EFFECT OF CALCIUM ADDITION ON THE DEFLUORIDATION CAPACITY OF BONE CHAR

P Jacobsen* and E Dahi*
Copenhagen, Denmark

SUMMARY: Dosage of small amounts of calcium chloride to fluoride water prior to contact with bone char which has already been saturated with fluoride is shown to provide an additional fluoride removal capacity. The additionally obtained removal capacity increases with slower filtration velocities and increasing calcium dosage. A filtration velocity of 0.07 m/h, corresponding to a contact time of about 2 hours, and a dosage of 100 mgCa/L, are shown to provide an additional removal capacity of about 3 mgF/g, i.e. almost a doubling of the genuine removal capacity of the bone char. The process is shown to be capable of reducing the fluoride concentration form 10 to about 0.5 mgF/L. The additionally saturated column is shown to be regenerated by simple adjustment of the pH of the water to 11 and allowing to flow for a few bed volumes. The useful regeneration capacity, where the fluoride concentration is reduced from 10 to less than 1.5 mg/L is determined to be about 1.0 mg/g.

Key words: Bone char; Fluoride; Calcium; Defluoridation capacity; Regeneration; Contact precipitation.

INTRODUCTION

Several methods have been studied for defluoridation of drinking water. Few of them have been tested and utilized in practice. One of the most studied and practiced method is the use of bone char in sorption filters. Bone char is an excellent selective sorbing agent for fluoride. Its capacity to absorb the fluoride is relatively high, 2-6 mg/g.[1] Furthermore, if bone char is prepared properly it would, apart from removing the fluoride, improve the raw water quality in general.[2]

However, the use of bone char in a simple sorption process has a couple of serious limitations. Firstly the change of the medium upon saturation is a cumbersome job. Secondly the good quality bone char may be unaffordable to most local peoples in fluorotic areas. Thirdly, the availability of good quality bone char is limited, if not non-existing, in most of these areas. Many efforts have therefore been brought about in order to develop methods by which the usability of the bone char could be improved. Three of these methods may be distinguished: The regeneration, the surface coating and the contact precipitation.

The ***regeneration*** method has been used at a large scale in Briton, USA, where a plant was operated for many years.[3] Thus it is proven that bone char can be saturated and regenerated for several hundreds cycles. The regeneration is carried out by the use of a 1 % alkaline solution, where the process is assumed to be an ion exchange between the fluoride ions and the hydroxyl ions:

$$BC\text{-}F^- + OH^- \Rightarrow BC\text{-}OH^- + F^-$$

The ***surface coating*** has been studied in the laboratory by Christoffersen et al..[4] According to this method, fluoride saturated bone char, if immersed in an acidic solution of calcium and phosphate or of bone char powder, would take up a fresh layer of hydroxyapatite on its surface. The so surface coated bone char will behave as fresh bone char and be able to absorb a new amount of fluoride. The saturation and

* *Environmental Development Cooperation, EnDeCo, Thulevej 16, DK 2860 Søborg, Denmark endeco@image.dk*

surface coating processes has been demonstrated to function for several cycles, of declining capacities though. The bone char powder is normally produced as a waste material in the preparation of grained bone char.

The ***contact precipitation*** method has been reported recently. It has been tested for defluoridation of drinking water in a primary school in Tanzania for a couple of years.[5] According to this method, appropriate amounts of calcium and phosphate compounds are added to the raw water prior to its flow through the fluoride saturated bone char filter. The bone char, being rich with fluorapatite, would catalyze the precipitation of fluoride mainly in agreement with the following equation:

$$10\ Ca^{++} + 6\ PO_4^{---} + 2\ F^- \Rightarrow Ca_{10}(PO_4)_6F_2$$

It has been proved that raw water containing approximately 10 mg/L fluoride could be treated on long term basis at an efficiency of 95 %, i.e. residual concentration of about 0.5 mg/L, by addition of 120 mg/L calcium and 150 mg PO_4/L phosphate. The main mechanism behind the contact precipitation is attributed to the production of fluorapatite. However, if all the removed fluoride was precipitated as pure fluorapatite, higher dosage of phosphate would have been needed. It has therefore been concluded that the process, at least at the employed relatively high initial fluoride concentration, may involve some precipitation of calcium fluoride.[5]

The purpose of this study is to investigate the processes taking place when calcium alone is added to the fluoride water prior to flow through the fluoride saturated bone char column.

METHODS

Fluoride water. Tap water from the water supply at Ngurdoto, Tanzania, was used through out the experiments. The fluoride concentration, which was between 9.5 and 11.5 mg/L of drinking water, was standardized to 10 mg F/L of raw water for treatment. This was done either by addition of sodium fluoride in stock solution or by dilution with rainwater.

Saturated bone char. Cattle bones collected at village level were charred in a locally developed kiln packed with charcoal. The charring took about 15 hours, during which the access of atmospheric oxygen was restricted and the temperature controlled at between 400 and 500°C. The charred bones were crushed and sieved into grain size 0.5 -1.5 mm. Three kg of bone char medium were added to 9 liters of a solution containing 1gram fluoride per one liter of drinking water. The mix was stirred regularly for a period of 3 weeks. At the end the water had a fluoride content of 21 mg/L i.e. the bone char had absorbed 3 mg F/g bone char. This saturated bone char was drained, dried and then used through out this study.

Batch experiments. Batch experiments were carried out in plastic bottles containing one liter of fluoride water. In order to account for blind effects the experiment was carried out in triple, one where calcium but not saturated bone char was added, one where saturated bone char alone was added and one where both calcium and saturated bone char were added. The bottles were shaken by turning upside down 10 times and left idle for 8 hour. This was repeated 6 times in order to provide a total contact time of 48 hours, before the residual fluoride concentrations were measured.

Column experiments. Glass columns of 30 mm inner diameter and 300 mm height were packed with 106 mL or 80 g saturated bone char, the height of the bed being 150 mm. The height of the supernatant water was 50 mm. The columns were loaded with the fluoride tap water at rates of 50, 200 and 800 mL/hr, corresponding respectively to 2.1 h, 32 min. and 8 min. hydraulic retention times or to 1.13, 0.28 and 0.07 m/h flow velocities. The flow was controlled using an inlet of silicon-tubing and a regulating clamp in combination with a dripping device. The calcium chloride and or sodium hydroxide were added by, respectively during water treatment and regeneration of media. The outlet water was collected in batches and the average fluoride concentration was measured batch wise.

Fluoride and pH measurements. The fluoride concentrations were measured using a fluoride selective electrode (Metrohm 6.0502.150) and an Ag/AgCl reference electrode (Metrohm 6.0726.100) connected to a Metrohm 704 pH-meter. Five mL of samples was mixed with 5 mL of TISAB and compared with standard solutions of 1 to 10 mg F^-/L. pH was measured using a Metrohm electrode 6.0220.100.

RESULTS

Table 1 shows the effect of addition of calcium to fluoride water containing saturated bone char. It is seen that the dosage of calcium results in additional uptake of fluoride, but only in the presence of saturated bone char.

TABLE 1. Batch experiment where calcium is added to water containing10 mg/L fluoride with and without the presence of saturated bone char. Contact time is 48 hours.

Added materials	Flask I	Flask II	Flask III
$CaCl_2$ in mgCa/L :	360	0	360
Saturated bone char in g/L:	0	2	2
Fluoride residual (mg/L)	10	8.2	4.5
Add. F- removal cap. mg/g	0	0.9	2.8

The column experiments of different flow rates of fluoride water added 100 mg/L calcium are shown in Figure 1. Flow rates of 50, 200 and 800 mL/h are utilized. These correspond to hydraulic retention times of 2.1 hours, 32 minutes and 8 minutes or to flow-velocities of 0.07, 0.28 and 1.13 m/h respectively.

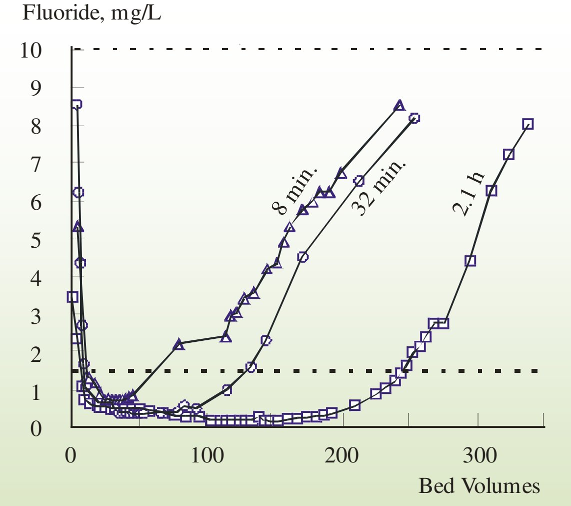

FIGURE 1. Column experiments where 10 mg/L fluoride water is added 100 mg/L calcium and the mix is passing the saturated bone char columns at three different rates of flow. Hydraulic retention time is indicated.

In the third campaign of experiments the same columns and water are used. The flow rate was fixed to 200 mL/h, but the dosage of calcium was different, respectively 0, 25 and 50 mg/L. The results are shown in figure 2.

The fourth set of experiment aimed at cycling between treat-ment of the fluoride water and regenerating the columns by use of sodium hydroxide. The results are presented in Figure 3.

DISCUSSION

It is well known that calcium can precipitate fluoride as calcium fluoride, CaF_2, the solubility constant Ks being $1.92 \cdot 10^{-11}$. The results of the batch experiments shown in table 1 illustrate that calcium and fluoride may remain dissolved in the water, after a contact time of 48 hour, even if the solubility product is exceeded by not less than 130 times. The results are in agreement with the fact that the fluoride can not be removed instantly from the water by simple addition of large quantities of calcium compounds.

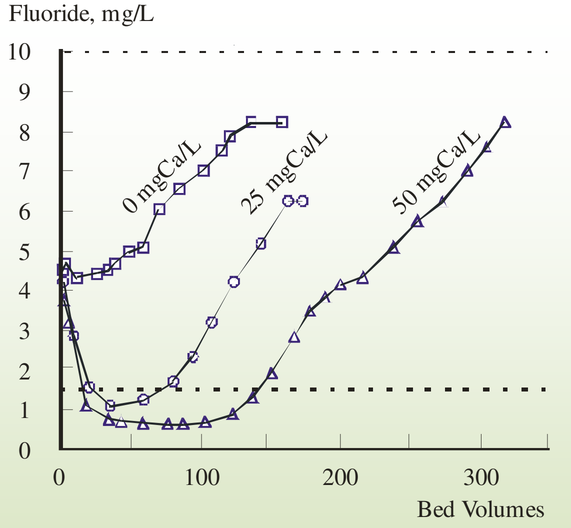

FIGURE 2. Column experiments where different amounts of calcium are added to 10 mg/L fluoride water. The columns containing saturated bone char are loaded with the water at a fixed flow velocity of 0.28 m/h corresponding to retention time of 32 minutes.

The results of the batch experiment illustrate furthermore the difficulty in defining the saturation point of bone char. Though the bone char was saturated after contact time of three weeks, ending in a steady residual fluoride concentration of 21 mg/L, it was able, at a later stage, to remove fluoride from water containing 10 mg/L. Though this additional removal capacity is limited, 0.9 mg/g, it illustrates the complexity of the bone char saturation processes. The experiments demonstrate however, that addition of calcium increases this additional removal capacity significantly. The additional removal capacity gained by addition of calcium is measured to be 2.8 mg/g, i. e. about doubling the genuine removal capacity of the bone char.

Fluoride is also removed from the water, as the fluoride water, after addition of 100 mgCa/L, passes through a saturated bone char column. Figure 1 shows that the bone char removal capacity increases with increasing hydraulic retention time, i.e. slower filtration velocities. If the breakpoint is defined to 1.5 mgF/L in the treated water, the additional removal capacities obtained in the columns are 0.8, 1.6 and 3 mg/g respectively for the flow velocities of 1.15, 0.28 and 0.07 m/h. The slowest flow utilized, which is giving the highest augmentation in the calcium-bone char removal capacity, corresponds to contact time of approximately one hour. Faster flow probably results in higher escape of the added calcium. As compared to the batch experiments, this may indicate that the observed removal process is not a simple filtration of already precipitated calcium fluoride, but that the precipitation, whether calcium fluoride or not, is facilitated by the saturated bone char in the column. A contact time of at least 1 hour, i.e. a hydraulic retention time of at least 2 hours, is required for the process to take place.

The results shown in Figure 2 confirm that the saturated bone char by it self is able to absorb more fluoride, but at very low removal efficiencies, i.e. 50 % or less. Again if an effluent concentration of 1.5 mgF/L is defined as acceptable water quality criteria,

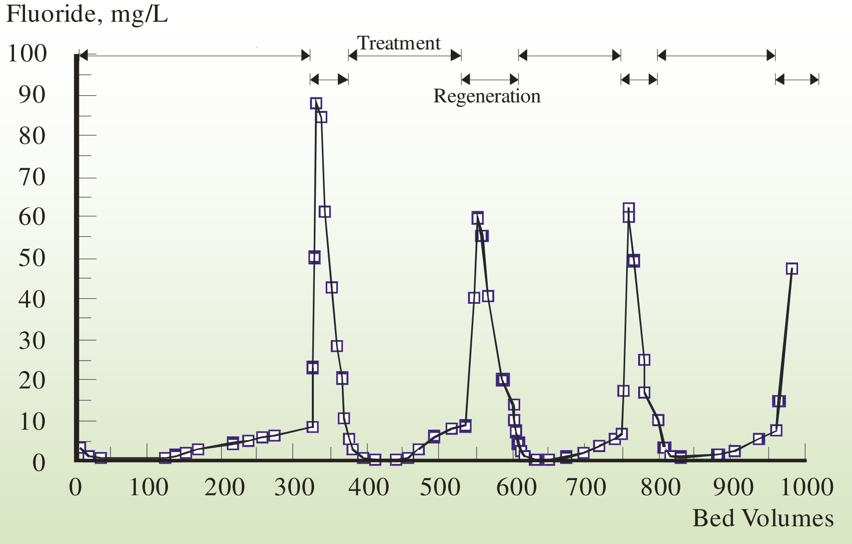

FIGURE 3. Cyclic treatment of 10 mg/L fluoride water in a column of saturated bone char. The regeneration is done by adjusting pH of the fluoride water to pH 11 using a NaOH solution. Hydraulic detention time is 32 min. Flow velocity is 0.28 m/h.

the number of treated bed volumes were 0, 40 and 120, for dosage of respectively 0, 25 and 50 mgCa/L. These represent additional efficient removal capacities of 0, 0.5 and 1.5 mg/g. It is therefore concluded that the amount of added calcium is crucial for the efficiency of the removal. The data are not conclusive about the optimum dosage. At flow of 200 mL/h, i.e. hydraulic retention time of 32 minutes, similar capacities, 1.5 and 1.6 mg/g, are obtained at dosage of respectively 50 and 100 mgCa/L.

The above mentioned results show clearly that the fluoride saturated bone char, if added calcium is able to absorb more fluoride, but only to become saturated again at higher capacity level. The results of the regeneration experiment, Figure 3, show that interruption of the treatment and adjusting pH to 11 elutes the additionally absorbed fluoride and renews the capability of the column to treat more water. The treatment capacity of the column is shown to be about 320, 150, 140 and 160 bed volumes. Counting on average effluent fluoride concentration of approximately 3 mg/l the removal capacity of the column in its four operation periods is respectively 3.0, 1.4, 1.3 and 1.4 mg/g. This indicates that the regeneration may be operated for equidistant cycles, i.e. at technical use, but at an efficient capacity of less than 1.4 mg/g. If the above mentioned criteria of 1.5 mg/L is defined as acceptable, then regenerative fluoride removal capacity would be about 1 mg/g, which is much lower than the additional capacity gained by addition of calcium, i.e. 2.8 mg/g, and the genuine capacity of the bone char, i.e. 2-4 mg/g.

The results presented in this study are in agreement with the previous studies of Christoffersen et al. 1991,[4] Larsen and Pearce 1992,[6] Bregnhøj 1995[1] and Dahi 1996,[5] all showing that calcium compounds are able to increase the fluoride removal capacity of the bone char. Yet the results are not conclusive about the mechanisms of the removal observed. It is known that bone char is not a perfect compound of hydroxy- and fluorapatite. The bone structures, especially after processing, storage or drying may be in deficit of calcium. If this calcium deficiency is covered through addition of e.g. calcium chloride, the bone char will be able to remove more fluoride from the water. The additional removal observed in this study could be attributed to coverage of this calcium deficit through contact precipitation of calcium fluoride and/or fluorapatite. It is unlikely that calcium fluoride is the only precipitate produced, as the residual fluoride concentration is much below the equilibrium concentration of saturation. It can however not be excluded that a simple ion exchange is playing a major role in the observed regeneration of the saturated bone char columns.

ACKNOWLEDGEMENT

Danida has kindly sponsored this study and the author's participation in the workshop through the Enreca Program and the Defluoridation Technology Project.

REFERENCES

29. Bregnhøj H, Processes and kinetics of defluoridation of drinking water using bone char. Ph.D. Thesis. Technical University of Denmark, 1995.
30. Dahi E and Bregnhøj H. Significance of oxygen in processing of bone char for defluoridation of water. p 84-90 in: *Proceeding of the 1st International Workshop on Fluorosis and Defluoridation of Water,* October 18-20, 1995. Eds. Dahi & Bregnhøj, ISFR Auckland.
31. Horowitz HS, Heifetz SB, Driscoll WS. Partial Defluoridation of a Community Water Supply and Dental Fluorosis. Final Evaluation in Britton, S. Dak. USA. *Health Services Reports 87* 451-4551972.
32. Christoffersen J, Christoffersen MR, Larsen R, Møller IJ. Regeneration by Surface-Coating of Bone Char Used for Defluoridation of Water. *Water Research 25* (2) 227-229 1991.
33. Dahi, E. 1996. Contact Precipitation for Defluoridation of Water. Paper presented at 22nd WEDC Conference, New Delhi, 9-13 September, 1996.
34. Larsen MJ, Pearce EIF. Partial Defluoridation of Drinking Water Using Fluorapatite Precipitation. *Caries Research 26* 22-28 1992.