/L. The models, estimated by the method of leat squares, are plotted as curves fitting the symbols in Figure 1 and in Figure 2. The estimated f_m and k values are shown in Table 1.

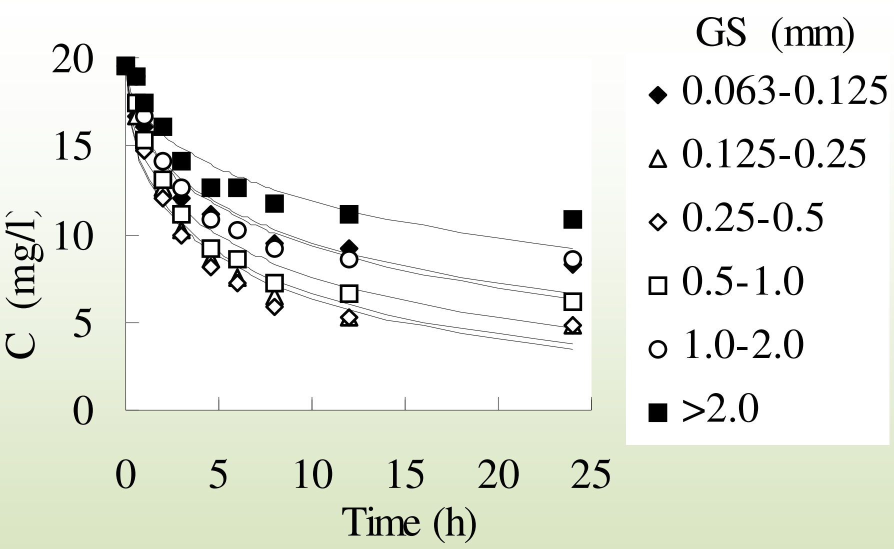

FIGURE 2. Fluoride concentration in water in Jar test experiments with C_0=19.6 mg/L and X=2.0 g/L. Grain sizes are indicated. Line and symbols like in Figure 1.

The method of least squares is also used to estimate the dynamic capacity parameter, f_m and the reaction rate parameter, k for the reddish clay laterite. The experiments are made by Bjorvatn and Bårdsen[2] and the results of the modelling can be seen in Figure 3 for laterite containing humus, and in Figure 4 for laterite without humus. The curves being the models estimates and the discrete symbols the measurements. The estimated f_m and k values for laterite with and without humus are shown in Table 1.

DISCUSSION

The two defluoridation agents, calcined magnesite and laterite, show very different capabilities in fluoride removal.

As seen in Figure 1 and Figure 3 and 4, the model seems to reproduce the experimental data well.

Magnesia Kinetics: Looking at the estimated model parameters in Table 1, the model is not that good. The reaction rate parameter, k, is subject to a wide variation, between

0.00076-0.0029 L/(mg·$h^{0.5}$) for C_0=10 mg/L, and between 0.00076-0.0018 L/(mg·$h^{0.5}$) for C_0=20 mg/L. Thus, the reaction rate parameter is in some way dependent on the dosage of magnesia.

The experimental results are shown as discrete symbols and the curves are best fit with individual f_m and k for each raw water, see Table 1.

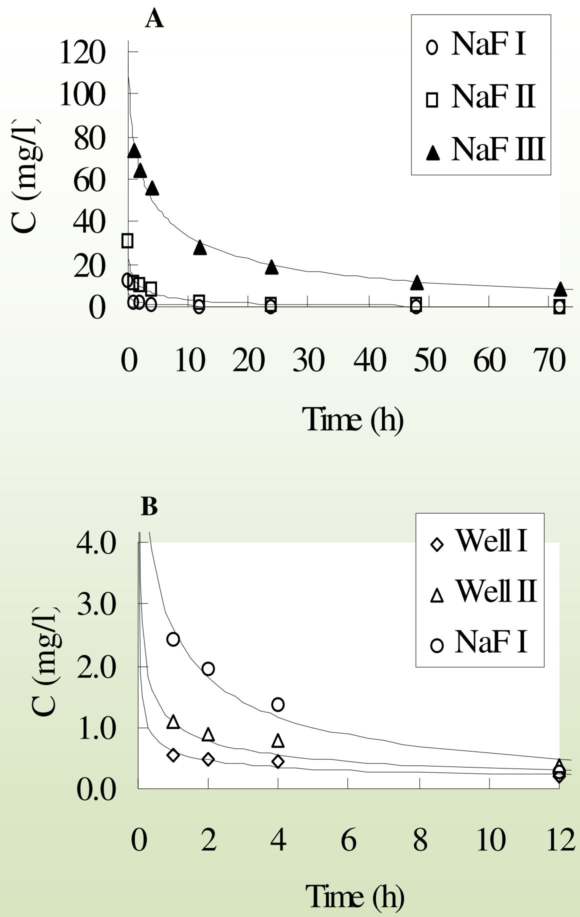

FIGURE 3. Fluoride concentration in water in Jar test experiments. The sample ID is indicated and the dosage of laterite without humus is X=100 g/L. The initial fluoride concentration is shown in Table 1.

The model does not fit the experimental results at all when using different grain sizes of calcined magnesite, as seen in Figure 2. The reaction rate parameter is varying between 0.00073 and 0.0017 L/(mg·$h^{0.5}$). Though, the capacity parameter f_m is indicating that calcined magnesite is very effective in removing fluoride from drinking water. The sorption capacity is high, approx. 56 mg/g compared to bones where f_m is 5.6 mg/g.

Laterite Kinetics: The estimated models reproduce the experimental data very well, both the data using laterite with humus and laterite without humus. The capacity parameter f_m is 0.77 mg/g for laterite containing humus and the reaction rate parameter, k, varying between 0.0031 and 0.0049 L/(mg·h$^{0.5}$).

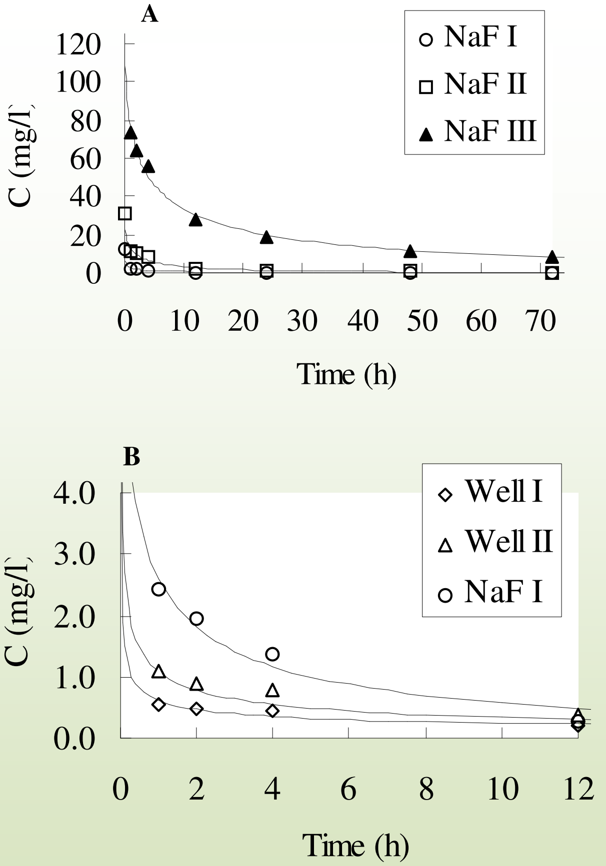

Figure 4 Fluoride concentration in water in Jar test experiments. The sample ID is indicated and the dosage of laterite without humus is X=100 g/L. The initial fluoride concentration is shown in Table 1. The experimental results are shown as discrite symbols and the curves are best fit with individual f_m and k for each raw water, see Table 1.

The variation in k is probably due to the wide variation in the initial fluoride concentration and the variation in the raw water quality, as sample "Well I- II" is Norwegian groundwater and "NaF I-III" is distilled water added sodium fluoride.

The estimated model parameters, f_m and k, for laterite without humus vary a lot (Table 1). The reaction rate parameter varies between 0.0017 and 0.80 L/(mg·h$^{0.5}$), and the capacity parameter between 0.054 and 1.95 mg/g. The estimated model parameters for laterite without humus are even more sensitive to the variation in raw water quality and the initial fluoride concentration than the estimated parameters for laterite containing humus. It seems like there is a relation between f_m and *k*, increasing f_m results in decreasing *k*.

TABLE 1. Estimated *k* and f_m values in Jar test experiment using calcined magnesite (this study) and laterite with and without humus[2] as defluoridation agent.

Defluoridation agent	Sample ID	C_0 mg/L	X g/L	GS mm	f_m mg/g	k L/(mg·h^{½})	Reference
Magnesia	-	10	0.25	0.25-0.50	56.0	0.0028	This study
			0.5			0.0029	
			1.0			0.0021	
			2.0			0.0021	
			4.0			0.0014	
			8.0			0.00076	
Magnesia	-	20	0.25	0.25-0.50	56.0	0.0017	This study
			0.5			0.0018	
			1.0			0.0014	
			2.0			0.0016	
			4.0			0.0012	
			8.0			0.00076	
Magnesia		19.6	2.0	0.063-0.125	56.0	0.0011	This study
				0.125-0.25		0.0017	
				0.25-0.50		0.0017	
				0.50-1.0		0.0014	
				1.0-2.0		0.0011	
				>2.0		0.00073	
Humus containing laterite	Well I	5.42	100		0.77	0.0044	2
	Well II	7.75				0.0049	
	NaF I	12.1				0.0036	
	NaF II	29.7				0.0033	
	NaF III	120				0.0031	
Laterite containing no humus	Well I	5.47	100		0.054	0.80	2
	Well II	7.75			0.079	0.37	
	NaF I	12.2			0.14	0.10	
	NaF II	31.2			0.56	0.010	
	NaF III	132			1.95	0.0017	

CONCLUSION

The model developed by Bregnhøj and Dahi[1] is better for describing uptake of fluoride on clay than on calcined magnesite. This is probably due to the fact that when dealing with calcined magnesite, the processes involved are not only uptake of fluoride, but also dissolution of MgO.

k is the parameter for quantitatively characterisation of the reactivity of the agent as well as experimental set-up, including grain sizes, temperature, mixing velocity and water quality. Using magnesia the model parameter *k* is not constant, even though the experimental set-up is the same for the results presented in Figure 1.

The model also has some limitations in estimating the model parameters when using clay. Very different raw water qualities, like different initial fluoride concentrations result in a wide variation in both f_m and *k*.

ACKNOWLEDGEMENTS

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MODELING DEFLUORIDATION OF WATER IN BONE CHAR COLUMNS

H Bregnhøj[*], E Dahi[*] and M Jensen[**]

ABSTRACT: Two series of fluoride uptake on bone char in flow columns are presented. Experimental fluoride concentration profiles at different times are established. A mathematical model is developed, based on a batch kinetic model, which is of first order with respect to the fluoride concentration in water, the deficit towards saturation of the bone char and the inverse square root of time. The analytical solution to the mass balance equation estimates the theoretical fluoride concentrations profiles and time of breakthrough, properly fitting the experimental data. The column sorption is determined by the dynamic capacity parameter $f_{m,f}$, estimated to be 3.5 and 6.6 mg/g for two different bone char materials, and the reaction rate parameter k, estimated to be $10^{-2} L \cdot mg^{-1} \cdot h^{-½}$. Two empirical constants, S_{min} and t_1, must be determined for use in the model. The significance of smaller grain sizes is reflected in higher k values, independent of $f_{m,f}$. According to the experimental data, and in agreement with the model predictions, the amount of water which can be defluoridated in a column is larger for higher hydraulic retention time. The model may provide an appropriate tool for sizing bone char columns for water defluoridation.

Keywords: Modelling, Defluoridation, Bone char, Column experiments, Sorption capacities.

INTRODUCTION

Defluoridation of drinking water using bone char in filter columns was performed in USA in the 1950's and 60's.[1,2] Today bone char is among the most promising methods considered for defluoridation in developing countries.[3] Column sizing and operation is usually based on continuous monitoring of effluent fluoride concentrations and on experience with existing treatment systems, but not on mathematical modelling of the process.

Only one trial has been made to develop a model for fluoride uptake in bone char columns. A simple model, based on the assumption of a homogeneous reaction chamber and a instantaneous equilibrium has been developed by Mwaniki and Nagelkerke.[4] The model fits their experimental results, but has difficulties with interpretation of different flows.

To get a better basis for sizing columns and a further understanding of the fluoride removal kinetics in columns, this paper describes two series of experiments and a mathematical model which fits the results. The model can be used for sizing of filters.

Definitions: The fluoride concentration S in the water decreases as the water proceeds through the column. This decreasing curve of S as a function of distance, l, measured at a fixed time, is referred to as the *fluoride concentration profile* or just the *profile*. A front point of the profile defined by a small concentration S_{min} is called the *fluoride front*. The curve of S as a function of time, t, at the outlet of a column is called the *breakthrough curve.*

[*] *Center for Developing Countries, Technical University of Denmark, Building 208, DK-2800 Lyngby, Denmark.*

[**] *Engineering College of Copenhagen, DK-2750 Ballerup, Denmark.*

MATERIALS AND METHODS

Two series of flow experiments have been made with two different bone char materials. The two sets of bone char are the same used in batch experiments presented elsewhere.[5] Bone char 1 was used in Series 1, and bone char 2 was used in Series 2.

TABLE 1. Summary of Experimental Conditions

Para-meter	Unit	Column no.							
		1.1	1.2	1.3	1.4	1.5	2.1	2.2	2.3
L	m	0.88	0.88	0.88	0.87	0.87	0.8	0.8	0.8
A	cm^2	1.12	1.14	1.15	1.15	1.16	2.8	2.8	2.8
X_{BC}	g/l	838	801	796	822	796	781	781	781
d_l	mm	0.25	0.5	0.5	1.4	1.4	1.2	1.2	1.2
d_h	mm	0.5	1.0	1.0	2.0	2.0	2.0	2.0	2.0
$\in$	-	0.70	0.70	0.69	0.70	0.70	0.73	0.73	0.73
v_D	m/hr	0.70	0.70	0.69	0.70	0.70	2.14	1.11	0.64
T_h	h	0.88	0.88	0.88	0.86	0.86	0.27	0.53	0.91
T_{tot}	hr	168	168	173	173	116	313	341	318
S_0	mg/l	22.8	22.8	22.8	22.8	22.8	13.8	13.8	13.8

EXPERIMENTS:

Series 1, Columns 1.1-1.5. Varying grain sizes. Bone char 1 was packed in transparent soft PVC tubes. The tubes were propped up with wooden constructions. Nylon sponge at inlet and outlet ensured that bone char were immobilized in the tube. Syringe needles, stuck through the wall to the center of the tubes, were placed with equal distances along the tubes. Samples of 1 mL for fluoride analysis were taken regularly with syringes through the needles and from the effluent. A constant water flow was kept by the use of an Ismatec tube pump, type VP-MS/CA12. During the experiments the tubes were covered with aluminum foil, to avoid algae growth. All other tubing at inlet and outlet were PVC transparent soft tubes connected with plastic connectors. Grain sizes of the bone char were in Col. 1.1: d = 0.25-0.5mm, col. 1.2 and 1.3: d = 0.5-1.0mm, col. 1.4 and 1.5: d = 1.4-2.0. Other system parameters are listed in Table 1.

Series 2, Columns 2.1-2.3. Varying flow velocities / retention times. Bone char was packed in pieces of opaque water hose. Nylon sponge at inlet and outlet ensured that bone char were immobilized in the tube. Samples of 1-2 mL were taken regularly with syringes and needles, which were stuck through the wall to the center of the tubes at equal distances along the tubes. Effluent concentrations were followed for 14 days period. A constant water flow was ensured by a constant head tank with an overflow device at the inlet, and regulation of the outlet water height as the head loss in the columns increased. All other tubing at inlet and outlet were PVC transparent soft tubes connected with plastic connectors. Hydraulic retention times were Col. 2.1: T_h = 0.27h, Col. 2.2: T_h = 0.53h, Col. 2.3: T_h = 0.92h. Other system parameters are listed in Table 1.

Fluoride concentrations were monitored in a period of 1-2 weeks. For both series the water flow was stopped sometimes by accident. The time periods with no flow have been subtracted in the presentation of the results. These periods add up to 5-20 % of the total experiment time.

PREPARATION OF BONE CHAR:

Bone char 1 (Columns 1.1-1.5). A mixture of all sorts of farm animals bones and teeth has been used. The bone materials were delivered from the Danish bone meal and animal feed factory DAKA, after being boiled, washed, dried and crushed down to 2-3 cm particle size. Four kilogram bone material were charred in a programmable ceramic oven SK 35 S from Scania-Oven AS. The temperature was gradually raised at a rate of 2°C/min from room temperature to 500°C, and kept constant for 2 hours. The oven was then allowed to cool down during overnight to ambient temperature before opening. The bone char was further ground in a plate crusher and sorted out in a test sieve shaker type EFL2 mk3 from Endecotts LTD to grain sizes d = 0.25-0.5 mm, 0.5-1.0 mm, and 1.4-2.0 mm.

Bone char 2 (Column 2.1-2.3) Rib bones from goats and sheep bred in the fluoride affected areas of Arusha, Tanzania, were used. The bones were sun dried and crushed into pieces of 2-3 cm grain size. The bone materials were then calcined in a 1-L cane open to atmospheric air on a kerosene pressure cooker. The temperature was controlled using a Viking 1000 thermometer with Viking type UHT3 bimetallic sensor. The temperature was kept between 500 and 600°C for 10-15 minutes. The bone char which appeared grey on the surface and black in the interior was then ground and sorted out as mentioned above in a grain size d = 1.2-2 mm.

ANALYSES:

Fluoride was measured with a Radiometer F1052 fluoride selectrode, a Metrohm reference electrode with sleeve diaphragm and a Metrohm 691 pH-meter. Samples and standards were diluted with distilled water and mixed with tisab according to Standard Methods.[6] pH was measured with a combined Metrohm pH-electrode according to Standard Methods.[6]

RESULTS

results of the interior fluoride profiles for Columns 1.1-1.5 and 2.1-2.3 are shown as discrete points in Figures 1.a-1.c and Figures 2.a-2.c respectively. Breakthrough curves for experiments 2.1-2.3 are shown as discrete points in Figure 3.

The influence of grain size is visualized in Figures 1.a-1.c. Experiments 1.1, 1.2/1.3 and 1.4/1.5 are made with three different grain sizes (experiments 1.2 and 1.3 are identically made and so are exp. 1.4 and 1.5), while all other parameters are the same. Sampling from the interior of the columns at different positions reveals certain profiles (t constant), which are "moving" down stream through the column with time. Samples from exp. 1.2 and 1.3 (and exp. 1.4/1.5) are taken at slightly different times.

Similarly the influence of flow is shown in Figures 2.a-2.c. Three samplings from the three columns are made after approximately the same number of bed volumes, i.e. not at the same experimental time. In Column 2.1 fluoride is measurable in the effluent at all three samplings, in Columns 2.2 and 2.3 only the last. Effluent concentrations are followed beyond the time of sampling from the interior. The results are shown in Figure 3.

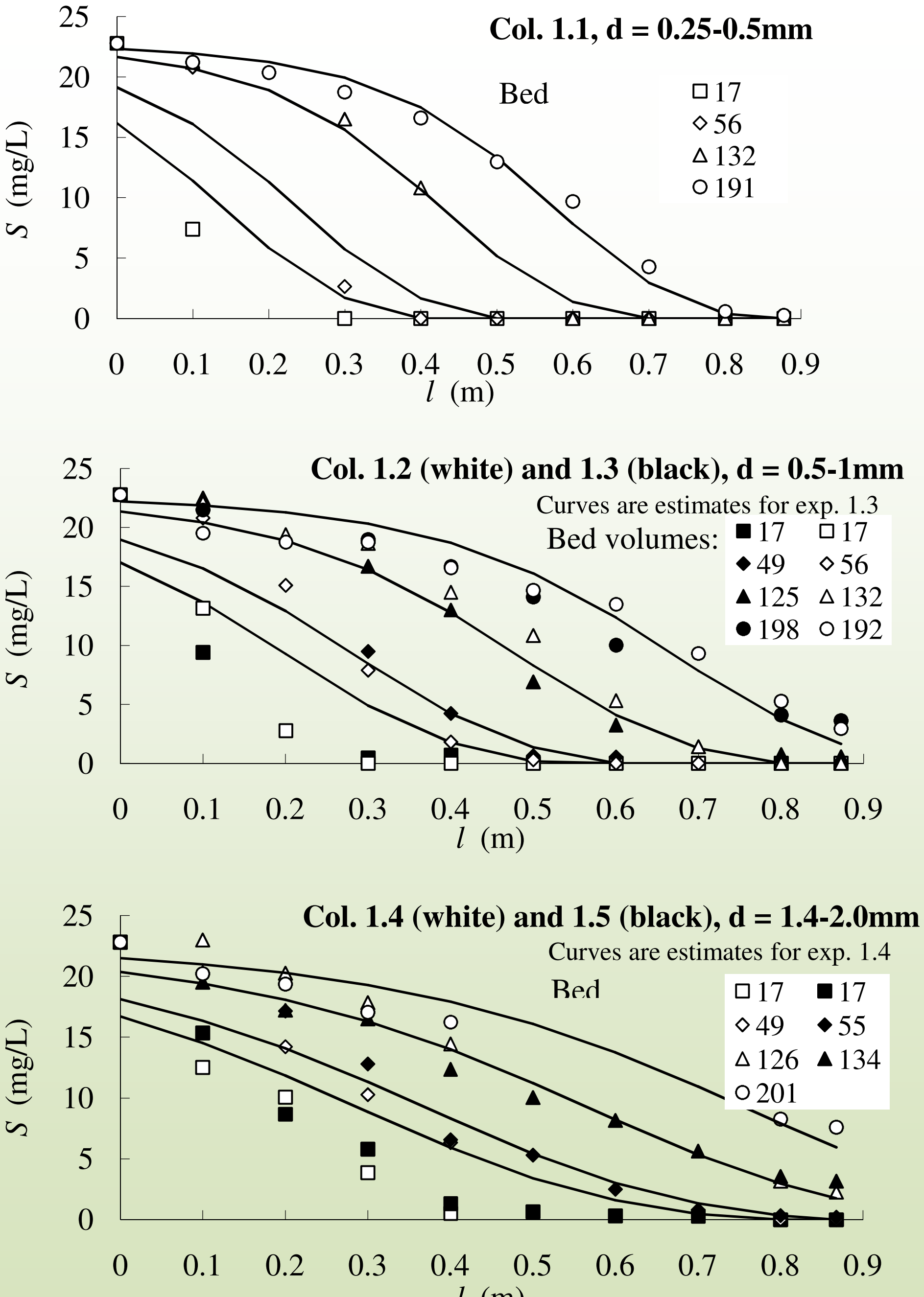

FIGURE 1. Measured fluoride concentrations in bone char columns 1.1-1.5 at different times and positions (dots). Experiments 1.2/1.3 and 1.4/1.5 are replicates. Profile curves are drawn from the estimated model parameters in table 1.

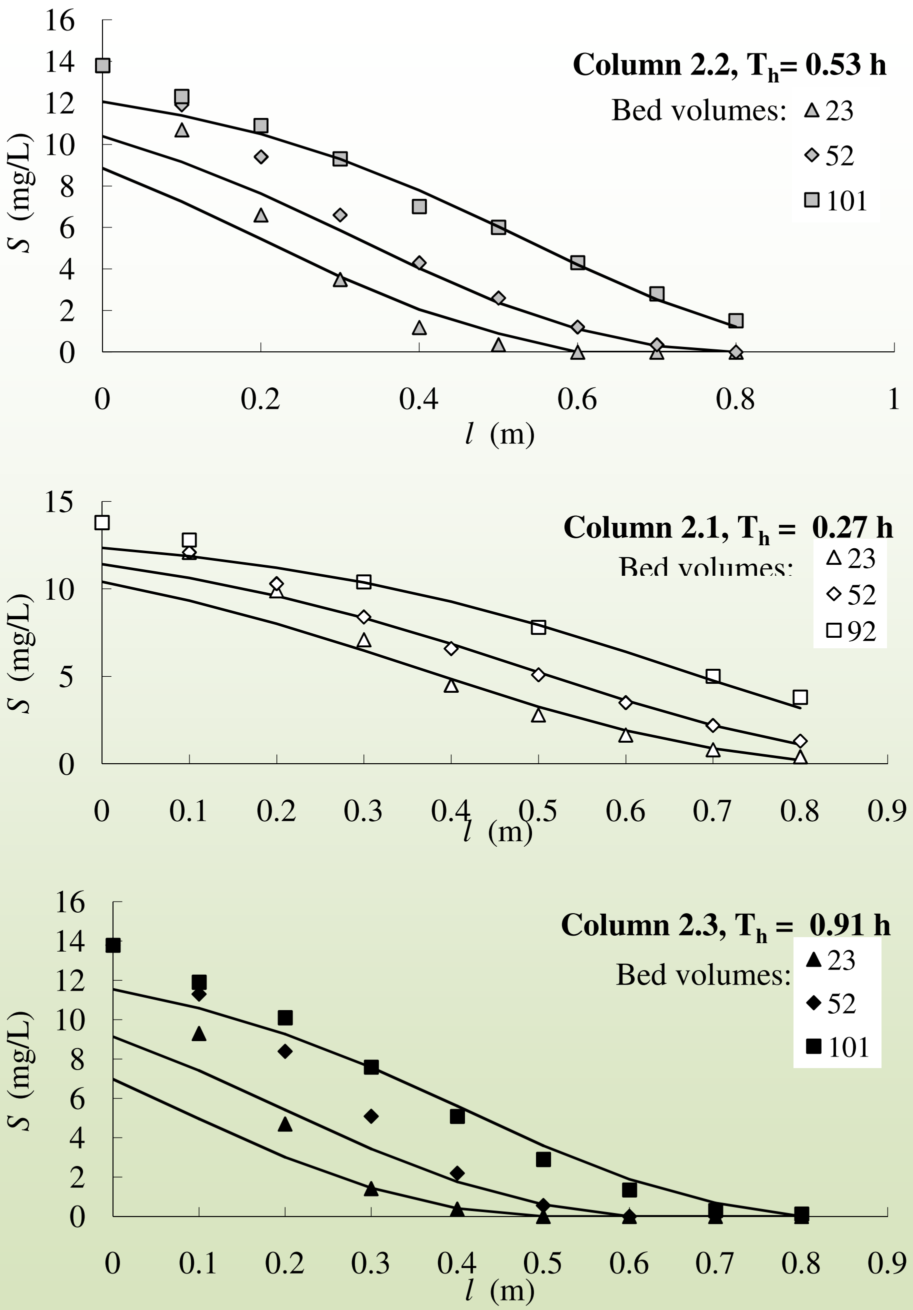

FIGURE 2. Measured fluoride concentrations in bone char columns 2.1-2.3 at different times and positions (dots). Profile curves are drawn from the estimated model parameters in table 1.

A KINETIC MODEL FOR FLUORIDE PROFILES IN COLUMNS:

In batch experiments the following mathematical model for the kinetics of fluoride uptake on bone char has proven to be valid[5]:

$$\frac{dS}{dt} = -k \cdot X_{BC} \cdot \left(f_{m,b} - f\right) \cdot S \cdot t^{-o.5} \qquad \text{Eq. 1}$$

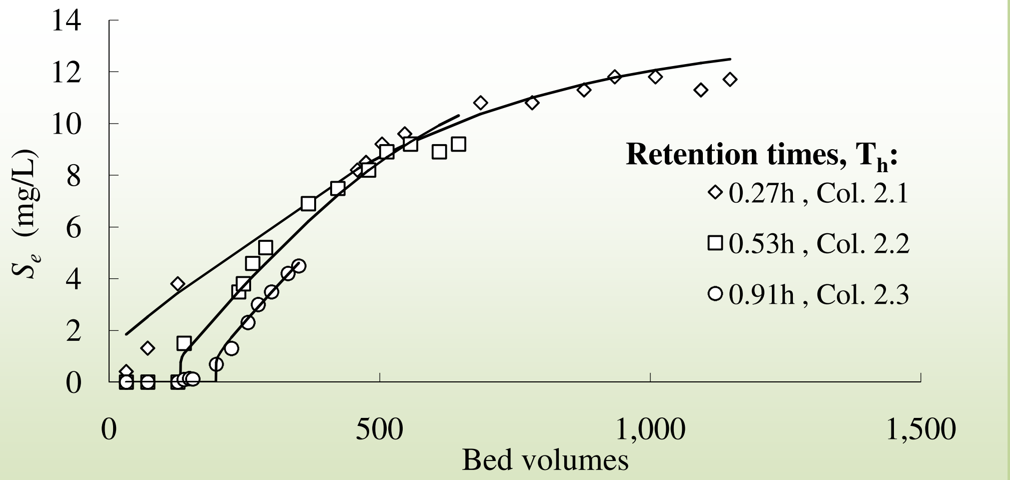

FIGURE 3. Measured fluoride concentrations in the effluent of bone char columns 2.1-2.3 at different times (dots). Breakthrough curves are drawn from the estimated model parameters in table 1.

The reaction rate is proportional to the fluoride concentration and driven by the deficit of fluoride sorbed on bone char. t is the contact time between bone char and fluoride. The fluoride front moves through the column more slowly than the water front and reaches a certain point in the column at $t=t_0$, where t_0 is a function of the distance from the inlet. Every point at the column can be expressed as the corresponding retention time $x = l/v_{lin} = l \cdot \epsilon / v_D$. The reaction rate is therefore written for columns for $t > t_0$ ((t-t_0) is the bone char-fluoride contact time):

$$\frac{dS}{dt} = -k \cdot X_{BC} \cdot \left(f_{m,f} - f\right) \cdot S \cdot \left(t - t_0(x)\right)^{-o.5} \qquad \text{Eq. 2}$$

A mass balance for an infinitesimal piece of column, see Figure 4, for the water phase and for the solid phase:

Balance for the water phase volume between l and l +dl :

$$\begin{array}{lclclcl} \text{IN} & = & \text{OUT} & + & \text{SORBED} & + & \text{ACCUMULATED} \\ Q \cdot S & = & Q\left(S + \frac{\partial S}{\partial l} \cdot dl\right) & + & r \cdot A \cdot \varepsilon \cdot dl & + & \frac{\partial S}{\partial t} \cdot A \cdot \varepsilon \cdot dl \end{array}$$

$$Q \cdot \frac{\partial S}{\partial l} + A \cdot \varepsilon \cdot \frac{\partial S}{\partial t} + A \cdot \varepsilon \cdot r = o \qquad \text{Eq.3}$$

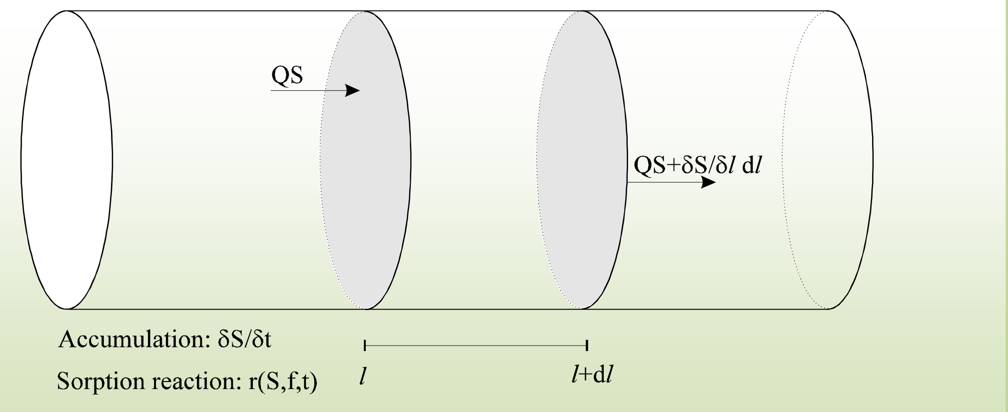

FIGURE 4. Fluoride mass flow in a bone char column

The reaction rate (sorption rate) r is according to Eq. 2 above. Eq. 2-4 form together a 1st order partial differential equation (PDE) system in both f and S. This PDE can not be solved analytically without certain assumptions. *We make the assumption that the fluoride concentration is a pure function of the time of contact with fluoride* and not both with time and position:

Balance for the solid phase in volume between l and l+dl:

IN	=	OUT	+	ACCUMULATED
$r \cdot A \cdot \varepsilon \cdot dl$	=	0	+	$\frac{\partial f}{\partial t} * X_{BC} * A * dl$

$$X_{BC} \cdot \frac{\delta f}{\delta t} - r \cdot \varepsilon = 0 \qquad \text{Eq. 4}$$

$$S = \bar{S} \cdot (t - t_0) = S(u) \qquad \text{Eq.5}$$

Using the boundary conditions $(u,S) = (\infty,S_0)$ and $(u, S, f_{m,f} - f) = (0, S_{min}, f_{m,f})$, where S_{min} is a small concentration defining the fluoride front, the following solution can be shown to be valid:

$$S = \bar{S} \cdot = \frac{S_0 \cdot S_{min}}{S_{min} + (S_0 - S_{min}) \cdot e^{-2k \cdot \varepsilon \cdot S_0 \cdot u^{0.5}}} \qquad \text{Eq. 6}$$

Where

$$u = t - t_0 = t + t_l - R \cdot x \qquad \text{Eq. 7}$$

t_l is a constant like S_{min}, emerging from the derivation of the equations. R is the retention parameter, describing how many times the fluoride front is delayed compared to the water front.

ESTIMATION OF MODEL PARAMETERS FROM RESULTS:

The mathematical model, Eq. 6-8, contains four constants to be determined. Two of them, $f_{m,f}$ and k, have the physical explanations of being a dynamic capacity constant and a dynamic reaction rate, while t_1 and S_{min} are integration constants and have no known physical significance.

The most probable values for the parameters can be estimated by non-linear regression. By changing the four parameters in an iterative procedure, the difference between the measurements and the model values (as the sum of squares of deviation) can be minimized.

Initial trials of estimating parameters for the experimental results showed some trends that may prove to be general:

- The fit of the results are not good in the first part of the column in the first hours of treatment. This is due to the constants t_1 and S_{min}, which make the model behave unexpected in the beginning of the experiment.
- $f_{m,f}$ can be considered constant for the same bone char, thus it can be kept as a common parameter during estimation of the other parameters.
- S_{min}, t_1 and k are interrelated. Similar curves can be obtained with S_{min} varying in a wide range, 1 to 10^{-9} mg/L, and k and t_1 are varied in the intervals 0.01-0.08 $L \cdot mg^{-1} \cdot h^{-½}$ and 50-900 h.
- In order to find a significant k, S_{min} can therefore be chosen as a constant in a series of experiments. For any chosen constant S_{min}, there is an approximately linear correlation between optimized k's and t_1's of experiments made with the same bone char, i.e. $t_1 = c_1 k + c_2$.

We have used results of $t > 45$ hours and $l > 0.30$ m only for estimation of parameters. When the interior profiles for the two sets of experiments were evaluated, $S_{min} = 0.1$ mg/L was appropriate, while $S_{min} = 0.7$ mg/L was more appropriate for the breakthrough curves for exp. 2.1-2.3.

TABLE 2. Estimated Model Parameters

Parameter	Unit	Experiment no.										
		1.1^a	1.2^a	1.3^a	1.4^a	1.5^a	2.1^a	2.2^a	2.3^a	2.1^b	2.2^b	2.3^b
k	10^2 $L \cdot mg^{-1} \cdot h^{-½}$	1.71	1.57	1.58	1.27	1.34	3.54	2.69	2.16	1.44	1.20	0.93
$f_{m,f}$	mg/g			6.6				3.3			3.5	
S_{min}	mg/L			0.10				0.10			0.72	
t_1	h	119	157	155	236	217	63	86	101	83	83	83
c_1	$mg \cdot L^{-1} \cdot h^{1.5}$			-26,768				-2,697			0	
c_2	h			577				159			83	
St. dev.	mg/L	1.42	1.61	1.17	1.56	1.49	0.31	0.39	0.50	0.69	0.51	0.15

[a] Estimates from column profiles. [b] Estimates from breakthrough curves

Table 2 is a summary of the best fit values of the parameters estimated for each experiment. For experiments 1.1-1.5 and 2.1-2.3 the parameters are estimated from the sampling of the interior of the column. For experiment 2.1-2.3 additional parameters are estimated from the breakthrough curves. The interior samplings are mainly (exp. 2.2-2.3) obtained before breakthrough, so there is a difference in time between interior and exterior sampling in the second series of experiments.

From these parameters are generated curves for the experimental conditions, which are shown in Figures 1-3 together with the measured results. To make reading easier, only estimates of experiments 1.3 and 1.4 is included in Figures 1.b and 1.c respectively.

DISCUSSION

Correlation of the model with experimental results*:* Figure 1 through 3 show good agreement between the model and the experimental results, both in shape and size of profiles and breakthrough curves. The model curves emphasize the S-shape of the profiles. The S-shape profiles were noted earlier based on the experimental data. This type of profile is characteristic of sorption columns and is reported in previous studies.[7]

The fit of the curves are acceptable in these experiments from approximately 50-200 bed volumes, at the time of breakthrough. However, the estimated parameters for the interior profiles, do not apply to the breakthrough curves of columns 2.1-2.3. This can be due to insufficiency of the model, but also that the experimental results are determined with some uncertainty, due to problems of keeping the flow constant for a 2 weeks period. In this case the best determined parameters are the ones for the breakthrough curves, since they represent the whole treatment period.

The two parameters t_l and S_{min} have apparently no physical meaning, just emerging as necessary constants in the development of the flow kinetic model. The linear relation between t_l and k are totally empiric, based on these few results. Further and more precisely performed experiments should show if this relation is valid, or other correlations can be established for t_l and S_{min}.

Variation of Reaction Rate Parameter and Dynamic Capacity Parameter*:* It is shown in Table 2 that the k-values for the interior samplings of the two types of bone char apparently are higher for bone char 2 than bone char 1. This is in contrast with the conclusions from batch experiments, that obviously showed that bone char 2 is a poor quality field manufactured bone char.[5] Because k is correlated with t_l this comparison cannot be made directly. More uniformly made experiments would apparently be necessary for comparison between two different bone chars, as e.g. exp. 1.1-1.5 can be used for comparison of the influence of different grain sizes.

The dynamic capacity parameter $f_{m,f}$ is estimated at 6.6 and 3.3-3.5 mg/g for the two bone char materials (Table 2). These capacities are slightly higher, but in the same order as the $f_{m,b}$ = 5.6 and 2.0 mg/g estimated in batch experiment using the same kinetic expression.[5] It is expected that higher capacities can be found in columns, because water in the upstream end of the filter can be saturated at fluoride concentrations close to the inlet concentration.

The influence of grain size on fluoride uptake in filters: When parameters are estimated for each experiment 1.1-1.5, the value of $f_{m,f}$ falls between 5.7 and 7.8 mg/g (not shown in the table) with no tendency for $f_{m,f}$ to increase with lower grain sizes.

We therefore assume that $f_{m,f}$ is constant for the three grain sizes. This was the same conclusion drawn for $f_{m,b}$ in batch experiments.[5]

The effect of the grain size can instead be read in the dynamic rate constant, *k*. Smaller grains have a higher *k* value and are faster reacting. The same trend is found for batch experiments with other bone char materials.[5,8,9] There is a linear correlation (negative slope) between the average *k* values of experiments 1.1, 1.2/1.3 and 1.4/1.5 and the average grain sizes $d = \sqrt{d_l \cdot d_h}$. The sample size is too small to reliably determine the correlation coefficient between *d* and *k* but, it is apparant smaller *d* results in higher reactivity *k*.

The influence of retention time on fluoride uptake in filters*:* The influence of retention time on fluoride uptake can be read easiest in Figure 3. Not only does the breakthrough of the filter occur sooner at higher flows, but also at smaller total discharge, i.e. smaller amounts of water can be treated before breakthrough appears when the flow is higher. Lower fluoride removal at higher flow rates are also found by Mwaniki and Nagelkerke[4] in their experiments, indicating that an equilibrium model is not sufficient to describe this effect.

The effect of better fluoride uptake at lower retention times is included in the kinetic model developed in this paper. It is expected that k is independent of T_h and flow, since flow is already included by way of the flow mass balance (Eq. 3 and 4). The results in Table 2 indicate however that *k* varies by a factor 1.6 between the lowest and highest flow, *k* is higher (opposite the fluoride uptake) for high flow rates. Whether this is an effect of experimental uncertainty or the model inadequacy is not known.

Further comparisons of batch and flow experiments with the same bone char can show if there can be established a correlation between the *k* and f_m values in the two types of experiments (and general rules for t_l and S_{min}). It will be a great advantage if a general batch test experiment can reveal kinetic constants usable in flow experiments and flow treatment plants, because batch experiments are much more simple to perform than flow experiments.

Practical applications. *Sizing of filters:* When appropriate constants have been established for a bone char from laboratory experiments, the kinetic formula should be usable for sizing of filters for various types of waters and different water consumption / flow rates. The basis for approving the model is limited to the presented series of experiments, which are in fact made under difficult experimental conditions, resulting in a number of pauses in the flow. Our experience gained from the flow breaks are that they result in short termed improved fluoride uptake, when the pause is omitted from the experimental time. We suppose that the difference will be smaller on a long term basis.

By rearrangement of Eq. 6 and 7 the model can be used for sizing of bone char filters. The bed volume, *BV*, of a bone char column that can treat a daily water amount D_d during a daily filtration time T_d for an operation period T_{OP} (till bone char media should be shifted), until the effluent concentration reach a maximum concentration of S_{max} is:

$$BV = A \cdot L = \frac{D_d}{T_d \cdot R \cdot \varepsilon} \cdot \left\{ \frac{T_d}{24 \cdot h} \cdot T_{OP} + t_1 - \left[\frac{\ln\left(\dfrac{\frac{S_0 - S_{min}}{S_{min}}}{\frac{S_0 - S_{max}}{S_{max}}} \right)}{2 \cdot k \cdot \varepsilon \cdot S_0} \right] \right\} \qquad \text{Eq. 9}$$

On the background of the limited experimental evidence of this model, it should only be regarded as a suggestion, which needs further proof to be accepted for practical application for column sizing. The model is not mentioning any preferences of *L*/*A*-ratio. According to usual dispersion theory (dispersion is not included in this model), less dispersion (which is preferred) is obtained at higher linear water velocities. Long thin columns would for this reason be better than short thick columns. Flow friction loss and edge effects may however favour larger diameters.

CONCLUSIONS

It is seen for the first time from interior sampling in flow experiments with bone char columns, that fluoride concentrations is reduced as S-shaped curves. This behavior is described by a kinetic model, from which can be generated usable parametres for future sizing of filters. With support from the mathematical model the experimental results further show that smaller grain sizes of the bone char makes fluoride sorption faster and that smaller flow velocities or larger retention times makes the bone char more effective.

ACKNOLEGMENTS

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NOTATION

A = Cross sectional area of column (m^2)
c_1 = Model parameter, correlating k with t_1 (mg·L^{-1}·h$^{1.5}$)
c_2 = Model parameter, correlating k with t_1 (h)
d = Average grain size of a bone char sample (mm)
d_l = Size of sieve mesh retaining a bone char sample (mm)
d_h = Size of sieve mesh just allowing the bone char sample to pass (mm)
D_d = Daily water amount required for filtration (L)
f = Fluoride concentration in the bone char (mg/g)
$f_{m,f}$ = Capacity parameter for fluoride uptake on bone char in flow (mg/g)
$f_{m,b}$ = Capacity parameter for fluoride uptake on bone char in batch (mg/g)
k = Reaction rate parameter (L·mg^{-1}·h$^{-½}$)
L = Length of a filter column (m)
l = Distance from the inlet of the column (m)

Q = Water flow (L/h)
r = Reaction rate, = $-dS/dt$ ($\text{mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$)
S = Fluoride concentration in the water phase (mg/L)
S_0 = Fluoride concentration in the raw water (mg/L)
S_{max} = Maximum acceptable fluoride concentration in treated water (mg/L)
S_{min} = Empirical model parameter, concentration defining the fluoride front (mg/L)
t = Time (h)
t_0 = Time for fluoride front to reach position x (h)
t_l = Empirical Model parameter (h)
T_d = Daily filtration time (h)
T_h = Hydraulic retention time in the filter (h)
T_{OP} = Filter operation period (h)
T_{tot} = Total experimental time (h)
u = Contact time between fluoride and bone char = $t-t_0$ (h)
x = Hydraulic retention time corresponding to position on column = l/v_{lin} (h)
X_{BC} = Density / concentration of bone char in the filter (g/L)
v_D = Surface loading / Darcy velocity ($m^3\ m^{-2}\ h^{-1}$)
v_{lin} = Linear velocity of water = $v_D/$ (m/h)
BV = Bed volume of a bone char filter (L)
ε = Porosity measured in column

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SIGNIFICANCE OF OXYGEN IN PROCESSING OF BONE CHAR FOR DEFLUORIDATION OF WATER

E Dahi* and H Bregnhøj*

SUMMARY: The significance of duration and temperature of bone char processing and the admission of air oxygen during charring is investigated. Different quality criteria are used, i.e. the defluoridation capacity and the specific surface area of the treated bone, along with the pH and alkalinity of the defluoridated water. Processing temperatures between 300 and 800°C and duration between ½ and 5 hours are used. It is found that when admission of oxygen is restricted, i.e. the process is run as of pyrolysis, all measured quality parameters, including defluoridation capacity, are at optimum, independent of charring time and temperature. When bones are exposed to atmospheric oxygen, i.e. the process is run as a calcination, the defluoridation capacity is drastically reduced for temperature above 500°C. Similarly, pH and alkalinity of the defluoridated water are found to increase during the calcination. The specific surface area is highest for pyrolysed bone, and much lower for calcined bone. The results indicate that pyrolysis, when carried out completely, provides the best bone char quality, where the product is all over black and has the highest possible defluoridation capacity. If treated properly pyrolysed bone may even be able to improve the aesthetic water quality rather than deteriorating it.

Keywords: bone char, defluoridation, pyrolysis, calcination, charring procedure, surface area, capacity, optimisation.

INTRODUCTION

Bone char has been used for defluoridation of drinking water in USA in the 1950's and 1960's.[1,2] At that time bone char was commercially widely available, because of its use in the large scale sugar industry. Today the use of bone char in the sugar industry is replaced by synthetic ion exchange resins. As the manufacturing of bone char was previously empirically established for the sugar industry, very few studies have been carried out on its manufacturing for use in drinking water defluoridation. Today there is an increasing interest in using bone char for defluoridation of drinking water in third world countries, and hence the need to investigate how to prepare and to measure a high quality bone char for treatment of fluoride contaminated drinking water.

It has been reported that the defluoridation ability deceases with increasing charring temperatures and duration time even when treated at 550°C for 30 minutes compared with 400°C for 1 hour[3] or 450°C compared to 350°C (time not indicated).[4] Bone char is reported to change its colour from black to grey to white as it is heated from 350°C to 600°C and "black bone char" has therefore been regarded as the good bone char.[4,5] According to this study, these colour changes are only observed when bones are *calcined*, i.e. heated in the presence of atmospheric oxygen. In principle, the end product of such a calcination is pure bone minerals, i.e. compounds related to

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* *Center for Developing Countries, Technical University of Denmark, Building 208, DK-2800 Lyngby, Denmark.*

hydroxyapatite. All organic materials are combusted and gassed off. All organic carbon is transferred into carbon dioxide.

The original procedure of charring bones for the sugar industry was different, in the sense that no or limited flow of oxygen was admitted to the process.[6] When the bones thus are *pyrolysed*, the organic material is mainly cracking, and a significant part of the organic carbon is converted to inorganic carbon, graphite. The end product of this treatment will be black. No colour changes at all are observed. The above mentioned criteria of colour changes as a means of characterising the product and the preparation, as described by Phantumvanit et al.[5] and Mwaniki[4] is thus unusable in the case of pyrolysis of bones.

MATERIALS AND METHODS

Preparation of bones: A mixture of all sorts of farm animal bones and teeth has been used as raw bones. The bone materials were delivered from the Danish bone meal and animal feed factory DAKA, where the genuine bones are boiled, washed, dried and crushed down to 2-3 cm particle size.

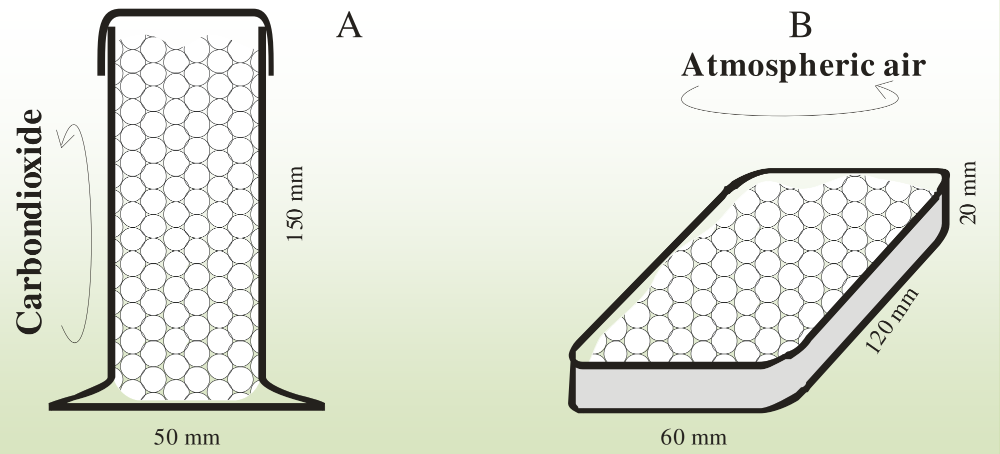

FIGURE 1 Illustration of the containers used for respectively pyrolysis (A) and

The DAKA bones were crushed to a size 4-10 mm in a Morgårdshammars, B-92 plate type crusher. Samples of bone char were placed in two types of containers, type A for pyrolysis and type B for calcination, see figure 1. The bone materials were then charred in a programmable ceramic oven SK 35 S from Scania-Oven A/S. The temperature was gradually raised at a constant rate of 3̃C/min from the room temperature and up to the treatment temperature. This temperature was then kept constant for a selected treatment duration. As treatment temperatures for the different batches 400, 500, 550, 600 and 700°C were used. As treatment duration ½, 1, 2, 3 and 5 hours were used. After the said time of treatment samples were taken out for cooling and testing. Pyrolysed samples were cooled down in a CO_2 atmosphere. The bone char was further crushed and sorted out in a test sieve shaker type EFL2 mk3 from Endecotts LTD to grain size diameter between 1 and 2 mm. Samples were weighed before and after charring in order to assess the weigh loss.

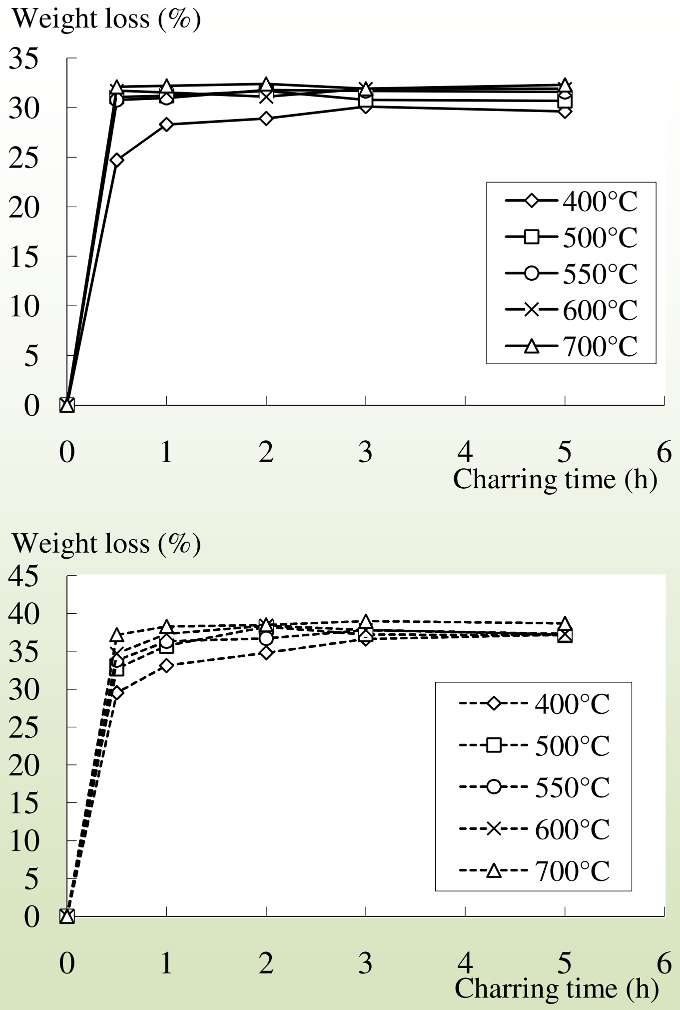

Figure 2. The weight loss in % as a function of heating time and duration. The upper results are obtained through pyrolysis. The lower results are obtained through calcination in atmospheric air.

Defluoridation capacity testing: Four gram samples of bone char having grain size 1-2 mm were added to 1 litre distilled water containing 20.0 mg/L fluoride in plastic beakers at time zero. The beakers were stirred using a Jar test apparatus Type 7790-402 from Phipps & Birds at a speed of 60 rpm. After stirring in 24 hours, samples of the water were taken for analysis.

Analysis: The fluoride concentrations in the water samples were measured using a Radiometer F1052 fluoride electrode and an Ag/AgCl reference electrode with sleeve type diaphragm (Metrohm 6.0726.100) connected to a Metrohm 692 pH-meter. Five ml samples were mixed with 5 ml tisab[7] for measurements and readings, compared to standards of 2 and 20 mg/L F^-, according to Standard Methods[8].

pH was measured in the defluoridation capacity samples using a combined glass electrode (Metrohm 6.0233.100) in connection with a Metrohm 691 pH-meter.[8]

Total alkalinity (TAL) was measured in the defluoridation capacity samples by autotitration of 100 ml solution to pH = 4.5 with standardised 0.1 M H_2SO_4[8], using a titrator set of Metrohm 691 pH-meter, Metrohm 614 Impulsomat and Metrohm 665 Dosimat.

The specific surface (BET-method) was measured in a Micromeritics Flowsorp II 2300.

RESULTS

Figure 2 shows the results of bone char weight loss as a function of 5 different temperatures and 5 different duration times, for pyrolysis as well as calcination. The average weight loss after 5 hours of pyrolysis at 400 to 700°C is 31.2 % standard deviation being 1.05. The average weight loss after 5 hours calcination at 400 - 700 °C is 37.5, the standard deviation being 0.68.

The defluoridation capacity is calculated in the jars from the determination of fluoride concentrations before and after 24 hours of contact time, according to the following equation:

$$DC = \frac{S_0 - S_{24h}}{X_{BC}}$$

Where:

DC_{BC}	Defluoridation capacity of bone char (mg/g)
S_0	Beginning concentration in defluoridation capacity measurements (mg/L)
S_{24h}	Concentration after 24 hours in defluoridation capacity measurements (mg/L)
X_{BC}	Added bone char (g/L)

The defluoridation capacities are shown in figure 3 for all selected temperatures and duration times. When temperatures below 550 °C and duration timed shorter than 2 hour are excluded, the results shows that the utilised bone, on an average, has a defluoridation capacity of 2.27 (± 0.18) mg fluoride per g of bone char when pyrolysed, but only between 0.2 and 1.6 mg/g when calcined.

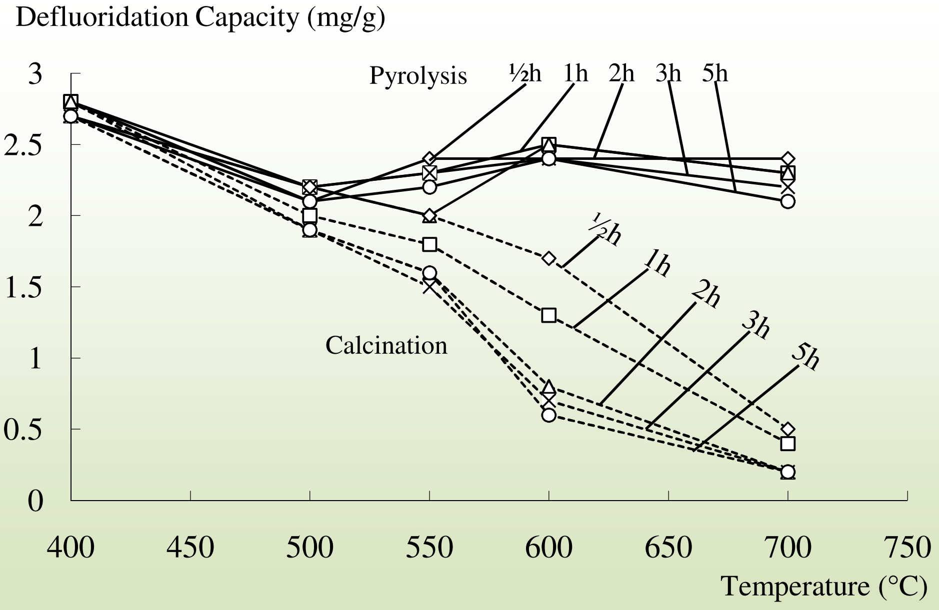

FIGURE 3. The defluoridation capacity of bones pyrolysed and calcined for different temperatures and heating durations.

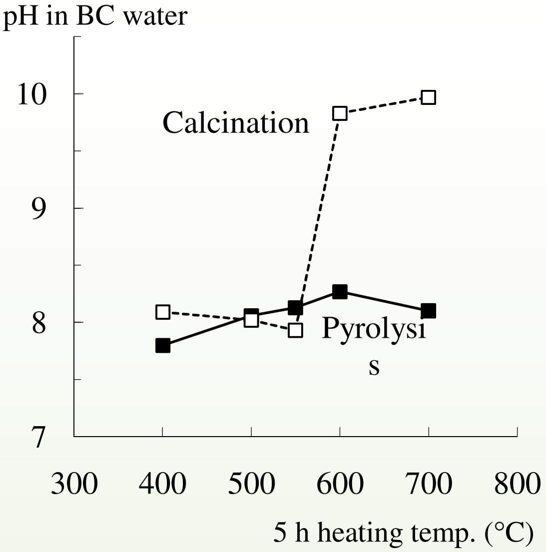

Figure 4. pH in the distilled water contain-ing 20 mg/L fluoride, after treatment for 24 hours with 4 g/L bone char heated for 5 hours at the given temperatures.

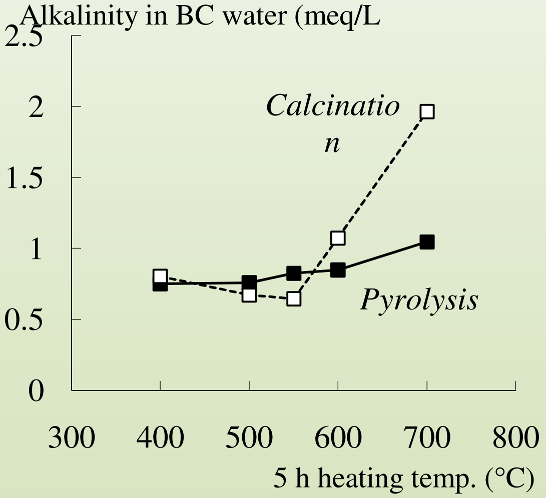

FIGURE 5. The alkalinity in the distilled water containing 20 mg/L fluoride, after treatment for 24 hours with 4 g/L of bone char heated for 5 hours at the given temperatures.

The exclusion of the low temperatures and duration times is made to avoid poor taste, smell and colour in the water treated by the bone char treated under these conditions.

pH in the waters treated with bone char heated for 5 hours are illustrated in figure 4. The pyrolysed bone waters have pH between 7.8 and 8.3, while the calcined bone char waters have pH between 8.1 and 10.0. The alkalinity of these samples, as shown in figure 5 is similarly stable for the pyrolysed bone, between 0.8 and 1.0 me/L, but increasing for the calcined bone, between 0.8 and 2.0 me/L.

Figure 6 shows the measured specific surface area of the heated bones. On an average BET is 131 ± 12 m^2/g for pyrolysed bones, while BET is falling from 94 to 11 m^2/g for the calcined bone. The BET for the not heated bone is measured to less 5 m^2/g .

DISCUSSION

The results of weight loss analysis in this study, figure 2, show that when bone is heated slowly (3°/min) in a well insulated oven, most of the organic materials are lost already ½ an hour after the target end temperature is reached. This is at least valid when the end temperature is more than 400 °C. Through weight loss analysis, it is thus impossible to distinguish between treatment duration of 1-5 hours and temperatures of 500-700 °C.

On the other hand as all pyrolyses are resulting in the same degree of weight loss (about 31 %) and all calcinations are coming up to a higher loss (about 38 %), the weight loss, along with the colour changes may be most useful for characterisation of the admissibility of oxygen during the treatment. Samples which all through are black after being heated for more than a couple of hours at 500-700°C, i.e. properly pyrolysed, would probably contain not less than 10 % pure (activated) carbon. This is of course most important as this graphite carbon may be used in the water treatment depending upon the raw water quality.

The measurements of the specific surface area of the treated and not treated bone, figure 6, indicate that the high surface area is produced during the heating. In case of pyrolysis the surface area will remain at maximum for all temperatures and duration times, contrary to calcination, where the specific surface area decreases with heating temperature.

The defluoridation capacity of the treated bone seem to follow the same pattern as the surface area as illustrated in figure 7. The raw bone has both a low defluoridation capacity and a small surface area, probably because of organic material covering the pores. When this material is removed by heating more surface is made available for adsorption. The defluoridation capacity is preserved all through the pyrolysis and partly destroyed in the calcination process. This is at least valid for temperatures above 550 and less than 800 °C, even when the treatment is as short as ½ an hour, figure 3.

The increase in pH and alkalinity are

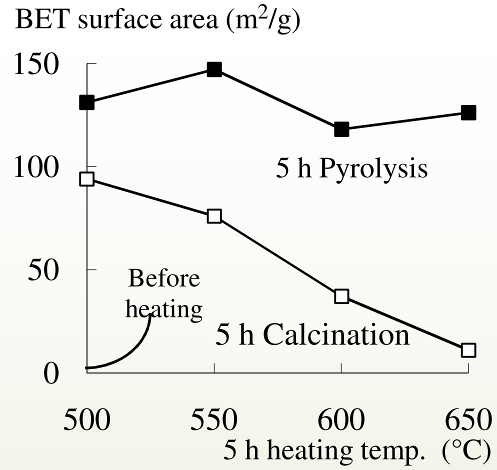

Figure 6. The specific surface area of bone before and after heating for 5 hours at the indicated temperatures, without and with the admission of atmospheric oxygen.

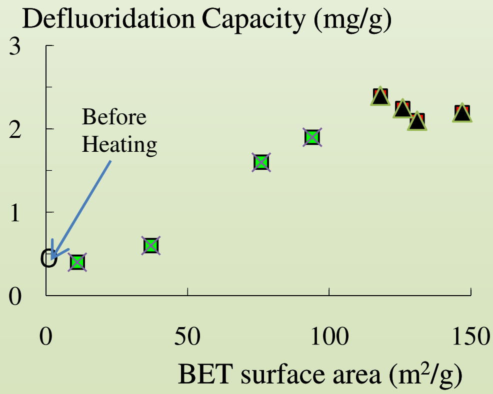

FIGURE 7. Defluoridation capacity as a function of BET surface area of raw bone and 5 h heat treated bone.

probably due to destruction of some of the apatite, where mainly CaO is produced. As this compound is only slightly soluble in the water, the production of CaO may be expressed through the increased pH and alkalinity. This is in agreement with the fact that the decreases in the defluoridation capacities during calcination, up to about 90 % of full capacity as per pyrolysis, are stoichiometrically more significant than the observed corresponding increases in alkalinities. It must be noted that even pyrolysed bone does add alkalinity to the water. This alkalinity increase is however only slightly above the equivalent reduction of fluoride, indication that the pyrolysed bone, in the contrary to calcined bone, does not contain any significant alkalinity.

It may be argued that if the defluoridation capacity is preserved during the short time and low temperatures, this is because the oxygen admitted is only consumed by the organic materials. Thus the apatite structure may not be exposed to entire calcination condition as long as oxygen is consumed by the organic materials.

The heating of bone for water defluoridation should therefore be carried out as a pyrolysis, i.e. where the admission of air oxygen is restricted, in order to:

Preserve the apatite structure uncalcined and hence the defluoridation capacity of the bone at maximum.

Allow for maximum specific surface area of the treated bone, including its contents of pure carbon, which may be used as a general sorption agent in the water treatment.

Minimise the potential of introducing alkalinity and too high pH in the treated water due to destruction of apatite compounds in the calcination process.

As apatite is believed to be durable even in atmospheric air at 400 to 700°C, this study does not give a direct answer to the mechanisms behind the defluoridation capacity deterioration during calcination. One explanation could however be that much higher temperatures are obtained at a micro (molecular) level, as a consequence of burning the organic materials in the bone during the process of calcination.

It has to be added that this study does not recommend certain temperatures and duration times. The experiences gained in the laboratory and in the field show that laboratory experiences can not be directly extrapolated to field conditions. Further more the volume and the design of the container may play an important role in selection of these parameters. Field testing indicate however that the necessary preheating periods are longer, and hence more energy consuming, in the pyrolysis process.

CONCLUSION

The following major conclusions can be drawn from the presented results.

- The best quality bone char is obtained through heating where the air oxygen is prevented or restricted (pyrolysis).

- The bone defluoridation capacity and its contents of black carbon are durable under several hours' exposure to temperatures up to 700. This is valid for the pyrolysis, but not for the calcination.
- The weight loss is an ambiguous indicator in the control of the bone char preparation; maximum weight loss is only obtained in case of calcination, where the bone char quality may be deteriorated.
- Colours of bone char can be used as indicators of defluoridation ability only if the bone char has been calcined. All pyrolysed bone char is black.
- The pyrolysis process, which ensures the maximum defluoridation capacity, would as well result in better defluoridated water quality, with respect to pH, alkalinity and may give rise to a higher potential for removal of colour, taste and turbidity in the raw water.

ACKNOLEGMENTS

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MEASUREMENT OF FLUORIDE IN MAGADI

J M Nielsen* and E Dahi*
Copenhagen, Denmark

SUMMARY: The concentration of fluoride is measured in a crystalline magadi sample, originating from Lake Magadi, after it has been pre-treated in three different ways. The results show that the measured fluoride concentration is independent of the amount of magadi dissolved in water, though high concentrations, like 30 g magadi/l, results in high ionic strength of the solution, which may interfere in the fluoride analysis. A big lump is crushed into small pieces and these are analysed for fluoride. The concentrations measured are subject to wide variation and there are significant differences in the concentrations. The concentration seems to follow a logarithmic distribution. Crushing and sieving before analysing, results in significant differences in the measured concentrations. Grains smaller than 1.0 mm have a significant higher concentration than grains bigger than 1.0 mm. Additionally crushing of grains bigger than 4.0 mm does not result in variation in the concentration.

Key words: Magadi; trona; fluoride concentration; sieving; dilution.

INTRODUCTION

The special geological and hydrological conditions at the East African Rift Valley cause both ground water and surface water in big parts of Kenya and Tanzania to be alkaline and contaminated with fluoride (low Ca^{2+}, high Na^+, CO_3^{2-} and F^-). As a result, salt deposits are formed at the alkaline lakes and on the earth's surface due to evaporation. The salt deposits consist mainly of trona ($Na_2CO_3{\cdot}NaHCO_3{\cdot}2H_2O$) contaminated with fluoride. This is locally called magadi.

In trona, fluoride is occurring as villiaumite (sodium fluoride) and it has been observed[1] that well-formed cubic crystals of villiaumite is occurring as inclusions in the larger trona crystals and it also occurs as clots of crystals adhering to the margins of the trona crystals. The fluoride concentration in magadi varies a lot, 0.2-14.9 mg F^- /g magadi[1-4] not only depending on the origin.

This paper evaluates three different pre-treatments before measurement of fluoride concentration in magadi solutions and the influence of the pre-treatment on the measured value.

MATERIALS AND METHODS

Magadi Samples: The magadi samples used in the investigation is from Lake Magadi, Kenya and was bought at the market in Magadi town November 1993. The sample is crystalline and grey in colour. The crystals have form like needles to a length of 30 mm.

Crushing and Sieving: The magadi sample is crushed in a mortar and dissolved in distilled water. Thereafter the fluoride concentration is measured.

Fluoride measurements: The fluoride concentration is measured using a Radiometer F1052 fluoride electrode and a Metrohm Ag/AgCl reference electrode with a sleeve type diaphragm connected to a Metrohm potentiometer (692 pH/Ion Meter). A 10-ml sample of the solution is mixed with 10 ml CDTA-tisab and the fluoride

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* *Center for Developing Countries, Technical University of Denmark, Building 208, DK-2800 Lyngby, Denmark.*

concentration is measured using the calibration method according to Standard Mehods[5]. If the reading on the potentiometer is higher than a concentration equal to 10 mg/l the sample is diluted additionally.

Preparation of solutions: The magadi is treated in three different ways before it is dissolved in distilled water. In the first investigation a big lump (40 g) is crushed into powder. Different dilutions, 5.0, 10, 20, and 30 g magadi/l, are prepared (4-5 replicates) and analysed for fluoride. In the second part a big lump (500 g) is crushed into 20 smaller parts. These small samples are crushed into powder and dilutions of 20 g/l are prepared (2 replicates) and analysed for fluoride. In the last investigation a lump of 150 g is crushed into small particles and sieved in a electrical shaker for 5 minutes using the sieve sizes: 0.50, 0.71, 1.0, 1.4, 2.0, and 4.0 mm. Dilutions of 20 g/l are prepared (3 replicates) for each grain size fraction and analysed for fluoride.

RESULTS AND DISCUSSION

Magadi Solutions: The results from the experiment with different magadi dilutions can be seen in Table 1. The ionic strength of the solution, I, is calculated according to the Debye-Hückel theory[9], $I=\frac{1}{2}\sum m_i \cdot z_i^2$, assuming that the magadi sample is pure sodium sesquicarbonate ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$).

It is seen that the measured fluoride concentration varies for different amount of dissolved magadi in distilled water. A single factor ANOVA (ANalysis Of VAriance) shows that there is no significant difference between the fluoride concentrations in the different dilutions. No relation between the ionic strength and the fluoride concentration can be found either.

TABLE 1: The fluoride concentration in a magadi sample and the ionic strength (I) of the solution according to the Debye-Hückel theory[6].

Dilution g-magadi/L	No of Samples	Con. mg-F/g-magadi	I mol/L
5.0	5	0.291	0.088
10	5	0.280	0.177
20	5	0.265	0.354
30	4	0.285	0.531

The ionic strength of the solution has to be taken into consideration though. The CDTA-tisab is mixed with the dilution to keep a constant ionic strength, resulting in a hardly varying activity coefficient. The addition of CDTA-tisab to a water sample with low ionic strength (for example drinking water) results in a ionic background strength of 2.0 mol/l[7] and addition of 30 g sodium sesquicarbonate to 1 litre of distilled water results in a ionic strength of 0.53 mol/l. Therefore different amounts of dissolved magadi result in varying ionic strength and therefore higher uncertainties in determination of the fluoride concentration. Thus, small amounts of magadi have to be dissolved in distilled water before measurement of fluoride concentration when using the calibration method.

Distribution Differences: The fluoride concentration (average of 2 replicates) in the 20 small samples can be seen in Figure 1. The cumulative frequency is plotted versus the fluoride concentration on logarithmic probability paper. It is obvious that the fluoride concentration is subject to a wide variation and a single factor ANOVA shows significant differences between the measured fluoride concentrations in the small samples. The concentration ranges from 0.09 to 0.20 mg-F/g-magadi and the fractiles of 25, 50, and 75% being 0.102, 0.115, and 0.137 mg/g. From the plot in

Figure 1 it is seen that the fluoride concentration in the magadi sample seems to follow a logarithmic distribution.

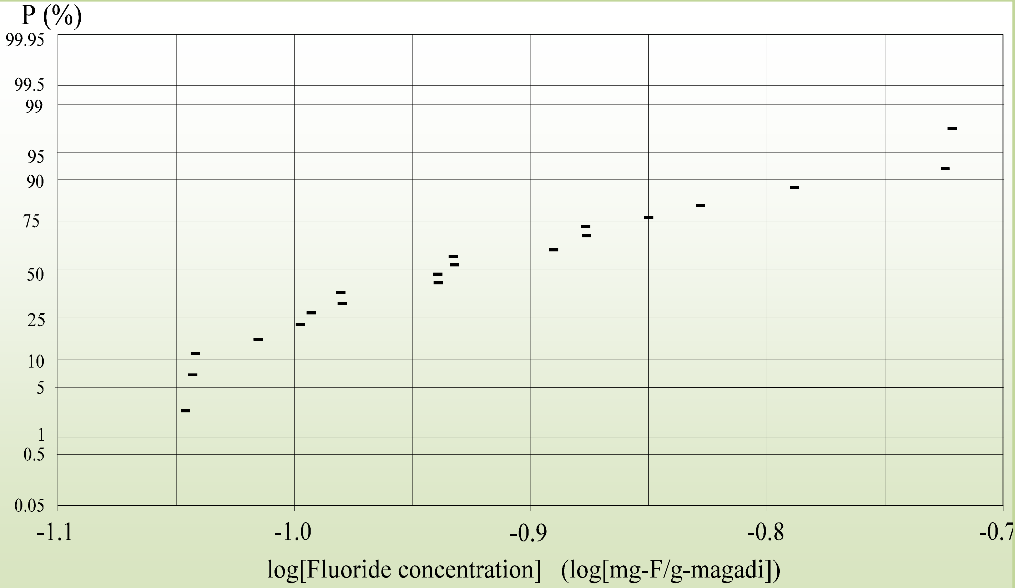

FIGURE 1. The fluoride concentration in 20 small samples from the same lump plotted on logarithmic probability paper.

Grain sizes: The results from the sieving investigation can be seen in Figure 2. The measured fluoride concentrations (3 replicates) are plotted versus the geometric mean grain size, GS_{gm}.

From Figure 2 an obvious dependency between the grain size and the fluoride concentration is observed, that is the fluoride concentration is decreasing for increasing grain sizes. It seems as the concentration stabilises at a certain level for GS_{gm} higher than 1.18 mm. A single factor ANOVA shows a significant difference between the grain sizes and a Newman-Keuls Range Test shows that the concentration for GS_{gm}, equal to 0.22, 0.59, and 0.8 mm are significantly higher than the concentration for the other grain sizes. All grains bigger than 1.0 mm (GS_{gm}=1.18) has the same

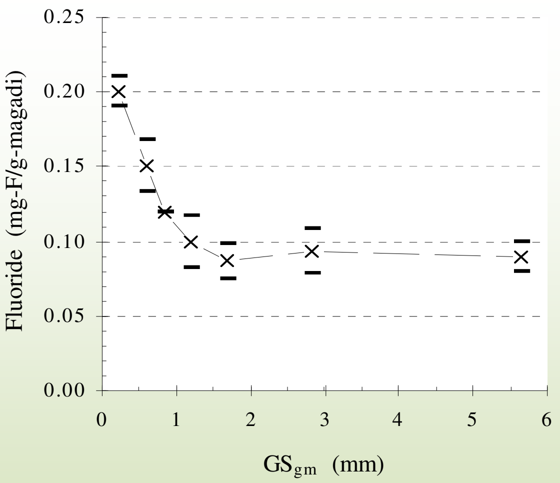

FIGURE 2. The fluoride concentration (3 replicates) versus the geometric mean grain size, GSgm. x indicates the mean, and - indicates the standard deviation.

fluoride concentration, approximately 0.09 mg F^-/g magadi.

For further investigations of the relationship between the fluoride content and the grain size, grains bigger than 4.0 mm (GS_{gm} = 5.66 mm) are additionally crushed and sieved using the mesh sizes 0.125, 0.18, 0.25, 0.50, 0.71, 1.0, and 1.4 mm. Dilutions of 20 g/l are prepared (single measurement) for each grain size fraction and analysed for fluoride. The result of a single measurement can be seen in Figure 3.

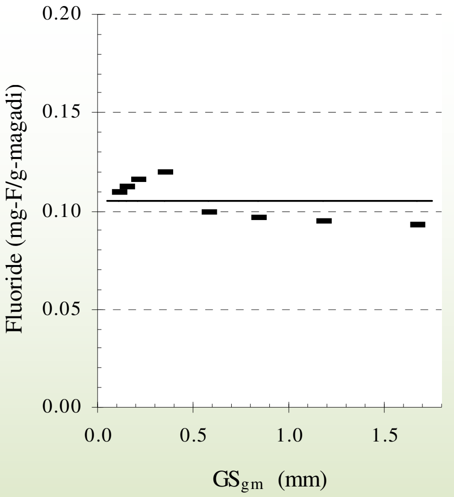

FIGURE 3 Single measurement of the fluoride concentration in a magadi sample (d>4.0mm) versus the geometric mean grain size, GS_{gm}, after additional crushing and sieving. - indicates the measurements and the straight line indicates the average.

It is observed that the fluoride concentration is stable, 0.105 mg-F^-/g-magadi for all grains after additional crushing and sieving of grains bigger than 4.0 mm. This is not in agreement with Baker[1] who found that fluoride was mainly present in the +4mm and -60 mesh B.B.S. (≈0.50 mm) fractions of crushed magadi. Baker[1] also found that when crushing the coarser fraction fluoride passed into the fine products.

From the above given results it is recommended that a big sample is crushed into powder and mixed well before analysing for fluoride. If only a small amount of magadi is available it should be kept in mind that the measured fluoride concentration is not a very good estimate of the true fluoride concentration.

ACKNOWLEDGEMENTS

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WATER DEFLUORIDATION FOR RURAL FLUORIDE AFFECTED COMMUNITIES IN TANZANIA

F J Gumbo* and G Mkongo**

Summary: Fluoride is present in high concentrations in drinking water from a large number of boreholes and wells in many districts in Tanzania. This create major fluorosis problems, and a lack of appropriate alternative water sources. The Ministry of Water, Energy and Minerals has constructed a pilot scale defluoridation plant. The plant allowed for investigations of the efficiency of the Nalgonda technique and the magnesite technique to remove fluoride from drinking water. The Nalgonda technique involves addition of high concentrations of alum and lime, while the Magnesite technique involves contact with magnesia (MgO), obtained by calcination of Magnesite ($MgCO_3$). Addition of 800 mg/l alum and 80 mg/l lime could reduce fluoride concentration in the water from 22 mg-F/l to 3.5 mg-F/l. By filtering the treated water through a filterbed filled with calcinated magnesite the fluoride concentration could be reduced further by approximately 1 mg-F/l. However the pH of the water which has passed the magnesite filterbed, has raised to around 10, and require further treatment.

Key words: Defluoridation; aluminium sulphate; lime; magnesite.

INTRODUCTION

Excessive consumption of fluoride by man and animals is known to cause adverse affects on calcified tissues. The effects associated with regular and prolonged consumption of water containing high concentrations of fluoride have been studied and documented by various researchers. It has now been generally accepted that while drinking water with the optimum amount of fluoride, significantly reduces dental carries, excess fluoride will produce adverse effects that range from mild dental fluorosis to crippling skeletal fluorosis.

Fluorosis is a major public health problem in some parts of Tanzania. Endemic fluorosis is a well defined clinical entity characterised by dental mottling and skeletal manifestations. Ever since the first fluoride surveys were made by MacQuillan, 1944[1] in the Northern part of Tanzania a number of scientific papers on the problem have been written and tremendous interest has been shown over the past few years. Several investigators have studied different aspects of the problem in Tanzania such as the clinical, epidemiological and biochemical nature of the disease. Grech et.al. 1964[2] and Latham M.C. 1967[3] studied the extent of the problem in Kilimanjaro and Arusha regions. Their studies highlighted the areas in which fluorosis exists in the endemic form, and elucidated the extent of the problem and the factors underlying the cause of the disease.

Apart from the health effects associated with high fluoride uptake by man, fluorosis also has socio-economic implications. In Tanzania, for instance, there has been a decline in the implementation of water supply programmes in the fluoride regions of

** Central Water Quality Laboratory, Ministry of Water, Energy & Minerals, PO Box 35066, Dar es Salaam, Tanzania.*

*** Ministry of Water Energy and Minerals, Dar es Salaam, Tanzania.*

Kilimanjaro, Arusha, Shinyanga, Mwanza and Mara. The fluoride regions are semiarid and depend most on groundwater as sources of water, which unfortunately has high levels of fluoride resulting in many shallow and deep boreholes, costing millions of shillings to drill, being abandoned.

Researchers in many countries of the World have, since the early 1930's, been trying to develop a suitable defluoridation method to reduce fluoride concentrations in water. While several methods have achieved some degree of success, no universally acceptable method has been developed so far.

This paper reviews the defluoridation work carried out by the Ministry of Water, Energy and Minerals (MAJI) in Tanzania. The defluoridation work concentrated on improving existing defluoridation technologies which have been tried elsewhere. The technologies should preferable use raw materials which are easily available at affordable prices in Tanzania. The objective of the work was to search for a possibility to apply the technology to the rural communities in the fluoride affected regions.

FLUORIDE AND FLUOROSIS IN TANZANIA

In Tanzania the issue of excessive fluoride levels in drinking water in some parts of the country is well known to experts from the water, health, nutrition and agricultural sectors. Studies by various researchers have indicated that most people from Kilimanjaro, Arusha, Singida, Shinyanga, Mwanza and Mara regions drink water with fluoride levels well above the WHO drinking water quality guideline value of 1.5 mg-F/l. As a result, some people have developed fluorosis problems ranging from mottled teeth to crippling fluorosis. It has also been observed that the diet of the people from the fluoride regions add to the total fluoride uptake from drinking water. Kitefu village in Arusha region for instance, received water from Maji ya Chai River until 1966, which has a fluoride content of 22 mg-F/l; at the same time people from the village used salt crusts (magadi) whose fluoride concentration varied from 2,000 to 14,000 µg-F/g-magadi for cooking purposes[4]. Mungure J.S. 1987[4] also verified that 34 % of the people in Kitefu village were suffering from skeletal fluorosis and 77% from dental fluorosis.

TABLE 1 Fluoride concentrations in selected water sources of Arusha, Singida and Shinyanga regions.

Region	Source & Location	Conc. mg-F/l
Arusha	Maji ya Chai, Arumeru District	20.0
	Lemongo spring	10.5
	Kikati B/H 113/79	11.0
	Masai Furrow-Tingatinga	32.0
	B/H 186/81 - Hanang	46.0
Singida	S/W 8/78 - Ngorongoro	11.6
	Senene	10.5
	Well camp Doromoni	21.3
	Fish camp Migilango village	12.5
	S/W 5H2 Doromoni	10.0
	Hot spring - Manyoni	10.5
Shinyanga	S/W Mkokolo	17.0

Source: Water Qwality Laboratory in Arusha

Source: Water Quality Laboratory in Arusha.

The fluorosis situation in Arusha region is not different from the other fluoride stricken regions. Table 1 shows examples of water sources, some of which are boreholes with fluoride levels well above the WHO guideline value of 1.5 mg-F/l.

The prevalence of high concentrations of fluoride in water supply schemes has greatly affected the implementation of the water supply programme in the fluoride hit regions of Arusha, Kilimanjaro, Singida, Shinyanga, Mwanza and Mara regions. Large sums of money have been lost in the fluoride regions as most of the developed water supply schemes especially boreholes had to be abandoned due high levels of fluoride. Table 2 shows the percentage of water supply schemes mostly boreholes which should be abandoned due to high levels of fluoride when observing the WHO fluoride guideline value and the Tanzanian temporary fluoride standard.

TABLE 2. Percentage of water supply schemes which should be abandoned due to high concentrations of fluoride.

Region	Above WHO Guideline value of 1.5 mg-F/l.	Above Tanzanian Temporary Drinking Water Quality Standard of 8.0 mg-F/l.
´Arusha	55	18.0
Kilimanjaro	29	5.5
Singida	72	24.0
Shinyanga	61	12.0
Mwanza	59	10.0
Mara	49	3.5

Source: Proceeding of the Workshop on Domestic Water Health Standards with emphasis on fluoride - Arusha 21 - 23 June, 1982.

Various researchers including Horowitz, H.S and Heifez, S.B, 1972[5] have proved that by providing a community with defluoridated water, the prevalence and severity of fluorosis is reduced. These conclusions were drawn in Texas, USA where in 1952 a defluoridation plant reduced the fluoride level of the water source of Bartlett from 8 mg-F/l to an average of 1.08 mg-F/l. Studies carried out in 1954 and fifteen years later gave the different degrees of fluorosis as presented in Table 3.

TABLE 3. Percentage Distribution of children in Bartlett by fluorosis classification in the years 1954 and 1969.

Year	Normal	Questionable	Very Mild	Mild	Moderate	Severe
1954	2.3	1.5	3.0	43.9	34.9	14.4
1969	49.0	32.5	12.1	5.7	0.6	0.0

DEFLUORIDATION TECHNOLOGIES STUDIED

Various water defluoridation techniques has been studied by scientists around the World. After reviewing, it was decided in 1985 that the Nalgonda technique and the Magnesite technique were the cheapest, the easiest to operate and that both could be carried out by using locally available materials. A pilot plant for experiments was constructed and completed 1990.

Nalgonda Technique. Developed in India, the Nalgonda technique involves flush mixing of alum and lime solutions with the raw water, flocculation, sedimentation, and filtration in a way similar to what is practised in conventional water treatment. To be effective the method requires careful control of the alkalinity of the water.

TABLE 4. Jar tests on alum dosage and fluoride removal capacity. Raw water quality are the average over a 10 month period.

E.C.:Electrical Conductivity. TDS: Total Dissolved Solids.

Alum (mg/l)	pH	E.C. µS/cm	TDS mg/l	Fluoride (mg-F/l)
0	8.7	892	448	21.10
100	7.5	850	430	19.95
200	7.2	850	440	15.64
300	6.9	900	450	13.30
400	6.7	930	460	11.30
500	6.5	950	470	10.23
600	6.3	970	490	9.12
700	6.0	1,010	510	8.55
800	5.8	1,030	520	8.55
900	5.6	1,060	530	10.00
1000	5.1	1,080	540	10.20
1100	4.8	1,130	570	11.30
1200	4.7	1,150	580	11.30
1300	4.6	1,170	590	11.30
1400	4.4	1,240	620	10.85
1500	4.3	1,290	650	10.42

TABLE 5. Jar test experiment indicating the fluoride removal capacity of Alum and lime on raw water supplied to the pilot plant. Alkalinity of the raw water was 367 mg/l.

Jar No.	Alum mg/l	Lime mg/l	pH	Conc. mg-F/l
1	800	80	6.5	3.39
2	800	85	6.8	4.52
3	800	90	6.9	4.62
4	800	95	7.0	4.78
5	800	100	7.1	5.12
6	800	105	7.3	5.43
Raw water	0	0	8.8	23.3

Magnesite Defluoridation. Raw magnesite from Chambogo in Same, was collected and burned at different temperatures. Portions of magnisite burned at 900 °C were crushed and sieved to the size of 0.5 to 1 mm and packed in plastic buckets. Treated water from the sedimentation tank water was passed through and the efficiency of the magnesite in further removing fluoride was recorded (Table 6).

Determination of dosages of alum and lime. In order to optimise the pilot plant, jar test experiments were carried out using the standard laboratory jar test apparatus with six stirrers and one litre beakers. The stirrers were rotated at 150 revolutions per minute for 1 minute for flush mixing and at 40 revolutions per minute for 15 minutes for flocculation. The water was allowed to stand for 1 hour and supernatant sampled for analysis. results of experiments with different alum additions are presented in Table 4, while results of experiment with alum addition fixed at 800 mg/l and lime addition varying from 80 to 105 mg/l are presented in Table 5.

DISCUSSION

The Nalgonda technique was able to reduce fluoride concentrations in water from 22.1 mg-F/l to an average of 3.5 mg-F/l. Lower levels of fluoride would have been reached if dosages of more than 800 mg/l alum were applied. With addition of 800 mg/l alum, residual sulphate was found to be below 600 mg/l.. In a pH range of 6.0 - 8.0, where pH 6.5 is the optimum residual aluminium was found to be below 0.2 mg-Al/l.

Water defluoridated by the Nalgonda technique was passed through a filter bed consisting calcined magnesite granules, fluoride was adsorbed by the magnesite granules thus reducing further the fluoride concentration in the treated water, however rise in pH to above 10.0 in the finished water created a need of adjustment. Although magnesite reduces fluoride, it needs to be regenerated regularly, a situation which would not be easy in the rural areas.

TABLE 6. Efficiency of Fluoride removal from pilot plant sedimentation tank when passed through a magnesite filterbed. TAL:Total Alkalinity

	Before Magnesite filter bed					After Magnesite filter bed				
Day	Time	pH	TAL mg/l	Hardness mg/l	F^- mg/l	Time	pH	TAL mg/l	Hardness mg/l	F^- mg/l
1	13.20	7.8	123	74	3.6	13.20	8.9	287	176	2.9
	14.20	7.9	130	76	3.5	14.20	9.9	346	177	1.4
	15.20	7.8	123	73	3.5	15.20	10.2	257	137	1.5
	16.20	7.9	128	78	3.6	16.20	10.0	207	121	1.4
	17.20	7.9	128	76	3.5	17.20	10.2	190	104	1.6
	18.20	8.1	129	74	3.5	18.20	9.9	177	98	1.7
2	12.35	7.9	134	70	3.4	12.35	10.1	158	79	2.1
	13.35	7.8	134	72	3.6	13.35	10.0	146	76	2.2
	14.35	7.6	136	72	3.6	14.35	10.0	158	79	2.3
	15.35	7.8	133	71	3.7	15.35	10.0	147	74	2.5
	16.35	-	-	-	-	16.35	10.0	152	73	2.5
	17.35	7.7	136	67	4.1	17.35	10.0	167	86	2.8
	18.35	7.7	131	75	4.0	18.35	10.0	148	78	2.8

CONCLUSIONS AND RECOMMENDATIONS

The raw water which had been used in the defluoridation experiments has a high fluoride level (22.1 mg-F/l). The data in Table 6 clearly indicates that defluoridation by the Nalgonda Technique is possible. However, the technology is at present expensive since aluminium sulphate is not produced locally. Once the plant is constructed, operation and maintenance costs are affordable especially when the water from the source flows by gravity. For other types of schemes costs could be a bit higher. For the pilot plant already constructed which can serve a village of about 2,000 people, the capital construction costs was estimated at TSh.15 mill. and monthly operational costs at about TSh.10,000/=.

Now that it has been proved that defluoridation is possible, immediate action is needed to disseminate the technology to fluoride affected rural communities in Arusha, Kilimanjaro, Singida, Shinyanga and Mara regions. External financial support is vital in order to ensure the success of the exercise.

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THE APPLIED ICOH DEFLUORIDATOR

S Rajchagool*
Thailand

SUMMARY: The ICOH defluoridator has been accepted as appropriate technology. It uses charred bone meal which is prepared by heating, in an electric furnace. After ten years of using the ICOH defluoridators in the community, the problem of dental fluorosis is still unsolved. This project was carried out by three high school children, who improved the ICOH defluoridator by making it simple. This paper shows 1) the effectiveness of the student-made defluoridator, 2) the potential of the villagers in solving a problem which concerns them. The paper demonstrates that development of human resources is a very important point in solving any communities' problems.

Key words: defluoridator, dental fluorosis, bonechar.

INTRODUCTION

The ICOH defluoridator was developed in co-operation by the Intercountry Centre for Oral Health, Chiang Mai, the Dental Faculty of Chulalongkorn University and the World Health Organisation more than 10 years ago[1]. The defluoridator suitable for individual households, is based on the filtration and absorption principle and uses charcoal and bonechar.[2] (Figure 1: The ICOH defluoridator) bonechar used in the ICOH defluoridator is prepared by bone meal of 40 - 60 mesh size, produced for agricultural or industrial purposes. The bone meal is activated by heating in an electric furnace to a temperature of 600 °C for 20 minutes. The bonechar of the ICOH defluoridator remains active for 1 - 3 months, depending on the initial fluoride level and the amount of water consumed. The filter of the defluoridator has to be periodically changed. Ready-to-use filter bags prepared by ICOH were sold to the villagers. After several years, ICOH was no longer able to supply the ready-to-use filters to the community. Children born during the period of the experiment still have dental fluorosis, so the problem remains unsolved.

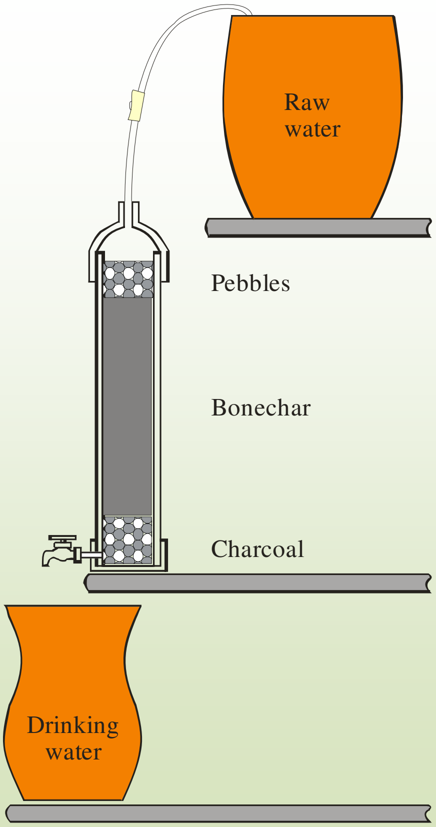

FIGURE 1. The original ICOH defluoridator.

* Intercountry Centre for Oral Health, Chiang-mai Lumphun Rd. Nong Hoi, Muang, Chiang Mai 50000, Thailand.

One weak point of the original ICOH defluoridator is the method of preparing the bonechar which has proved inappropriate. The electric furnace used in burning bone meal is expensive and the villagers cannot produce bonechar themselves.

This project was initiated by three high school children who live in a high fluoride area. With the assistance of ICOH, they made their own defluoridator. Their approach was that a defluoridator made by themselves will be used, and that the technology will be appropriate for their community, and their lifestyle. This study was designed and run by the students in order to determine the effectiveness of the defluoridator.

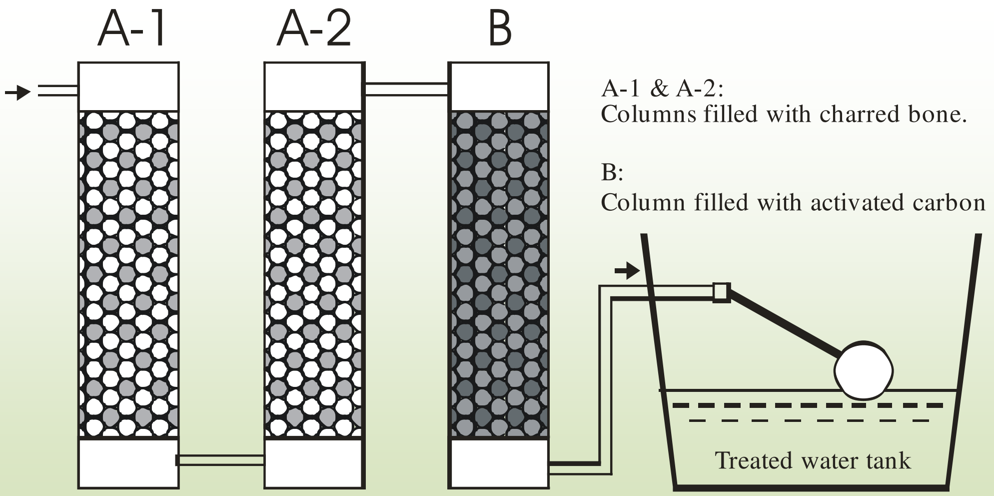

FIGURE 2. Schematic presentation of the applied ICOH defluoridator.

MATERIALS AND METHODS

The details of the Applied ICOH defluoridator are shown in Figure 2. Bonechar was prepared by burning fresh bovine bone, bought from a market, in outdoor until it turned black. When cooled it was crushed into small pieces of 0.5 cm in diameter. Cylinder A1 and 2 were filled with 10 litres of black bonechar. Cylinder B was filled with 4 litres of resin and 4 litres of activated carbon. Two sources of water were used in this experiment; water from a 120 m deep artesian well in the school grounds and a 50 m deep artesian well in the temple grounds. The fluoride concentrations were measured at the Faculty of Science, Chiang Mai University, with a fluoride electrode. The defluoridation efficiency of the defluoridator was examined at the following flow rates: 15, 12, 6, 4, 3, and 2 l/h. Water samples were kept in plastic bottles, containing 750 ml.

RESULTS

Results of measurements after filter A1 and A2 are presented in Table 1. All results are averages of four repetitions of sampling, the standard deviation being 7 % in average.

TABLE 1: Results of defluoridation by column using various flows with water from two sources.

Measured water	Flow L/h	Water from School mg/l	St..Dev.	Water from Temple mg/l	St..Dev.
Raw water	-	8.3	±0.2	4.3	±0.3
After A1	15	6.6	±0.2	2.6	±0.1
After A1+A2	15	5.3	±0.1	2.0	±0.1
After A1+A2	12	1.0	±0.1	1.2	±0.1
After A1+A2	6	0.68	±0.09	0.69	±0.08
After A1+A2	4	0.59	±0.03	0.49	±0.03
After A1+A2	3	0.40	±0.05	0.42	±0.02
After A1+A2	2	0.23	±0.03	0.38	±0.02

DISCUSSION

The results show, that after the water has flown through the first of the two cylinders (A1) at the rate of 15 l/h, the concentration of fluoride was reduced but the concentration was still higher than standard. After the second cylinder (A2) the concentration of fluoride was further reduced but not sufficient. In order to gain an acceptable concentration of fluoride in the water, the flow of water must be adjusted. According to this experiment an adjustment of the flow rate to 6 l/h, gave adequate reduction in the fluoride concentration in the water from both sources (down to about 0.7 mg-F/l). The flow rate of 6 l/h are considered to be optimal for the designed filter. After passing the third cylinder (B) filled with activated carbon and resin, the aesthetically quality of the water was tested. The water had no smell and was suitable for drinking.

This defluoridator is better than the original ICOH in three ways 1) It can be made in the villages with local materials. 2) It gives an optimum concentration of fluoride 3) It provides ready to drink water, stored in a storage tank with an automatic switch. The lifetime of the charred bone meal and the biological properties of water was not tested in this experiment.

The main point of this paper was to show the potential of the villagers to solve their own community problems. The ICOH company assisted the school children, only by information about the ICOH defluoridator. The design of the applied defluoridator and plan for the experiment were the school children's own work. Their work demonstrated that villagers can solve problems appropriately. The technology the villagers use must be appropriate technology for that specific community, though It may not be appropriate in other communities. However, development of human resources is very important in solving any communities' problems.

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