Bone Char Quality and Defluoridation Capacity in Contact Precipitation

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SUMMARY: Samples from six different brands of bone char are tested for their capacity to remove fluoride from water in batch. Initial concentrations of 10 mg/L and contact times of 6 hours are used. The removal capacities observed are 0.6 –1.1 mg/g, 0.9 mg/g on an average, s.d. being 0.16. In agreement with previous data the carbon-rich black-coloured bone char is on the higher end of this range.

Addition of calcium and phosphate compounds to the jar experiments results in more than doubling of these capacities, on an average 1.9 mg/g, s.d. being 0.14.

One of bone char products is setup in columns and fed with fluoride water, 100 mg/L, for saturation. Hereafter the columns are fed with water of 10 mgF/L where calcium and phosphate are added as in the contact precipitation process. The results show that the columns are able to remove up to 700 bed volumes, before the concentration of fluoride in the effluent water breaks through, above 1.5 mg/L. The operational removal capacities observed are 7 and 9 mg/L, depending on contact time and the dosage of chemicals.

It is discussed that longer contact time and higher dosage of calcium and phosphate may result in longer operation periods in the contact precipitation columns.

Key words: Bone char, contact precipitation, sorption, batch experiment, flow-experiment, defluoridation, jar test, pyrolysis, calcination, operational removal capacity, dynamic removal capacity.

INTRODUCTION

One of the appropriate methods for defluoridation of drinking water in developing countries is adsorption of fluoride on bone char in columns. The bone char needs to be of a quality that may be difficult to produce locally in developing countries and the lifetime of the defluoridation filters is limited due to saturation of the bone char. Contact precipitation has therefore been introduced as an alternative method for defluoridation. Contact precipitation is an addition of calcium and phosphate that leads to precipitation of fluoride when the solution is in contact with bone char. The bone char is a necessary catalyst in order to precipitate the fluoride [1].

Charring of bones for bone char can basically be done in two ways: As calcination where bones are heated in the presence of continuous supply of oxygen from the atmospheric air or as pyrolysis where no oxygen is present during the heating. In calcination the organic carbon is converted to CO_2 that is stripped off while in pyrolysis the organic carbon is converted to inorganic carbon that remains in the bone char. Pyrolysed bones are therefore always totally black while calcined bones are

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brown -grey - white, depending of the access of oxygen and thereby degree of charring [2]. Pyrolysis is much more fuel demanding and therefore more expensive.

Investigations of bone char for fluoride adsorption has revealed that calcined bone char produced at high temperatures inhibits the adsorption process [2]. It has though been found that bone char produced by partly calcination are suitable for adsorption provided that the charring temperatures do not exceed 500 °C and the charring time is sufficient [3]. White types of bone char produced with a high degree of calcination are therefore regarded as unsuitable for adsorption purposes. The adsorption capacity is however unimportant in connection with contact precipitation and it has never been investigated how calcined bone char influence the processes of contact precipitation. It is therefore possible that the manufacture of good quality bone char for contact precipitation is less complicated and cheaper to manufacture than bone char for adsorption.

The processes of uptake of fluoride on bone char are complicated to describe, consisting of more than one process. Direct adsorption in empty sites on the bone char surface seems to be an important reaction for fluoride binding on bone char. Also re-crystallisation, where hydroxyapatite is dissolved and fluorapatite is precipitated, is considered to be important in the process [4]. The following model has been developed for the kinetics of fluoride uptake on bone char in batch:

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

Where fluoride concentration is characterised for a given dosage of bone char (X_{BC}) and a given initial fluoride concentration (So) by the means of the parameters: dynamic capacity ($f_{m,b}$) and reaction rate (k).

The exact chemical process of contact precipitation are not known, but it is assumed that it is basically a combination of precipitation of fluorapatite, $Ca_{10}(P0_4)_6F_2$, and fluorite, CaF_2. Precipitation of fluorite can occur if there already are precipitated compounds to initiate the process e.g. bone char. Precipitation of fluorapatite will only occur in contact with the apatite structure in the bone char and is dependent of the pore water velocity and contact time in the filter [5].

Calcium and fluoride concentrations will decrease due to precipitation of both fluorite and fluorapatite as parallel reactions. The precipitation products depend on the concentrations of phosphate and calcium. At high concentrations both fluorapatite and fluorite will precipitate while at lower concentrations the solubility constant for fluorite will be reached and further removal of fluoride must be due to precipitation of fluorapatite alone [6].

Objective. The aim of these investigations was A) to compare different bone char products with respect to ability to adsorb fluoride, B) to investigate the influence of bone char quality in contact precipitation and C) to investigate possible limitations in the defluoridation capacity by contact precipitation.

METHODS

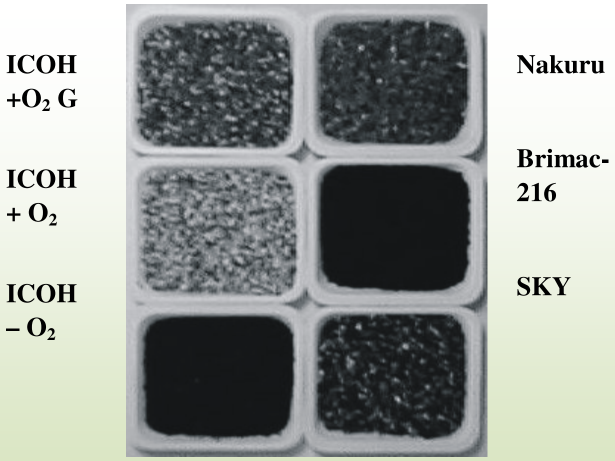

FIGURE 1. Picture of the six samples of bone char utilised

Bone char samples. Six samples of different brands bone char were prepared/collected, cf. Figure 1. Three of them were prepared at Intercountry Centre for Oral Health, ICOH, especially for this study under specific air access and heating conditions. One sample was provided from a Catholic Church defluoridation project in Nakuru, Kenya. One sample was a commercial bone char product purchased from Scotland (Brimac-2 16). The last one is prepared locally in Thailand. The last sample was purchased from Ban San kayom (SKY) in the northern Thailand where bone char is produced for local defluoridation at village level.

The six samples were examined with respect to grain size distribution, density and porosity. A known volume of bone char was soaked with water. Water was removed by use of a pipette until the water level was equal to the bone char level. The amount of water was determined by weighing the measuring glass before and after addition of water. The porosity was measured as a double determination, cf. Table 3.

Fluoride analysis. The concentrations of fluoride were measured in samples added 10 % TISAB using the ion-selective electrode and Ag/AgCl-reference electrode according to the Standard Methods [7].

Batch experiment. The batch experiments were carried out using a jar test apparatus; a six paddle-stirrer from Phipps & Birds Stiffer 7790-402. The parameters were set as given in Table 1. Solutions were made from respectively sodium fluoride, NaF, sodium dihydrogen phosphate, $NaH_2PO_4 \cdot H_20$, and calcium dichloride, $CaC1_2 \cdot 2H_20$. The used molar ratio proportionate fluorapatite F:P:Ca=1:3:5. Carbonate was added as Sodium hydrogen carbonate, $NaHCO_3$, in order to secure total alkalinity on a level of 5 meq, which is common for drinking water. The jar test was carried in two series: I) Adsorption and II) Adsorption + Precipitation where phosphate and calcium were added.

TABLE 1. Specification of experimental conditions for the jar test utilised.

Parameter	SYMBOL	UNIT	VALUE
Bone char dosage at t = 0	X_{BC}	g/L	4
Volume of batch	V_0	L	1
Grain size of medium	GZ	mm	0.2 - 0.85
Stirring rate	-	RPM	**60**
Fluoride concentration, initial	$S_{F,O}$	mg/L	10
Fluoride concentration, initial		mM	0.526
Phosphate concentration (series II)	$S_{P,O}$	mM	1.58
Calcium concentration (series II)	$S_{Ca,O}$	mM	2.63
Molar ratio	F:P:Ca	-	1:3:5

The solutions were prepared in each jar and the bone char was added at time zero. Samples of ## mL volumes were collected for fluoride analysis every 30 minutes. Each experiment series was carried out in duplicate.

TABLE 2. Specification of parameters in the column experiment for contact precipitation.

Parameter	Symbol	Unit	CP I	CP II	CP III
Fluoride concentration	$S_{F,O}$	mg/L	10	10	10
Grain size	GZ	mm	0.2 - 1.41	0.2 - 1.41	0.2 - 1.41
Porosity	ε	-	0.80	0.80	0.80
Bone char	M_{BC}	g	150	150	75
Flow	Q	L/h	0.35	0.35	0.35
Diameter of column	$Ø_{BC}$	cm	0.34	0.34	0.34
Height of bone char	H_{BC}	cm	26	26	13
Bedvolume	V_{BC}	L	0.24	0.24	0.12
Retention time, V_{BC}/Q	T_h	min	40	40	20
Contact time, $t_c=V_{BC}\ \varepsilon/Q$.	t_c	min	32	32	16
Molar ratio	F:P:Ca	-	1:1.5:2.8	1:2.3:3.9	1:2.3:3.9

The dynamic capacities and the reaction rates were estimated for the different types of bone char by non-linear regression of the experimental data sets from the jar tests. The non-linear regression was carried out by computer iteration using a function that minimises the deviation between the measured data and the model calculated data.

TABLE 3. Characteristics of utilised bone char samples.

Type of bone char	**ICOH +O_2**	**ICOH+O_2 G**	**ICOH -O_2**	**Nakuru**	**Brimac-216**	**SKY**
Preparation conditions:						
Incinerator type	ICOH (gas)	ICOH (gas)	ICOH (gas)	Charcoal furnace	Electrical furnace	ICOH (gas)
Max. charring temp.	500 □C	500 □C	500 □C	400-500 □C	1000-1100□C	400-700□C
Time at max. temp	3h	3h	3h	8h	>12h	2h
Access of oxygen	+ O_2	+ O_2	- O_2	+/- O_2	- O_2	+/- O_2
	Calcination	Calcination	Pure pyrolysis	Partly calcination	Pure pyrolysis	Partly calcination
Laboratory characterisation:						
Colour	White Grey (Brown)	Grey Brown	Black	Grey Brown	Black	White Grey Black
Grain size GS in mm	0.2 - 0.85	0.2 - 0.85	0.2 -0.85	0.2 - 0.85	0.5 - 0.85	0.2 - 0.85
Density □ , kg/L	0.58	0.60	0.60	0.58	0.64	0.65
Porosity □	0.80	0.80	0.80	0.78	0.90	0.78
Dynamic capacity; estimated $f_{m,b}$, mg/g:						
	0.81	1.5	1.9**	2.0	1.7	1.7
Kinetic rate constant; estimated k, $L \cdot mg^{-1} \cdot min^{-0.5}$						
	0.005	0.003	0.002**	0.003	0.003	0.002
Removal Capacity; Initially 10 mg/L, at t=360 min, mg/g						
Without Ca and PO_4	0.64	0.91	1.01	1.10	0.94	0.89
With Ca and PO_4	1.85	2.05	1.83	2.15	1.79	1.93

* ICOH +O_2 G is the same product as ICOH +02 but Graded by a manual removal of all visible white parts of the bones before crushing, resulting in a more dark type of bone char.

** The results from jar tests with ICOH-O_2 did not fit the kinetic model well and dynamic capacity is thereby found with less certainty.

Column experiment. The flow experiments were carried out in six identical plexiglas columns assembled as three pairs for double determination. The parameters for the experiment are given in Table 2. The amount of bone char and molar ratio of F:P:Ca was varied while all other parameters were kept constant.

The columns were closed in both ends with a rubber stopper with a glass pipe for connection to inlet and outlet hoses. A piece of sponge with the same diameter as the column was placed in the bottom to prevent bone char particles passing through the outlet. The bone char was produced for this investigation as described in Table 3 as ICOH $+O_2$. The columns were fed by gravity from feedwater tanks that were elevated 3 m. The effect of draw down in the feedwater tank was assumed to be insignificant. The treated water from the outlet was collected in separate reception tanks to facilitate measurement of treated volume. The flow deviated within 10 % during the experiment.

The bone char in the columns were saturated by feedwater of 100 mg/l fluoride at a flow of approximately 0.1 1/h for 8 days. After the saturation the bone char was rinsed with water of 10 mg/l fluoride. Measurement of the effluent concentrations of fluoride verified that the bone char was satisfactory saturated with respect to 10 mg/l fluoride. The inlet concentration of fluoride was kept constant at 10 mg/l for all columns during the experiment.

The columns where initially fed with approximately 40 litres at molar ratios F:P:Ca of 1:3:5 and 1:2.3: 3.9, respectively. These concentrations resulted in a total removal of fluoride therefore the molar ratios were decreased to respectively 1:2.3:3.9 in CP I & CP III and 1:1.5:2.75 in CP II for the main part of the experiment.

RESULTS

Bone char samples. As shown in Table 3, the six different samples had approximately the same grain size distributions, porosity and density except Brimac-2 16, which had grain size at the higher end of the interval. The bone char samples appeared however to be very different products, Figure 1.

Batch experiment. The production methods are briefly described in table 3 along with the measured characteristics of the bone char types.

The results from the jar test series are depicted as discrete points in Figure 2. The upper six series are the results from the jars with plain adsorption as an average of double determination for each type of bone char. The curves through these points are the best fit based on the kinetic model (eq. 1). The lowest six series are the results from the jars with both adsorption and contact precipitation as an average of double determination for each type of bone char.

Nakuru bone char seems to have the best ability to adsorb fluoride while ICOH $+O_2$ has adsorbed the lowest amount of fluoride. All six types of bone char was able to catalyse the contact precipitation.

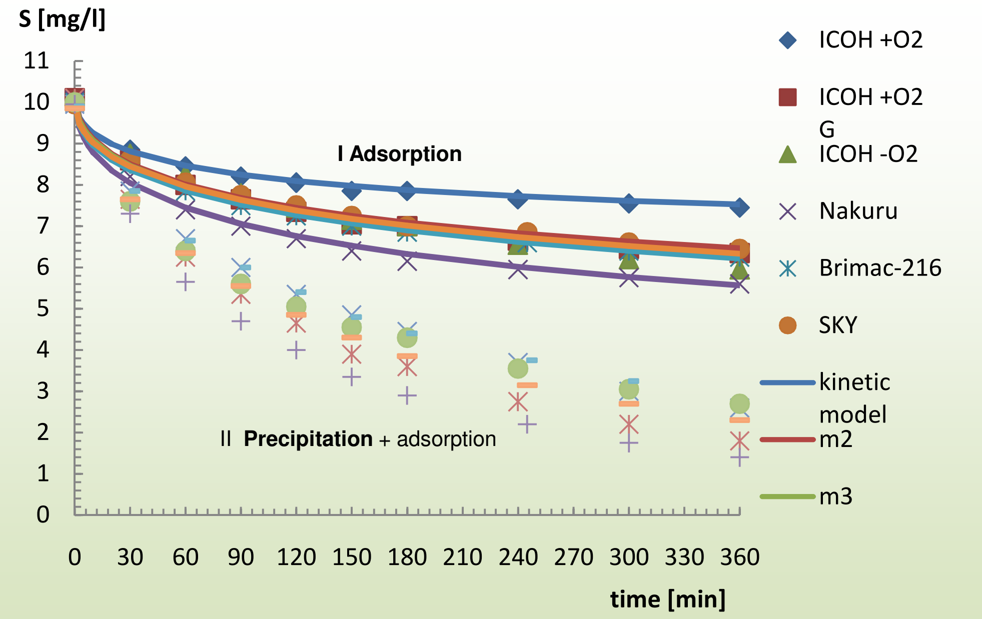

FIGURE 2. Concentration of fluoride in jar test versus time for the six different types of bone char. Series **I** is from jar tests with adsorption only and series **II** is from jar tests with simultaneously adsorption + precipitation.

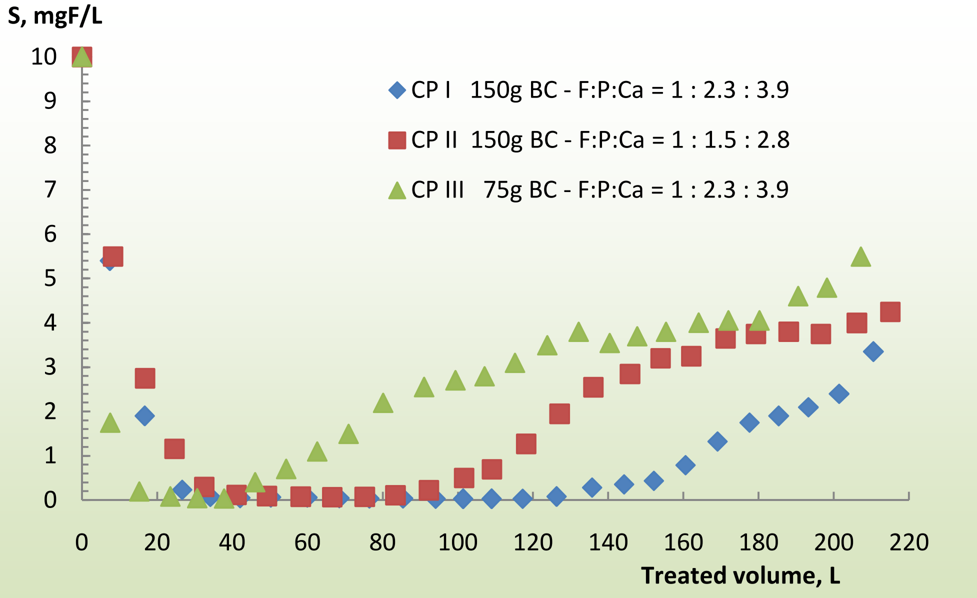

FIGURE 3. Fluoride concentration in the effluent from the columns as a function of the amount of treated water.

Flow experiment. The results from the column experiments are depicted as discrete points in figure 3. The results are shown as average for the double determination in each pair of columns.

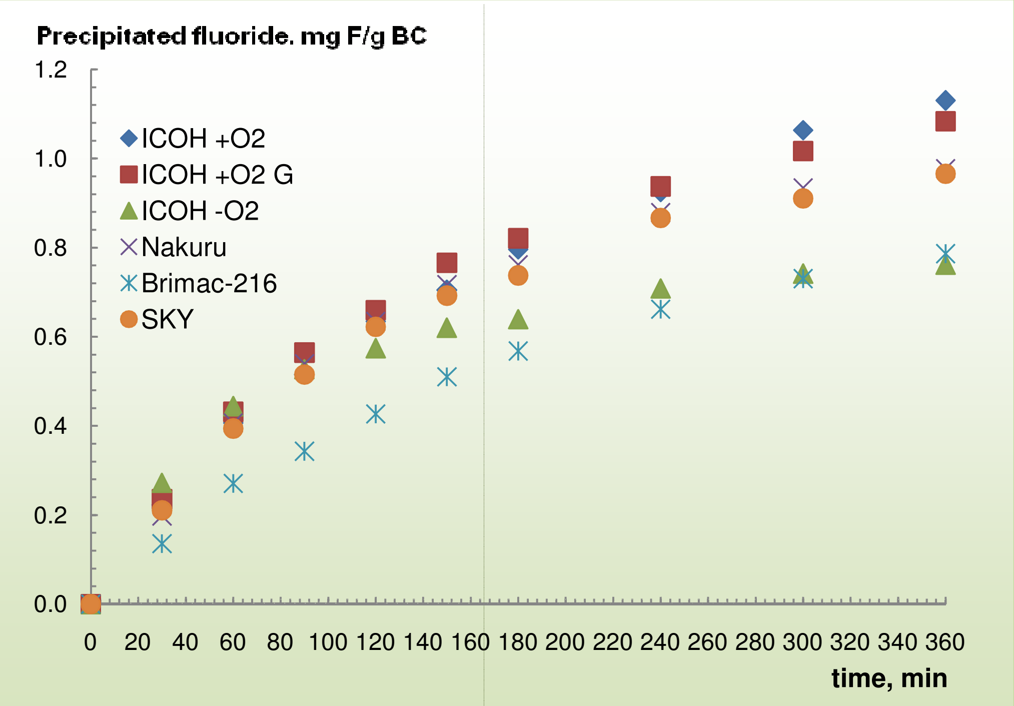

FIGURE 4. Precipitated fluoride versus time in jar test for the six different types of bone char.

DISCUSSION

Bone char characteristics. The six different samples of bone char were examined with respect to grain size distribution, density and porosity. This was done in order to detect other possible reasons for the difference in adsorption capacity and ability to catalyse contact precipitation than the production methods. The bone char all had approximately the same grain size distributions, porosity and density except Brimac-2 16, which had grain size at the higher end of the interval. Because of the higher uniformity of the grains the porosity is also higher. Slightly larger grains result in lower adsorption capacity [2].

The picture in Figure 1 is in black and white colours and does therefore not reflect other colour nuances as for example brown. ICOH - O_2 and Brimac216 produced by pyrolysis are totally black without any grey or white parts. Nakuru and SKY are also dark with only a few white grains due to a partly calcination. The graded bone char produced at ICOH (ICOH +O_2 G) is mainly dark grey and brown but with more white grains than Nakuru and SKY. ICOH +02 is the most white bone char of the 6 types.

Sorption capacity. The kinetic model, eq. 1, where used to estimate the dynamic capacities and reaction rates for the six different types of bone char. The estimated values are shown in table 3. Figure 1 illustrates that the model fits well to the experimental data. It is also noted that the estimated dynamic capacities are consistent with the results from the jar tests. ICOH +02 and ICOH +02 G with the lowest dynamic capacities had adsorbed the smallest amount of fluoride. Nakuru with the highest dynamic capacity adsorbed the largest amount of fluoride.

The difference in adsorption capacity must be due to the production method since the other characteristics for the six types of bone char were uniform. The results substantiate previous findings [2, 3], as the bone char produced by pyrolysis and partly calcination was found to be better for adsorption than the white types of bone char produced by calcination. It was not possible to detect differences in the quality of the black and dark grey types of bone char.

The six different bone char samples seem to have sorption capacities of the same magnitude, between 0.8 and 2 mg/g, 1.6 mg/g on an average. The dynamic capacities found in this experiment are smaller but in the same order of magnitude as values found in previous experiments [4]. This implies that results of $f_{m,b}$-determination from different tests of bone char quality may not be directly comparable due to variations in the design of the experiments. The estimated dynamic capacities from small-scale experiments like the jar test can therefore not be used as an exact determination of the capacities. They are however very useful for the purpose of comparing different types of bone char and rank them by quality for adsorption.

Contact precipitation. The jar tests for examination of contact precipitation was carried in two series: I) Adsorption and II) Adsorption + Contact Precipitation where phosphate and calcium was added. Unpublished results show that adsorption and contact precipitation can run simultaneously and independently. The amount of adsorbed fluoride can be determined directly from series I while the amount of precipitated fluoride has been estimated by an additive model equivalent to the difference between the series I and II.

$$m_{F,\text{precipitated}} = m_{F,\text{total removed(II)}} - m_{F,\text{adsorbed(I)}}$$

Series of the calculated amount of precipitated fluoride per gram bone char are depicted as discrete points in figure 4.

ICOH +O_2, which is the whitest type of the examined bone char, had the best ability to catalyse the precipitation of fluoride. The very black types of bone char Brimac-216 and ICOH - O_2 had the lowest ability to catalyse the contact precipitation.

The detected differences in amount of precipitated fluoride for each type of bone char are not very significant. There is though a tendency that pyrolysed bone char has a lower ability to catalyse the contact precipitation even when the uncertainty from use of the additive model is considered. This indicate that calcination of bone char, which is the cheapest and least complicated production method, may be the most suitable for defluoridation by contact precipitation.

Limitations in the defluoridation capacity by contact precipitation. The flow experiment with contact precipitation in columns was designed to investigate the influence of calcium- and phosphate dosages and the effect of different contact time during the precipitation. The results prove that both chemical dosages and the contact time influences the amount of precipitated fluoride as expected.

Most interesting is perhaps that the experiments show a limitation in the ability to remove fluoride. The columns CP I and CP II remove all fluoride until a certain point where the ability to precipitate the fluoride decrease and effluent concentrations increase. This limitation has not been reported before.

The amounts of water that can be treated before effluent concentrations of fluoride increases to exceed the WHO guideline [8] of 1.5 mg/L are given in table 4, together with the number of treated bedvolumes and the amount of precipitated fluoride.

Field investigations of contact precipitation in larger scale have been carried out at the primary school in Ngurdoto, Tanzania [1]. The school filter was still able to reduce fluoride almost completely after 2300 bedvolumes, compared to the 710 bedvolumes in these experiments. The amount of precipitated fluoride in the filter after treatment of 2300 bedvolumes can be estimated as 27.7 mg/g.

TABLE 4. Exceeding of WHO guideline 1.5 mg/L

Columns	Unit	CP I	CP II
Treated volume	L	170	120
Number of treated bedvolumes	-	710	500
Precipitated fluoride	mg/g	9.1	6.6
Molar ratio F:P:Ca	-	1:2.3:3.9	1:1.5:2.8
Concentration of phosphate	mM	1.2	0.8
Consumption of $NaH_2PO_4 \cdot H_2O$	g/L	0.18	0.12
Concentration of calcium	mM	2.1	1.5
Consumption of $CaC1_2 \cdot 2H_2O$	g/L	0.30	0.22

The amounts of treated water and precipitated fluoride are lower than the findings from Ngurdoto school plant. The difference may partly be explained by the higher concentrations of phosphate and calcium in Ngurdoto, which seems to provide for longer operation time, see below. The intermittent flow and long resting times for the filter in Ngurdoto may also favour the lifetime, which has also been observed for adsorption in filters. Finally there is always variation between a small-scale laboratory experiment and a field investigation of a pilot plant where the parameters are less controlled and the day to day running of the plant are more heterogeneous. The lifetime of a filter may therefore in practise be a lot longer than found in these experiments.

The experiment clearly show that an increase in concentrations of phosphate and calcium (from CP II to CP I) results in a longer durability of the filter. By increasing the concentration of phosphate with 50 % and calcium with 40 % the filter was able to treat a 40 % larger amount of water. Adding higher amounts of phosphate and calcium can thus extend the durability of a filter for defluoridation. If the price of bone char is low and the expenses for chemicals are the limiting factor in the running of defluoridation plant it may however be more appropriate to exchange the bone char more often.

The investigation also showed that the contact time influences the removal efficiency of fluoride by contact precipitation. The columns CP I and CP III were examined at identical additions of calcium and phosphate, but with a effective contact time of respectively 32 minutes in CP I and 16 minutes in CP III. Doubling the contact time, or the filter size, improve the lifetime of the filter to more than double. This is the same tendency, which is seen in fluoride adsorption in columns [9].

The reason for the limitations in filter lifetime has not been investigated in detail. Based on the understanding that fluoride is removed by precipitation it could be assumed that the lifetime of filters for contact precipitation in theory should be boundless until precipitate is filling the filter pores [1]. This is however in contradiction with the result that the highest loading of calcium and phosphate, CP I, which have given the highest amount of precipitate, at least a bit more than in CP II, has also the longest lifetime.

It has been made probable that the precipitate is a mixture of fluorite, CaF_2, and fluorapatite, $Ca_{10}(P0_4)_6F_2$ [1]. Based on assumptions of the amounts that precipitate either as fluorapatite or fluorite, the increase in bed weight from precipitation is in the order of 20 % during the lifetime in these experiments. The precipitation, presumably of fluorapatite, needs reaction time as seen from the result that large filters, CP I, are better than small, CP II. Normal reaction kinetics prescribes that higher concentration of the reactants, i.e. calcium and phosphate, make faster precipitation. This may mean the difference that prolongs the lifetime of the filter in the situation where contact time is lowered because of the precipitated products.

CONCLUSION

The investigation has shown that calcined bone char, which is the cheapest and least complicated production method, may be better in contact precipitation that pyrolysed bone char as opposed to experiences with adsorption.

Filters with fluoride saturated bone char are demonstrated to remove more fluoride due to addition of calcium and phosphate compounds, the so-called contact precipitation process. However, the results of this study sow that the process is of a limited durability. After a period of total removal of fluoride, the fluoride breaks through and the filter medium must be exchanged or regenerated. The amount of water that can be treated before the effluent concentrations of fluoride rise depends on contact time and concentrations of phosphate and calcium. Longer contact time will result in increased durability. Increased concentrations of calcium and phosphate will likewise result in increased durability.

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