KINETICS OF UPTAKE OF FLUORIDE ON BONE CHAR IN BATCH

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SUMMARY: A new series of data concerning the uptake of fluoride on bone char were obtained from experiments using both a chemostat, maintained at a constant temperature and pH and a jar test apparatus. A model for the sorption kinetics is developed, based on first order reaction with respect to the deficit towards saturation and first order reaction with respect to the concentration of the fluoride in solution and the inverse square root of time. The model fits the data collected during this study as well as data taken from the literature. The kinetic pattern can be described completely, for any given dosage and initial fluoride concentration, by means of a dynamic capacity parameter, $f_{m,b}$, and the reaction rate parameter, k. Both are subject to considerable variation, $f_{m,b}$ between 0.8 and 5.6 mg/g, and k between 0.002 and 0.12 L mg^{-1} h$^{-0.5}$. A high dynamic capacity parameter would probably reflect proper bone charring independent of the grain size, while higher reaction rates are observed for smaller grain sizes.

Key words: defluoridation, bone char, batch, mathematical model, capacity, reaction rate.

INTRODUCTION

In spite of the facts that charred bone has been proposed as an agent for defluoridation of water more than five decades ago[1], that it has been used as such in water works in USA[2], and that it is one of the most promising defluoridating agents for use in developing countries[3], the basic batch kinetics of the fluoride uptake on bone char are yet to be established. A literature survey has revealed that only a few batch experiments have been reported. Some are carried out in shaken containers[4,5], others in jar test apparatus where the paddle stirring is assumed to be more reproducible.[6,7] Whatever experimental setup, the results, which are often shown as fluoride concentration versus time, seem to have deviating patterns. Some show that the fluoride uptake is very fast in an initial phase, followed by a second phase of slow reaction.[4,6] Others show a relative continuous pattern.[4] In some cases the uptake is still going on even after one week of observation time[5], in others the curve is illustrated to be brought to an equilibrium within few hours.[6,7]

It is therefore not surprising that establishment of mathematical models to describe the uptake kinetics on bone char materials has been difficult. It is natural to consider similar studies of fluoride uptake on other hydroxyapatite (HAp) materials like bone meal[8], dental enamel[9] and synthetic Hap.[10-12] If such studies are considered, three different models may be distinguished:

- Larsen[9], using dental enamel, and Bhargava and Killedar[6], using bone char, describe the uptake as a simple first order process kinetics with respect to the fluoride concentration in water, that is:

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$$\frac{dS}{dt} = -k_1 \cdot S \qquad \text{Eq. 1}$$

- Christoffersen *et al.*[11], using synthetic HAp, describe the uptake as first order with respect to the fluoride concentration in water and first order with respect to the fluoride saturation deficit in HAp, that is:

$$\frac{dS}{dt} = -k_1 \cdot X_{BC} \cdot (f_{m,b} - f) \cdot S - k_2 \cdot X_{BC} \cdot f \qquad \text{Eq. 2}$$

- Bhargava and Killedar[6], without introducing the (differential) rate equation, describe the uptake on bone char as an (integrated) empirical equation dependent on two parameters a and b:

$$S = S_0 \cdot (1 - \frac{t}{a + b \cdot t}) \qquad \text{Eq. 3}$$

In this model a and b are derived as mathematical functions of the initial fluoride concentration, S_0, and the initial bone char dosage, X_{BC}, plus not less than six different rate constants, which have to be determined empirically.

In addition to the above mentioned models, the authors tested, among others, a "semi-infinite linear diffusion model" used by Stumm[13] for diffusion limited sorption in porous media in general, where the uptake is proportional with not only S and X_{BC} but also the reciprocal of square root of contact time:

$$\frac{dS}{dt} = -k_1 \cdot X_{BC} \cdot S \cdot t^{-0.5} \qquad \text{Eq. 4}$$

The tested models, fit some of the data collected as part of this study very well, but none of them seem to fit in general for all different experimental conditions and results obtained. This is in agreement with Gasser *et al.*[12], who concluded that the uptake of fluoride on HAp can not be described by a simple function if different series and experimental conditions are included.

The objectives of this paper is to present a new series of sorption data and to present a model for the kinetics of fluoride uptake on bone char as obtained in these experimental series as well as in series carried out by other workers.

MODEL DESCRIPTION

The idea of this model development is to describe the change of the fluoride concentration in water in batch as a function of time by means of an explicit mathematical equation, including as few as possible experimental variables and rate parameters. The model should be applicable for drinking water treatment, as it may take place in fluoride affected areas in developing countries, without any use of advanced characteristics of media like for example bulk density, bulk porosity, grain size, grain size uniformity, particle spherity, surface area and porosity. It was also set as a precondition that the model should fit the data collected in this study as well as data given in selected literature.

Using a trial and error approach considering many different models, both some reviewed in this paper and some not, the following differential equation was developed and adopted:

$$\frac{dS}{dt} = -k_1 \cdot X_{BC} \cdot (f_{m,b} - f) \cdot S \cdot t^{-0.5} \qquad \text{Eq. 5}$$

As f is the concentration of fluoride uptaken in the bone char and $f_{m,b}$ is a measure of the maximum concentration of possible uptake, ($f_{m,b}$ - f) would represent a deficit towards saturation of the bone char. $X_{BC}\cdot(f_{m,b}$ - f) is thus the total potential uptake per volume of batch. So far the equation may be accepted logically and considered as a modification of Fick´s law for diffusion quite similar to the normal uptake of gasses in liquid media.[14]

This part of the equation expresses that the rate of fluoride uptake is first order with respect to the fluoride concentration in the water, S, as well as first order with respect to the deficit of saturation of bone char, $X_{BC}\cdot(f_{m,b}$ - f). However, when testing the data it was found inevitable to attach the inverted square root time function $t^{-0.5}$. This term seems to be necessary to get an acceptable model fit to the data, not only to the fluoride uptake on bone char but also to its uptake on other media and in many other diffusion limited processes.[13]

Assuming that the initial concentration of fluoride in the bone char is negligible, that is $f_0 = 0$, f may at any time be given as $f = (S_0\text{-}S)/X_{BC}$. By substitution into equation 5 and integration of the equation, the concentration of fluoride in the water is given as a simple function of time:

$$S = \frac{X_{BC} \cdot f_{m,b} - S_0}{\frac{X_{BC} \cdot f_{m,b}}{S_0} \cdot e^{2(X_{BC} \cdot f_{m,b} - S_0) \cdot k \cdot t^{0.5}} - 1} \qquad \text{Eq. 6}$$

Thus the S-t curve of uptake of fluoride is characterised for a given dosage of bone char, X_{BC}, and a given initial fluoride concentration, S_0, by the means of only two parameters $f_{m,b}$ and k, where $f_{m,b}$ is a dynamic capacity parameter and k is a reaction rate parameter.

MATERIALS AND METHODS

Two types of experiments were carried out, one using a chemostat regulated at constant temperature and pH and the other using a jar test apparatus.

pH-chemostat. Batch experiments were carried out in 1-L plastic beakers in a water bath thermostated at 25°C. The beakers contained 1 L of NaF-solutions in distilled water at different given initial concentrations. The solutions were kept stirred using a paddle rotating at 100-150 revolutions per minute (rpm). The speed was adjusted in order to keep the bone char particles evenly suspended in the solution. The bone char was added at time zero in different given dosages. The control for this set of experiments contained no bone char. The concentration of fluoride and pH in the water were monitored continuously by potentiometric measurements. Experiments were run for 5-10 hours. The pH were kept constant using a Metrohm system of pH-

meter 691, Impulsomat 614 and Dosimat 715. The pH of these systems was adjusted using a 0.25 M HNO_3 solution. Each experiment was carried out in 2-4 replicates.

Jar test experiments. Experiments were carried out in 1-L glass beakers, using a Jar test apparatus (Phipps & Birds Stirrer 7790-402). Each of the six beakers was filled with 1 liter of naturally occurring spring water from the Ngurdoto National Park pumped directly to the Defluoridation Research Station in Arusha, Tanzania. The water had a pH of 8.2 and a fluoride concentration of 21 mg/L and total alkalinity of 6.7 meq/L. Stirring was carried out at 25 rpm, just enough to keep the water totally mixed without moving the bone char particles. The bone char was added at time zero in different given dosages. The control for this set of experiments contained no bone char. Five mL samples were taken at the different given times for filtration and fluoride measurement. These experiments were run for 4 hours.

Bone char preparation. In the *chemostat experiments* a mixture of various farm animals bones and teeth were used. The bone materials were delivered from the Danish bone meal and animal feed industry 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 (Scandia-Ovnen AS SK 35 S). The temperature was gradually raised at a rate of 2°C/min from room temperature to 500°C, and then kept constant for 2 hours. The oven was then allowed to cool down during overnight to ambient temperature before opening. The bone char was ground further in a plate crusher and sorted out in a test sieve shaker (Endecotts LTD EFL2 mk3). The grain size, d_h < 45µm, was used in the experiments. The specific surface was tested according to BET method and found to be 69±3 m^2/g, for particles of both $d < 0.053$ mm and $0.3 < d < 0.6$ mm, that is independent of the grain size.

In the *jar test experiments* rib bones from goats and sheep grown up 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 can 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 temperatures were 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 3 fractions to grain sizes of $d_h < 0.2$ mm, 1.2-2-mm and 3-4-mm.

Fluoride & pH-measurements. The fluoride concentrations were measured directly in the water using a Radiometer F1052 fluoride electrode and Metrohm Ag/AgCl reference electrode with sleeve type diaphragm connected to a Metrohm 691 pH-meter. Every one hour 5-ml samples were taken, filtered through 0.45 µm membrane filters (Schleider & Schuel) and measured for fluoride contents after addition of TISAB, according to Standard Methods.[15]

pH were measured according to Standard Methods[15] using a Metrohm combined glass electrode in connection with the above mentioned pH-meter.

RESULTS

Experimental results. The results from the pH-chemostat series of experiments are shown as discrete points in Figure 1a for initial fluoride concentrations of 10 mg/L

and bone char dosage, X_{BC}, of 1-, 2-, 3- and 4-g/L, and in Figure 1b for initial fluoride concentrations of 20 mg/L and bone char dosage of 2-, 3- and 4-g/L.

The results from the jar test series of experiments are shown as discrete points in Figure 2a for bone char grain size < 0.2 mm, the dosage being 3.55, 7.0, 13.0 and 32.5 g/L.

Figure 2b shows the results from the similar experiments, where bone char of grain size 1.2 - 2 mm was used, the dosage being 5.6-, 11.2-, 20.8- and 32.5-g/L. Figure 2c show the results from the similar experiments, where bone char of grain size 3-4-mm was used, the dosage being 8.5-, 16.9-, 31.2- and 78-g/L. The initial fluoride concentration in all jar test experiments is 21.0 mg/L.

Model Simulations. The dynamic capacity parameter $f_{m,b}$ and the reaction rate parameter k may be estimated by means of non-linear regression. This is carried out by computer iteration, using a function which minimises the deviation between the measured data and the model calculated data (as sum of squares) by changing k and $f_{m,b}$. The parameters are listed in Table 1 for as well the series of this study as the series selected from reported studies.

Figures 1a-b & 2a-c, illustrate the model estimates of the uptake kinetics as curves, in comparison with the experimental data of this study. Similarly, Figure 3a-c illustrates the model estimates of the uptake kinetics as compared to the experimental data of selected reported studies. The kinetic parameters of these simulations are also presented in Table 1.

DISCUSSION

The two types of experiments represent different approaches. The pH-chemostat experiments being controlled in the laboratory, while the jar test experiments rather represent the field practise and the poor quality bone char. Yet, as seen in Figures 1a-b & 2a-c, the model seems to reproduce the trends of the experimental data very well.

Even when the literature data are taken into consideration, and thus including the broad variation of experimental conditions and charring techniques, the model seems to reproduce the trends of the experimental data surprisingly well. This is illustrated in Figure 3a-c.

Based on this it seems feasible to use $f_{m,b}$ quantitatively first and foremost as a parameter for characterization of the bone char capacity to uptake the fluoride. Moreover, to use k quantitatively first and foremost for characterization of the reactivity of the bone char as well as experimental setup, including the influence of grain size, the temperature, the intensity of mixing and of the water quality in the batch system.

From Table 1 it may be seen that $f_{m,b}$ is subject to considerable variation, between 0.8 and 5.6 mg/g. Especially the data of Larsen *et al.*[5] and Bhargava and Killedar[6] illustrate that $f_{m,b}$ is very much dependent on the heating procedure used for bone char preparation. The low sorption capacities encountered is probably a direct result of destructive charring. Also with the data of this study $f_{m,b}$ seem to vary between 2 mg/g for the jar test experiments, where pH is 8-9 and 5.6 mg/g for the chemostat experiments where pH is controlled to 7. Probably the bone char preparation is, at least in part, responsible for these discrepancies.

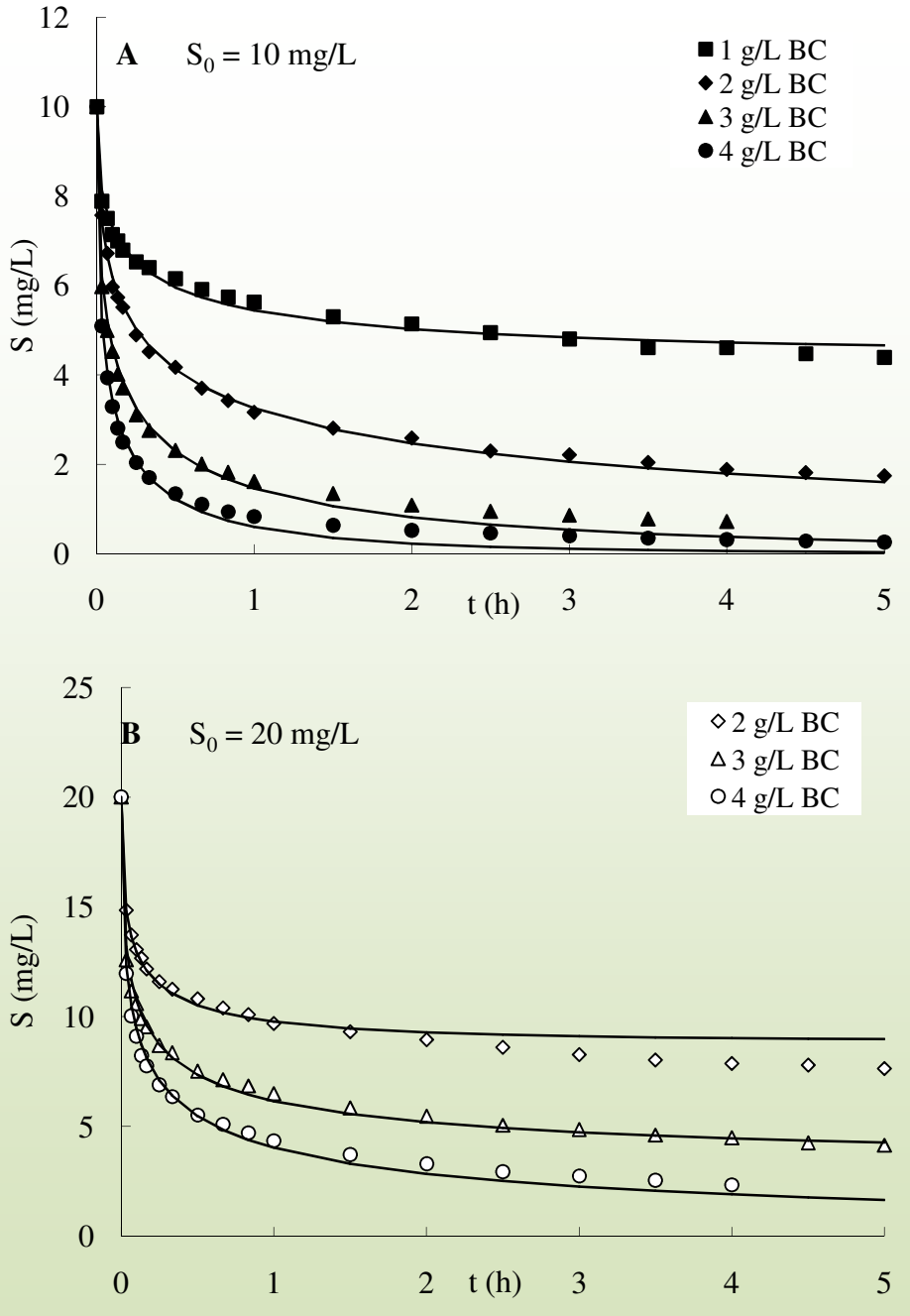

FIGURE 1A & 1B. Fluoride uptake on bone char in batch chemostat, pH is kept at 7.0. Initial fluoride concentrations and dosages are indicated. The experimental results are shown as discrete symbols, while the curves are generated by the model for best estimates of $f_{m,b}$ = 5.6 mg/g and individual k for the different series, see Table 1.

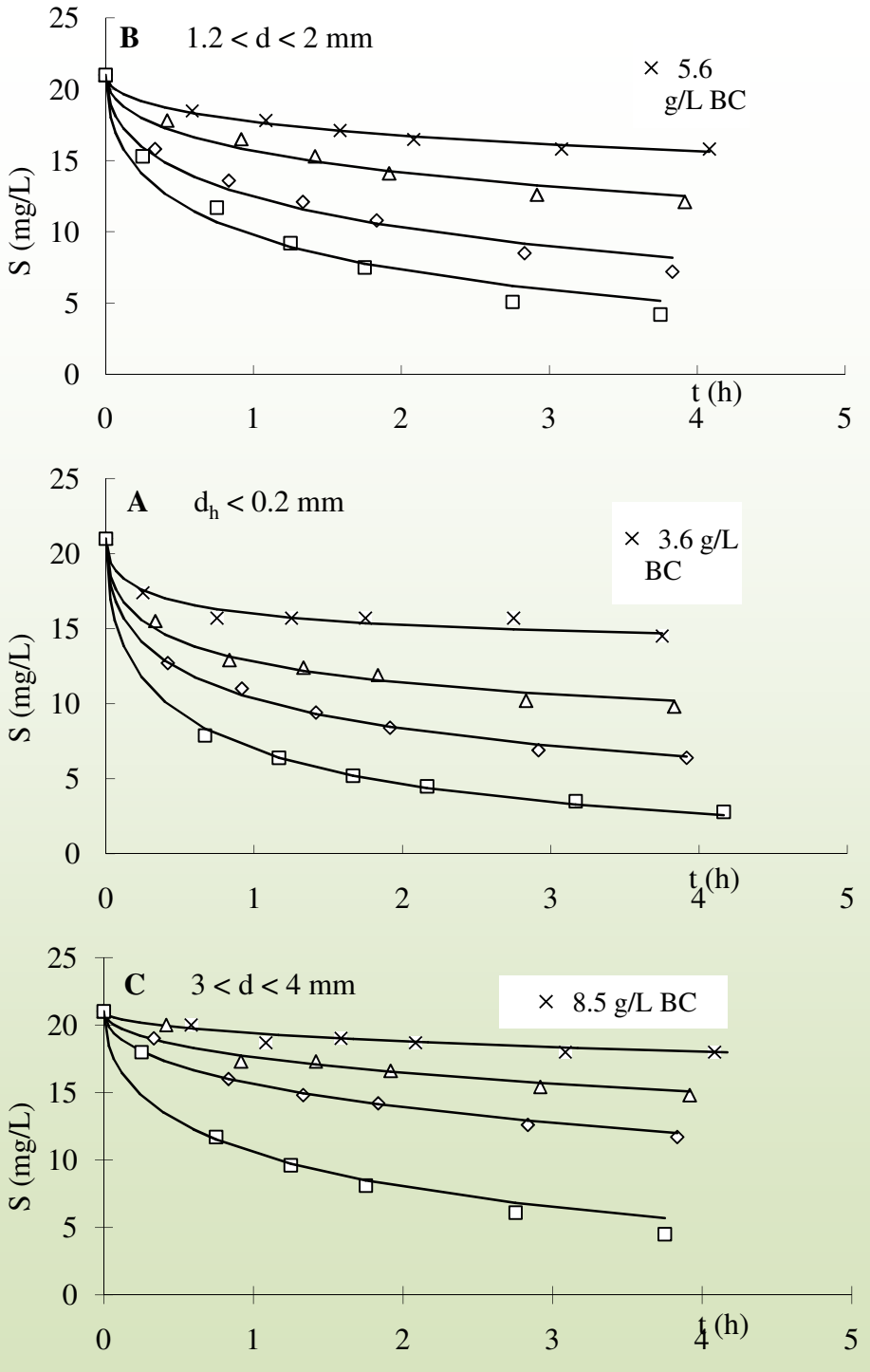

FIGURE 2A-C. Fluoride uptake on bone char in jar test experiments with gentle stirring (25 rpm) S_0= 21 mg/L. Dosages of bone char and the grain sizes are indicated. The experimental results are shown as discrete symbols, while the curves are generated by the model for best estimates of $f_{m,b}$= 2.0 mg/g for all series and individual k for the different series, see Table 1.

TABLE 1. Estimated k's and fm,b's in pH-chemostat and Jar test experiments of this study in comparison with selected data from the literature.

Experiment type	Charring	S_0 (mg/L)	X_{BC} (g/L)	d (mm)	Period (h)	$f_{m,b}$ (mg/g)	k $L \cdot mg^{-1} \cdot h^{-½}$	Ref
Chemostat 100-150 rpm	550 °C 2 h	10	1	<0.045	0-5	5.6	0.12	
			2				0.09	
			3				0.09	
			4				0.09	
		20	2				0.10	
			3				0.09	
			4				0.075	
Jar test 25 rpm	Ca. 600°C 0.5 h Kerosene cooker	21 Natural water source	3.55	< 0.2	0-4	2.0	0.036	
			7				0.028	
			13				0.018	
			32.5				0.010	
			5.6	1.2-2.0			0.0087	
			11.2				0.0076	
			20.8				0.0072	
			32.5				0.0067	
			8.5	3-4			0.0027	
			16.9				0.0028	
			31.2				0.0025	
			78				0.0023	
Gently shaken containers	400°C, 1 h	10	2.5	0.1-1.5	0-144	6.37	0.009	9
	400°C, 4 h					4.24	0.024	9
	550°C, ½ h					2.84	0.023	9
	550°C, 4 h					1.76	0.030	9
	550°C, 48h					0.81	0.018	9
Agitated containers	350 °C	200	50	< 0.42	0-8	3.98	0.008	4
				1.2 - 2.1			0.0012	4
				3 - 5			0.0009	4
Jar test 100 rpm	1000°C 2 h	10	4	0.09- 0.125	0-9	2.51	0.021	6
				0.125- 0.18			0.010	6
				0.18- 0.355			0.008	6
				0.355 - 0.6			0.007	6
				0.6 - 0.85			0.005	6

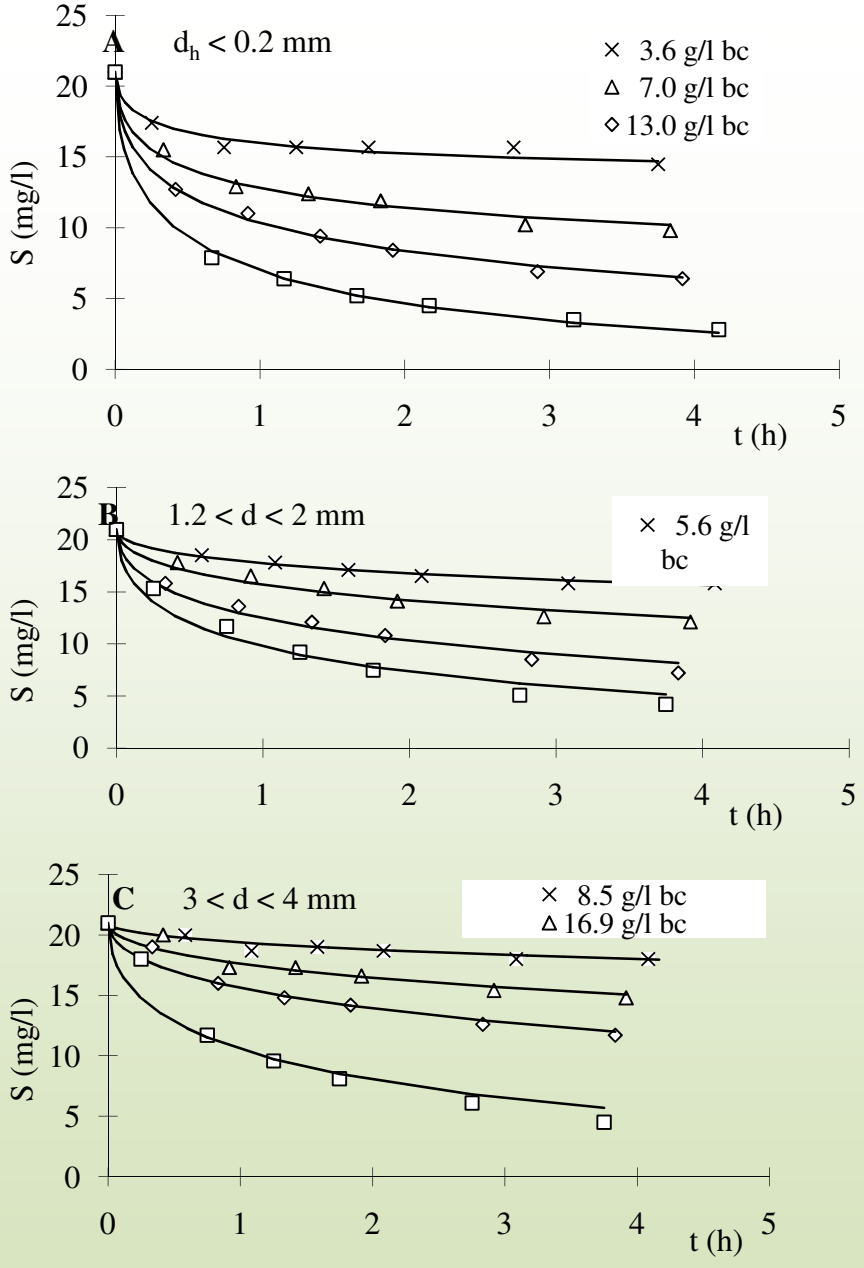

FIGURE 3A-C. Fluoride uptake on bone char as reported by A: Larsen et al.[5], B: Mwaniki[4], and C: Bhargava and Killedar[6]. Dosage of bone char are A: 2.5 g/L, B: 50 g/L and C: 4 g/L, and the utilized grain size A:0.1-1.5 mm, B & C: indicated. The experimental results are shown as discrete symbols, while the curves are generated by the model for best estimates of fm,b= A:0.8-6.4, B:4.0 and C:2.5 mg/g and individual k for the different series.

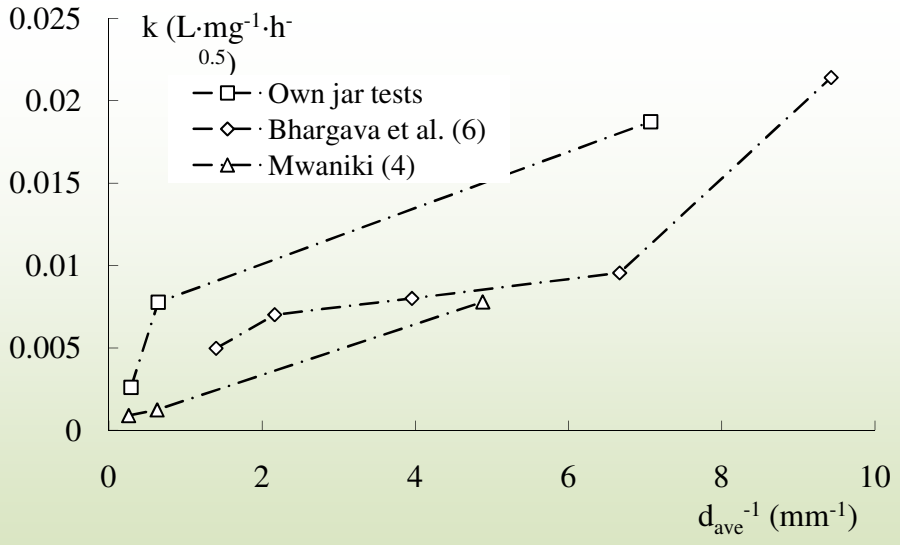

FIGURE 4. Variation of the reaction rate parameter k as a function of the reciprocal average grain size. Estimates are made from our own jar test experiments (average for each grain size) and results from the literature[4,6]. Values are from table 1.

It must be mentioned that experiences gained in our laboratory indicate very clearly that charring at 350°C may result in high or even highest possible fluoride removal capacity, but is not sufficient for the removal of bad taste and colour given by residuals in the bone char. Moreover, that the use of extremely high dosages of bone char and high concentration of fluoride may favour the precipitation of calcium fluoride in comparison with the fluoride sorption taking place in normal water treatment. It is worth noticing that the dynamic capacity parameter is almost totally independent of the grain size of the bone char.

This is in the line with the results given by Mwaniki[4], where the capacity of the bones are relatively preserved during the low temperature used for charring. Also that the capacity parameter is of the same order of magnitude, in spite of the fact that Mwaniki[4] utilises extremely high fluoride concentrations and correspondingly high dosage of bone char.

Reaction Rate Variation. From Table 1 it is seen that the rate parameter variation is subject to even wider variation than observed by $f_{m,b}$, the estimated k´s are between 0.0009- to 0.12-L mg^{-1} $h^{-0.5}$. The rate parameter is low for bone char heated at too high temperature, cf. data of Bhargava and Killedar[6], and for bone char of gross grain size. In contrast to the dynamic capacity, the reaction rate parameter is observed to be very much dependent on the grain size, the smaller the grain size, the higher is the reaction rate parameter, Figure 4.

The grain size for a fraction of bone char is normally given as an interval between the size of the sieve opening which retain the smallest grains (d_l), and the size of the sieve opening which all the grains have passed (d_h). In some cases, for the finest fraction, the grain size is given as < d_h. From the assumption that the grain size in any sample is logarithmically normal-distributed, an average grain size in a fraction can be calculated as $d_{ave} = (d_l\, d_h)^{½}$.

When the grain size is given as < d_h this definition does not apply. However, in this case, for d_h < 0.2 mm, an arbitrary value of $d_{ave} = (0.1 \cdot 0.2)^{½} = 0.14$ mm has been applied. The data are seen in Figure 4. This Figure illustrates that the rate parameter varies almost directly proportional with the reciprocal of grain size. However, a mathematical relationship is not established as the grinding process, the grain fractioning and the determination of the grain size are all subject to high variation.

The reaction rate to grain size relationship is in agreement with the findings in the studies of Bhargava and Killedar[6] and Mwaniki.[4] Moreover, this study indicates that dynamic capacity parameter $f_{m,b}$ of the bone char can not be directly related to the reaction rate. Thus the capacity of the different grain size fractions of a given batch of bone char may be of the same order of magnitude in spite of the fact that the reaction rate for the different fraction is higher the smaller is the grain size.

In order to describe the kinetic properties of the bone char with respect to uptake of fluoride from water, it seem most appropriate to use the dynamic capacity and the rate reaction parameters as these would reflect the complete sorption pattern.

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LIST OF SYMBOLS

a,b	Reaction constants in eq. 3
d	Grain size of a bone char sample, (mm (interval))
d_{ave}	Average grain size of a bone char sample, (mm)
d_l	Size of sieve opening retaining a bone char sample, (mm)
d_h	Size of sieve open. just allowing the bone char sample to pass, (mm)
f	Fluoride concentration in the bone char, (mg/g)
f_0	Fluoride concentration in the bone char at t=0, (mg/g)
$f_{m,b}$	Capacity parameter for fluoride uptake on bone char, (mg/g)
k	Reaction rate parameter, (L mg^{-1} $h^{-0.5}$)
k_1,k_2	Reaction rate constants in eq. 1, 2, and 4
S	Fluoride concentration in the water phase, (mg/L)
S_0	Fluoride concentration in the water phase at t = 0, (mg/L)
t	Time, (h)
X_{BC}	Dosage of bone char, (g/L)

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