MODELING DEFLUORIDATION OF WATER IN BONE CHAR COLUMNS

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

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

INTRODUCTION

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

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

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

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

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MATERIALS AND METHODS

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

TABLE 1. Summary of Experimental Conditions

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

EXPERIMENTS:

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

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

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

PREPARATION OF BONE CHAR:

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

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

ANALYSES:

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

RESULTS

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

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

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

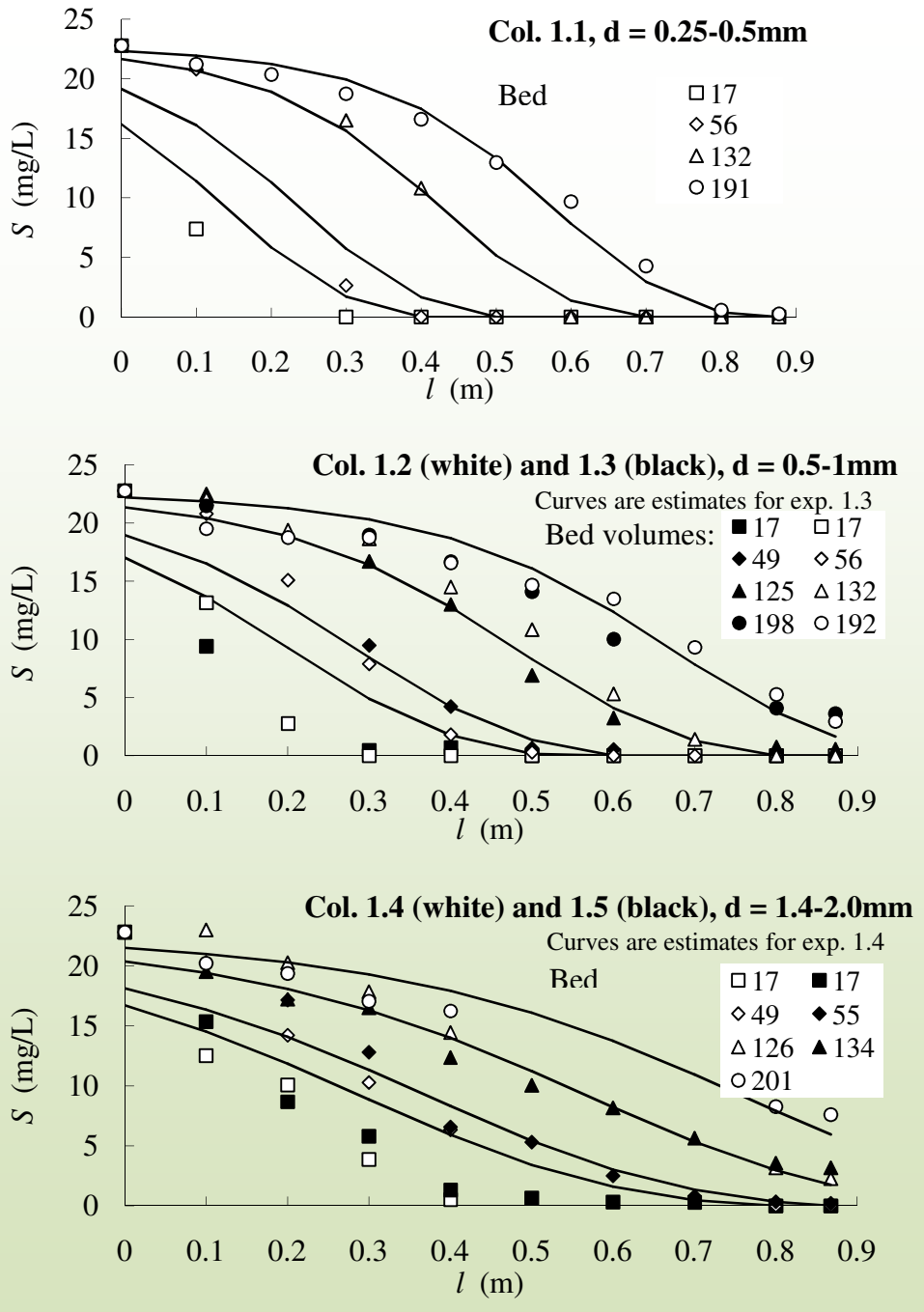

FIGURE 1. Measured fluoride concentrations in bone char columns 1.1-1.5 at different times and positions (dots). Experiments 1.2/1.3 and 1.4/1.5 are replicates. Profile curves are drawn from the estimated model parameters in table 1.

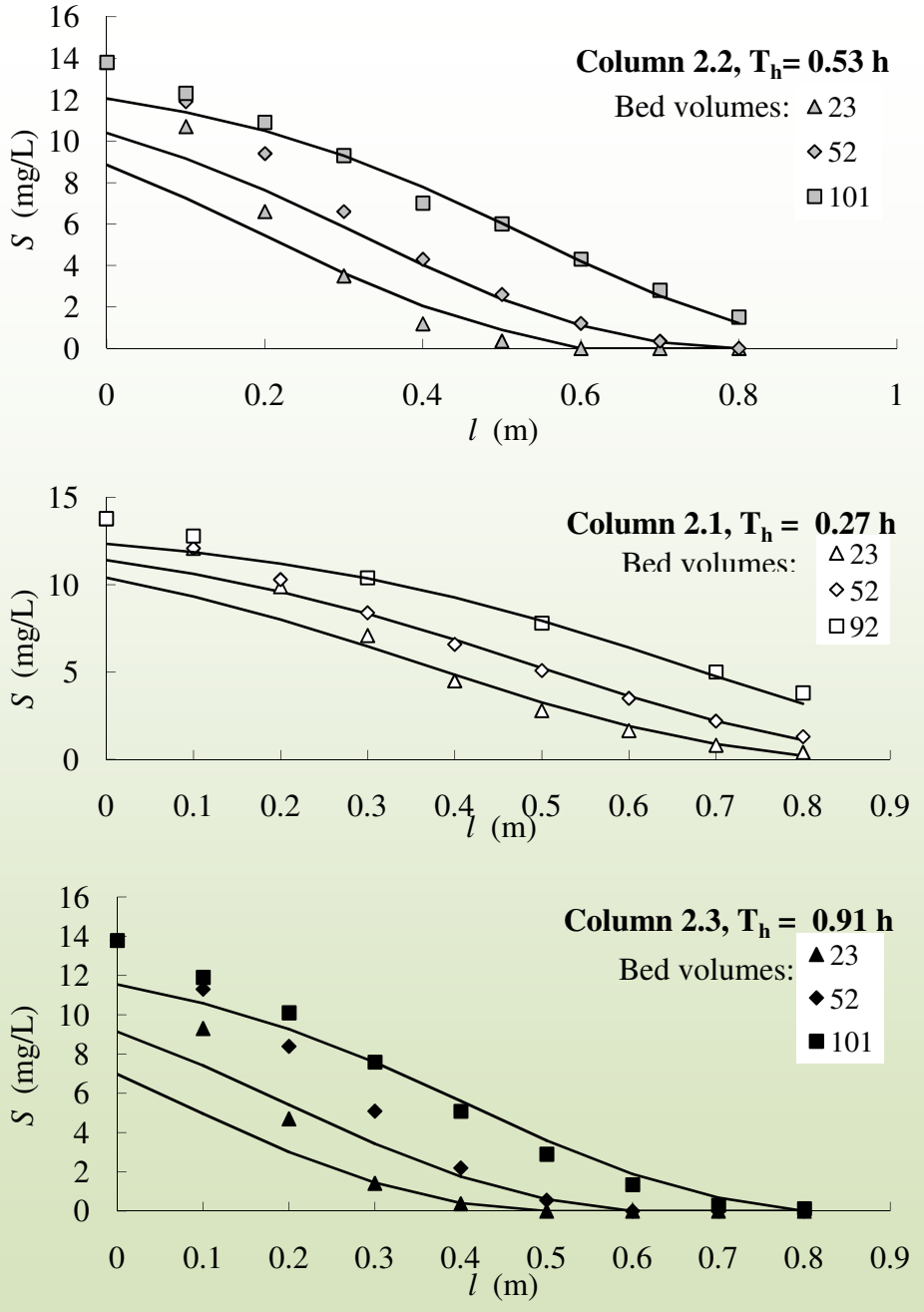

FIGURE 2. Measured fluoride concentrations in bone char columns 2.1-2.3 at different times and positions (dots). Profile curves are drawn from the estimated model parameters in table 1.

A KINETIC MODEL FOR FLUORIDE PROFILES IN COLUMNS:

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

$$\frac{dS}{dt} = -k \cdot X_{BC} \cdot \left(f_{m,b} - f\right) \cdot S \cdot t^{-0.5} \qquad \text{Eq. 1}$$

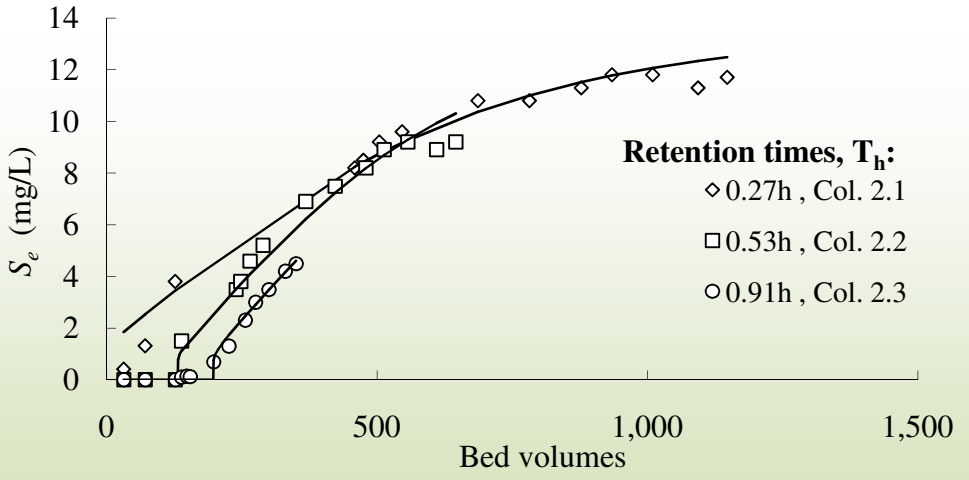

FIGURE 3. Measured fluoride concentrations in the effluent of bone char columns 2.1-2.3 at different times (dots). Breakthrough curves are drawn from the estimated model parameters in table 1.

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

$$\frac{dS}{dt} = -k \cdot X_{BC} \cdot \left(f_{m,f} - f\right) \cdot S \cdot \left(t - t_0(x)\right)^{-0.5} \qquad \text{Eq. 2}$$

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

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

IN = OUT + SORBED + ACCUMULATED

$$Q \cdot S = Q\left(S + \frac{\partial S}{\partial l} \cdot dl\right) + r \cdot A \cdot \varepsilon \cdot dl + \frac{\partial S}{\partial t} \cdot A \cdot \varepsilon \cdot dl$$

$$Q \cdot \frac{\partial S}{\partial l} + A \cdot \varepsilon \cdot \frac{\partial S}{\partial t} + A \cdot \varepsilon \cdot r = 0 \qquad \text{Eq.3}$$

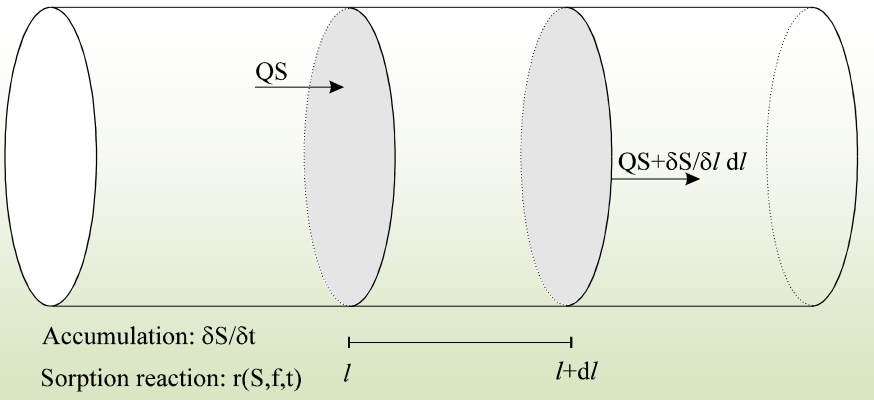

FIGURE 4. Fluoride mass flow in a bone char column

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

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

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

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

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

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

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

Where

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

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

ESTIMATION OF MODEL PARAMETERS FROM RESULTS:

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

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

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

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

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

TABLE 2. Estimated Model Parameters

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

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

Table 2 is a summary of the best fit values of the parameters estimated for each experiment. For experiments 1.1-1.5 and 2.1-2.3 the parameters are estimated from the sampling of the interior of the column. For experiment 2.1-2.3 additional

parameters are estimated from the breakthrough curves. The interior samplings are mainly (exp. 2.2-2.3) obtained before breakthrough, so there is a difference in time between interior and exterior sampling in the second series of experiments.

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

DISCUSSION

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

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

The two parameters t_1 and S_{min} have apparently no physical meaning, just emerging as necessary constants in the development of the flow kinetic model. The linear relation between t_1 and k are totally empiric, based on these few results. Further and more precisely performed experiments should show if this relation is valid, or other correlations can be established for t_1 and S_{min}.

Variation of Reaction Rate Parameter and Dynamic Capacity Parameter*:* It is shown in Table 2 that the k-values for the interior samplings of the two types of bone char apparently are higher for bone char 2 than bone char 1. This is in contrast with the conclusions from batch experiments, that obviously showed that bone char 2 is a poor quality field manufactured bone char.[5] Because k is correlated with t_1 this comparison cannot be made directly. More uniformly made experiments would apparently be necessary for comparison between two different bone chars, as e.g. exp. 1.1-1.5 can be used for comparison of the influence of different grain sizes.

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

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

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

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

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

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

Further comparisons of batch and flow experiments with the same bone char can show if there can be established a correlation between the *k* and f_m values in the two types of experiments (and general rules for t_1 and S_{min}). It will be a great advantage if a general batch test experiment can reveal kinetic constants usable in flow experiments and flow treatment plants, because batch experiments are much more simple to perform than flow experiments.

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

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

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

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

CONCLUSIONS

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

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NOTATION

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

Q	=	Water flow (L/h)
r	=	Reaction rate, = -dS/dt ($mg \cdot L^{-1} \cdot h^{-1}$)
S	=	Fluoride concentration in the water phase (mg/L)
S_0	=	Fluoride concentration in the raw water (mg/L)
S_{max}	=	Maximum acceptable fluoride concentration in treated water (mg/L)
S_{min}	=	Empirical model parameter, concentration defining the fluoride front (mg/L)
t	=	Time (h)
t_0	=	Time for fluoride front to reach position x (h)
t_1	=	Empirical Model parameter (h)
T_d	=	Daily filtration time (h)
T_h	=	Hydraulic retention time in the filter (h)
T_{OP}	=	Filter operation period (h)
T_{tot}	=	Total experimental time (h)
u	=	Contact time between fluoride and bone char = $t-t_0$ (h)
x	=	Hydraulic retention time corresponding to position on column = l/v_{lin} (h)
X_{BC}	=	Density / concentration of bone char in the filter (g/L)
v_D	=	Surface loading / Darcy velocity ($m^3\ m^{-2}\ h^{-1}$)
v_{lin}	=	Linear velocity of water = $v_D/$ (m/h)
BV	=	Bed volume of a bone char filter (L)
ε	=	Porosity measured in column

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