KINETICS OF DEFLUORIDATION OF WATER BY CALCINED MAGNESIA AND CLAY

E Dahi*, J J Singano**, and J M Nielsen*

SUMMARY: Series of fluoride removal by means of calcined magnesite are obtained from Jar test experiments. The model developed by Bregnhøj and Dahi[1] is tested on these results and on experiments made by Bjorvatn and Bårdsen[2] using laterite. The model do not describe the results very well when using calcined magnesite, especially not for different grain sizes. The reaction rate parameter, *k*, varies between 0.00076 and 0.0029 L/(mg·h$^{0.5}$) for a capacity, f_m, as high as 56 mg/g. This variation is probably because other processes than defluoridation are determining the kinetics, like the change of MgO into $Mg(OH)_2$. The model describes the laterite kinetics well, though it has some limitations in estimating both parameters if there is a big variation in the raw water quality. The f_m is estimated to 0.77 mg/g and *k* varies between 0.0031 and 0.0049 L/(mg·h$^{0.5}$) for humus containing laterite.

Key words: Defluoridation, magnesia kinetics, laterite kinetics, drinking water treatment, sorption capacity

INTRODUCTION

A model for describing the sorption kinetics on bone char in batch has been developed by Bregnhøj and Dahi.[1] This model is based on a first order reaction with respect to the deficit towards saturation and a first order reaction with respect to the concentration of fluoride in the solution and the inverse square root of time. The fluoride concentration in the water, *C,* is given as a function of time:

$$C = \frac{X \cdot f_m - C_0}{\left[\frac{X \cdot f_m}{C_0} \cdot \exp\left(2(X \cdot f_m - C_0) \cdot k \cdot t^{0.5} \right) \right] - 1}$$

The C-t curve can be characterised for a given dosage of sorbent, *X*, and a given initial fluoride concentration, C_0, by means of only two parameters, the dynamic capacity parameter f_m, and the reaction rate parameter *k*.

The objective of this paper is to estimate the model parameters, f_m and *k*, for defluoridation agents such as calcined magnesite, this study, and laterite with and without humus[2] and to elucidate whether the model is suitable for these materials.

MATERIALS AND METHODS

* Center for Developing Countries, Technical University of Denmark, Building 208, DK-2800 Lyngby, Denmark.

** Department of Civil Engineering, University of Dar es Salaam, P.O. Box 35131, Dar es Salaam, Tanzania.

The raw magnesite was crushed into small pieces and thereafter heated in an electrical oven. The temperature was raised with a gradient of 4°C per minute from room temperature to 750°C and kept constant for 4.5 hours.

he raw magnesite was crushed into small pieces and thereafter heated in an electrical oven. The temperature was raised with a gradient of 4°C per minute from room temperature to 750°C and kept constant for 4.5 hours.

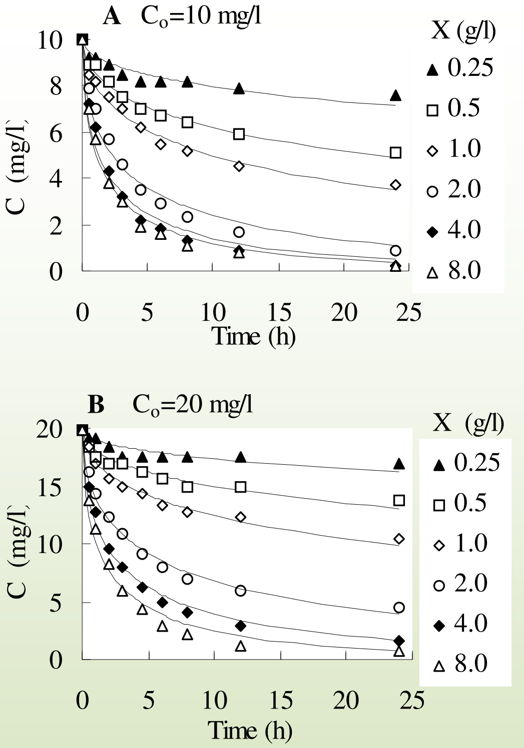

FIGURE 1. Fluoride concentration in water in Jar test experiments. Initial fluoride concentration and dosages of calcined magnesite are indicated and GS=0.25-0.5mm. The experimental results are shown as discrete symbols and the curves are best fit with f_m=56mg/g and individual k for each dosage, see Table 1.

The oven was allowed to cool to room temperature before opening. The calcined magnesite was sieved into different grain size fractions using an electrical shaker before the experiments were made.

The experiments were carried out in 1 L plastic beakers using a Jar test apparatus. Each beaker was filled with distilled water containing NaF equivalent to 10 and 20 mg/L F^-. Stirring was carried out at 45 rpm. The magnesia was added at time nil in different dosages and in different grain sizes. The experiments were run for 24 hours.

The fluoride concentration was measured using a Radiometer F1052 fluoride electrode and a Metrohm Ag/AgCl reference electrode with a sleeve type diaphragm connected to a Metrohm potentiometer. At given times 5 ml samples were taken and mixed with CDTA-Tisab before analysing for fluoride using the calibration method according to Standard Methods.[3]

RESULTS

The results from the Jar test experiment series are shown as discrete symbols in Figure 1a for an initial fluoride concentration of 10 mg/L using the grain size 0.25-0.50 mm, the dosages being 0.25, 0.50, 1.0, 2.0, 4.0, and 8.0 g/L. Figure 1b shows the results from a similar experiment where the initial fluoride concentration was 20 mg/L.

In Figure 2 the results of adding different grain sizes can be observed. The initial fluoride concentration was 19.6 mg/L and the dosage of calcined magnesite was 2.0 g/L. The models, estimated by the method of leat squares, are plotted as curves fitting the symbols in Figure 1 and in Figure 2. The estimated f_m and k values are shown in Table 1.

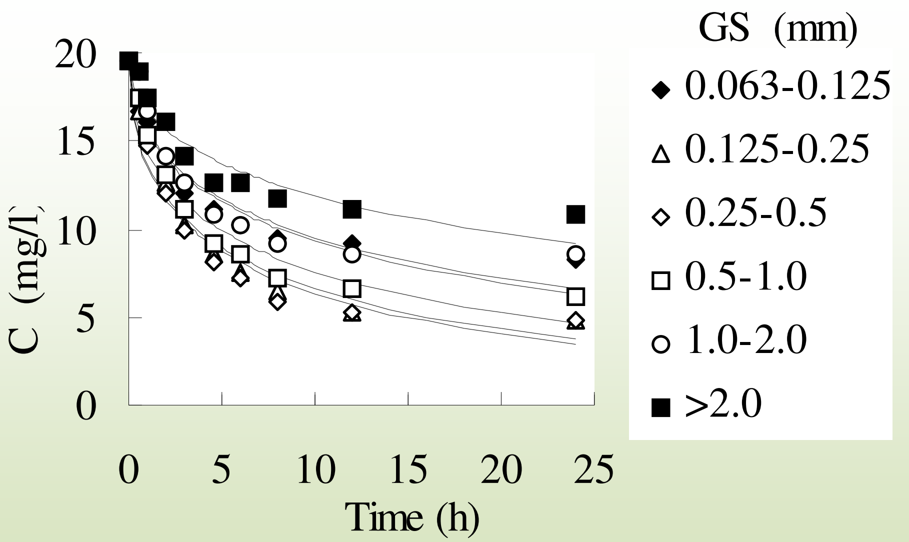

FIGURE 2. Fluoride concentration in water in Jar test experiments with C_0=19.6 mg/L and X=2.0 g/L. Grain sizes are indicated. Line and symbols like in Figure 1.

The method of least squares is also used to estimate the dynamic capacity parameter, f_m and the reaction rate parameter, k for the reddish clay laterite. The experiments are made by Bjorvatn and Bårdsen[2] and the results of the modelling can be seen in Figure 3 for laterite containing humus, and in Figure 4 for laterite without humus. The curves being the models estimates and the discrete symbols the measurements. The estimated f_m and k values for laterite with and without humus are shown in Table 1.

DISCUSSION

The two defluoridation agents, calcined magnesite and laterite, show very different capabilities in fluoride removal.

As seen in Figure 1 and Figure 3 and 4, the model seems to reproduce the experimental data well.

Magnesia Kinetics: Looking at the estimated model parameters in Table 1, the model is not that good. The reaction rate parameter, k, is subject to a wide variation, between

0.00076-0.0029 L/(mg·h$^{0.5}$) for C_0=10 mg/L, and between 0.00076-0.0018 L/(mg·h$^{0.5}$) for C_0=20 mg/L. Thus, the reaction rate parameter is in some way dependent on the dosage of magnesia.

The experimental results are shown as discrete symbols and the curves are best fit with individual f_m and k for each raw water, see Table 1.

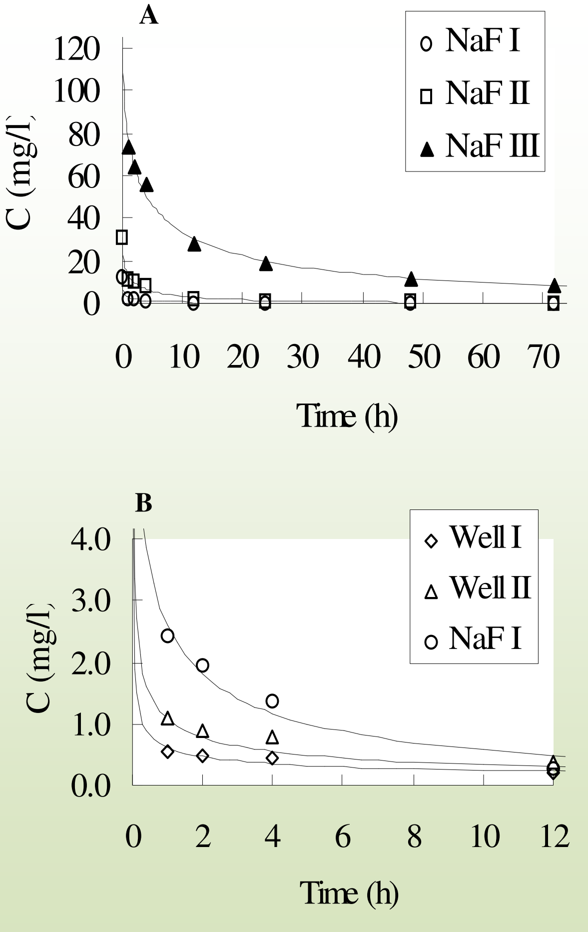

FIGURE 3. Fluoride concentration in water in Jar test experiments. The sample ID is indicated and the dosage of laterite without humus is X=100 g/L. The initial fluoride concentration is shown in Table 1.

The model does not fit the experimental results at all when using different grain sizes of calcined magnesite, as seen in Figure 2. The reaction rate parameter is varying between 0.00073 and 0.0017 L/(mg·h$^{0.5}$). Though, the capacity parameter f_m is indicating that calcined magnesite is very effective in removing fluoride from drinking water. The sorption capacity is high, approx. 56 mg/g compared to bones where f_m is 5.6 mg/g.

Laterite Kinetics: The estimated models reproduce the experimental data very well, both the data using laterite with humus and laterite without humus. The capacity parameter f_m is 0.77 mg/g for laterite containing humus and the reaction rate parameter, k, varying between 0.0031 and 0.0049 L/(mg·h$^{0.5}$).

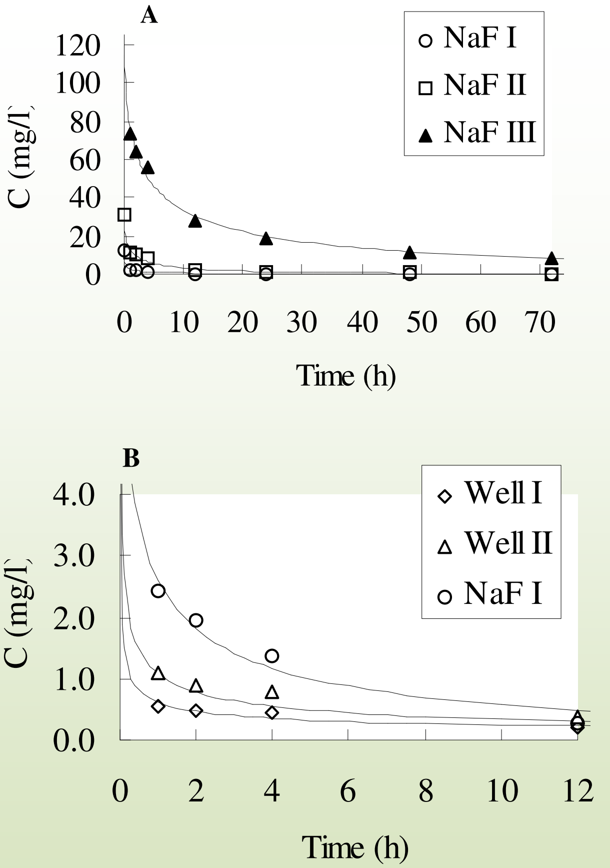

Figure 4 Fluoride concentration in water in Jar test experiments. The sample ID is indicated and the dosage of laterite without humus is X=100 g/L. The initial fluoride concentration is shown in Table 1. The experimental results are shown as discrite symbols and the curves are best fit with individual f_m and k for each raw water, see Table 1.

The variation in k is probably due to the wide variation in the initial fluoride concentration and the variation in the raw water quality, as sample "Well I- II" is Norwegian groundwater and "NaF I-III" is distilled water added sodium fluoride.

The estimated model parameters, f_m and k, for laterite without humus vary a lot (Table 1). The reaction rate parameter varies between 0.0017 and 0.80 L/(mg·h$^{0.5}$), and the capacity parameter between 0.054 and 1.95 mg/g. The estimated model parameters for laterite without humus are even more sensitive to the variation in raw water quality and the initial fluoride concentration than the estimated parameters for laterite containing humus. It seems like there is a relation between f_m and k, increasing f_m results in decreasing k.

TABLE 1. Estimated k and f_m values in Jar test experiment using calcined magnesite (this study) and laterite with and without humus[2] as defluoridation agent.

Defluoridation agent	Sample ID	C_0 mg/L	X g/L	GS mm	f_m mg/g	k L/(mg·h^{½})	Reference
Magnesia	-	10	0.25	0.25-0.50	56.0	0.0028	This study
			0.5			0.0029	
			1.0			0.0021	
			2.0			0.0021	
			4.0			0.0014	
			8.0			0.00076	
Magnesia	-	20	0.25	0.25-0.50	56.0	0.0017	This study
			0.5			0.0018	
			1.0			0.0014	
			2.0			0.0016	
			4.0			0.0012	
			8.0			0.00076	
Magnesia		19.6	2.0	0.063-0.125	56.0	0.0011	This study
				0.125-0.25		0.0017	
				0.25-0.50		0.0017	
				0.50-1.0		0.0014	
				1.0-2.0		0.0011	
				>2.0		0.00073	
Humus containing laterite	Well I	5.42	100		0.77	0.0044	2
	Well II	7.75				0.0049	
	NaF I	12.1				0.0036	
	NaF II	29.7				0.0033	
	NaF III	120				0.0031	
Laterite containing no humus	Well I	5.47	100		0.054	0.80	2
	Well II	7.75			0.079	0.37	
	NaF I	12.2			0.14	0.10	
	NaF II	31.2			0.56	0.010	
	NaF III	132			1.95	0.0017	

CONCLUSION

The model developed by Bregnhøj and Dahi[1] is better for describing uptake of fluoride on clay than on calcined magnesite. This is probably due to the fact that when dealing with calcined magnesite, the processes involved are not only uptake of fluoride, but also dissolution of MgO.

k is the parameter for quantitatively characterisation of the reactivity of the agent as well as experimental set-up, including grain sizes, temperature, mixing velocity and water quality. Using magnesia the model parameter *k* is not constant, even though the experimental set-up is the same for the results presented in Figure 1.

The model also has some limitations in estimating the model parameters when using clay. Very different raw water qualities, like different initial fluoride concentrations result in a wide variation in both f_m and *k*.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge K. Bjorvatn and A. Bårdsen, Faculty of Dentistry, University of Bergen, Norway for the contribution of data to the laterite kinetics.

REFERENCES

1. Bregnhøj H, Dahi E. Kinetics of Uptake of Fluoride on Bone Char. Proceedings of the First International Workshop on Fluorosis and Defluoridation, Ngurdoto, Tanzania, 1995.
2. Bjorvatn K and Bårdsen A. Use of Activated Clay for Defluoridation of water. Proceedings of the First International Workshop on Fluorosis and Defluoridation, Ngurdoto, Tanzania, 1995.
3. Standard Methods. Standard Methods for the Examination of Water and Wastewater. AP Health Association, 18th ed., Washington 1992, ISBN 0-87553-207-1.