

## DEVELOPMENT OF THE CONTACT PRECIPITATION METHOD FOR APPROPRIATE DEFLUORIDATION OF WATER

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**SUMMARY:** This paper describes the development of defluoridation of water by contact precipitation, where fluoride water is mixed with calcium and phosphate and brought in contact with bone char which is already saturated with fluoride. The process is studied in jar test, in manually stirred buckets and in continuously fed columns. Furthermore in a “fill, mix and filter” column both in laboratory and in a pilot plant for a period of two years. An appropriate setup is then designed and constructed using low-cost, corrosion-resistant and robust locally available materials. The removal efficiencies obtained in the batch systems were relatively low especially when manually stirred. The fill, mix and filter technique demonstrated surprisingly high removal efficiencies, 95-98 %, without any sign of break through or saturation, at dosage levels corresponding to calcium/phosphate/fluoride weigh ratio of 8.5/10.8/1. It is discussed that the main processes behind may be a crystal growth or a catalysed precipitation of fluorapatite and/or calcium fluoride, as the components are brought in close contact with fluoride saturated bone char.

**Key words:** Defluoridation; Drinking water; Contact precipitation; Bone char; Pilot plant; Tanzania; Removal mechanisms; Fill, mix and filter technique; Apatite; Crystal growth.

### INTRODUCTION

Millions of people, mainly in developing countries, are known to suffer from fluorosis due to the high fluoride concentrations in their drinking water,<sup>1</sup> and numerous methods and media, including low cost ones, are known to be able to remove fluoride from water.<sup>2, 3</sup> Yet none of these methods has so far been reported to be carried out successfully as a routine in any developing country.<sup>4</sup> This oddity is probably attributed to the fact that the available methods suffer from one or more serious drawback(s), e.g. low removal efficiency, low removal capacity, complex preparation of medium, complex procedures of regeneration, the need of monitoring in order to avoid the break through and deteriorated treated water quality. It is worth mentioning that the most promising methods of today, e.g. the bone char sorption, the activated alumina ion exchange and the alum/lime co-precipitation, have all been well known already in the thirties.<sup>5, 6</sup>

This paper describes the scientific background and the development of a new method, ascribed as contact precipitation.

### MATERIALS AND METHODS

**Fluoride Measurements.** The fluoride concentrations were measured using a Metrohm fluoride electrode and a Metrohm Ag/AgCl reference electrode with a sleeve type diaphragm connected to a Metrohm potentiometer (691 pH Meter). An aliquot of 10.0 mL of the sample solutions was mixed with 10.0 mL CDTA-tisab and the fluoride concentration was measured according to the Standard Methods.<sup>7</sup>

**Bone char preparation.** The bone material was delivered from the Danish bone meal factory DAKA, where the bone material has been boiled, washed, dried and crushed into small particles of grain size < 4.0 mm. The bone material was pyrolysed in a

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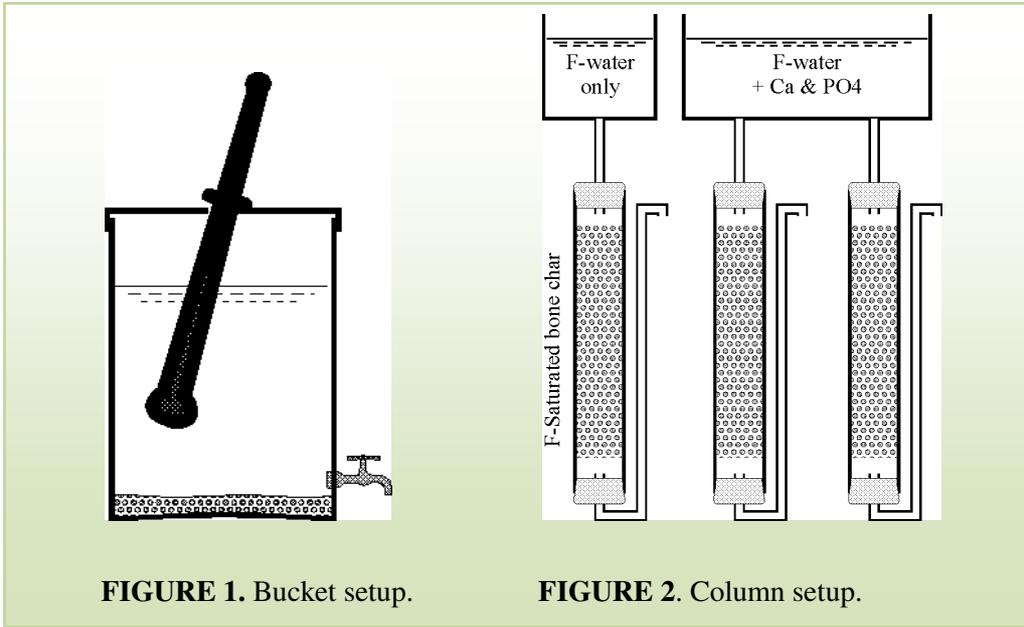


FIGURE 1. Bucket setup.

FIGURE 2. Column setup.

programmable ceramic oven (Scandia Oven, Type SK 355) in a covered steel container, where the access of atmospheric oxygen was restricted. The temperature was raised at a rate of  $4^{\circ}\text{C}/\text{minute}$  from room temperature to  $600^{\circ}\text{C}$  and then kept constant for 4 hours. The charred bone material was allowed to cool down to room temperature before the oven was opened. Bone char of 2.0-2.8 mm grain size was sorted out using a test sieve shaker (Endecotts EFL2 mk3).

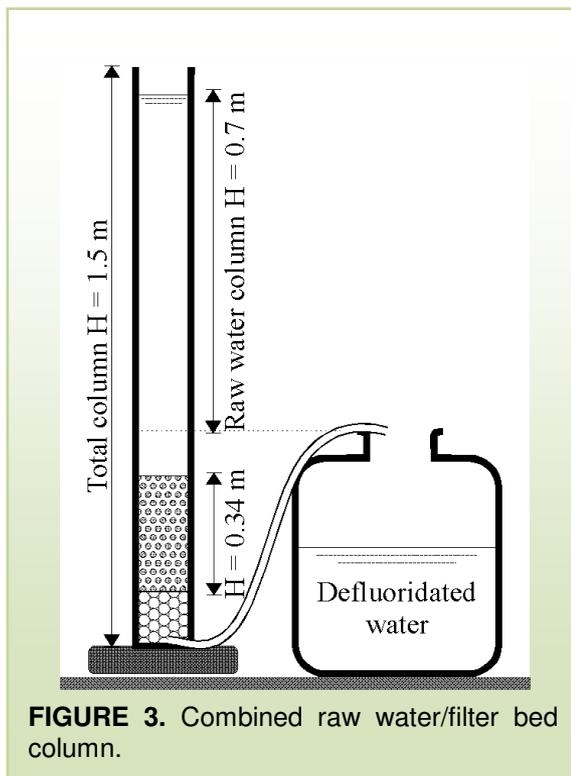
**Saturated bone char.** For the jar test, the bucket and the column experiments saturated bone char was prepared by packing the fresh bone char in a column of 50 cm height and circulating of 13 mg/L fluoride water. The sorption was continued until the effluent concentration was as high as the influent concentration, i. e. for a period of one week.

For the field testing large quantity of bone char was saturated by suspending the fresh bone char medium in a solution containing 1 g fluoride per litre of drinking water. The mix was stirred regularly for a period of 2 weeks. At the end the water had a fluoride content of about 18 mg/L. At this point of saturation the bone char had absorbed 2.5 mg F/g bone char. The bone char was transferred directly to the village school plant contact chamber and brought to equilibrium with the local drinking water containing 8.2 – 13 mg/L fluoride.

**Jar test setup.** One litre plastic beakers each containing 1 L Danish municipality water enriched with fluoride to contain 13 mg/L fluoride were stirred in the Jar test apparatus (Phipps & Birds Stirrer 7790-402) at a stirring frequency of 140 revolutions per minute. Different media were added at time nil with and without chemicals, i.e. calcium chloride and calcium monohydrogen phosphate. The level of dosage being 159 mg Ca/L and 226 mg  $\text{PO}_4/\text{L}$ . Six batches were added respectively fluoride saturated bone char, marble, quarts sand, unsaturated (fresh) bone char and saturated bone char. All media were added at same volume dosage of 100 ml/L and of same grain size, 2.0-2.8 mm. In parallel one batch was left as a blank and stirred separately without any addition. After 2 hours of stirring samples were taken, filtered through a

0.45  $\mu\text{m}$  Minisart GF filters before determination of the residual fluoride concentrations.

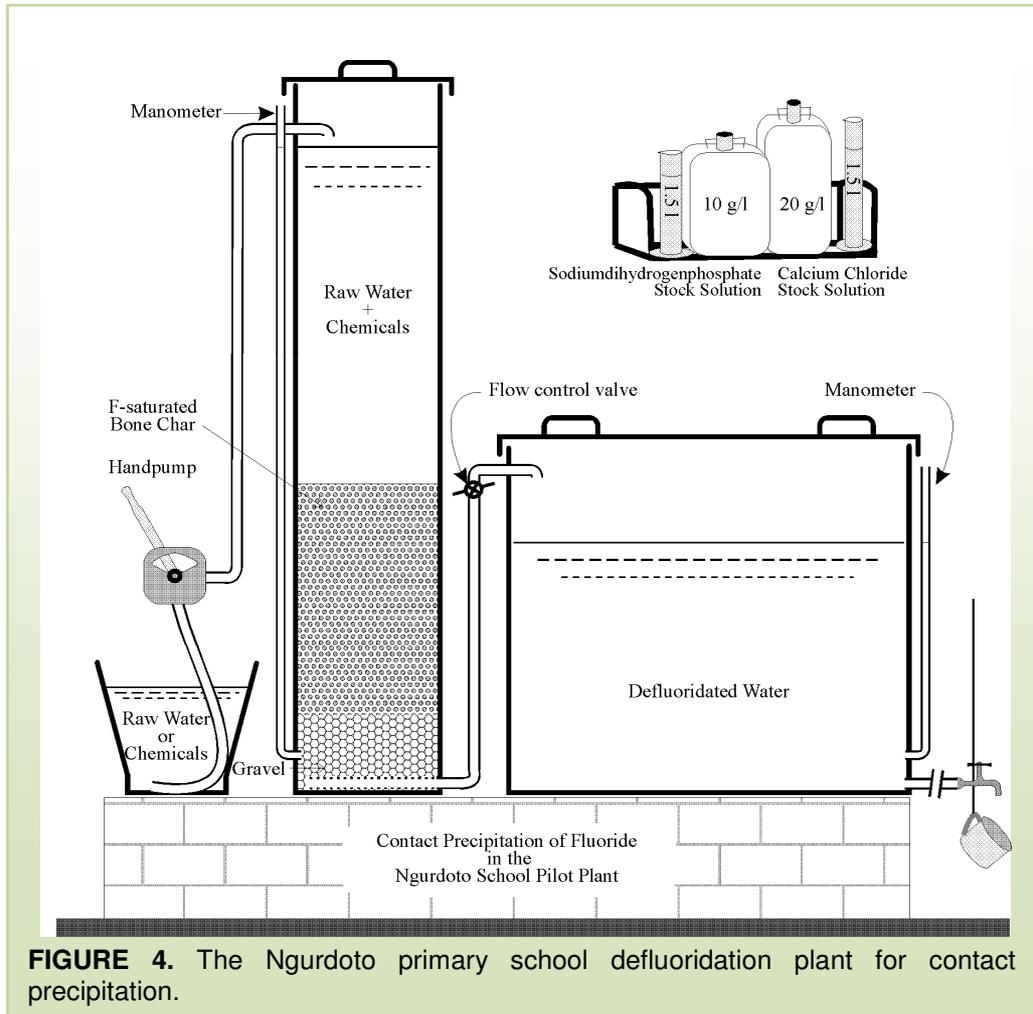
**Bucket setup.** Different volumes of natural piped water containing 15 mg F/L were poured into 20 L plastic buckets, as normally used in the households in the Arusha region of Tanzania. The buckets were supplied with taps at a level of 5 cm above the bottom in order to allow for decanting of medium. A wooden device was used for mixing, as illustrated in Figure 1. Saturated bone char was added to the water, grain size 2.0 – 2.8 mm, 83 g/L. Then at time nil calcium chloride and calcium monohydrogen phosphate were added, the dosage level being 237 mg Ca/L and 337 mg  $\text{PO}_4$ /L. The suspensions were stirred, about 100 RPM, manually for 3 minutes every 15 minutes. The residual fluoride concentrations were measured vs. time as mentioned above.



**FIGURE 3.** Combined raw water/filter bed column.

**Column setup.** Glass columns 1.9 cm in diameter and 50 cm in length were packed using 118 g of bone char, fluoride saturated as described above. The bone char had grain size 2.0-2.8 mm, porosity 0.65 and bulk density 0.83 g/mL. The columns were loaded with fluoride water containing 16 mgF/L at two different flow rates, 0.19 and 0.095 L/h corresponding to flow velocities of 0.67 and 0.34 m/h and a hydraulic retention time of  $\frac{3}{4}$  and  $1\frac{1}{2}$  hours respectively. One column was used as a reference without additions of chemicals in order to account for the residual sorption (or desorption) capacity of the saturated bone char. Two columns were loaded with the same water after addition of 237 mg Ca/L and 337 mg  $\text{PO}_4$ /L. The flow was controlled by a peristaltic pump, which however was only run during working hours, 8 hours per day.

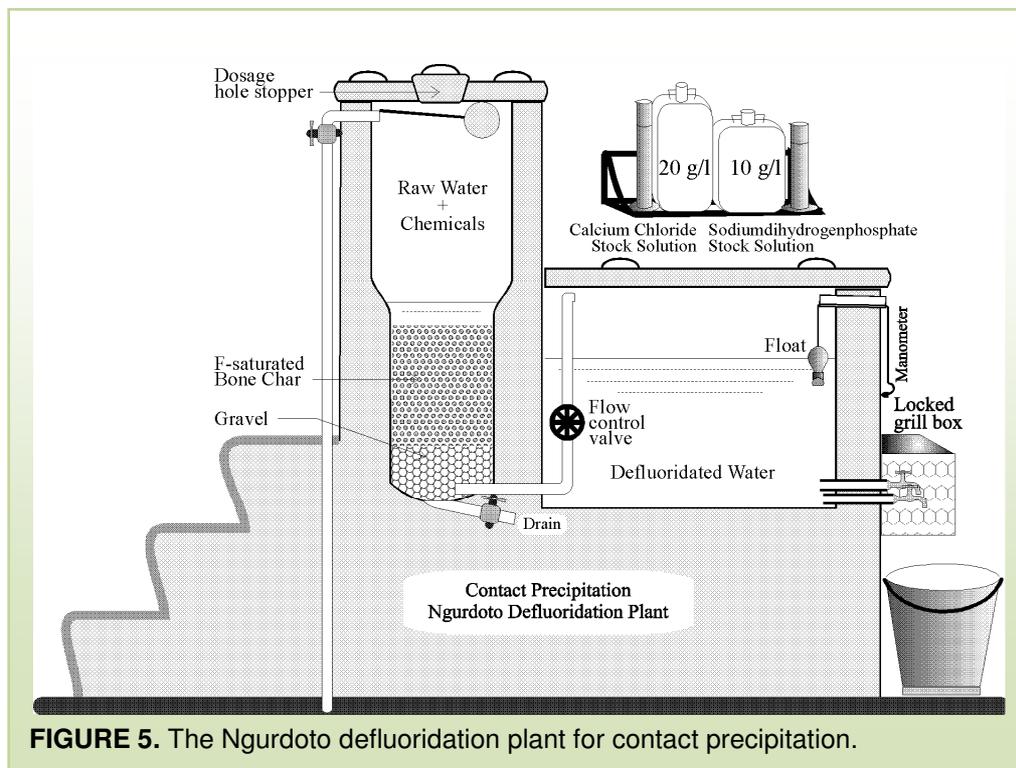
**Fill and filter contact column.** A combined raw water and filter bed column was set up for testing the significance of declining rate contact filtration in a simple “fill and contact filter” system, Figure 3. The column was packed with 20 cm gravel in the bottom, then with 3.28 kg of fluoride saturated bone char of grain size 1-2 mm. Eleven litres of water containing 20 mg/L fluoride were added each day to the compartment above the bone char, along with 470 mg/L anhydrous calcium chloride and 1100 mg/L calcium monohydrogen phosphate dihydrate, corresponding to dosage of 169 mg Ca/L and 415 mg  $\text{PO}_4$ /L. The water was allowed to flow slowly at declining rate until the raw water compartment of 11 L was emptied. In most cases the filtration time was between 10 and 20 minutes.



**FIGURE 4.** The Ngurdoto primary school defluoridation plant for contact precipitation.

**School pilot plant.** A plant was set up at the Ngurdoto Primary School, Arusha Region, Tanzania, to cover the need for drinking water of about 500 people during the day hours of the weekdays. The plant, Figure 4, consisted of one column 0.32 m in inner diameter and 1.4 m height. The column was packed with 20 L gravel, 0.25 m height and grain size 5-10 mm, and 18.7 kg of fluoride saturated bone char, 0.28 m in height and grain size 1-4 mm. The upper part of the column, 1.1 m in height, equal 100 L, was left as a raw water chamber in which the chemicals were added daily and mixed with the raw water. After mixing the water was allowed to flow at a declining slow rate through the saturated bone char compartment to a large clean water tank. This tank was supplied with a pipe and a tap at the schoolyard for convenient water intake by the people and the teachers.

One senior school pupil was employed as a caretaker and operated the plant as follows: The caretaker arranges for fetching the water in buckets every morning. Then starts closing the flow control valve completely. One and half litres of each of the two stock solutions containing Ca and  $\text{PO}_4$  are pumped to the raw water column after mixing with the raw water from the first two buckets. The remaining water is then



**FIGURE 5.** The Ngurdoto defluoridation plant for contact precipitation.

pumped to fill the raw water column, in total about seven buckets. As raw water is falling into the raw water column, the supernatant water is completely mixed. The flow control valve is then opened, but only to allow slow flow through the contact bed, the average filtration velocity not exceeding 1 m/h. A water sample is taken by the plant keeper for testing. This procedure is carried out once a day, apart from holidays. However, in between, the procedure is omitted or carried out twice in the same day in order to meet the demand for drinking water. The design and operation and maintenance procedures are described elsewhere in more details.<sup>8</sup>

**Stock Solutions.** The caretaker prepares the two stock solutions once every 10<sup>th</sup> operation day. Two special measuring cups are used for volumetric portioning of the chemicals, respectively 300 g calcium chloride (311 mL CC) and 150 g Sodiumdihydrogenphosphate (142 mL MSP). The chemicals used are both from the Swedish Kemira LTD. CC is fabricated as technical grade flakes containing 77-80 % calcium chloride MSP is fabricated as Bolifor Granular containing 24 % P and 20 % Na. The dosage used corresponds to 85 mg Ca/L and 110 mg PO<sub>4</sub>/L. The chemicals are dissolved separately, each in 15 L defluoridated water. The stock solutions containers along with the respective chemical bags and the measuring cups and cylinders are coloured respectively in red and green in order to minimise the risk of failure dosage.

**Appropriate design.** After successfully testing of the Ngurdoto pilot plant for a period of 2 years, a more appropriate design was developed and constructed in the Arusha region, using corrosion resistant, robust, low cost and locally available materials. The plant is used for demonstration purposes, Figure 5, the dimensions and dosage are given in Table 1.

**TABLE 1.** Design parameters of the contact precipitation process as shown in figure 5.

Raw water chamber:			Contact bed:			Clean water reservoir:		
Width	cm	50	Diameter	cm	35	Width	cm	120
Breadth	cm	80	Height	cm	42	Breadth	cm	80
Height	cm	75	Volume	L	40	Height	cm	83
Volume	L	300				Volume	L	800
Bone Char			Calciumchloridedehydrate			Sodiummonohydrogenphosphate		
Weight	kg	34	Bulk density	kg/L	1.06	Bulk Density	kg/L	0.96
Volume	L	40	Stock solution	g/L	20	Stock solution	g/L	10
Grain size	mm	1-4	Dosage	mgCa/mgF	8	Dosage	mgCa/mgF	10
Porosity	-	0.65	mg chemical/L		15	mg chemical/L		30

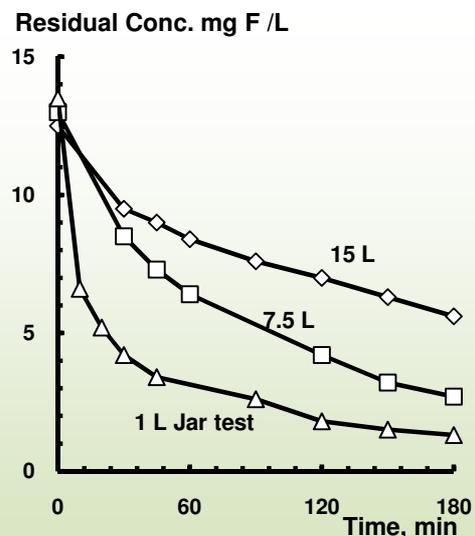
**TABLE 2.** Residual fluoride concentration in jar test, where water containing 13 mg F/L is added different media with and without dosage of calcium and phosphate. Dosage of medium 100 mL/L. Contact time is 2 hours, stirring 140 RPM.

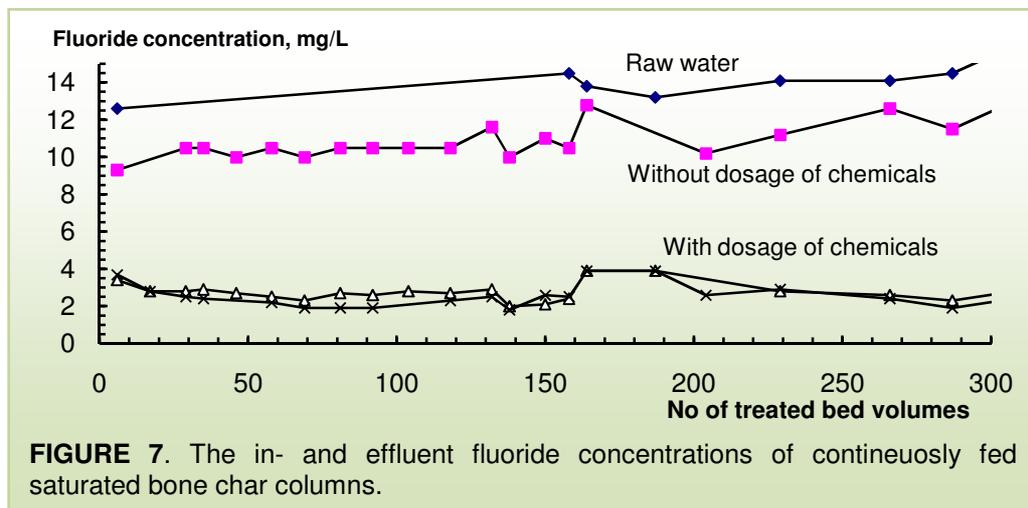
Batch	Medium	CaCl <sub>2</sub> ·2H <sub>2</sub> O*	CaHPO <sub>4</sub> ·2H <sub>2</sub> O	Residual F <sup>-</sup> , mg/L
0	Not added	Not added	Not added	13.0
1	Not added	159 mgCa/L	226 mgPO <sub>4</sub> /L	12.8
2	Marble	159 mgCa/L	226 mgPO <sub>4</sub> /L	13.0
3	Quarts sand	159 mgCa/L	226 mgPO <sub>4</sub> /L	12.2
4	Fresh bone char	159 mgCa/L	226 mgPO <sub>4</sub> /L	0.3
5	Saturated bone char	Not added	Not added	14.1
6	Saturated bone char	159 mgCa/L	226 mgPO <sub>4</sub> /L	3.2

\* The dosage of calcium is calculated as the sum of calcium originated from calcium chloride + the calcium originated from calcium monohydrogen phosphate.

## RESULTS

**Jar test experiments.** The experimental results of the jar test are shown in Table 2. It is seen that fluoride is not removed if only saturated bone char is added to the water. It is also seen that the fluoride removal is negligible in case calcium and phosphate are added to fluoride water alone or along with marble or sand. Similarly other media like charcoal, bone ash were tested and found indifferent with respect to the fluoride removal. Only in case calcium and phosphate are added to fluoride water that contain saturated bone char the removal process seem to take place to a significant extent, 75 %. The removal is thus moderate compared to

**FIGURE 6.** Kinetics of contact precipitation in buckets and jar of different volumes.



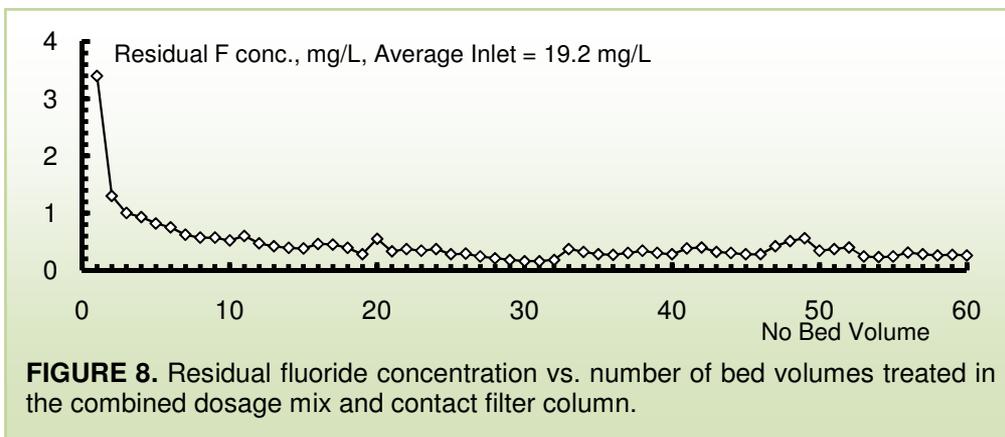
defluoridation by means of fresh bone char, which at a dosage level of 83 g /L resulted in 98 % removal after 2 hours of contact time.

Bucket experiments. The significance of batch volume on the fluoride removal rate is shown in Figure 6. While the 15 and the 7.5 L batch experiments are carried out in the bucket setup, the 1 L batch experiment is carried out in the Jar test apparatus. The bucket technique resulted, after mixing time of 3 hours, 57 % removal, i.e. significant but far from sufficient. The removal was improved, to 80 and 90 %, by reducing the volume of water without any changes in the dosage or the amount of saturated bone char added.

Continuously fed column. The fluoride removal in the continuously fed saturated bone char columns is shown in figure 7. It is seen that what is supposed to be a saturated column may still be able to remove fluoride. The removal efficiency is 24 %. In the chemical added columns the removal efficiencies are much higher, i.e. 82 and 84 %. It has been demonstrated that the efficiency could be improved slightly by increasing the contact time in the column from 30 minutes to one hour by decreasing the flow rate.

Fill, mix and filter column. Figure 7 illustrates the fluoride removal obtained in the fill, mix and filter column. The fluoride removal is shown to be high, 83 % in the first filtration cycle, improving to 93.5 % in the second and to more than 97 % from the 6<sup>th</sup> cycle and hereafter. If the result from the first day is neglected, the removal, on an average, is 98 %. Furthermore, at the time where the experiment was brought to an end, after treatment of 60 bed volumes of water, there was no sign of breakthrough. Rather, the removal seems to improve as the filter gets mature. Due to chemical addition pH was increased from about 7 to about 8 in the raw water. However, pH was 7.29 in the treated water. Similarly, the water alkalinity was 5.3 me/L in the raw water chemical mix, but falling down to 3.3 me/L in the treated water. The calcium content was 96 mg/L on an average in the treated water, indicating that the water is slightly enriched with calcium compared to the raw water, and that most of the added calcium is retained in the filter.

**Long term testing in pilot plant.** The plant operation was initiated on 6<sup>th</sup> November 1995 and terminated in October 1997. During this period one raw water column of water was treated every day, apart from holidays.



Thus the total effective operation period was 586 days. The raw water contained between 8.2 and 13 mg F/L, subject to seasonal fluctuation. The fluoride removal was as high as 92 % in the first filter operation day, improving to 94 % in the second day and then stabilising at about 95-98 %. At the time where the experiment was brought to an end, after treatment of 51.8 m<sup>3</sup> of water, there was no sign of breakthrough. Rather, the removal seemed to improve as the filter gets mature. Only a slightly increase in the filter resistance was observed. During long holidays the plant was standing idle, but this did not affect the organoleptic or microbial quality of the water.

## DISCUSSION

The results obtained from the jar test experiments show clearly that the fresh bone char process may be of extremely high efficiency in batch systems, but this would at the expense the capacity. Table 2 shows that fresh bone char is able to remove 98 % of the initial fluoride concentration of 13 mg/L, but at a capacity level as low as 0.15 mg F/g. The fluoride removal in the contact precipitation process is 75 %, i.e. significant but insufficient.

The jar test results demonstrate that saturated bone char can not, by it self, remove fluoride from water. Furthermore, addition of calcium and phosphate to fluoride water, is not able to remove fluoride from the water unless the water and the chemical mix is brought in contact with fluoride saturated bone char. This catalysis effect of the saturated bone char seems to be unique compared to other media like sand, charcoal, marble or bone ash.

The bucket experiments demonstrate that the removal is not only dependent on the dosage of chemical and the amount of the saturated medium available, but also on the mixing that facilitate the contact between what is assumed to be reagent and the catalysis medium. Apparently this is another limitation of the contact precipitation in batch. Moderate intermittent mixing even for two hours is not sufficient to carry out the contact precipitation at optimum. Therefore it is concluded that the batch technique, especially if carried out in bucket, is not capable to facilitate efficient contact precipitation of the fluoride.

On the contrary to the batch system, the column system seems to facilitate the contact precipitation efficiently. The removal efficiencies obtained being on an average 82 % and 84 % in the continuously fed columns, 98 % in the fill, mix and filter lab column

and 95-98 % in the fill, mix and filter column of the school pilot plant. It is unclear whether the mix and flow pattern can be held responsible for this difference in the results. It has to be mentioned that the phosphate compounds utilised, as stated under Materials and Methods, have been different.

Probably higher removal efficiency in the contact precipitation is obtained by using more soluble calcium and phosphate compounds. Sodium dihydrogen phosphate, or MSP, is preferred to be used at large scale due to high solubility, relative high phosphate content, relative neutrality and still reasonable price.

The mechanisms of the contact precipitation are yet not fully understood. One of the main questions, which was repeatedly discussed during the invention of the contact precipitation technique, is whether the observed removal reveals through a steady state condition, or through a non-steady state. In the first case the removal is likely to continue as long as the chemicals are added and the bottleneck in the process would probably be the decrease in filter permeability. The original permeability can then easily be re-established through rejuvenation, without the need to replace or to regenerate the filter medium. In second case the bone char would be moving towards a saturation of the bone char at a higher capacity level, and thus would need to be renewed or regenerated at final saturation. It is already well documented that bone char, which has been saturated with respect to a given concentration of fluoride in water, may prove to be able to uptake additional fluoride. Addition of calcium ions, drying, and resting, e.g. during night-time, are factors known to facilitate additional removal capacities.<sup>9,10</sup>

The second question which had to be clarified was whether the observed removal is a kind of regeneration of the bone char as described in the literature,<sup>11, 12</sup> or it is a contact precipitation of the added chemical along with the fluoride from the water. According to Christoffersen et al.,<sup>12</sup> treatment of saturated bone char in a solution of calcium and phosphate regenerate the bone char by coating it with a fresh layer of hydroxyapatite.

The mechanism of regenerations through surface coating seems not to explain the contact precipitation satisfactorily. This is, among other things, because simultaneous addition of the chemicals is more efficient than pre-treatment of the bone char. It is clear that the fluoride/calcium mix is over-saturated with respect to calcium fluoride. However, the residual fluoride concentration in the treated water is brought down to a level where a simple precipitation of calcium fluoride can not explain the results.<sup>9</sup> It is also clear that the fluoride/calcium/phosphate mix is over-saturated with respect to fluorapatite. The results may thus be explained as a precipitation of fluorapatite, a process which is only taking place if catalysed in a saturated bone char bed, i.e. a kind of heterogeneous crystal growth phenomenon, where the adjacent water is rich with the precipitate components.

The calcium/phosphate/fluoride weight ratio is 10.5/15/1 in fluorapatite. But the added calcium/ added phosphate/removed fluoride ratio has been 8.5/20.7/1 and 8.5/10.8/1 respectively in the lab and field long term testing, where the very high removal was obtained. Thus both calcium and (in the field testing) phosphate are added at lower levels than required for production of fluorapatite. If fluorapatite crystal growth is the mechanism behind contact precipitation it can not be the only one. Probably some of removal is taking place as a precipitation of calcium fluoride.

The contact precipitation method seems to be most promising, especially because it is environmentally safe, socially acceptable, economically affordable, highly efficient and reliable, without much need for skills and monitoring.<sup>8</sup> However, the challenge in its implementation remains to be at least two sided: motivation of users and availability of the chemicals at user points.

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