KINETICS OF SORPTION OF FLUORIDE ON CALCINED MAGNESITE IN BATCH

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SUMMARY: A series of sorption of fluoride on calcined magnesite are obtained from thermostatic pH-chemostat and jar test experiments. The fluoride removal is observed not to start instantly, as normal, but after a lag time of up to ½ an hour of contact time. A model for sorption kinetics is developed, based on first-order reaction with respect to the concentration of fluoride. The rate constant is directly proportional to the dosage. The model takes into accounts the lag time observed. The kinetical model can be described for any given dosage and initial fluoride concentration in the water. The reaction rate parameter, K, varies however slightly for different initial concentrations of fluoride in the water and different dosage of calcined magnesia. These relationships are described separately by two linear equations. It is discussed that the observed lag time is due to the fact that magnesia cannot remove fluoride without hydrolysis, and it is probably this hydrolysis which constraint the start of the removal.

Key Words: Fluoride Removal; Defluoridation; Drinking Water Treatment; Sorption Kinetics; Magnesite; Calcination; Modelling.

INTRODUCTION

The use of drinking water containing fluoride at high levels, which affect the public health, is a serious problem for communities in fluorotic areas in many developing countries. A number of defluoridation methods have been developed and tested.[1] These include the bone char, the contact precipitation, the Nalgonda technique, the activated alumina and the clay sorption techniques, just to mention the prominent ones. This paper presents the kinetical aspects of defluoridation by means of calcined magnesite.

Already in the 1930´s the magnesium oxide, i.e. calcined magnesia, has been proposed for the removal of fluoride from drinking water.[12] Though it has not been successfully implemented so far, the calcined magnesia is one of the most promising defluoridating agents, especially in countries like Tanzania, where magnesite can be harvested from locally available mines.[2-6]

In spite of reported high fluoride removal capacity,[6] the basic batch kinetics of the fluoride uptake by magnesia has not been established yet. A literature survey has revealed that only a few batch experiments using jar test apparatus have been reported.[3,5,7] In most cases the results show the fluoride concentration versus time. Apparently there is no correlation between the surface area of the calcined magnesite and the fluoride removal capacity.[3,7] There seems to be a correlation between the dosage of calcined magnesite and the fluoride removed from the water.[3] Some results show that the fluoride uptake, for a dosage of 2 g/L, initial concentration of 20 mg/L and after a contact time of 12 hours, is almost negligible for smaller particle media, 0.063 mm, meanwhile there is a substantial fluoride uptake by bigger grain particle media, even up to 24 hours.[3] One of the developed models predicts that fluoride uptake is a slow and a continuous process which is taking place even after a contact time of 52 hours for dosage of 7.0 g/L, initial fluoride concentration of 20 mg/L and grain size of 2.0-4.0 mm.[5] On the contrary, another model predicts that the equilibrium concentration in the aqueous phase would be achieved after a contact

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time of 15 hours with varying sorption constant K for dosage of 8.0 g/L, initial fluoride concentration of 20.0 mg/L and grain size of 0.25-0.5 mm.[3] The magnesia used in these studies, i.e. Nielsen[3] and Jackson and co-workers[5] was calcined at 700°C for a duration of 4.5 hours.

An advanced mathematical model was developed by Bregnhøj and Dahi[9,10] to describe the uptake kinetics on bone char media. The model was tested for validity on calcined magnesite, but it was concluded that it does not fit well.[8] The reaction rate parameter, K, varied between 0.00076 and 0.0029 L/(mg.h$^{0.5}$) for a capacity, f[*] as high as 56 mg/g.[8]

The objective of this paper is to present a new series of sorption data and to propose a more-simple model for kinetics of fluoride uptake by calcined magnesite in agreement with the obtained experimental data.

MATERIALS AND METHODS

Two types of experiments are carried out; one using jar test equipment and another using a chemostat regulated at constant temperature and pH.

Preparation of Magnesia. Magnesite was collected 230 km east of Arusha town at Chambogo mines in Same district, the Kilimanjaro region in northern part of Tanzania. The material was crushed to small grain sizes of 0.063 - 2 mm on an electrical crushing machine and then calcined in a furnace. The temperature was raised at a rate of 4°C per minute from room temperature to 700°C, and then kept constant for 4.5 hours. The oven was then allowed to cool to room temperature before opening. The electrical furnace used was of type Scandia micro programmable TC - 15/45 and of type Nabertherm, model L9/R. After calcination the magnesia was sorted out in a test sieve shaker type Endecotts LTD EFL2 mk3 and type Vibro (VM1) to different sizes fractions. The grain size 0.063 - 0.125 mm diameter was used. The specific surface area was tested according to BET method.

Jar test experiments. The jar test experiments were carried out by setting six 1 litre beakers each containing equal quantity of raw water under a stirring paddle. The jar test apparatus was of type Phipps and Birds Stirrer 7790-402. Two different series of experiments were made. The first set of experiments was made using a constant initial fluoride concentration of 20 mg/L for different dosage of 0.5 - 4 g/L. The second set was made at constant dosage of 0.5 g media per litre for different initial fluoride concentrations of 5 - 31 mg/L. Stirring was carried out at 25 RPM. Five mL samples were taken at the different contact times, up to 6 hours. The samples were filtered through 0.45 μm membrane filters from Schleider and Schuel, before measurement of the fluoride concentrations.

pH-chemostat. The chemostat experiments were carried out using a Dosimat 715, 614 Impulsomat, Water-bath themostated at 25°C type Julabo U3, two 691 pH Meters Metrohm type, burettes, multiple stirrer, 1 litre beaker, pH and fluoride electrodes. The pH was kept constant at 10.5 at different given initial fluoride concentrations. The solutions were kept stirred using a paddle rotated at about 100 RPM to keep the magnesia particles evenly suspended in the solution. Before starting each experiment, the thermostat, pH and fluoride electrodes were submerged in the fluoride solution in the beaker. Readings of pH and mV were recorded. The electrodes used were Radiometer F1052 fluoride electrode and Metrohm Ag/AgCl reference electrode with sleeve type diaphragm connected to a Metrohm 691 pH-meter. pH was monitored

using a Metrohm 691 pH meter and combined pH electrode. The Impulsomat was set correctly before adding magnesia to the fluoride solution in the beakers. The dosimat, which was connected to the impulsomat, was feeding a 0.25 M nitric acid solution to the beaker, automatically as pH tends to raise above 10.5. Controlling pH below 10.5 was made manually by adding 0.25 M potassium hydroxide using a glass burette, supplied with a peristaltic pump. The experiment was carried out for a duration of 4 hours. Samples were taken before starting, after 15 minutes and at the end of each experiment. The samples were filtered using a SM 16510/11 polycarbonate filter holder through 0.22 µm membrane filter paper from Schleider and Schuel. The samples were tested for fluoride, total alkalinity and hardness. The results of pH, mV readings and net acid added were recorded at different intervals. Each experiment was carried out in 2 replicates.

Fluoride and pH-measurements. The fluoride concentrations were measured directly using Radiometer F1052 fluoride electrode and Metrohm Ag/AgCl reference electrode with sleeve type diaphragm connected to a Metrohm 691 pH-meter. pH was monitored using a Metrohm 691 pH meter and combined pH electrode. Both pH and fluoride concentration were measured according to Standard Methods.[11]

RESULTS

The results from the jar tests series of experiments are presented in Figure 1 A & B. The rate of fluoride removal is plotted versus contact time in order to illustrate the observed lag time before the uptake of fluoride starts taking place.
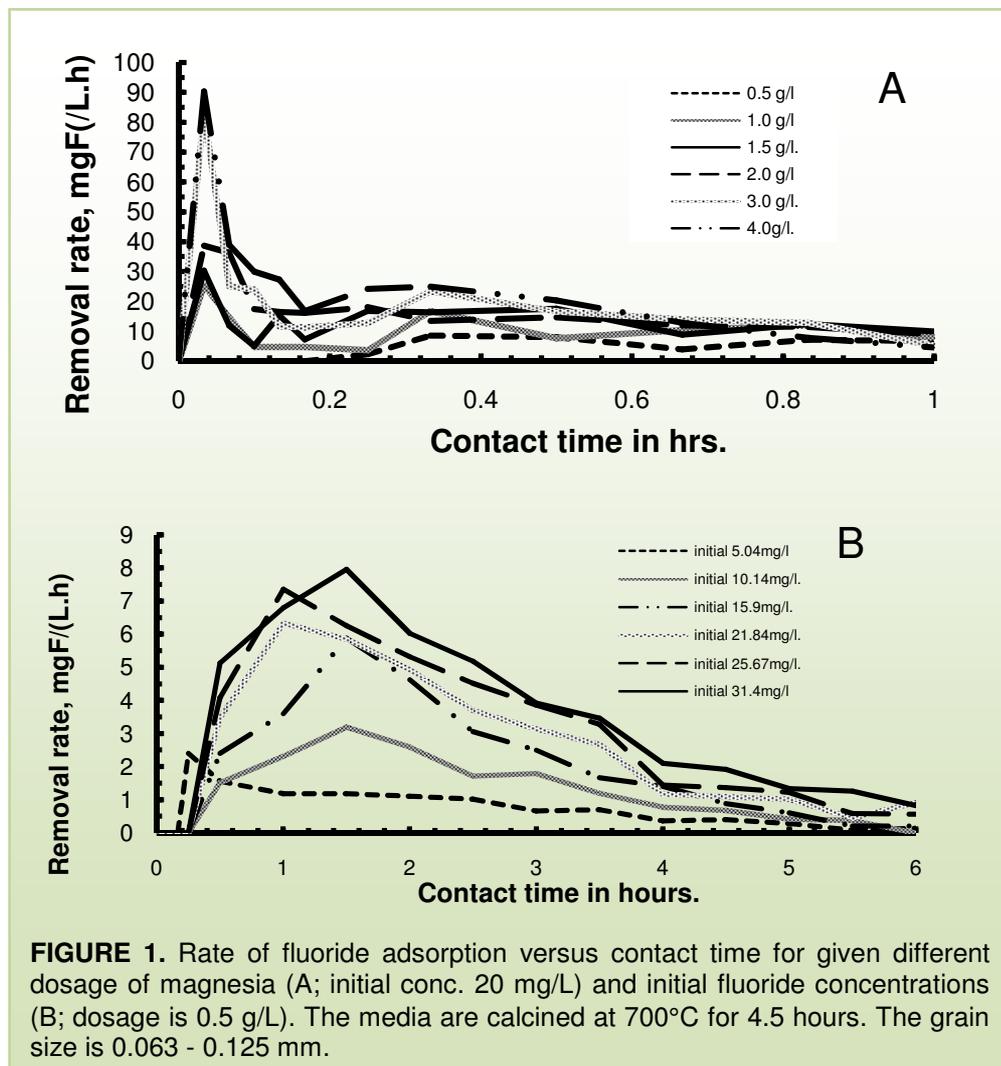
MODEL DEVELOPMENT

Order of reaction. As the rate of removal is not following a continuously decreasing pattern, the data obtained would not be following a simple kinetic of a well defined order. Thus plotting the data as $\ln(F_{R,t}/F_{R,0})$, as $1/F_{R,t}$ and as $F_{R,t}^{1-n}$ have confirmed that the order of the reaction, if any, is not of 1st or 2nd order. It varies between 1.2 - 1.8, and it does not take into account the lag time. It was concluded that the reaction pattern is complex and the reaction order changes within the same run. However, for engineering practise, since the rate of reaction is high within the first 2 hours and it fits the first order pattern within this time, it was found appropriate to adopt a simple 1st order kinetics, but where the model takes into account the lag time as observed.

In an advanced description of the sorption kinetics, the rate of the reaction is dependent on the residual fluoride concentration in the water as well as the simultaneous residual of defluoridation capacity of the sorbing medium. A literature study has revealed that such derivations would always result in complex expressions containing multiple variables and constants, cf. e.g. Nielsen 1993.[3] In this study, therefore, an attempt is made to develop a simple model, which describes the change of fluoride concentration in water as a function of time. The model should however is pragmatic and compromises about the precision of fitting the pattern in order to limit the expression using as few variables and rate parameters as possible.

Model description. The model adopted is as below:

$$F_t = F_0 \exp[-K \cdot X_T \cdot (t-t_{lag})]$$

FIGURE 1. Rate of fluoride adsorption versus contact time for given different dosage of magnesia (A; initial conc. 20 mg/L) and initial fluoride concentrations (B; dosage is 0.5 g/L). The media are calcined at 700°C for 4.5 hours. The grain size is 0.063 - 0.125 mm.
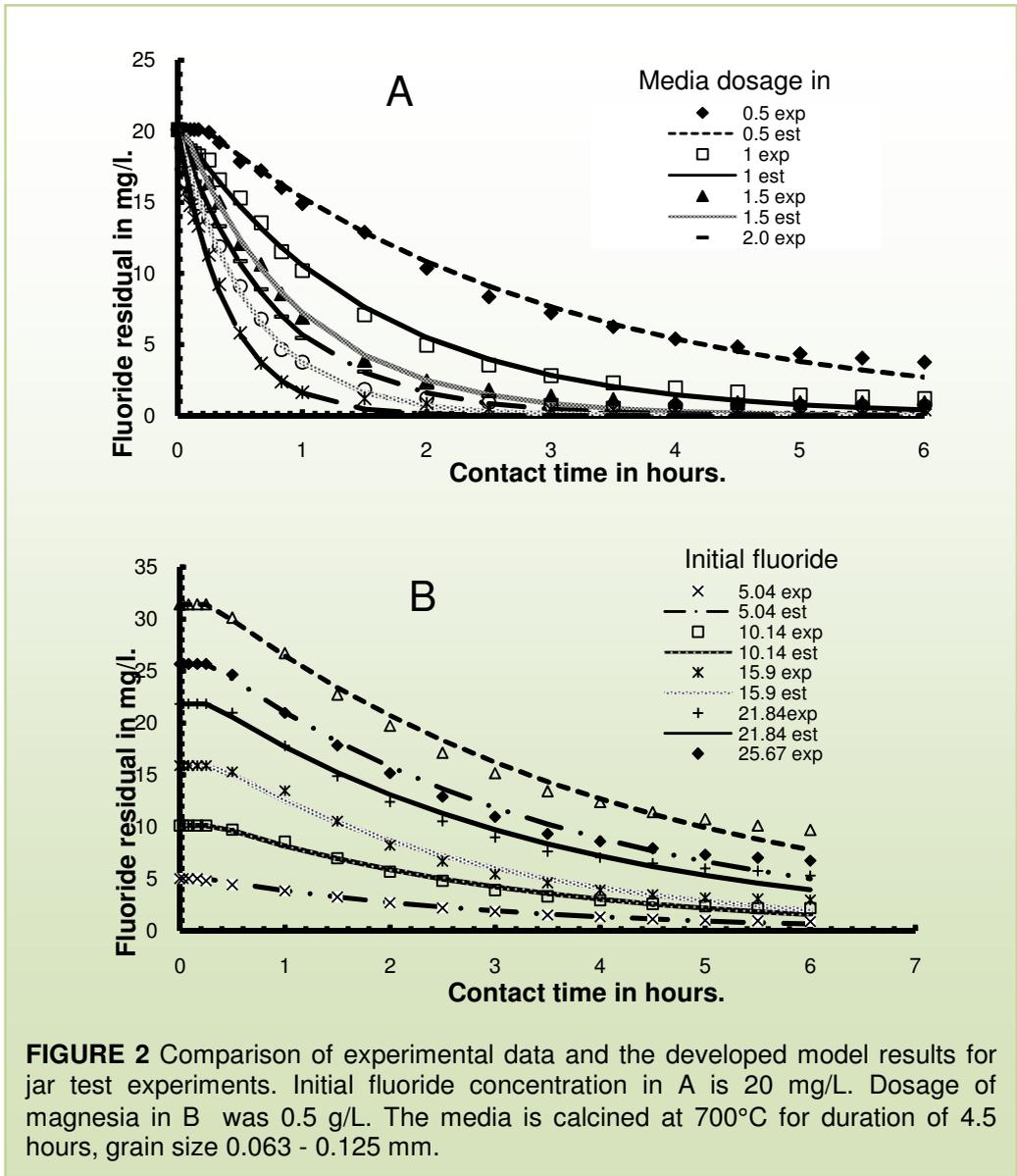
Thus the model takes into account:

- The rate of removal follows a simple 1st order kinetics with respect to the residual fluoride concentration, F_T.
- The rate constant being k is not a constant, but is dependent on the dosage, X_T.
- k is approximately directly proportional to the dosage X_T, thus $k = K \cdot X_T$.
- The reaction does not start at t = 0, but at $t = t_{lag}$.

DISCUSSION

Derived parameters. Figure 2 A shows that addition of 0.5 g/L to water containing 20 mgF/L resulted in a concentration of less than 5 after a contact time of 6 hours.

This means a removal capacity of about 30 mg/g, which is extremely high compared to other mineral media and even to bone char.[1]

The experimental and estimated model results are presented graphically in Figure 2. It shows that the model reproduces the trend of the experimental data very well for both at high as well as low dosage.

FIGURE 2 Comparison of experimental data and the developed model results for jar test experiments. Initial fluoride concentration in A is 20 mg/L. Dosage of magnesia in B was 0.5 g/L. The media is calcined at 700°C for duration of 4.5 hours, grain size 0.063 - 0.125 mm.
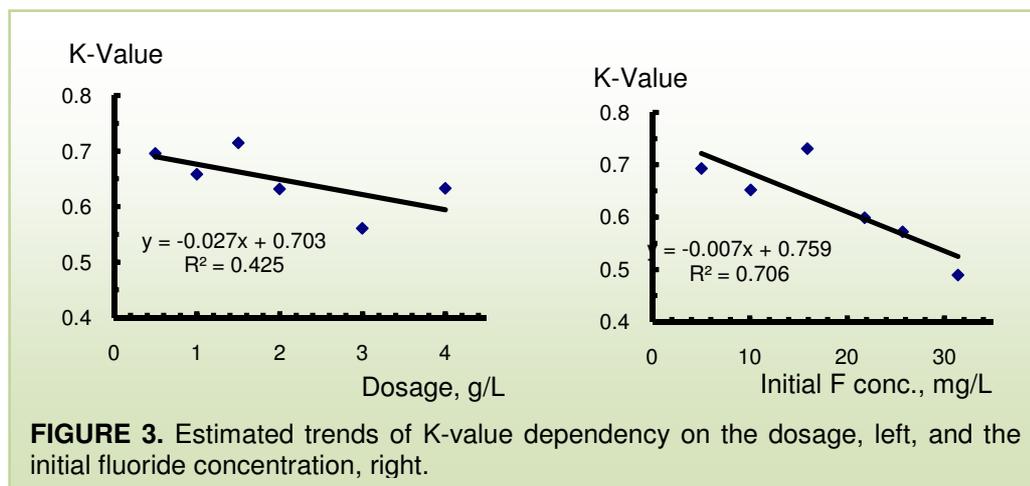
The estimated values of K are presented in table 1, including the results observed from different dosage, different initial fluoride concentrations and the chemostat series where pH was controlled at 10.5.

From the deviation of the estimated K, respectively 8.4, 14.1 and 33.9 % of the average value, it may be concluded that the model is most sensitive towards variations in the initial fluoride concentration, especially when pH is controlled where estimation of an average K becomes of no use.

This is in agreement with the above-mentioned fact that the process is not a simple 1st order reaction. Figure 3 illustrates the trends of K-values when estimated for different dosage and initial fluoride concentration.

TABLE 1. Estimated reaction values, K, of the proposed model.

Batches of different dosage			Batches of different initial F			Chemostat pH = 10.5		
F_0 mg F/L	X_T g/L	K $L \cdot g^{-1} \cdot h^{-1}$	F_0 mg F/L	X_T g/L	K $L \cdot g^{-1} \cdot h^{-1}$	F_0 mg F/L	X_T (g)	K $L \cdot g^{-1} \cdot h^{-1}$
20.1	0.5	0.696	5.04	0.5	0.693	10.6	0.5	0.36
20.1	1.0	0.658	10.1	0.5	0.652	11.3	0.5	0.32
20.1	1.5	0.715	15.9	0.5	0.731	11.7	0.5	0.33
20.1	2.0	0.632	21.8	0.5	0.599	20.0	0.5	0.41
20.1	3.0	0.561	25.7	0.5	0.572	21.7	0.5	0.66
20.1	4.0	0.633	31.4	0.5	0.489			
SUM $(F-F_{est})^2$ = 41.5			SUM $(F-F_{est})^2$ = 30.1			SUM $(S-S_{est})^2$ = 14.5		
Average K		**0.649**			**0.623**			**0.416**

FIGURE 3. Estimated trends of K-value dependency on the dosage, left, and the initial fluoride concentration, right.

Also the t_{lag} value is found to be dependent on the dosage as well as the alkalinity of the water. The lower the dosage and the higher the alkalinity, the higher is the value of lag time. For dosage of 0.5 g/L to water of no alkalinity, of the t_{lag} was found to be 15 minutes. The same dosage to natural water with initial alkalinity the lagging was about 30 minutes.

The developed model fits to both jar and pH-chemostat experiments though the two types of experiments represent different approaches. The pH-chemostat experiments represent a controlled experiments in the laboratory, while jar test experiments represent the experiments which can be done practically in the field.

The observed lag time has not been reported in connection with other defluoridation media. On the contrary the defluoridation process is known to start instantly at maximum rate.[10] The delay in case of magnesia, is believed to be due to hydrolysis processes which apparently have to take place, prior to defluoridation. This may indicate that magnesia by it self can not remove fluoride. Its hydrolysis product on the other hand is highly efficient in taking up the fluoride from the water.

ACKNOWLEDGMENTS

LIST OF SYMBOLS

t   time, (h).

t_{lag} lag time before the reaction starts taking place, (h).

X_T concentration of sorption media or the dosage, $(g \cdot L^{-1})$

K   reaction rate parameter, $(L \cdot g^{-1} \cdot h^{-1})$

k   reaction rate constant or specific rate, (h^{-1}) where n is order of reaction.

REFERENCES

1. Dahi, E Small community defluoridation of water; The state of the art. 32 pp. Chapter 6 IN: Fluoride in Drinking Water. IN PRESS by WHO 1999.

2. Singano J. *Defluoridation of Drinking Water by using Magnesite and Polyaluminium Chloride.* M.Sc. Thesis. Department of Civil Engineering, Tampere University of Technology, Finland. 77p 1991.

3. Nielsen JM. *Defluoridation of Water by means of Magnesite.* M.Sc. Centre for Developing Countries, Technical University of Denmark, Copenhagen. 98p 1993.

4. Viswanadham CR, Purushottam D, Rao GM, Vaidyanadham D, Francis PG. Defluoridation of Water with Magnesium Oxide. *Proceedings of Symposium on Fluorosis.* Hyderabad, India. p 249-271, 1974.

5. Jackson T, Levin AKM, Rasmussen K, Sørensen J. *The Potential of using Magnesite in Defluoridation of Drinking Water in Arusha region, Tanzania.* Field Study report at Centre for Developing Countries, Technical University of Denmark. 88p. 1991.

6. Singano JJ, Mashauri DA, Dahi E, Mtalo FM. Effect of pH on Defluoridation of water by Magnesite. *Proceedings of the First International Workshop on Fluorosis and Defluoridation of Water,* Ngurdoto, Tanzania. p 30-34. 1995.

7. Zettlemoyer AC, Zettlemoyer EA, Walker WC. Active Magnesia. II. Adsorption of Fluoride from Aqueous Solution. *Journal of America Chemical Society 69* 1312-1315 1947.

8. Dahi E, Singano J, Nielsen JM. Kinetics of Defluoridation of Water by Calcined Magnesia and Clay. *Proceedings of the First International Workshop on Fluorosis and Defluoridation of Water*, Ngurudoto, Tanzania. p 67-71. 1995.

9. Bregnhøj H, Dahi E. Kinetics uptake of Fluoride on Bone Char in Batch. *Proceedings of the First International Workshop on Fluorosis and Defluoridation of Water,* Ngurdoto, Tanzania. p 55-66. 1995.

10. Bregnhøj H. *Processes and Kinetics of Defluoridation of Drinking Water using Bone Char.* Ph.D. Thesis. Institute of Environmental Science and Engineering. Technical University of Denmark. 112p 1995.

11. Standard Methods. *Standard Methods for the Examination of Water and Wastewater.* Greenberg AE, Clesceri LS, Eaton AD. APHA, AWWA, WEF. 18th ed. Washington DC 1992.Evolve, E . Removal of Fluorides from Drinking Water. United States Patent Office, Patent no. 2,207,725, 1940.