

EFFECT OF pH ON DEFLUORIDATION OF WATER BY MAGNESITE

JJ Singano*, DA Mashauri** E Dahi*** and FW Mtaló**

SUMMARY: The dissolution of fluoride in water as well as its adsorption on defluoridation agents is very much influenced by the pH of the solution. Studies carried out showed that magnesite calcined into magnesia has an optimum fluoride removal capacity at pH levels between 10.0 and 11.0. For cases where the initial pH was lower than the optimum range, the reaction increased the pH to the optimum range. For drinking water quality purposes, it is recommended to have pH adjusted after treatment.

Key words: Calcined magnesite, magnesia, fluoride, defluoridation, pH.

INTRODUCTION

In Tanzania magnesite is locally available in the northern part at Chambogo in Same District, Loporosite in Kiteto District and Longido in Monduli District. At present magnesite is being exploited at Chambogo mines¹.

In defluoridation of drinking water by using magnesite, fluoride is removed by ion exchange or by chemical reaction with the adsorbent. Removal in this paper refers to total mechanism of adsorption and ion exchange.

The general principles of the surface chemistry of oxides in contact with an aqueous solution are as follows: The hydroxyl groups behave amphotericly. The hydroxide ion association reaction are as shown in equation 1 for positively charged surfaces, in equation 2 or 3 for neutral surfaces and in equation 4 for negatively charged surfaces.



Equation 1 is favoured at low pH, while equation 4 is favoured at high pH.²

Despite the high affinity of fluoride for the metal on the surface of adsorbents, fluoride ions are adsorbed mainly by the positively charged surface as shown in equation 5 and 6. However, to some extent it can also be adsorbed by an ion exchange mechanism even when the surface is neutral as shown in equation 7.²

At positive surfaces:



At neutral surfaces:

* Ministry of Water, Energy and Minerals, PO Box *, Dar es Salaam Tanzania.

** Faculty of Engineering, University of Dar es Salaam, PO Box , Dar es Salaam Tanzania.

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



As the pH decreases, positively charged complexes are formed and at the same time the hydroxyl ion association will be further positively charged. Thus there will be an electrical repulsion between the positively charged complex and the positively charged surface. At the same time, when the pH increase beyond an optimum value, the hydroxyl groups (-M-OH) will gradually disappear forming more negatively charged surfaces as shown in equation 3. In addition OH⁻ will compete with fluoride ions for available sites left on the surface^{1,2}.

Hence effect of pH plays a big role in defluoridation by magnesia (MgO). In order to examine the effect of pH on defluoridation by using magnesia, chemo-stat experiments were carried out.

MATERIALS AND METHODS

Preparation of Magnesia: Pieces of magnesite from Chambogo were calcined at 700°C for 4.5 hours.

Chemo-stat Experiments. The different experiments were carried out in series under different conditions, namely: (a) fluoride and pH were kept constant. (b) fluoride was constant and pH was not controlled. (c) pH was constant and fluoride was not controlled.

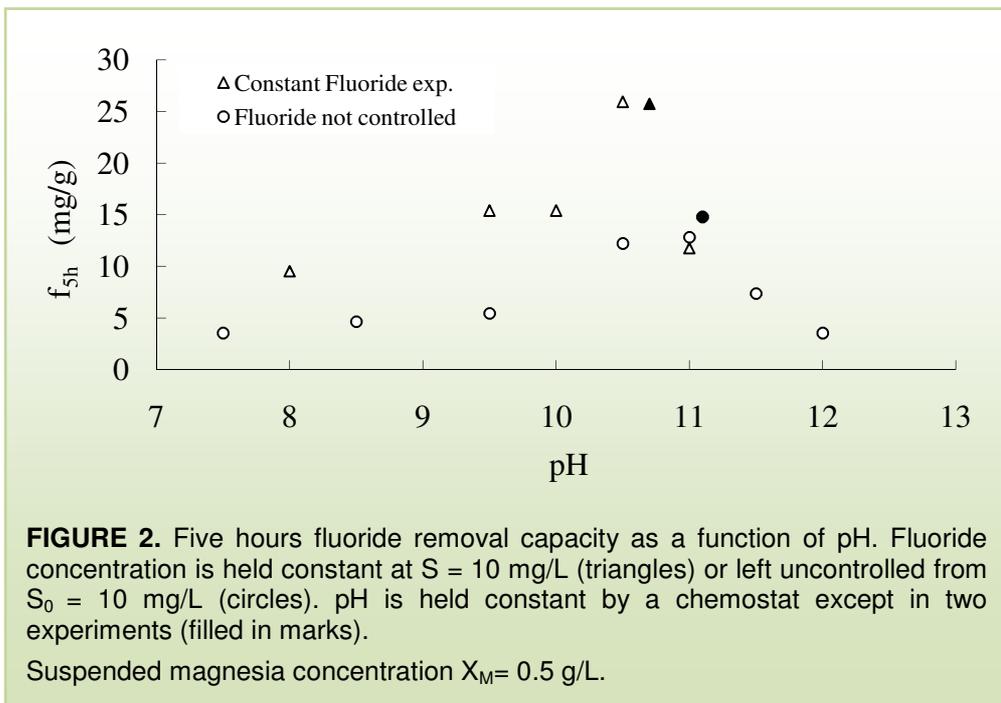
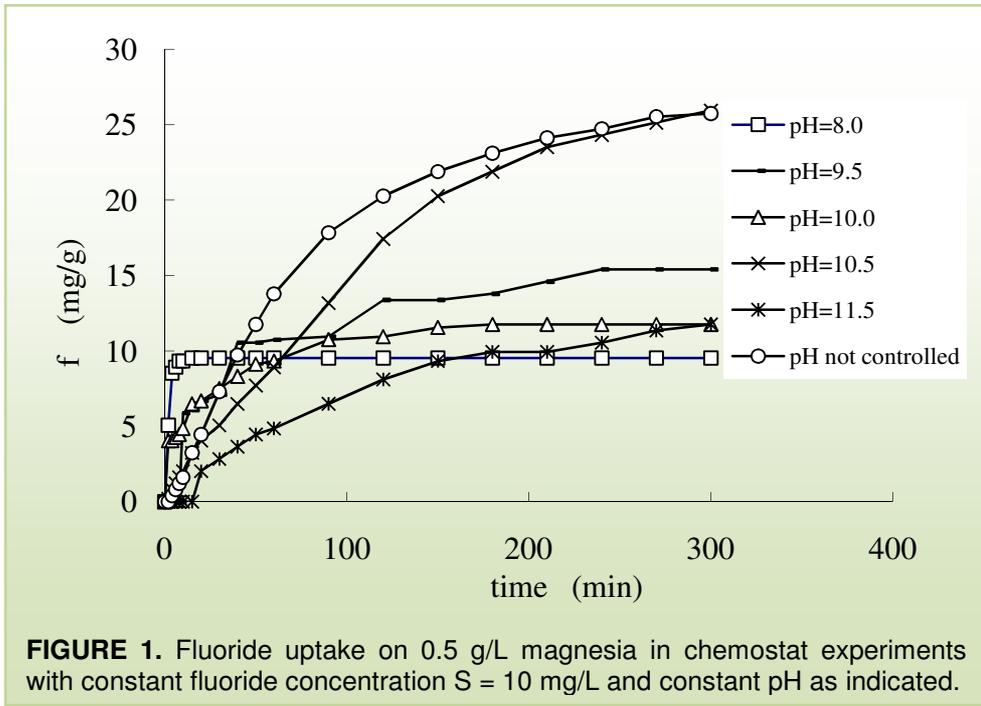
The chemo-stat consisted of three units from Metrohm: 715 Dosimat, 614 Impulsomat and a 691 pH Meter. In experiments (a) and (b) fluoride was added automatically to the reaction beaker from a stock fluoride solution on the dosimat of 2.00 g F/L. In experiment (a) acid or base was added manually from stock solutions in burettes of 0.25 M HNO₃ and 0.25 M KOH. In experiment (c) acid was added by the dosimat. The reaction beaker contained 1 L 10 mg F/L (NaF in distilled water). The beaker was placed in a Julabo 3U water bath at 25°C and the solution was stirred by a paddle stirrer. The fluoride concentrations were recorded directly in the reaction beaker using a Radiometer F1052 fluoride electrode and Metrohm Ag/AgCl reference electrode with sleeve type diaphragm connected to the Metrohm 691 pH-meter. pH were measured using a Metrohm combined glass electrode in connection with a Metrohm 691 pH-meter.

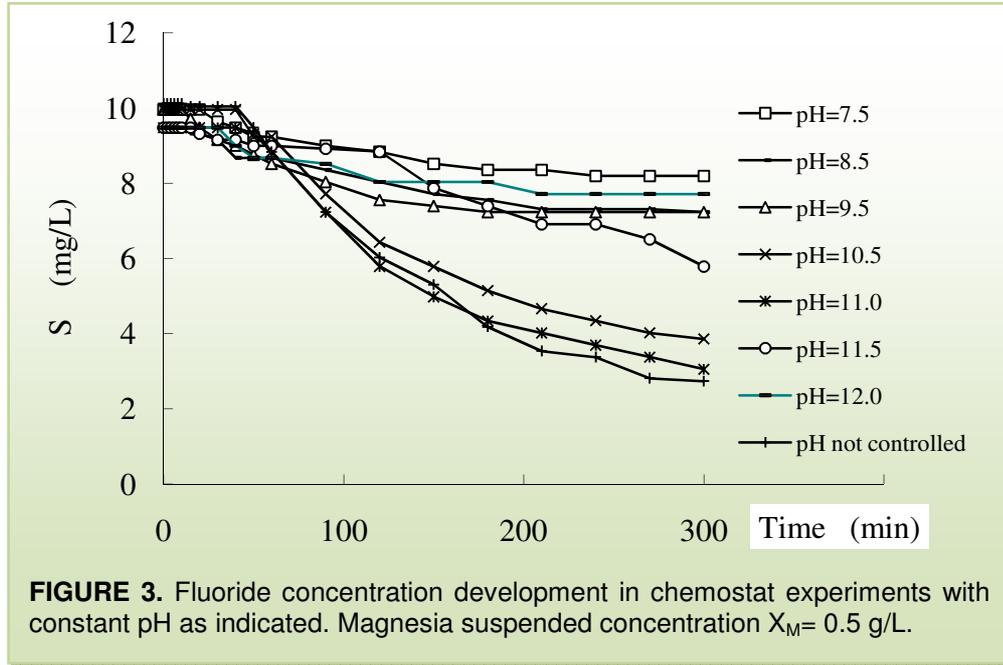
At time zero 0.5 g magnesia was added to the reaction beaker. All experiments were run for 5 hours. In (a) and (c) pH was kept constant at different values between 7 and 12. Recordings were made of fluoride added, pH, mV readings and acid added.

Batch experiment: In another experiment neither pH nor fluoride were kept constant. All other conditions as in the chemo-stat experiments.

RESULTS

Experiments with constant fluoride concentration. Figure 1 shows the fluoride uptake on magnesia, measured as the amount of fluoride added to keep a constant fluoride electrode potential in the solution, at the various constant pH-values together with the experiment with no control of pH. The 5 hours fluoride removal capacity is in this context defined as:





$$f_{5h} = \frac{V \cdot \sum m_{F^-}}{X_M} \quad \text{Eq. 8}$$

Where:

f_{5h} is the specific fluoride removal capacity at 5 hours experiment (mg/g)

V is the volume of water (L)

$\sum m_{F^-}$ is the amount of fluoride added after 5 hours (mg)

X_M is the suspended concentration of magnesia (g/L)

f_{5h} is shown as a function of pH in Figure 2. The results show that the optimum pH for fluoride removal is at about 10.5 to 11.0.

Experiments with no addition of fluoride. Figure 3 shows fluoride concentrations as a function of time in experiments with and without control of the pH. A 5 hours fluoride removal capacity is defined similar to the experiments with addition of fluoride:

$$f_{5h} = \frac{S_0 - S_{5h}}{X_M} \quad \text{Eq. 9}$$

Where

S_0 is the fluoride concentration at time zero (mg/L)

S is the fluoride concentration after 5 hours experiment (mg/L)

f_{5h} is shown in Figure 2 as a function of pH, together with results of the constant fluoride concentration experiments. It also shows that the fluoride removal is highest when pH is about 11.0.

DISCUSSION

It is demonstrated through the present experiments that calcined magnesite from Chambogo in Tanzania is able to adsorb fluoride from water in batch systems. The uptake curves seem to differ from usual adsorption curves by a certain lag period or delay before adsorption starts, as seen in Figure 3. This has no influence on practical defluoridation as defluoridation using magnesite is thought to be carried out in columns.

The results clearly show that pH is extremely important for defluoridation by magnesite. Figure 2 demonstrates that adsorption has a maximum at pH 10.5-11.0. This result is obtained in two different types of experiments, in some experiments fluoride concentration was kept constant and in others it was falling during adsorption. The optimum is thought to be related to the surface chemistry of magnesite. At very high pH the surface will be negatively charged and fluoride will compete with OH⁻ for adsorption.

An important result of this study is also that the magnesite is by itself exactly adjusting the pH to the optimum pH = 10.5-11.0. Although the magnesite is very sensitive to pH, it is for practical applications therefore not necessary to adjust pH for optimization of treatment.

However it should be stressed that for practical applications pH needs to be adjusted *after* treatment. The resulting pH is far above the WHO guidelines of 6.5-8.5. More investigations are needed to find a way of regulating the pH, which is appropriate for use in Tanzania.

ACKNOWLEDGMENTS

The authors thank Danida for their financial support to the Defluoridation Technology Project.

REFERENCES

1. Singano J. Defluoridation of Drinking Water by using Magnesite and Polyaluminium Chloride. M.Sc. Thesis. Department of Civil Engineering, Tampere University of Technology, Finland. 77 p 1991.
2. Choi WW, Chen KY. The Removal of Fluoride from Water by Adsorption. Journal of American Water Works Association 71 562-570 1979.