DTU

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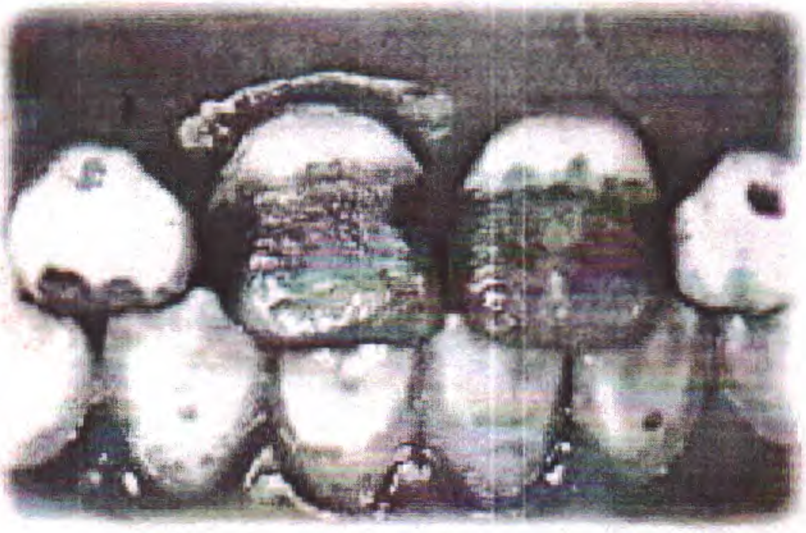

Preparation for Field Studies in Developing Countries

Methods in Defluoridation
by Contact Precipitation and Bone Char

Student Report

July 1999
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Preparation for Field studies in Developing Countries

Methods in Defluoridation by Contact Precipitation and Bone Char

Prethesis

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The experimental work has been carried out by the students, supervised by professionals from the Technical University of Denmark.

The report is not an institutional publication and does not necessarily reflect the supervisors understanding of the results.

Abstract

The objectives of the present report were to obtain knowledge of the subject defluoridation. There have been given a literature review fluorosis, bone char preparation and defluoridation by bone char and contact precipitation. Further was defluoridation by adsorption on bone char and contact precipitation studied by batch experiments. Three types of bone char were examined. The results showed a similar adsorption capacity for fluoride by all types of bone char. Differences in ability to catalyse contact precipitation were observed. The resulting water quality after defluoridation was briefly examined and some types of bone char causes a decrease of the water quality.

Project description

Background: Defluoridation is carried out on drinking water in order to prevent fluorosis. A promising, but relatively unexplored, method for defluoridation is contact precipitation using bone char, which has high removal efficiency, operational reliability combined with low cost.

The bone char consists mainly of hydroxyapatite that acts as a catalyst for precipitation of fluorapatite when calcium and phosphate is added to the water that contains flour. Investigations of mechanisms and processes that take place in contact precipitation are limited but earlier experiments with the method have shown high efficiency.

If contact precipitation should be used for defluoridation on household level in developing countries it is necessary to examine the optimum conditions for the method.

Idea: The aim of the project is to design, test and optimise household defluoridation units using the "fill and filter"- contact precipitation in columns with bone char.

Contents:

- Literature review of fluorosis, bone char preparation and defluoridation by bone char and contact precipitation.
- Tests of methods of analysis.
- Experiments with bone char defluoridation and contact precipitation.

Supervisor: Henrik Bregnhøj

Preface

This report is the result of a preparation and introduction project to respectively a field study in developing countries and a master thesis. The project is carried out from the end of June to the middle of July, with 3 weeks of actual work. The workload in the course is equal to 5 points. Both the field study and the master thesis, that treats issues of defluoridation, will be carried out in Chiang Mai, Thailand, from September to December 1999.

The project and the report are a co-operation between two students. The definition of the project and the experimental work has been made in co-operation while the report has been partly co-operation and individual work. Thus Chapter 2 "Theory" and chapter 3 "Contributions in the area" are written by Augusto Bravo while chapter 4 "Methods" and chapter 5 "Results" are written by Jane Albertus.

We would like to thank our supervisor Assist. Res. Prof. Henrik Bregnhøj for outstanding guidance, inspiration and patience during the project. Further we would like to thank Birthe Ebert and Anders Torp Gundersen for technical assistance during practical work in the laboratories at IMT.

Lyngby DK. 28-07-99
Jane & Augusto

1 Introduction

Fluoride is for most people known as the most effective remedy for improving oral health, for example as an active agent in toothpaste. Fluoride can however be injurious to health when it is consumed in larger doses for a period of time. This is a serious problem in many countries where the ground water contains unhealthy high amount of fluoride. More than 260 million people all over the world consume drinking water with unacceptable high concentrations of fluoride. The majority of these people live in developing countries. [WHO 1984]

The first symptom caused by excessive intake of fluoride is dental fluorosis also known as mottled enamel, which as the name says causes damage on the teeth. Individuals exposed to continuously over many years may develop the severe skeletal fluorosis, which causes skeletal deformities and immobilisation of joints. [ICOH 1999]

Defluoridation is carried out on drinking water in order to prevent fluorosis, and several methods have been developed. There is however a need in developing countries for improved defluoridation methods that are effective, simple and cheap.

1.1 Background and Motivation

A promising, but relatively unexplored, method for defluoridation is contact precipitation using bone char, which has high removal efficiency, operational reliability combined with low cost.

The bone char consists mainly of hydroxyapatite that acts as a catalyst for precipitation of fluorapatite when calcium and phosphate is added to the water that contains flour. Investigations of mechanisms and processes that take place during contact precipitation are limited but earlier experiments with the method have shown high efficiency.

If contact precipitation should be used for defluoridation on household level in developing countries it is necessary to examine the optimum conditions for the method.

Further it will be beneficial to compare the advantages and disadvantages of the method with the better-known method defluoridation by adsorption on bone char.

1.2 Aim of the Project

The primary purpose of this project is to form a foundation of theoretical and practical experience as introduction and preparation for a field study in a developing country.

The aim of the project is therefore to obtain:

- knowledge of the subject defluoridation by a literature review of fluorosis, bone char preparation and defluoridation by bone char and contact precipitation.
- general view of previous student project on the subject.
- experience in production of bone char.
- experience of methods of analysis by small scale experiments.

2 Theory

This chapter presents an overview of the fluorosis and its afflictions, the background theory on defluoridation and bone char production and the latest research papers in the area, with focus on DTU work.

2.1.1 Delimitation

In view of the still recent affords put in the defluoridation area and extent number of parameters involved, added to the complexity of phenomena's describing the subject, the theory review is limited to most relevant points to this work.

2.2 Fluorosis

2.2.1 Diverse sources of fluoride

The intake of fluoride by humans and animals occurs by inhalation as well as orally. The amount of intake by air is very reduced, exception made to highly contaminated atmosphere, as in phosphate factories, for instance. The oral intake happens by ingestion of foodstuffs and drinking. From these two, the amount of fluoride in the foodstuff is very low, as for example in vegetables, were concentrations are normally less than 10 mg/kg. Moreover, the body cannot absorb the entire content of fluoride present in foodstuffs. Therefore, the main fluoride intake is via drinking water [Bregnhøj 95].

The World Health Organisation [WHO 1993] sat a guideline of 1.5 mgF/l of water. It is accepted that a higher intake of fluoride per day would definitely contribute for the development of fluorosis. The current guideline for maximum values of fluoride in Thailand is 1 mg/l [ICOH 1999].

2.2.2 The affliction

Mottled enamel or dental fluorosis is the first outcome of fluorosis. The characteristics are coloured stains and breakage of the teeth surface. In more severe cases, skeletal fluorosis may appear, which can be identified by stiff and painful joints, reaching a further stage were deformation of the hard tissue is observed – the so-called crippling fluorosis [Bregnhøj 95].

2.3 Bone Char – Structure and Production

Hard tissues in the body are essentially constituted of 35% of collagen and 65% of hydroxyapatite (HAP), $Ca_{10}(PO_4)_6(OH)_2$. This bone apatite is not "pure"; for example, some of the ions in the structure may be substituted by CO_3^{2-} or just being vacant. Other substitutions may also occur, what can increase the solubility of the apatite by a factor of up to 10^7, when compared with perfect HAP [Bregnhøj 95].

In order to prepare bone char, bones and teeth, whole or in grains, are heated up to a temperature that optimally may vary from around 500°C to 800°C, in presence or absence of oxygen, for a period that can vary from 30 minutes to a few hours [Dahi 95]. In this way, the collagen is burned/volatised, remaining only the hydroxyapatite.

When the intended use of bone char is fluoride removal, it seems that charring of bone char – heating in absence of oxygen – is recommended, since the process becomes very little dependent on temperature, meaning that the quality of the product is as good at 500°C as it is at 800°C [Dahi 95].

2.4 Defluoridation

In its structure, HAP resembles fluorapatite (FAP), the only difference been the hydroxide anion substituted by the fluoride anion. HAP has a solubility constant which is larger than FAP, $Ca_{10}(PO_4)_6F_2$. Therefore, when some HAP dissolves, the calcium, phosphate and fluoride might bind together, forming FAP, which will precipitate. This process is known as recrystallisation. The apatite will remain insoluble as long as the solution is not acidic. It is worth to note that this is a small portion of the fluoride removal, compared with ion exchange, for instance, since HAP itself has a very small solubility at drinking water pH levels.

Another process when considering removal of fluoride from water is adsorption. Among the various processes that form the adsorption process is ion exchange between OH^- and F^-, which seems to be an important part of the bone char adsorption. Adsorption is likely to occur, since fluoride atoms "fit" on the oxygen position in the apatite structure. The fluoride anion will dislocate the hydroxide anion, changing HAP to FAP [Bregnhøj 95].

As seen from above, bone char structure has a limited adsorption capacity. After a while in contact with fluoridated water, the replacement hydroxide-fluoride in the bone char reaches an equilibrium state and the bone char is said to be saturated, indicating the end of its fluoride adsorption capacity. When that occurs, the char can then be disposed or regenerated. The latter would consist in treating the bone char with a slightly acidic solution of calcium and phosphate, in order to coat the char surface with an apatitic layer [Phantumvanit 91].

The bone char apatite has much larger solubility than other possible precipitating compounds, as CaF_2, for instance. Thus, theoretically, apatite will be the main compound for the fluoride removal.

Defluoridation can occur in batch or column filters. While batch filters – where chemicals are added to a bucket or similar - are easy to "operate" and can be used at household level, its removal efficiency is limited and it is time and working demand. Column filters are more sophisticated, due to its construction and operation, but has much larger effectiveness, due to sorption kinetics' properties [Bregnhøj 95].

Among the defluoridation techniques, the Nalgonda is an exception in the sense that it does not use adsorption as the principle for removing fluoride. Here, the principle is co-precipitation, in which well-stirred water with alum and lime is let to settle; the flocs formed sediments and take down with it the fluoride in the water [Bregnhøj 91/92]. This method has been successfully applied in India.
Another co-precipitation technique is the two-step brushite ($CaHPO_4{\bullet}2H_2O$) saturation, apatite precipitation method, which consists in treating fluoridated water with brushite

in order to create a state of supersaturation with respect to fluorapatite and then to seed the solution with hydroxyapatite (bone char) to provoke precipitation and consequently removal of fluoride [Pearce 93]. In opposition to the Nalgonda technique, this method, as far as we know, has not been applied in practice.

2.5 Contact Precipitation

The inconvenient of having to regenerate the bone char brought a new development in defluoridation, the contact precipitation. This technique uses the bone char as a catalyst, acting in a solution of fluoridated water, calcium and phosphate. It is observed that fluoride will react with calcium and phosphate to precipitate as fluorapatite or similar compounds. The latter will precipitate on the surface of the bone char and thus no regeneration is needed. The covering layers of fluorapatite continue to act as precipitation seed for the new-coming deposition.

It is rather uncertain the proportions among the various reagents, but the stoichiometric proportions are used as initial approach. Calcium can be obtained from calcium chloride and phosphate from sodium hydrogen phosphate. Contact precipitation is also more efficient than bone char sorption with respect to fluoride removal capacity [Bregnhøj 95].

3 Contributions in the area

This section will present the goals and results of the latest works on bone char and contact precipitation, mostly from DTU, as a way to elucidate more detailed parameters concerning the above theory and to establish the present stage in defluoridation achievements.

Several projects have recently worked on production and optimisation of bone char. Apparently, for bone char adsorption, the preparing temperature has little influence when the char is charred (in absence of oxygen). Temperatures from 300°C to 800°C were used, showing the same adsorption capacity. But when burning the bones (in the presence of oxygen), adsorption capacity is inversely proportional to temperature. [Tønnesen 94][Jacobsen 96][Dahi 95].

The charring/burning time, for temperatures up to 500°C, gives almost the same results in terms of adsorption capacity, for heat treatment from 0.5 to 5 hours. In the case with oxygen though, for temperatures above 500°C, a deterioration of the adsorption capacity is noted [Tønnesen 94][Dahi 95]. Moreover, Nielsen (1994) has observed that, for higher temperatures - 400°C and above, a slight loss in adsorption quality is present when increasing not only the burning but also the charring time. It is worth to mention that these last results were obtained from a heat treatment at a prototype oven, where many parameters are still being adjusted.

Bregnhøj (1995) reports that, in spite of the dynamic adsorption capacity be independent of the grain size, the reaction rate is inversely proportional to the grain diameter average.

Dahi (1996, 1998) describes a long-term prototype experiment of contact precipitation in which no deterioration of precipitation capacity and no clogging were observed, with no headloss in the filter even after more than one year of operation. An estimate made in the 1996 paper shows that after one year of plant operation, only 13% of the pore water in the bed compartment volume were replaced. Nevertheless, it is expected the need of backwashing in the future. On the opposite, Dyekjær-Hansen, Mondrup & Nedenskov [1994] comment – in spite of the lack of data in the report - about increase in filter resistance.

Other works have tried to explain the complexity of the adsorption and contact precipitation. Optimal pH for defluoridation is observed between 6 and 7, since higher pH will push hydroxide's to the apatite structure, releasing fluoride, and at lower pH-values the apatite itself will dissolve [Schouw 96]. Since fluorapatite has the lowest solubility constant, in the order of 10^{-121}, it is also by far the main fluoride specie to precipitate. The second lowest is hydroxyapatite, with a K_s of 10^{-116}. Calcium fluoride is hundreds of times more soluble, with K_s of $3.45x10^{-11}$ [Schouw 96].

In contact precipitation, though, since large amounts of calcium and phosphate are added to the solution, kinetics can favour the precipitation of other species, as calcium hydrogen phosphates, which becomes "waste", since it does not remove fluoride. Thus, the amount of calcium and phosphate added should be optimised, in order to yield maximum fluoride removal, avoid filter clogging and saving money in chemicals. Mondrup (1993) have shown that the more calcium and phosphate is added, the more fluoride is removed, but proportionally the removal becomes smaller the more calcium and phosphate there is in relation to fluoride [Schouw 96]. An optimum relationship seems to be a stoichiometric ratio of calcium and phosphate to fluoride between 1 and 2 (here a removal difference between both values is around 7%). That does not mean that only fluorapatite is precipitating. Some calcium hydrogen phosphate and some calcium fluoride might also be precipitating. In the case of calcium fluoride, precipitation is not undesirable, since much less calcium - and phosphate - is needed for the same fluoride removal, when comparing to FAp. Especially the amount of phosphate is interesting to have reduced, since microorganisms and algae's can use excess of it (mentioned in Dyekjær-Hansen, Mondrup & Nedenskov 1994).

4 Methods

In this chapter are the methods of analysis and the experimental work described.

4.1 Analysis

The description of analysis is not a detailed instruction but persons with chemical knowledge and laboratory experience should be able to understand and carry out the analysis on this background. The analysis is a mean to evaluate the efficiency of the defluoridation and compare the methods. It is relevant to measure the decrease in fluoride-, phosphate- and calcium concentrations and changes in total alkalinity and pH.

4.1.1 Fluoride

Fluoride is measured by an F^- electrode (Metrohm 6.0502.150), an Ag/AgCl-reference electrode (Metrohm 6.0726.100) and a multi meter (pH/Ion meter: Metrohm 692). Total Ionic Strength Adjustment Buffer (TISAB) is added to the samples for ion strength adjustment. The contents in - and production of TISAB is described in appendix III. Fluoride is measured in samples with 10 V% TISAB, which means that the result must be rectified according to the dilution of the samples. Fluoride should be measured with suitable stirring and at constant temperature.

A standard curve is found by measuring the potential at known solutions of 1mg l^{-1} F and 10 mg l^{-1} F. This will give two points on a straight line in a semilogaritmisk graph (log F1, E1) and (log F2, E2). α is supposed to be in the range [–54;-59]. The standard curve is an approximation to Nernst equation.

$$E = \alpha \cdot \log F + \beta \qquad \alpha = \frac{E_2 - E_1}{\log \frac{F_2}{F_1}} \qquad F = 10^{\frac{E-\beta}{\alpha}}$$

The standard curve can drift a bit during the experiments, due to lack of stability in the fluoride electrode. It is therefore necessary to measure the standard curve both before and after the measuring of the samples and if needed, rectify the results.

In order to compare the efficiency of the defluoridation in the experiments, the adsorption capacity f is calculated. f is the ratio of removed fluoride (F_0-F) and the amount of bone char X_{BC}. Due to the removal of fluoride in each measurement, f has to be rectified according to the actual batch volume.

$$f\left[\tfrac{mg}{g}\right]=\frac{(F_0-F)\left[\tfrac{mg}{l}\right]}{X_{BC}\left[\tfrac{g}{l}\right]}$$

4.1.2 Calcium

Calcium is measured by atomic absorption. In this case Ca was measured on a PERKIN ELMER 5000 Atomic Absorption Spectrophotometer. Another method for analysis of Ca is a titration by EDTA danish standard DS 248. This method is probably more appropriate for field work

The samples are filtered in order to prevent interference from precipitated and suspended P.

4.1.3 Phosphate

Phosphate is measured by spectrophotometer. Phosphate reacts with molybdenum in acid, which gives a blue colour (molybdenum blue) that can be measured. The analysis is developed on background of Standard methods 14th Edition 1975 page 481 "Manuel analysis for determination of o-phosphate, the ascorbic acid method".

In this case the molybdenum blue was measured on a TECHNICON™ AutoAnalyzer™(II), but it could just as well be measured on a HACK™ which would probably be more suitable for the purpose of field studies in developing countries.

The samples are filtered in order to prevent interference from precipitated and suspended P.

4.1.4 pH

pH is measured directly in the jars by pH electrode (Metrohm 6.0220.100) and pH meter (Metrohm 691).

4.1.5 Total Alkalinity – TAL

The samples for TAL should be stored in small plastic bottles. The bottles should be filled totally and closed to avoid contact between the sample and CO_2 in the atmosphere.

TAL is determined by acid titration with either H_2SO_4 or HCl. The end point of the titration is pH = 4.5. TAL is thereby calculated as:

$$\boxed{\mathrm{TAL} = \frac{V_{H2SO4} \cdot M_{H2SO4} \cdot 2 \frac{\mathrm{eq}}{\mathrm{mole\ H2SO4}} \cdot 1000 \frac{\mathrm{meq}}{\mathrm{eq}}}{V_{\mathrm{sample}}}}$$

TAL : Total Alkalinity [meq/l]

V_{H2SO4} : Volume of H_2SO_4 used at titration [ml]

M_{H2SO4} : Molarity of H_2SO_4 [mole/l]

V_{sample} : Volume of sample [ml]

4.2 Experimental work

Small-scale experiments are designed and carried out in order to obtain practical experience of laboratory work and presentation of results.

The experiments are carried out as small-scale batch on a Jar Test apparatus. The experiments are designed to enable examination of defluoridation and contact precipitation simultaneously. It is assumed that the fluoride removed by adsorption is the same whether contact precipitation occurs at the same time or not. This might be a rough estimation since the adsorption depends of concentration of fluoride. A better method would be to saturate the bone char completely before the contact precipitation. This is however very time demanding and the saturation methods are not very reliable. The principle is shown in figure 4.1 where the amount of fluoride removed by contact precipitation is assumed to be the difference in removed fluoride from Jar I to Jar II. The figure is not drawn to scale.

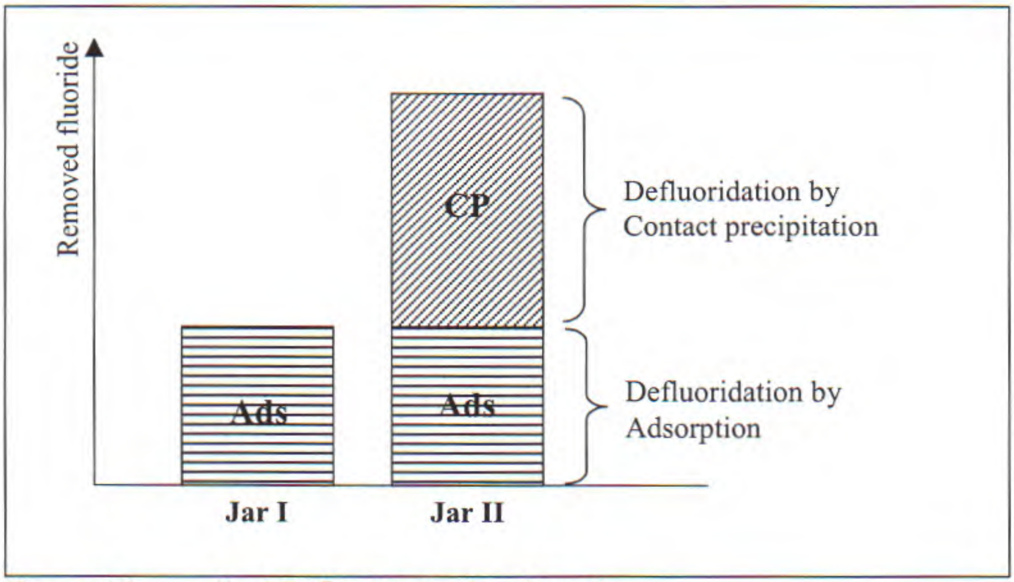


Figure 4.1: *Jar I Defluoridation by adsorption*
Jar II Defluoridation by adsorption and contact precipitation

4.2.1 Design of experiments

It is possible to vary several parameters during the experiments. The possible parameters are:

- Type of bone char (production parameters/methods and origin)
- Molar ration - ($F:PO_4:Ca$)
- Initial fluoride concentration - F_0
- Bone char amount - X_{BC}
- Grain size
- Stirring

It was decided to keep as many parameters as possibly constant and only vary one. Since the aim of these experiments is to compare types of bone char, this is the only parameter that is varied. A standard experiment was set up as shown in table 4.1. The different values are settled by experience from earlier experiments.

Table 4.1 Standard Experiment

X_{BC} (added at t=0)	(0.5) 4	[g/l]
V	1	[l]
F_0	10 0.526	[mg/l] mM
Grain size	0.2<GZ<0.85	mm
$F:PO_4:Ca$	1:3:5	mole
$[PO_4^{3-}]$	1.58	mM
$[Ca^{2+}]$	2.63	mM
TAL	5	meq
Stirring	60	rpm

The ratio for fluoride, phosphate and calcium is determined to proportionate FAP $Ca_{10}(PO_4)_6F_2$ which is $F:PO_4:Ca$ = 1:3:5. Solutions of fluoride, phosphate and calcium were made from respectively sodiumfluoride, sodiumdihydrogenephosphate monohydrate and calciumdichloride dihydrate. The used ammount of bone char was changed during the experiments from 0.5 to 4 g/l, which is explained in chapter 5 "Results". Total alkalinity was made by addition of $[HCO_3^-]$ to enable measuring of pH. See appendix III for further details.

4.2.2 Execution of experiments

Preparation

The bone char is parted in different fractions of grain size by sieves and the fraction between 0.2 and 0.85 mm is used in the experiments.

Solutions are made as described in appendix III. "Jartest apparatus" is prepared with 6 1 l beakers. 1000 ml calibrated flask is filled app. half with distilled water (to avoid precipitation of Ca and PO_4) before F, PO_4, Ca and HCO_3 is added. The flask is filled to 1000 ml after which the solution is poured to a 1 l beaker. The stirring is set to 60 rpm. At time 0 is the weigh out bone char added.

Adsorption: F_0= 10 mg/l ; X_{BC} =4 g (no addition of PO_4 and Ca)
Precipitation: F_0= 10 mg/l ; X_{BC} =4 g ; Ca:PO_4:Ca = 5:3:1
Control: F_0= 10 mg/l ; Ca:PO_4:Ca = 5:3:1 (no addition of BC)

Measuring

pH is measured before addition of bone char and by the end of the experiment. Optimum would be to also measure pH right after addition of bone char but this was not done in this project.

A small test-tube is made from a cut plastic flask of approximately 2 cm in diameter. 5 ml sample is added to 1 ml TISAB and 4 ml distilled water in the test-tube and the electrodes are placed in the test-tube with magnetic stirring. The resulting potential is read on the multimeter and the fluoride concentration is calculated by the standard curve. Addition of TISAB and distilled water results in a two times dilution of the sample. Suggestion for a record of the results is enclosed in appendix IV.

Samples are taken at the end of the experiment for determination of Ca, PO_4 and TAL. The samples are filtered to avoid precipitation. The amount of samples taken in this project was to small and TAL was therefore not measured.

The quality of the water with respect to colour, taste and odour is examined after the experiments.

4.3 Bone Char

Bone char has been produced in small scale with variation in access of oxygen and size of bone pieces. Further has different types of bone char been purchased in order to compare the "home made" bone char product with available commercial products.

4.3.1 Production of Bone Char

Four types of bone char were made in IMT's oven for small-scale manufacture. Supervisor Henrik Bregnhøj recommended the procedure for production of bone char.

The types differentiate in the size of the bone pieces that are used as basis material and the access or limitation of oxygen. This bone char will in the following be named "JAGU".

Type 1:	Crushed before burning. (+O_2) 500 °C
Type 2:	Crushed before burning. (-O_2) 500 °C
Type 3:	Crushed after burning. (+O_2) 500 °C
Type 4:	Crushed after burning. (-O_2) 500 °C

The bones were supplied as an unfinished product from DAKA bone meal factory. They where charred in an electric oven with a temperature gradient of 2 °C/min until 500 °C. This temperature was kept for respectively 5 hours in charring of crushed bone and 10 hours for charring of a larger amount of bigger bone pieces.

Bones burned with access of oxygen lost 37 % weight and were a mixture of black, brown and grey grains after burning. Bones burned without access of oxygen lost only 33 % and were homogenous black. The colour indicates the amount of carbon left after the burning. When there is access of oxygen most of the carbon convert to CO_2 and leave the bone char while limitation of oxygen will convert the carbon to activated carbon that remains in the bone char.

Visual inspection of the bone char shows a "typical" burned (+O_2) bone char uniformity and colour, when the temperature and length of the burning phase are considered. The charred type (-O_2) used in the experiments had also colour and uniformity in accordance to the literature.

The bone char was crushed in a home-made box for crushing and sieving. The box is made of a u-shaped metal sheet with wire netting mounted on the open sides. See figure 4.2. A solid iron cylinder was used as a mortar for crushing the bone char.

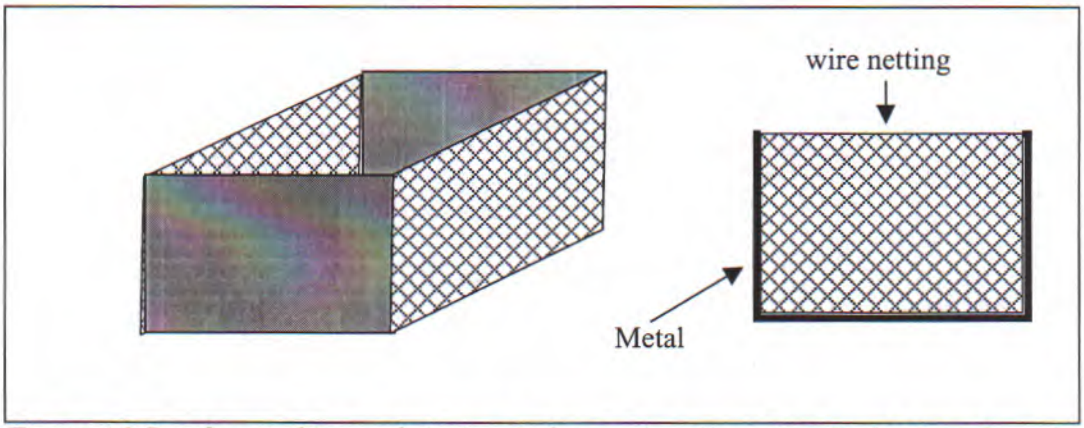


Figure 4.2 Box for crushing and sieving. Left: seen in perspective. Right: Seen from the side with wire netting.

After the bone char is crushed the box is shaken to separate the wanted grain size and keep the bigger grains in the box for further crushing. The crushed bone char is further parted in different fractions of grain size by sieves and the fraction between 0.2 and 0.85 mm are used in the experiments.

4.3.2 Description of Bone Char types in experiments

It was chosen to use JAGU type 4 since this method of burning without access of oxygen and crushing the bone char after is the most common method today.

In order to compare commercial available bone char with the "home made" was bone char from Kenya and from Scotland purchased. The three types of bone char are described in table 4.2.

JAGU-production Type 4 (Denmark)	Ngurdoto (Kenya)	Brimac 216 (Scotland)
Electric oven	Charcoal oven	Electric oven
Crushed after burning	Crushed after burning	Crushed after burning
- O_2	+/- O_2	-O_2
Max temp. 500°C for 10 hours	Max. temp. 400-500°C for 1 hour	Max temp. 1000-1100°C for 12 h

Table 4.2 types of Bone Char

Many parameters have been varied in the production of these types of bone char. It will therefore not be possible to determine the causes for possible differences in defluoridation capacity.

5 Results

The results from the experiments will be stated in this chapter and the graphic presentations will be commented. A more thorough evaluation of the results will be done in the following chapter 6 “Discussion of experiments”.

Please note that the points on the graphic presentations are connected to facilitate the distinction of the different Jar Tests, which means that the lines do not illustrate a curve.

It is emphasised that no kind of statistics has been carried out on the results, and all discussions of tendencies are therefore only indications for further investigations.

5.1 Preliminary Experiment

A preliminary experiment with one of the bone char types was carried out in order to verify if the experiments were viable and to detect needed changes in the standard experiment.

The experiment was carried out as explained in previous chapter 4.2.2. “Design of Experiments”, with bone char from Ngurdoto, $X_{BC} = 0.5$ g/l. There has been made one experiment for adsorption, one experiment for contact precipitation and further one experiment to examine the possibility of precipitation without addition of bone char.

Table 5.1 Preliminary Experiment

Jar test 1	Adsorption	$X_{BC} = 0.5$ g/l
Jar test 2	Control	F: PO_4:Ca = 1:3:5
Jar test 3	Contact precipitation	$X_{BC} = 0.5$ g/l F: PO_4:Ca = 1:3:5

Fluoride was measured at regular intervals and the final concentrations if calcium and phosphate were determined. There was no decrease of fluoride in Jar test 2 (control), which means that there has been no precipitation of fluoride, phosphate and/or calcium compounds. The results showing a decrease of fluoride content by time in Jar test 1 and 3 is to be found in figure 5.1.

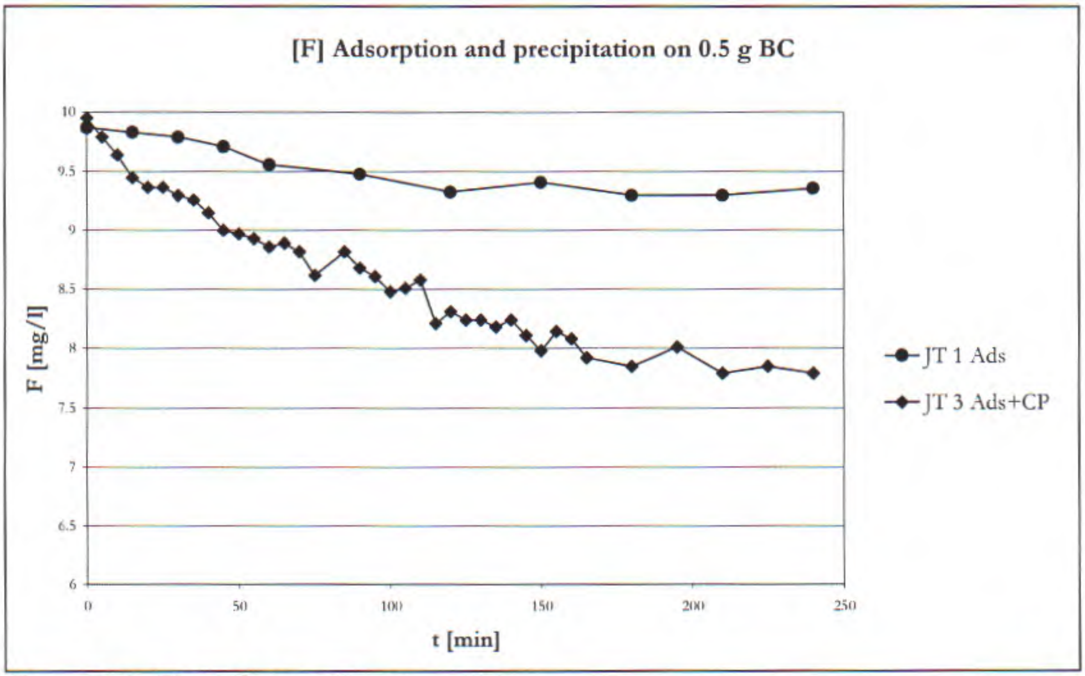


Figure 5.1: Fluoride concentration vs. time
Jar test 1 (adsorption) and Jar test 3 (contact precipitation)

The results show a decrease in fluoride concentration in solution, which is more distinct in Jar test 3 - with addition of phosphate and calcium - than in Jar test 1 - without the possibility of contact precipitation.

The results are presented for respectively f_{ads+cp}, f_{cp} and f_{ads} in figure 5.2.

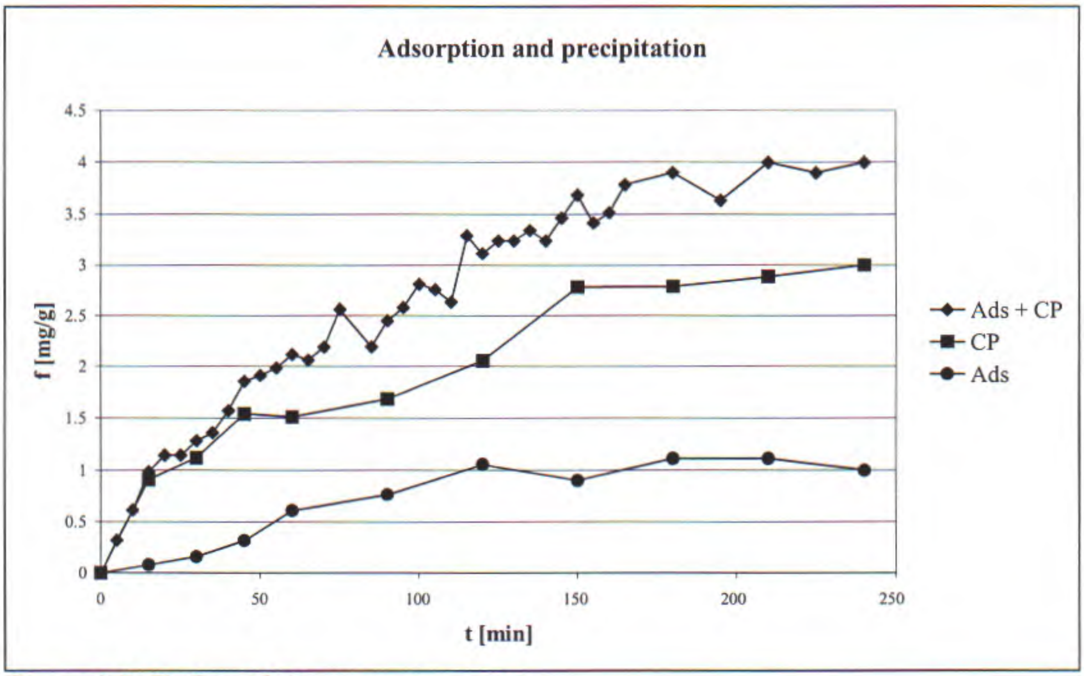


Figure 5.2: Defluoridation capacity vs. time

It is assumed that the adsorption is the same in Jar test 1 and 3. The results for contact precipitation are a subtraction of the results of Jar test 3 from Jar test 1. This gives the difference that represents the defluoridation by contact precipitation. This is seen in figure 5.2, where points from "ads" and "cp" in total gives "ads + cp".

From this experiment is possible to see the effect of the defluoridation by adsorption on bone char. Further it is seen that addition of phosphate and calcium seems to increase the defluoridation efficiency due to contact precipitation. The amount of bone char was increased in order to obtain a higher removal. A linear relation between X_{BC} and defluoridation was assumed. X_{BC} was therefore increased from 0.5 g/l to 4 g/l in the standard experiment, before the experiments to compare bone char types took place.

5.2 Comparison of Bone Char Types

Three types of bone char were compared in order to detect possible differences in adsorption capacity and ability to catalyse the contact precipitation. The three types: JAGU 4, Ngurdoto and Brimac 216 are described in chapter 4.3.2 "Description of bone char types in experiments".

The experiments were carried out as explained in chapter 4.2.2. "Design of Experiments". The series of Jar tests 4 to 9 is equal to the series of Jar test 10 to 15, which gives an opportunity to comment on the possibility of reproducing the experiments. Each series consist of one adsorption and one contact precipitation for all three types of bone char.

Table 5.2 Comparison of Bone Char Types

JT 4 & 10	Ads.	BC : JAGU 4 $X_{BC} = 4$ g/l
JT 5 & 11	Ads. + CP	BC : JAGU 4 $X_{BC} = 4$ g/l $F:PO_4:Ca = 1:3:5$
JT 6 & 12	Ads.	BC : Ngurdoto $X_{BC} = 4$ g/l
JT 7 & 13	Ads. + CP	BC : Ngurdoto $X_{BC} = 4$ g/l $F:PO_4:Ca = 1:3:5$
JT 8 & 14	Ads.	BC : Brimac 216 $X_{BC} = 4$ g/l
JT 9 & 15	Ads. + CP	BC : Brimac 216 $X_{BC} = 4$ g/l $F:PO_4:Ca = 1:3:5$

5.2.1 Results of fluoride measurements

All 12 Jar tests showed a decrease in fluoride concentration. The results of the fluoride measurements are shown in figure 5.3.

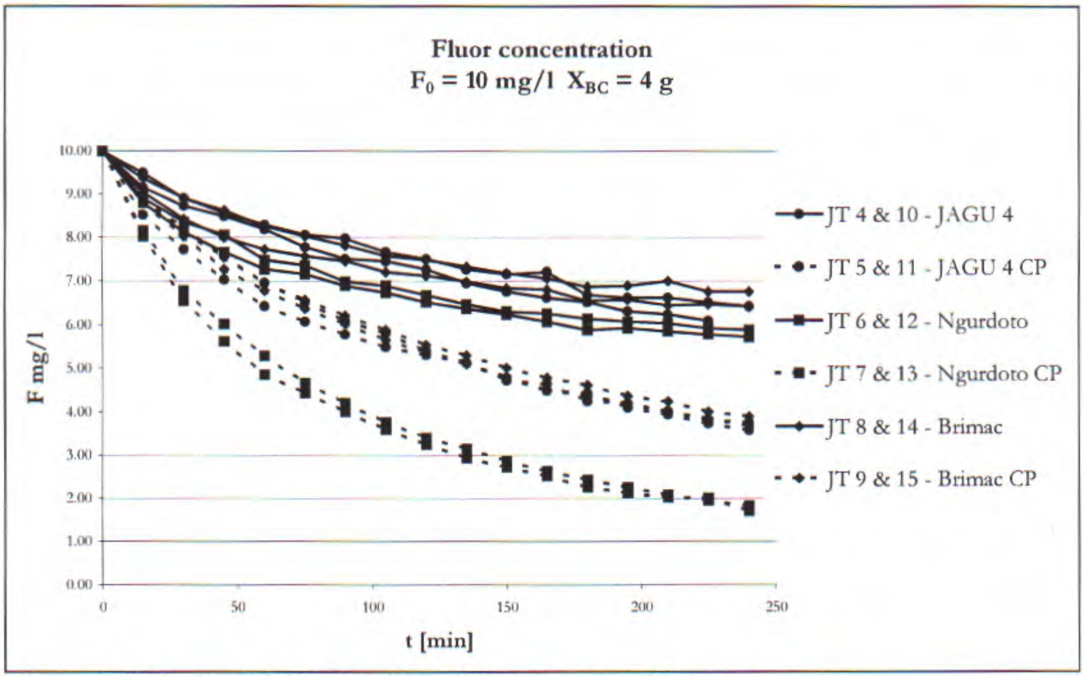
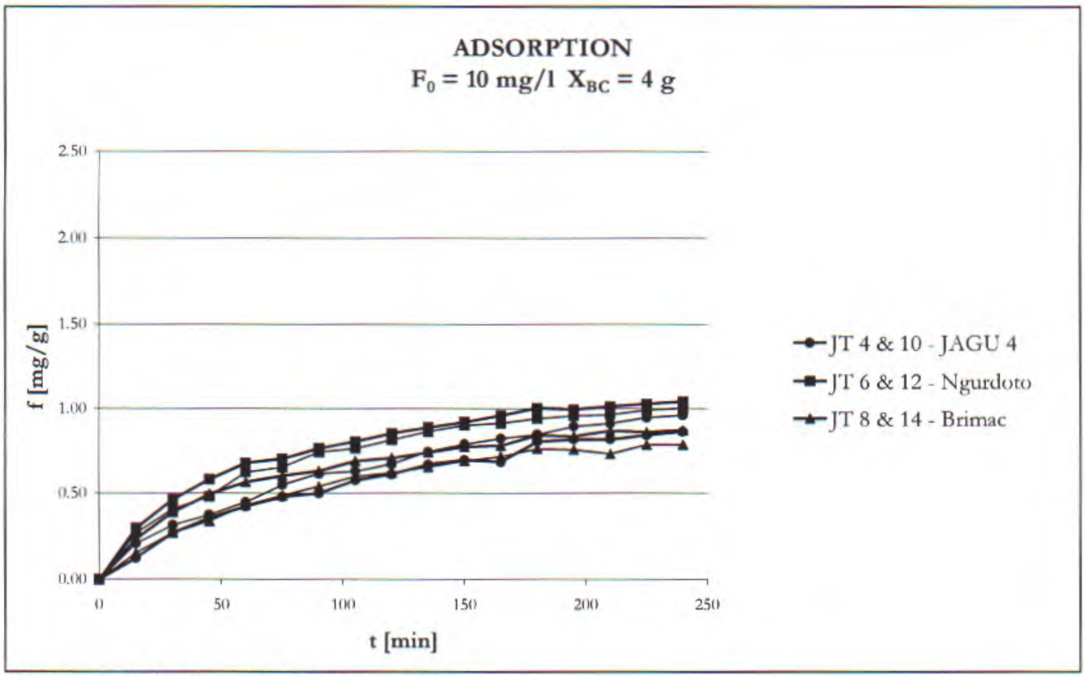


Figure 5.3: Defluoridation by three different types of BC.
Points connected by a full line illustrate defluoridation by adsorption.
Points connected by a dotted line illustrate defluoridation by CP.

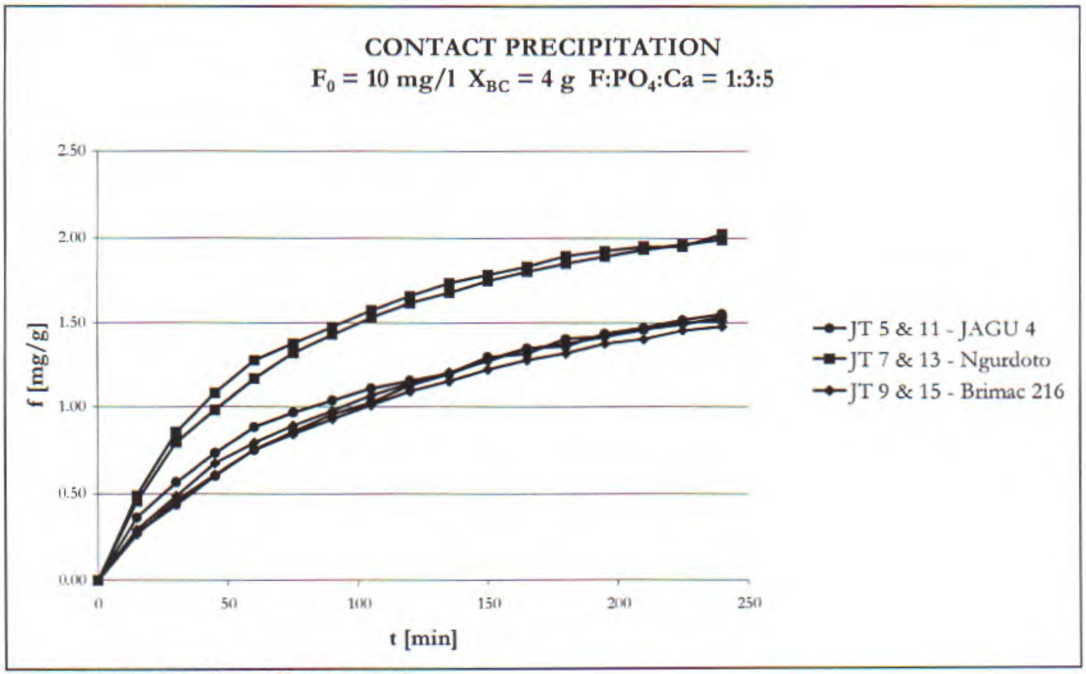
bone char from Ngurdoto seems to have a better effect on the defluoridation. The Jar test with contact precipitation indicates a larger difference than the adsorption tests. JAGU 4 and Brimac 216 seem to be almost the same effect.

f was calculated in order to examine these tendencies more thoroughly. f for defluoridation capacity and f for catalyst efficiency is illustrated respectively in figure 5.4 and figure 5.5.



ADSORPTION
$F_0 = 10$ mg/l $X_{BC} = 4$ g

Figure 5.4: Defluoridation capacity f_{ads}



CONTACT PRECIPITATION
$F_0 = 10$ mg/l $X_{BC} = 4$ g F:PO_4:Ca = 1:3:5

Figure 5.5: Catalyst efficiency f_{cp}.

From figure 5.4 it can be seen that all three types of BC has the ability to adsorb fluoride. It seems that Ngurdoto BC has a bit higher capacity than the two other types do.

Figure 5.5 shows that Ngurdoto is the best bone char in the contact precipitation tests, but all three types have the ability to act as precipitation catalyst.

In all cases, the ability to catalyse the contact precipitation reaction is similar or higher than the ability for defluoridation by adsorption.

5.2.2 Results of calcium and phosphate measurements

Samples for test of calcium and phosphate was taken at the end of the Jar tests in order to determine the removal of these compounds and find a molar ratio of $F:PO_4:Ca$. The results can be seen in table 5.3.

Jar Test	$[PO_4^{3-}]_{end}$ mM	$[Ca^{2+}]_{end}$ mM	$P_{removed}$ mM	$Ca_{removed}$ mM
2	1.60	1.33	0	0
3	1.60	1.26	0	0.07
5	Error in sampling		-	-
7			-	-
9			-	-
11	0.87	0.51	0.73	0.82
13	0.51	0.59	1.09	0.74
15	0.69	0.83	0.91	0.50

Table 5.3 End concentrations of F, PO_4 and Ca.

It is impossible to compare the results from the two series of Jar tests, due to an error in the sampling after Jar test 5, 7 and 9. The initial concentrations of PO_4 and Ca should be respectively 1.58 mM and 2.63 mM. These concentrations should in theory be found as end concentrations in Jar Test 2, since no reactions should occur in this control experiment. The concentration of PO_4 is as expected but the concentration of Ca is approximately half of the expected. This indicates a mistake in either the preparation of the solutions or a dilution error when measuring calcium. The error is assumed to be present in all measurements of calcium and it is therefore not possible to evaluate anything from these results.

An efficient method to evaluate the defluoridation by contact precipitation is to calculate the ratio of removed fluoride, phosphate and calcium. The ratio indicates what sort of compounds that has precipitated, as for example calcium fluoride (CaF_2), FAP ($Ca_{10}(PO_4)_6F_2$) or other calciumphosphate compounds. This however require reliable results and the experiments should therefore be repeated.

It is however possible to evaluate that fluoride, phosphate and calcium has decreased and it is therefore reasonable to assume that precipitation of FAP has occured.

5.2.3 Water Quality

The treatment with bone char can change the quality of the water. pH was therefore measured before addition of BC and after the Jar Tests. Colour, odour and taste was examined after the treatment.

pH changes both by type of bone char and treatment. Due to lack of pH measuring right after addition of bone char it is not possible to evaluate if the change is caused by reactions during the defluoridation or by addition of bone char.

6 Discussion of experiments

The theory of defluoridation and the over view of contributions in the area are treated in previous chapters where the findings are being both discussed and compared. This chapter is therefore a discussion and evaluation of the experiments and the results from these.

The primary objective of the experimental work was to obtain experience in the methods of defluoridation and to test the methods of analysis in practice. The experiments showed that it was possible to detect an effect of the defluoridation methods and the possibility of defluoridation without addition of bone char was excluded.

The secondary objective was to examine different types of bone char. Previous experiments have demonstrated that different types of bone char have different adsorption capacity and thereby different ability for defluoridation. It was assumed that the apatite structure in bone char has the same ability to act as catalyst for contact precipitation regardless of origin and production method. The hypothesis was therefore that the experiments would show difference in adsorption capacity but not a remarkable difference in ability to catalyse contact precipitation.

There was not found any significant difference in the defluoridation capacity f_{ads} [mg/g]. By the end of the experiment is the largest difference between Ngurdoto and Brimac 216 with the other results distributed in between. Further were the experiments with adsorption not clearly reproducible, since 2 batch tests were made, reaching similar results.

The bone char types ability to catalyse the contact precipitation is designated as catalyst efficiency f_{cp} mg/g. The experiments indicate that there is a difference between Ngurdoto bone char and the two other types. Measurements of Ngurdoto are remarkable higher compared to JAGU 4 and Brimac 216, which have very similar catalyst efficiencies. The experiments seem to be reproducible. This could indicate that bone char in general has similar ability to catalyse the contact precipitation, but something in Ngurdoto bone char seems to improve this ability.

As mentioned in chapter 5.2.2 it would be very beneficial to compare ratios of removed fluoride, phosphate and calcium, this is however impossible due to problems in sampling and measurements.

Eventual changes in water quality due to treatment with bone char are important to examine. Increased or decreased pH can cause health risk and changes in colour, taste and odour can make the water unpleasant and unqualified as drinking water.

JAGU 4 caused an unpleasant yellow brown colour of the water. This results in a strongly decrease in water quality due to the needed aesthetics of drinking water. pH remained unchanged on an acceptable level in all experiments except where Brimac 216 was used for adsorption. Water treated with Brimac 216 for adsorption had a pH of approximately 9.5, which is on the limit for what is acceptable for drinking water. Brimac 216 did not cause severe increase in pH when it was used for contact precipitation. This part of the experiments shows that it is important to examine the water quality for each type of bone char according to the purposes.

7 Recommendations

Since this project is a preparation for a master thesis and a field study, it is very relevant to consider possible improvements and relevant developments.

Primary it will be beneficial to enlarge the basic understanding of the physical and chemical aspects of HAP and FAP as for example structure, adsorption, precipitation and solubility products.

In future experiments it will be very interesting to examine the tendencies of the results in this project. Whether some types of bone char has a better ability in catalysing contact precipitation and if so, what causes this improved ability.

The experiments with adsorption had the highest uncertainty of reproducing the results. Therefore it might be useful to run several experiments under similar conditions to eliminate the variation in defluoridation capacity for each type of bone char.

The pore size and the porosity have influence in the efficiency and are relevant information when bone char types are evaluated. The porosity and the pore size have not been considered or determined in this project, but should be included in an extended investigation of bone char quality.

The experiments in this project have been based on small-scale batches. When defluoridation for household purposes are examined, it will be more relevant to increase the treated volume and examine both batch and columns or eventually just columns. Columns theoretically have a higher efficiency, which should be considered if matters of design are considered.

A better understanding of the composition of precipitated products could be obtained by an examination of the surface coating in the bone char. For example by EDAX analysis of bone char from a column exposed to contact precipitation during a longer period of time.

Experience from this project has shown that preliminary experiments to test the set-up and the analysis will prevent many errors in the actual experiments. Finally will careful planning ease the work and secure the relevance and standard of references of the results.

8 Conclusion

Knowledge of the subject defluoridation has been obtained by a literature review of theory behind fluorosis, bone char preparation and defluoridation by bone char and contact precipitation.

A general view of previous student project on the subject is given by describing and comparing contributions in the area. In spite of the reasonably well-known defluoridation processes and applications, lack of theoretical understanding is still considerable. Production of bone char for adsorption and contact precipitation techniques varies broadly in methodology and quality. However, the positive effects of these techniques for defluoridation are unarguable.

Experience in production of bone char has been obtained by producing four types of bone char (JAGU). The burned type was not use in these experiments, but visual inspection shows a "typical" burned bone char uniformity and colour, when the temperature and length of the burning phase are considered. The charred type used in the experiments had also colour and uniformity in accordance to the literature.

Experience of methods of analysis has been obtained by small-scale experiments. The aim of the experiments was to examine different types of bone char concerning defluoridation capacity and ability to catalyse contact precipitation. The hypothesis was that the experiments would show difference in adsorption capacity but not a remarkable difference in ability to catalyse contact precipitation. There was not found any significant difference in the defluoridation capacity. The experiments indicate that Ngurdoto bone char has a better ability to catalyse the contact precipitation than the two other types of bone char. The results of the experiments was therefore not as expected.
The experiments seem to be reproducible with respect to contact precipitation but more changeable, and thereby less reproducible, in experiments of adsorption.

The experiments shows that it is important to examine the water quality for each type of bone char. JAGU 4 caused an unpleasant yellow brown colour of the water, which is a decrease in water quality. Brimac 216 used for adsorption cause an increase in pH, which is also a decrease in water quality.

References

Bregnhøj 91/92	Bregnhøj, Henrik - "Defluoridation methods applicable to third world". Lecture note for 8807 Water supply in developing countries, Centre for Developing Countries, Technical University of Denmark, 1991/1992
Bregnhøj 95	Bregnhøj, Henrik - "Processes and kinetics of defluoridation of drinking water using bone char". Ph.D. thesis, Department of Environmental Science and Engineering, Technical University of Denmark, 1995
Dahi 96	Dahi, Eli - "Contact Precipitation for defluoridation of water". 22nd WEDC Conference: discussion paper, New Delhi, India, 1996
Dahi 98	Dahi, Eli - "Small community defluoridation of drinking water; the state of the art". Environmental Development Cooperation EnDeCo, 1998
Dahi 95	Dahi, Eli & Bregnhøj, Henrik - "Significance of oxygen processing of bone char for defluoridation of water". Proceedings of the first international workshop on fluorosis and defluoridation of water, Ngurdoto, Tanzania, 1995
ICOH 1999	Dr. Sunsanee Rajchagool, et.al. - ICOH Newsletter, March-June 1999 Volume 7, Number 1
Jacobsen 95	Jacobsen, Peter - "Charring of bone for defluoridation of drinking water". Centre for Developing Countries, Technical University of Denmark, 1995
Pearce 93	Pearce E. I. F & Larse, M. J. - "Defluoridation of drinking water by co-precipitation with apatite". Basic Sciences, Caries Res. 1993:27:378-386 1993
Phantumvanit 91	Phantumvanit, P. & Guay, M. - "Regeneration of bone char for recycling water defluoridation". Dept.of Biochem., Sch. of Dent., Chulalongkorn Univ., Bangkok & ICOH, Chiang Mai, Thailand, 1991
Schouw 96	Schouw & Christensen - "Mechanisms in Contact Precipitation of fluorapatite". Centre for Developing Countries, Technical University of Denmark, 1996

Tønnesen 94	Tønnesen, A. & Nielsen, D. K. - "Thermodynamics in bone charring for drinking water defluoridation". Centre for Developing Countries, Technical University of Denmark, 1994
WHO 1984	The World Health Organisation - "Guidelines for drinking-water quality". Geneva, WHO, 1984

List of symbols

Parameters

α	**Slope on standard curve**	
β	**Intersection of standard curve**	
X_{BC}	**Bone char added**	**g BC/l**
V	**Volume of Batch**	**l**
ppm	**parts per million**	**mg/l**
TAL	**Total Alkalinity**	**meq/l**
$(F:PO_4:Ca)$	**Molar ratio between F^-, PO_4^{3-} & Ca^{2+}**	
f_{ads}	**Defluoridation capacity by adsorption**	**mg/g**
f_{cp}	**Catalyst efficiency for contact precipitation**	**mg/g**

Concentrations

$[Ca^{2+}]$	**Calcium concentration in aquatic phase**	**mM**
$[Ca^{2+}]_0$	**Calcium concentration at t=0**	**mM**
$[PO_4^{3-}]$	**Phosphate concentration in aquatic phase**	**mM**
$[PO_4^{3-}]_0$	**Phosphate concentration at t=0**	**mM**
F	**Fluoride concentration in aquatic phase**	**mM or mg/l**
F_0	**Fluoride concentration at t=0**	**mM or mg/l**

Abbreviations

Ads.	**Adsorption**
BC	**Bone char**
CP	**Contact precipitation**
FAP	**Fluorapatite**
HAP	**Hydroxyapatite**
JT	**Jar Test**
rpm	**rounds per minute**
TISAB	**Total Ionic Strength Adjustment Buffer**
IMT	**Department of Environmental Science and Engineering**

APPENDIX I

TERMS OF REFERENCE by Jane Albertus

Optimisation and Pilot Implementation of Defluoridation by Contact Precipitation on Bone Char

Technical University of Denmark
Department of Environmental Science and Engineering

Background

More than 260 million people all over the world consume drinking water with unacceptable high concentrations of fluor. The majority of these people live in developing countries.

The first symptom caused by excessive intake of fluoride is dental fluorosis also known as mottled enamel, which as the name says causes damage on the teeth. Individuals exposed to continuously over many years may develop the severe skeletal fluorosis, which causes skeletal deformities and immobilisation of joints.

Defluoridation is carried out on drinking water in order to prevent fluorosis, and several methods have been developed. However, developing countries needs to increase the knowledge for improving defluoridation methods that are effective, simple and cheap.

A promising, but relatively unexplored, method for defluoridation is Contact Precipitation using Bone Char, which has high removal efficiency, operational reliability combined with low cost. The Bone Char consists mainly of hydroxyapatite that reacts as a catalyst for precipitation of fluorapatite when calcium and phosphate is added to the water that contains flour. Investigations of mechanisms and processes that take place in Contact Precipitation are limited but earlier experiments with the method have shown high efficiency.

If Contact Precipitation should be used for defluoridation on household level in developing countries it is necessary to examine the optimum conditions for the method. Further it will be beneficial to compare advantages and disadvantages of the method with better known methods as defluoridation by adsorption on Bone Char.

Objectives

The aim of the project is to design, test and optimise household defluoridation units using the "fill and filter"- contact precipitation in columns with bone char.

Output

The output of the master thesis is a written report and a oral presentation which will be evaluated by the 13-scale.

Activities

The project will be carried out during a 3-month stay at Intercountry Centre for Oral Health in Chiang Mai Thailand. Following activities will be carried out during the stay.

- Experiments in laboratory at ICOH to optimise the method of contact precipitation.

  The bone char produced at ICOH will be examined with respect to defluoridation capacity and ability to catalyse the contact precipitation. The optimisation process will attempt to determine the hydraulics, bone char preparation, addition of chemicals et cetera applicable to the columns for household defluoridation units.

- Design of household defluoridation units in co-operation with Thai engineering students and the future users.

- Pilot implementation of household defluoridation units and evaluation of the effect at the drinking water.

Supervisors

Intern supervisor	Assist. Res. Prof. Henrik Bregnhøj Department of Environmental and Engineering Science Technical University of Denmark
Extern supervisor	Dr. Sunsanee Rajchegool Intercountry Centre for Oral Health Chiang Mai, Thailand

APPENDIX II

TERMS OF REFERENCE by Augusto Bravo

Defluoridation

DTU and ICOH have long studied defluoridation techniques; Northern Thailand has significant problems with fluoride in potable water and a mutual collaboration between the two institutions could be advantageous.

It is the aim of this collaboration to study the roll of the filter media in the defluoridation process, specially concerning contact precipitation technique. For this, different bone char's, made by distinct processes will be evaluated. This will occur in lab and at site (village).

To implement it in villages, a prototype filter unit will be developed and tested both at lab and at site. From these experiences, prototype adjustments will be made and re-checked, as far as time allows it.

Social-economics will be evaluated at village levels, in order to draw people's acceptance for concept, technique and prototype. All adjustments will be, as much as possible, based on villager's understanding and participation in the project.

As major activities can be mentioned the design of bone char production, the design of the filter prototype, the village's "workshops" and the implementation phase at the village.

As a project output, a full report will be presented.

APPENDIX III

Reagents and Solutions

Electrodes:	3M KCl	: 223.7 g KCl in 1 l distilled water
Fluor:	2000 mg F l^{-1} = 0.105 M F	: 4.420 g NaF in 1 l distilled water
Calcium:	0.526 M Ca	: 77.3 g $CaCl_2 \bullet 2H_2O$ in 1 l distilled water
Phosphate:	0.316 M PO_4	: 43.6 g $NaH_2PO_4 \bullet H_2O$ in 1 l distilled water
TAL:	1M HCO_3	: 84.01 g $NaHCO_3$ in 1 l distilled water

TISAB (to be dissolved in1 l distilled water):

Potassium nitrate	1 M KNO_3	101.1 g
Potassium hydroxide	0.21 M KOH	11.78 g
DCTA (Triplex IV)	0.01 M $C_6H_{10}(N(CH_2COOH)_2)_2$	2.983 g
Potassium hydrogen phtalate	0.30 M $C_6H_4(COOK)(COOH)$	61.27 g

Adsorption: F_0= 10 mg/l ; X_{BC} = 4 g (no addition of PO_4 and Ca)
Precipitation: F_0= 10 mg/l ; X_{BC} = 4 g ; Ca:PO_4:Ca = 5:3:1
Control: F_0= 10 mg/l ; Ca:PO_4:Ca = 5:3:1 (no addition of BC)

Preparation for each Jar in 1000 ml calibrated flask:

Adsorption: 5 ml 0,105 M F^-, 5 ml 1 M HCO_3
Precipitation: 5 ml 0,105 M F^-, 5 ml 1 M HCO_3, 5 ml 0,526 M Ca, 5 ml 0,314 M PO_4
Control: 5 ml 0,105 M F^-, 5 ml 1 M HCO_3, 5 ml 0,526 M Ca, 5 ml 0,314 M PO_4

$M_{w\ F}$ = 18.998 g $mole^{-1}$
$M_{w\ NaH2PO4 * H2O}$ = 137.99 g $mole^{-1}$
$M_{w\ CaCl2 * 2H2O}$= 147.01 g $mole^{-1}$
$M_{w\ KCl}$ = 74.55 g $mole^{-1}$
$M_{w\ NaF}$ = 41.988 g $mole^{-1}$
$M_{w\ NaHCO3}$ = 84.007 g $mole^{-1}$
$M_{w\ KNO3}$ = 101.11 g $mole^{-1}$
$M_{w\ KOH}$ = 56.11 g $mole^{-1}$
$M_{w\ C6H10\ (N\ (CH2COOH)2\ )2}$ = 298.3 g $mole^{-1}$
$M_{w\ C4H14\ (COOK)(COOH)}$ = 204.22 g $mole^{-1}$