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S.V.R. Weerasooriya <sup>a</sup> , K.B.P.N. Jinadasa <sup>a</sup> & C.B. Dissanayake <sup>a</sup>

<sup>a</sup> Soil Vegetation and Health Study Group, Institute of Fundamental Studies, Kandy, Sri Lanka

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## DECONTAMINATION OF FLUORIDE FROM COMMUNITY WATER SUPPLIES

S.V.R. Weerasooriya\*, K.B.P.N. Jinadasa and C.B. Dissanayake Soil Vegetation and Health Study Group, Institute of Fundamental Studies, Kandy, Sri Lanka

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#### ABSTRACT

A chemical treatment method is described for enhancement of fluoride uptake by serpentinite in an aqueous medium. The powdered raw material is acidulated with concentrated HCl to a stoichiometric ratio for generating protonated serpentinite [SH]. This product is hydrolysed with a dilute base/distilled water, to yield SO<sup>+</sup>H<sub>2</sub>. A surface complex formation model is suggested to describe the adsorption of fluoride by the solid substrate. These reaction mechanisms can be identified as surface complex formations involving SOH and SO<sup>+</sup>H<sub>2</sub>.

#### INTRODUCTION

water supply schemes particularly in developing countries such as Many Sri Lanka, where groundwater forms the major source of drinking water, have excess levels of fluoride normally detrimental to dental health (1,2). A simple and rapid method of defluoridating these waters is required. It was observed that serpentinite forms a suitable starting material in the defluoridation process. Serpentine as a group name, denotes a class of minerals having a layer structure similar to that of kaolinite but with a di-octahedral Al layer. The major varieties of serpentine include chrysolite, lizardite and antigorite. When the serpentine particles occur in such proportions as to make up a major portion of the entire rock mass, it is termed serpentinite. However the identification of individual serpentine group minerals in such rock is often Several studies (4,5) have shown that the efficiency of difficult (3). serpentinite in removing excess fluoride from fluoride-rich water is limited, and it tends to be deactivated with repeated use.

In this report, we present a method for the chemical treatment of serpentinite to enhance the uptake of fluoride. Using this method, the concentration of fluoride can be lowered from 10 mg/L to less than 1 mg/L, [i.e. below the W.H.O. permissible level in drinking water (6)] under laboratory conditions.

The presence of diverse anions have been shown to affect the uptake of fluoride, favourably or adversely. It is known that  $SO_4^{2-}$  and  $Ca^{2+}$  has a favourable effect whereas in the case of HCO<sup>-</sup><sub>3</sub> the effect is adverse (7,8,9). The fluoride removal efficiency of serpentinite is, therefore, governed by the nature and concentration of ions present in the water.

#### Chemical Treatment of Serpentinite

The powdered serpentinite passed through mesh #120 was selected for the study. A sample of 100 g of the material was washed several times with distilled water to yield neutral serpentinite. Thereafter it was mixed with different quantities of concentrated HCl (60 ml - 200 ml) and the mixtures were aged for three months. Thereafter the mixtures were gently heated at 100°C in a water bath for 8 hrs and dried to form protonated serpentinite [SH]. The dried material was again washed with distilled water and/or dilute base until the pH of the solution was slightly acidic. Upon hydration the hydroxyl functional groups may be located at the surface sites of the protonated serpentinite  $[SO^+H_2]$ . This material was used for the defluoridation process.

#### Reactivation

The chemically treated serpentinite saturated with fluoride was mixed with 1% (w/v) NaOH at 60°C for 5 hrs and 12 hrs. The excess base was decanted. The material was then made to react with 10 M HCl and kept for 72 hrs. This method of treatment was found to restore its fluoride trapping ability.

#### Adsorption/Desorption Studies

All adsorption studies of fluoride ions onto serpentinite were carried out in 100 ml plastic beakers. (The ionic strength of the 100 ml reaction solution was maintained at the 0.1 M level with NaCl).

The concentration of fluoride was varied from 1 to 10 mg/L. The pH of the solution was initially adjusted to the range of 2-8 using either 0.1 M HCl or 0.1 M NaOH. The solutions were stirred for 24 hrs at room temperature. The mixture was filtered, and the fluoride concentration of the solutions was determined with an ion selective electrode (9,10).

#### RESULTS

Preliminary investigations indicate that the adsorption capacity of fluoride in serpentinite varies with the quantities of acid in the chemical treatment process. As illustrated in Figure 1 the fluoride uptake capacity of serpentinite reaches an optimum value at a serpentinite/HCl ratio of 1:1. The above ratio was maintained in all subsequent studies.

The data obtained by equilibrating the chemically treated serpentinite with fluoride ions in solution at various pH conditions are shown in Figure 2.

The results are presented as simple isotherms. The fluoride uptake by the solid substrate increases with the solution pH, and an optimum condition is reached at a pH value of 5.20. Afterwards it decreases with the further increases of pH. The pH determinations, made after the equilibrium period showed that the acidity (pH) did not vary by more than 0.1 - 0.2 pH units, as long as the pH of the initial solution is greater than this value, the pH increases with the amount of fluoride adsorbed onto the serpentinite.

According to these results a solution of pH 5.20 was selected for examining the kinetic behaviour of fluoride adsorption. As shown in Figure 3, initially, the fluoride adsorption rate was very rapid and it reached a maximum value after 6 hrs. After this time, the amount of adsorbed fluoride per given quantity of serpentinite was almost constant, indicating an apparent saturation of the solid substrate. Essentially we are dealing with a heterogeneous system in which the fluoride is distributed between the solution and the chemically treated

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FIGURE 2 •• The variation of fluoride adsorption in serpentinite with pH.



FIGURE H •• The variation of fluoride adsorption capacity in serpentinite with the amount of acid used in the treatment process





FIGURE 3 : The time dependence of fluoride adsorption

serpentinite. It has been shown (10) that a number of minerals in the solid mass are involved in the adsorption of fluoride.

We have noted that there was a remarkable constancy of the ratio of fluoride adsorbed by serpentinite to that present in the water. This constancy arises from the rapid establishment of the equilibrium.



FIGURE 4 : Fluoride adsorption isotherm

As shown in Figure 4, this equilibrium can be explained by the Langmuir equation.

$$E_s = E_{max} [F] / [C+F]$$

where  $E_s$  is adsorbed fluoride onto chemically treated serpentinite (mg/kg), and C is the half saturation constant. This expression is a non-linear relationship between adsorbed and dissolved fluoride, with an asymptotic approach to a maximum adsorbed value as the dissolved fluoride concentration becomes large.

#### DISCUSSION AND CONCLUSIONS

The physico-chemical properties which may be considered as being of significance to the binding of fluoride onto chemically treated serpentinite include pH, ionic strength and the presence of competing ions such as OH<sup>-</sup>, HCO<sup>-</sup>3 or SO4<sup>2-</sup>. In principle, there are two different ways for fluorides to be adsorbed by serpentinite. One is chemisorption through an ion exchange at the solid surface (11) and the other is by forming inorganic precipitates (12). Preliminary investigations indicate that the uptake of fluoride by chemically treated serpentinite does not depend on temperature. [Those results are not given in It is well known that except for a few salts of Ca and Mg the this paper]. solubility of an inorganic precipitate increases with temperature (13). Therefore, any inorganic precipitation of fluoride in the present study is not a deciding factor in the equilibration between the liquid and solid phase. Ion exchange reactions are fast, and as such will not be affected by temperature. Therefore, it is suggested that the uptake of fluoride by chemically treated serpentinite is an adsorption process involving anion exchange. Many models (14,15) (conceptual and numerical) have been advanced to describe the adsorption of anions onto hydroxy-solids. In this study we have selected a surface complex formation model (14) to describe the mechanisms involved in the fluoride adsorption.

According to this model the reaction between fluoride and serpentinite is thought to occur via the formation of solid fluoride complexes [SF]. The reaction can take place in two independent steps which are determined by the pH of the solution. One involves the surface hydroxyl groups with the release of  $OH^-$ , and the other involves the water molecules on the solid  $[SO^+H_2]$  without the release of  $OH^-$  or  $H^+$ . Therefore the exchange sites of chemically treated serpentinite show amphoretic behaviour for the variation of solution pH. These sites which are saturated with fluoride ions can be reactivated with the treatment of NaOH followed by HCl. The overall stoichiometry of the reactions can be represented according to the analogy of activated alumina and fluoride as described by Hao <u>et al</u>. (10), as follows:

A. Acidulation and hydration

 $S + H^+ = SH$ 

 $SH + H_2O = SO^+H_2 + H^+$ 

B. Fluoride adsorption

(i) <u>pH < 5.20</u>

 $SO^{+}H_{2} + F^{-} = SF + H_{2}O$ 

(ii)  $\underline{PH} > 5.20$   $SO^+H_2 + OH^- = SOH + H_2O$  $SOH + F^- = SF + OH^-$ 

C. Reactivation

SF + NaOH = SOH + F<sup>-</sup> SOH + HCl =  $SO^+H_2$  + Cl<sup>-</sup>

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