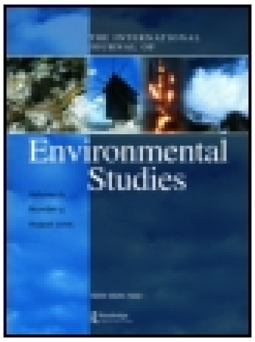

International Journal of Environmental Studies

ISSN: 0020-7233 (Print) 1029-0400 (Online) Journal homepage: http://www.tandfonline.com/loi/genv20

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To cite this article: K. B. P. N. Jinadasa , C. B. Dissanayake & S. V. R. Weerasooriya (1991) Use of serpentinite in the defluoridation of fluoride#rich drinking water, International Journal of Environmental Studies, 37:1-2, 43-63, DOI: 10.1080/00207239108710616

To link to this article: http://dx.doi.org/10.1080/00207239108710616

Intern. J. Environmental Studies, 1991, Vol. 37, pp. 43–63
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USE OF SERPENTINITE IN THE DEFLUORIDATION OF FLUORIDE-RICH DRINKING WATER†

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S. V. R. WEERASOORIYA§

(Received July 24, 1989)

A newly developed, HCl treated method is described for the enhancement of fluoride uptake by serpentinite in an aqueous medium. Fluoride adsorption and desorption reactions in treated serpentinite were investigated, over the range of fluoride concentrations (1–10 mg/l). The zero point charge of the variable charge components (pH_0), and total surface charge (σp) of serpentinite were also investigated. At equal concentrations of total fluoride in solution, fluoride retention was greatest at $pH = 5.2$ and decreased both at low and high pH. Thermodynamic properties for fluoride adsorption at 25°C and 50°C were investigated. The isosteric heat of adsorption (ΔH) was calculated for treated surfaces and heterogeneity of this surfaces was examined. Finally, Differential Thermal Analysis (DTA) and X-ray Diffraction (XRD) patterns were observed for raw, treated and fluoride-contacted surfaces. According to DTA and XRD patterns, structural changes were observed with HCl treatment.

KEY WORDS: Defluoridation, drinking water, serpentinite, fluorosis.

INTRODUCTION

Previous epidemilogical studies have shown that dental fluorosis is endemic in the lowland, dry zone of Sri Lanka, which is considered to be an area in which excess fluoride is present in drinking water supplies. The availability of inexpensive and effective materials for the removal of excess fluoride from potable waters at village levels would undoubtedly be a boon to the public health worker. It must be noted that even though there are many methods now available for the defluoridation of water, nearly all of these are expensive and suitable only for large central water supply schemes. This investigation is therefore aimed at providing a simple technique that could be used at community level, particularly in developing countries as exemplified by Sri Lanka.

It was observed that serpentinite could be used as 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 kaolonite but with a di-octahedral Al layer. The major varieties of serpentine include chrysotile, lizardite and antigorite. When the serpentine particles occur in such proportions so as to make up a major portion of the entire rock mass, it is termed serpentinite. In Sri Lanka, there is a large serpentinite body located at Uda Walawe and which covers an area of approximately 7 km^2. Other serpentinite bodies lie along the boundary of the Highland Group and Vijayan Complex.[1] A further serpentinite-marble deposit is found at Rupaha, in the Central Province. Several studies[2–4] have shown that the efficiency of serpentinite in

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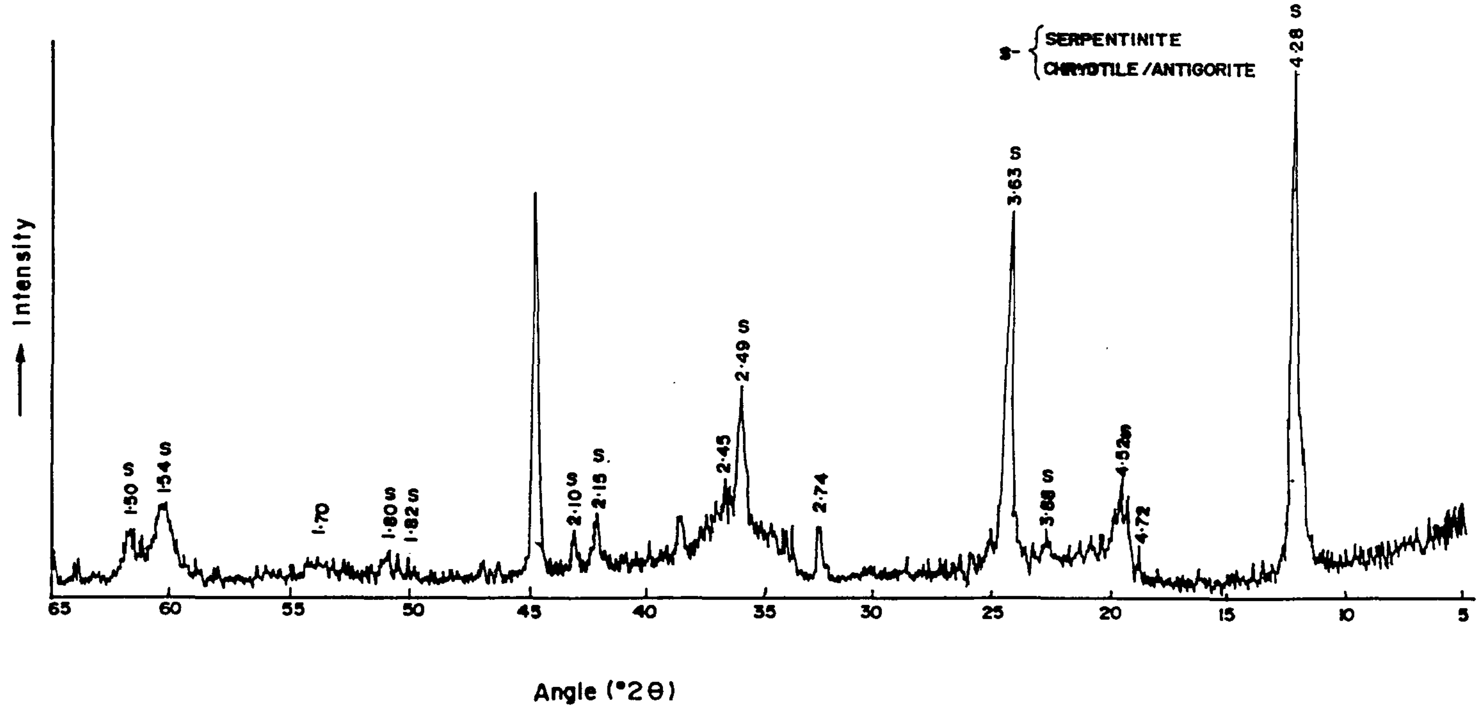

Figure 1 The X-ray diffraction (XRD) pattern for Uda Walawe serpentinite.

removing excess fluoride from fluoride-rich water is limited, and it tends to be deactivated with repeated use.

The physico-chemical factors which are of significance to the binding of fluoride onto chemically treated serpentinite are pH, ionic strength and the presence of competing ions[5] such as OH^{1-}, HCO_3^{1-}, or SO_4^{2-}. It is known that SO_4^{2-} and Ca^{2+} have a favourable effect on the uptake of fluoride whereas in the case of HCO_3^{1-}, the effect is adverse.[6,7] The fluoride removal efficiency of serpentinite is, therefore, governed by the nature and concentration of ions present in the water.

In this paper, a method for the chemical treatment of serpentinite to enhance the uptake of fluoride is presented. Using this method, the concentration of fluoride can be lowered from 10 mg/l to less than 1 mg/l (i.e. below the WHO permissible level in drinking water)[8] under laboratory conditions.

MATERIALS AND METHODS

1. *Chemical Composition and Mineral Analysis of the Uda Walawe Serpentinite*

Preliminary investigations of the X-ray diffraction patterns (using the Shimadzu model XRD spectrometer) for the minerals of the Uda Walawe serpentinite were carried out. (Figure 1) The total chemical analysis was carried out using X-ray fluorescence spectroscopy and the results are shown in Table I.

Table I X-ray fluorescence spectroscopic analysis of serpentinite

	Concent. (ppm)			Weight %	
Trace element	Ginegal-pallassa	Indikola-pallassa	Major element	Ginegal-pallassa	Indikola-pallassa
Ba	30	1	SiO_2	38.80	38.84
Cr	2,575	2,454	Al_2O_3	0.45	0.39
Cu	14	14	Fe_2O_3	8.76	7.28
Nb	13	20	MgO	37.54	35.92
Ni	2,588	2,358	MnO	0.08	0.07
Pb	7	5	CaO	0.07	0.11
Rb	3	3	Na_2O	0.31	0.28
Sr	3	3	K_2O	0.0003	0.0003
Th	2	2	TiO_2	0.0001	0.0001
U	6	13	P_2O_5	0.007	0.007
V	24	24	H_2O^+	12.67	13.58
Y	8	1	H_2O^-	0.93	2.12
Zn	61	38			
Zr	25	33	Weight %	99.61	98.59

2. *Chemical Treatment Process*

The first six 100 g samples of the powdered serpentinite which passed through a −120 mesh sieve were selected for study. The samples were mixed with different quantities of concentrated HCl in the range 60–200 ml, in the ratios of 100 g : 60 ml, 100 g : 80 ml, 100 g : 100 ml, 100 g : 120 ml. 100 g : 140 ml and 100 g : 200 ml. The HCl used for the preliminary study was the commercially available type and the analytical grade of HCl was used only for the final study. The mixtures were kept at room temperature for 1 hr, and later they were gently heated to 100°C in a water bath kept for 8 hrs. The mixtures were then dried to form a protonated serpentinite (SH), and the latter was lightly washed with distilled water until the pH of the solution was slightly acidic ($<$ pH 5). Finally, the SH serpentinite samples were dried and taken for adsorption studies.

3. *Adsorption/Desorption Studies*

For this investigation, duplicates of 1.0 g treated serpentinite (S:H = 100 g : 120 ml) samples were separately mixed with 20 ml of NaF in the concentration of 1 to 10 mg/l range (1, 3, 5, 8 and 10 mg/l, fluoride), in 100 ml plastic beakers. The serpentinite-fluoride mixtures were shaken for 10 min at room temperature and allowed to stand for 24 hours. Finally, the supernatant solution was removed for fluoride analysis. Langumuir and Freundlich equations were used to study the adsorption isotherms.

The serpentinite (S : H = 100 g : 120 ml) samples that adsorbed 17, 52, 76, 93 and 118 μg F^-/g serpentinite, were selected for the desorption study. One gram quantity of fluoride-adsorbed serpentinite sample was mixed with 1% (W/V) NaOH at a 1 : 20 ratio, and heated at 60°C in a water bath for 6 hrs. Thereafter the mixture was kept at room temperature (25°C) for 12 hrs and the supernatant fluoride measured.

4. *Determination of Surface Charge Properties of Raw and Treated Serpentinite*

(*a*) pH_0 determination. 100 g of a serpentinite sample was washed free of exchangeable cations and anions with a 1 M solution of KCl. The sample was washed with distilled water until the electrolyte concentration was reduced to a low value of 0.002 M K^+ as measured by atomic absorption spectrophotometry (Shimadzu model). Oven dried, duplicates of 4 g samples were added to 50 ml beakers with 0.002 M KCl and the pH adjusted with HCl and NaOH to span the expected pH_0 value. The final volume was adjusted to 20 ml with 0.002 M KCl and the suspensions allowed to equilibrate for 3 days, with occasional stirring, and the equilibrium $pH_{0.002\ M}$ was recorded. A 0.5 ml solution of 2 M KCl was added and gently shaken for about 3 hrs, and the pH ($pH_{0.05\ M}$) was measured. Subsequently Δ pH *vs.* $pH_{0.002\ M}$ was plotted to obtain the point where $\Delta \text{pH} = 0$. This is designated as pH_0, the pH value which is independent of salt concentration.

(*b*) *Permanent charge determination.* Duplicates of 4 g samples of oven dried serpentinite were placed in pre-weighed centrifuge tubes with 20 ml of 1 M KCl and shaken for 1 hr. The samples were centrifuged and the supernatant solution discarded. These samples were washed twice with 20 ml of 0.2 M KCl, and then three to five times with 0.01 M KCl adjusted to pH_0. After pH_0 and equilibrium had been established, the supernatant solutions were removed and retained for analysis of K^+ and Cl^-. The centrifuge tubes were weighed to estimate the entrained KCl. The K^+ and Cl^- were removed using 0.5 M NH_4NO_3. This was done by washing five times with five solutions of 20 ml 0.5 M NH_4NO_3. The K^+ and Cl^- concentrations were determined from a combination of the five solutions used in the washings with the help of the atomic absorption spectrophotometer and the Ion Selective Electrode. The adsorbed K^+ and Cl^- were calculated for meq/100 g. Then the permanent charge was calculated from the expression (K^+ adsorbed–Cl^- adsorbed).

5. *Fluoride Adsorption with pH*

In order to determine the effect of pH on fluoride adsorption on treated serpentinite (S : H = 100 g : 120 ml), duplicate samples of 1.0 g each were used. To measure the fluoride adsorption according to the variation of pH, buffered solutions were prepared from (NaOAc/HOAc) and (NaH_2PO_4/Na_2HPO_4). For each of the pH values, 10 mg/l fluoride solutions were prepared, and the serpentinite samples were added to 20 ml of each of these solutions, mixed for 10 min and allowed to stand for 24 hrs. Thereafter the supernates from each solution were taken for the measurement of fluoride. It was noted that a value of 5.6 was the optimum pH for the maximum fluoride adsorption process. The experiment was repeated with unbuffered solutions in the pH range 1.0 to 8.0 using HCl and NaOH. It was observed that the pH value of the solution had changed with the fluoride adsorption process.

6. *Fluoride Adsorption with Temperature*

The adsorption experiments were conducted again for the serpentinite-fluoride system, 1, 3, 5, 8 and 10 mg/l solutions with fluoride concentrations in a water bath at 25°C and 50°C. After 4 hrs the supernatant fluoride concentration was determined.

7. *Mineral Analysis Differential Thermal Analysis (DTA)*

In this experiment the DTA curves were obtained for raw, acid treated and fluoride contacted serpentinite samples. The temperature gradient used was 10°C/min and the selected temperature range was from 25°C to 1000°C. DTA curves were obtained using a NETZSCH Geratebau D-8672 Selb model.

8. *X-ray Diffraction Analysis (XRD)*

Raw, treated and fluoride contacted serpentinite were selected for study. The analyses were carried out using a Shimadzu model X-ray Diffractometer.

RESULTS AND DISCUSSION

1. *Adsorption/Desorption Studies on Serpentinite*

The adsorption and desorption curves for fluoride on acid treated serpentinite (S : H = 50 : 60) are shown in Figure 2. The XRD data showed that (S : H = 50 : 60), serpentinite structure had not changed during the treatment process. With the OH^- group in serpentinite being essential for the fluoride uptake, Rao *et al.*[3] showed that any attempt to replace it by sulphate or other ions renders the material inactive. This could mean that the OH^- is either replaced by F^- or is involved in the formation of a complex with it. That the exchangeable OH^- in serpentinite corresponds only to 1.65 m equiv., when there are eight OH^- sites in its structure, indicates that all of them are not involved in the process.[3] During the treatment with strong acids such as HCl, the structural metal ions are released, and significant F^- adsorption can be observed due to the greater abundance of binding sites as compared with untreated serpentinite. A comparision between treated and raw serpentinite on fluoride adsorption is shown in Figure 3.

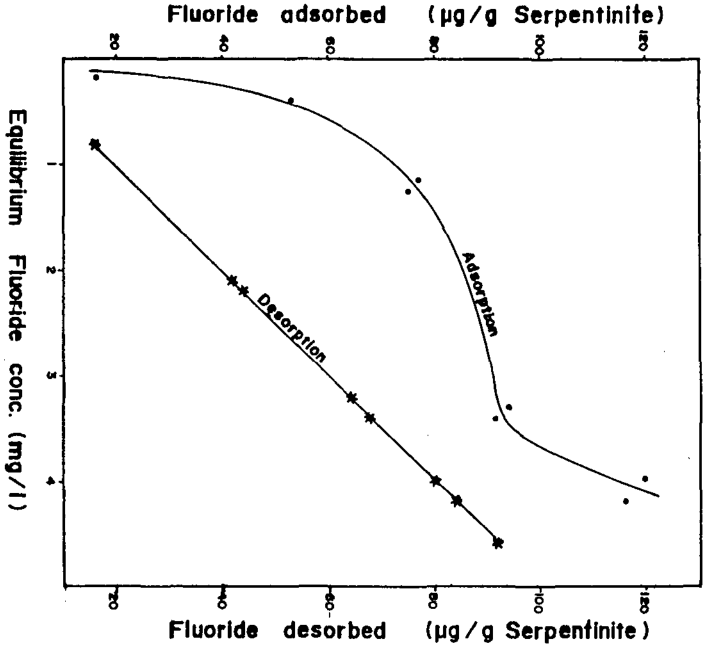

Figure 2 Adsorption and desorption for treated serpentinite.

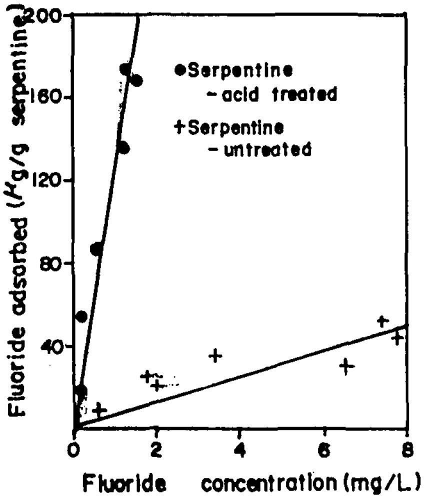

Figure 3 A comparison between treated and raw serpentinite on fluoride adsorption.

The fluoride adsorption conformed to both Langumuir and Freundich isotherms over the entire initial fluoride concentration which ranged from 1 to 10 mg/l, for treated serpentinite as shown in Figures 4 and 5. Earlier studies had shown that this treated serpentinite had a high positive charge (1.1 meq/100 g units). Houchin[9] reported that the surface charge is balanced by an equal amount of opposite charge in the solution adjacent to the solid surface, the charge separation being known as the

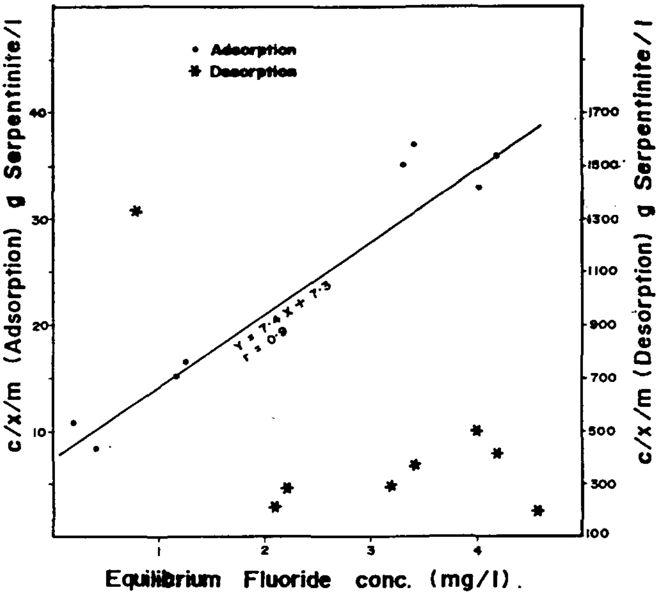

Figure 4 Langumuir isotherms of fluoride for (i) adsorption (ii) desorption.

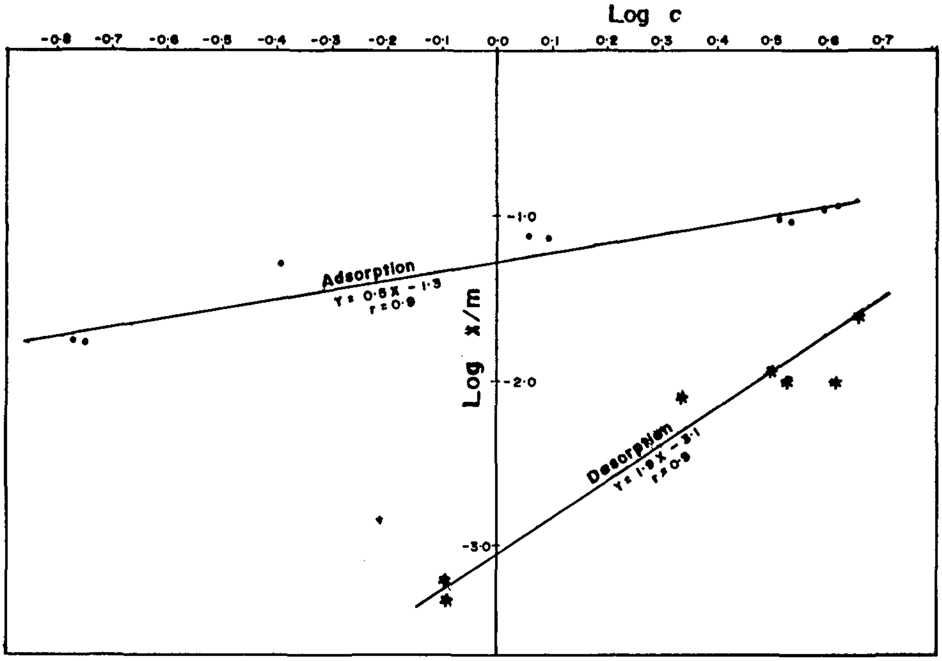

Figure 5 Freundlich isotherms of fluoride for (i) adsorption (ii) desorption.

electrical double layer. Thus it can form strong bonds between the positive surface and negative fluoride ions.

Desorption of fluoride by 1% (W/V) NaOH conformed only to the Freundlich isotherm for treated serpentinite. In comparing the Freundlich isotherm for adsorption and desorption, the line for fluoride desorption did not fall on the line plotted for fluoride adsorption, indicating possible hysteresis. The partial desorption process was carried out in a 1% NaOH (W/V) medium at 60°C. This shows the extraordinary high bond energy needed to break F^- ions from the serpentinite surface. Furthermore, the partial desorption of fluoride from 1% (W/V) NaOH solution is explained as being due to $OH^- \rightleftharpoons F^-$ exchange phenomena. It further suggests the possible occurrence of a F^- serpentinite complex that cannot be desorped easily.

2. *Surface Charge on Treated Serpentinite and its Relation to Fluoride Adsorption*

Preliminary investigation indicate that the adsorption capacity of fluoride onto serpentinite varies with the quantity of HCl used in the chemical treatment process. As illustrated in Figure 6, the uptake capacity of fluoride onto serpentinite reaches an optimum value at a serpentinite /HCl ratio of 50 g : 60 ml. The optimum fluoride adsorption process may depend on the chemical composition of the original serpentinite used, and hence a trial and error method has to be applied when determining the optimum conditions. The total surface charge of raw and acid treated serpentinite is shown in Table II. It is seen that raw serpentinite has a negative charge of −2.6, while the treated serpentinite (from S : H ratio 50 : 60) has a positive charge, the highest positive charge being observed for the S : H 50 : 60 ratio. The optimum fluoride adsorption was also observed for this ratio.

In raw serpentinite specific fluoride adsorption may generally take place as an exchange of OH^- and F^-. However, in treated serpentinite, non-specific adsorption can also take place due to the presence of a charge. Hence treated serpentinite may

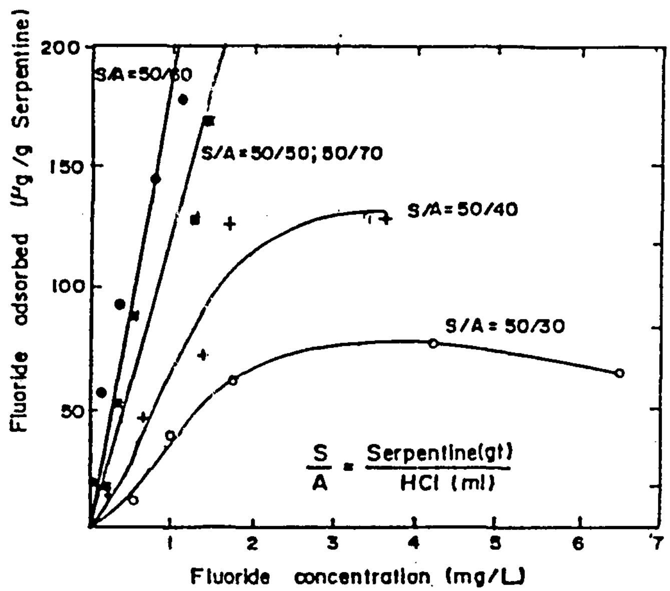

Figure 6 The adsorption curves of fluoride at various serpentinite/HCl ratios.

Table II Permanent charge properties of treated and raw serpentinite

Treatment (serpentinite : HCL)	K^+ adsorbed meq/100 g, serpentinite	Cl^- adsorbed meq/100 g, serpentinite	Permanent charge (σ_p) $\sigma_p = {}^-[K^+\text{adsorbed-}Cl^-\text{ adsorbed}]$
100 : 50	6.968	0.331	−6.637
100 : 100	7.691	2.976	−4.715
100 : 120	3.378	4.455	1.077
100 : 140	4.090	4.367	0.277
100 : 160	3.350	4.172	0.222
100 : 200	5.613	5.973	0.360
raw serpentinite	2.983	0.432	−2.551

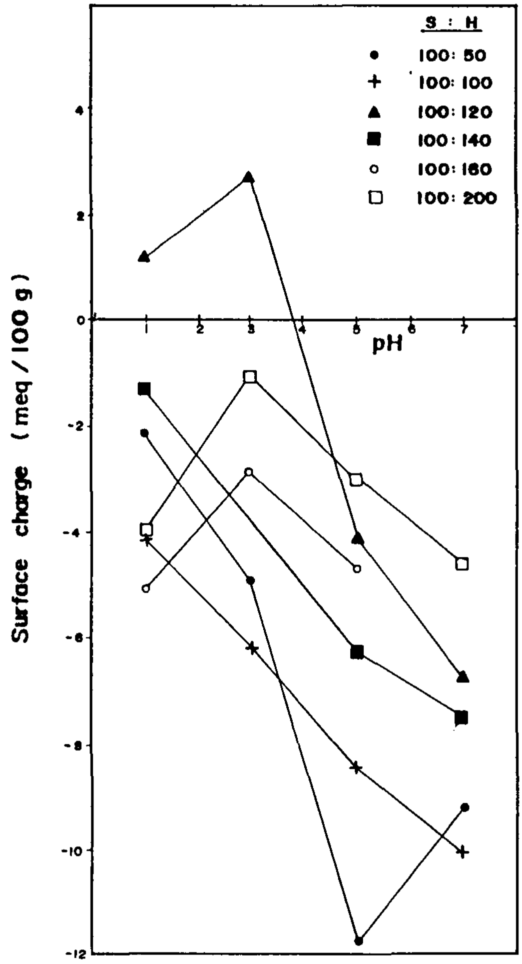

Figure 7 The surface charge variation with pH.

provide more adsorption sites for fluoride adsorption than raw serpentinite. Furthermore, the positive charge on the surface may provide more favourable electrostatic potential for fluoride adsorption than the negative surface in raw serpentinite. The amount of fluoride adsorption is normally related to surface area. In this case, strong reaction with conc. HCl may increase the surface area of the serpentinite.

The variation of the surface charge of the treated serpentinite with the variations of the pH of the media used is shown in Figure 7. The positive charge developed at low pH (1 and 3) and the negative charge developed at high pH (7) is observed only for treated serpentinite with a S : H ratio of 50 : 60. Other treated serpentinites showed a negative charge at low pH (1, 3) as well as at high pH (7). The positive charge developed at low pH and the excess negative charge developed at high pH are collectively known as the pH dependent charge.[10]

The efficiency of acid treated serpentinite in fluoride removal with pH_0 is shown in Figure 8. It is interesting to note that the fluoride adsorption ability of serpentinite decreases both at high and low volumes of HCl used and maximum total surface charge was observed at pH_0 (4).

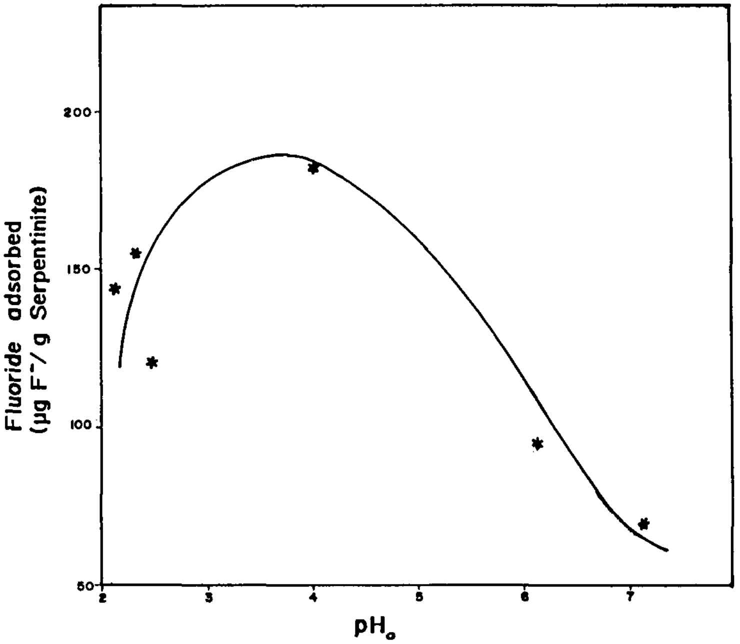

Figure 8 Fluoride adsorption with pH_o, on treated serpentinite.

3. *Variation of Fluoride Adsorption in Serpentinite with pH*

The data obtained by equilibrating the chemically treated serpentinite (S : H = 100 : 120) with fluoride ions in solution at various pH conditions are shown in Figure 9. The fluoride uptake by the solid substance increases with the solution pH and the optimum condition is reached at a pH value of 5.2. Subsequently it decreases with further increase of pH. The decrease of fluoride adsorption onto serpentinite in the acid medium cannot be thought of as a complexation mechanism with metals that

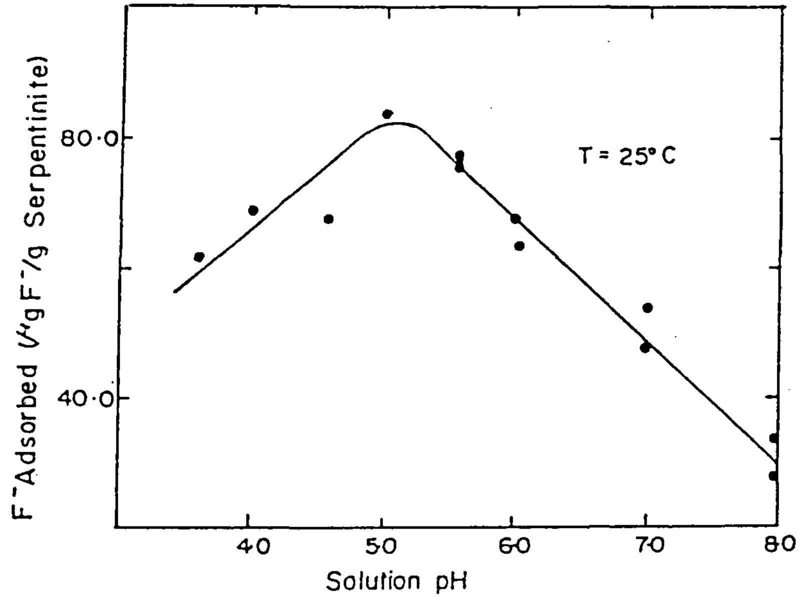

Figure 9 Fluoride adsorption with pH, on treated serpentinite.

are released from serpentinite. In the treatment process, considerable amounts of metals were released from serpentinite. Therefore in high acid media, fluoride can form a complex with H^+ forming (HF). As a result, the concentration of free fluoride ions in solution is negligible and the adsorption decreases. However, due to reaction with HF, ions of Al and Fe which are abundant in serpentinite may be released. It is a well known fact that F^- and Al^{3+} have the ability to form complexes. With decreasing acidity (by increasing pH) the solution is enriched with OH^- ions, that can react with positive sites in the solid medium. As a result, the polarity of the positive medium will be reversed and this may be a reason for the decrease of fluoride adsorption.

Many models, both conceptual and numerical[11,12] have been advanced to describe the adsorption of anions onto hydroxy-solids at various pH levels. In this study, a surface complex formation model was selected[12] to describe the mechanisms involved in the fluoride adsorption. According to this model, the reaction between fluoride and serpentinite occurs via the formation of solid fluoride complex (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 (SOH_2), without the release of OH^- or H^+. Therefore the exchange sites of chemically treated serpentinite show amphoteric behaviour for the variation of solution pH. The model uses the following mechanism.

(a) *acidulation and hydration*

$$S + H^+ \rightleftharpoons SH$$

$$SH + H_2O \rightleftharpoons SOH_2 + H^+$$

(b) *fluoride adsorption*

1) pH < 5.20

$$SO^{+}H_2 + F^{-} \rightleftharpoons SF + H_2O$$

2) pH > 5.20

$$SO^{+}H_2 + OH^{-} \rightleftharpoons SOH + H_2O$$

$$SOH + F^{-} \rightleftharpoons SF + OH^{-}$$

The variation of Δ pH with the amount of fluoride adsorbed onto serpentinite is shown in Figure 10. As expected the adsorption ability of serpentinite increases with increasing pH, indicating exchange of OH- ions into solution by F^-. When initial pH of the solution is 10, the adsorption capacity of serpentinite is reduced significantly. However, the observed adsorption of (70 μg F^-/g serp.) at pH (−1) could result from the direct release of H^+ into solution as indicated below.

$$SH + F^{-} \longrightarrow SH + H^{+}$$

4. *Thermodynamics of Fluoride Adsorption*

In this study, the fluoride–solid phase adsorption isotherms were constructed at 25°C and 50°C to calculate the isosteric heat of adsorption ($\overline{\Delta H_r}$) as described below.

$$\overline{\Delta H_r} = R \ln ((C_2/C_1)/(1/T_1 - 1/T_2))$$

Where $\overline{\Delta H_r}$= isosteric heat of adsorption (kJ/mole) at a given adsorption density *r*; *R* is gas constant, C_2 is the equilibrium concentration of the ion at temp. T_2 and

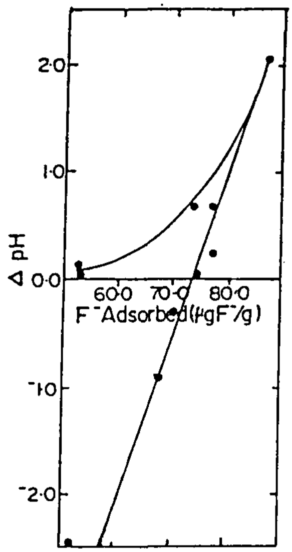

Figure 10 pH variation with fluoride adsorption on treated serpentinite.

given adsorption density; and C_1 is the equilibrium concentration of ion at temp. T_1 and the same adsorption density.

The data obtained by equilibrating serpentinite samples with various concentrations of fluoride (0.1 mM–1 mM) at 25°C and 50°C, respectively, is shown in Figure 11, and are presented as simple isotherms. From the results of the present study, it would appear that the fluoride adsorption depends on the temperature. The kinetically controlled process or reactions having a high activation energy would behave this way.[13] When we consider Figure 11 in one instance (S : H = 100/200), the fluoride adsorption at 25°C is well below that at 50°C indicating exothermic behaviour. The determination of isosteric heat of adsorption as a function of adsorption density gives an indication of the uniformity or nonuniformity of adsorption sites. As shown in Figure 12, the $\overline{\Delta H_r}$ varies with the adsorption density, suggesting that some treated surfaces are heterogeneous. If the isosteric heat of adsorption is independent of adsorption density then the surface is homogeneous and if the $\overline{\Delta H_r}$ decreases with increasing adsorption density, then the surface is heterogeneous. The decrease in $\overline{\Delta H_r}$ with increasing adsorption density can be due to different types of adsorption sites or the interaction of adsorption ions.[14]

With the increase of adsorption density for S : H ratios 50 : 40, 50 : 50 and 50 : 60 in treated samples, the $\overline{\Delta H_r}$ decreases, as shown in Figure 12. This indicates that these surfaces are heterogeneous. However, this effect is reversible in the S : H ratio of 50 : 70 treated sample surface.

5. *Action of Water on Treated Serpentinite*

The action of distilled water on treated serpentinite is shown in Table III. When a weighed quantity of serpentinite is made to react with distilled water, it is found that the conductivity of the solution increases gradually with a concomitant release of ions such as of chloride, while the fluoride concentration of the solution increases only to a very small extent. The pH of the solution also increases from 5.8 to 7.3. Pundssac[15] has shown that the aqueous solution containing the serpentinite is rendered alkaline in the process of hydrolysis.

Table III Water quality variation with time, in treated serpentinite (S : H = 100 : 120) when placed in contact with distilled water

Time (days)	Specific conductivity (μS)	pH (units)	Temp. °C	Alkalinity as $CaCO_3$ m.mol l^{-1}	F^- (mg/l)	Cl^- (mg/l)
0	2.5	5.75	24.6	—	—	—
1	38.0	6.90	23.3	1.0	0.02	7
2	44.8	6.70	22.6	1.0	0.04	12
3	47.4	7.10	23.1	1.0	0.05	12
4	52.3	7.30	24.4	1.0	0.05	12

6. *Differential Thermal Analysis (DTA) and X-ray Diffraction (XRD) Curves for Raw, Acid Treated and Fluoride Adsorbed Serpentinite*

Figure 13 shows the DTA curve for raw serpentinite obtained from Uda Walawe. In this material the first endothermic peak is at 150°C, due to loss of hydroscopic water and the second endothermic peak is at 680°C, caused by the loss of structural water.

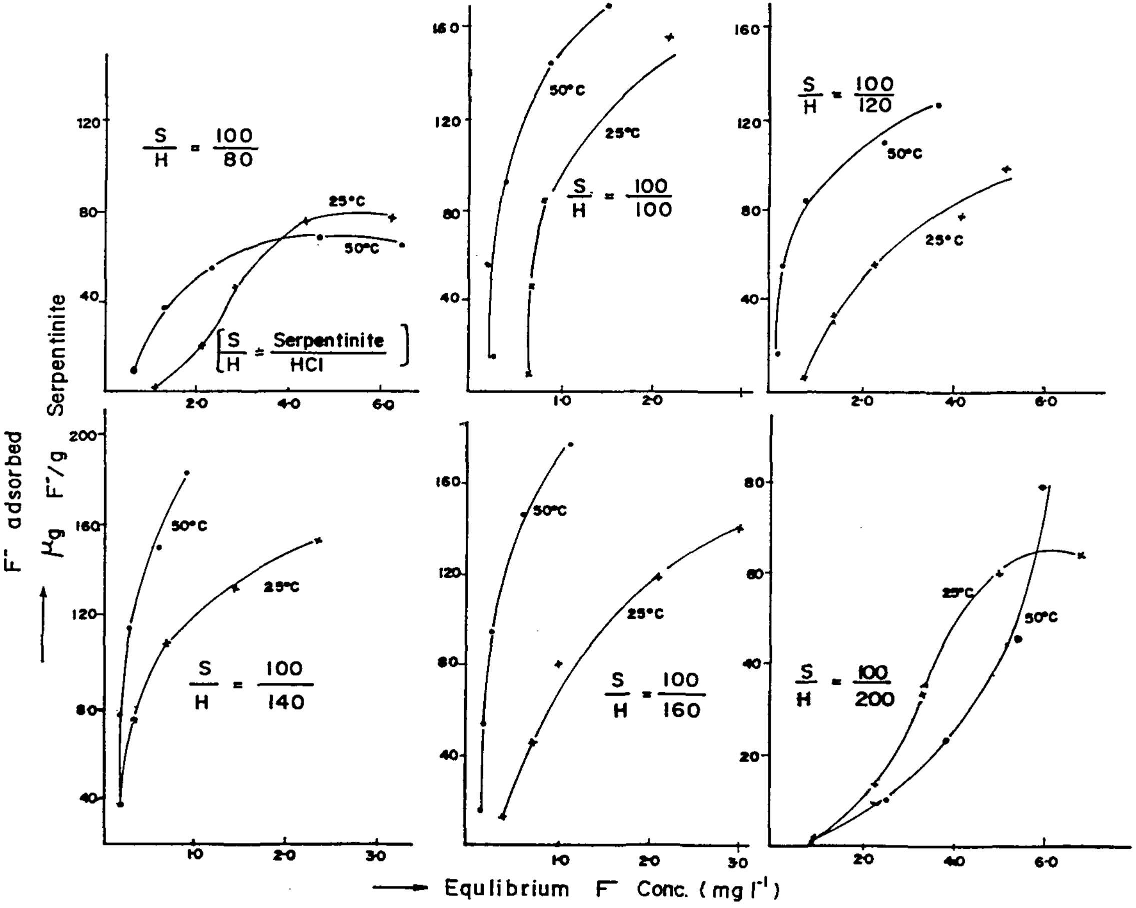

Figure 11 Fluoride adsorption at 25°C and 50°C from serpentinite.

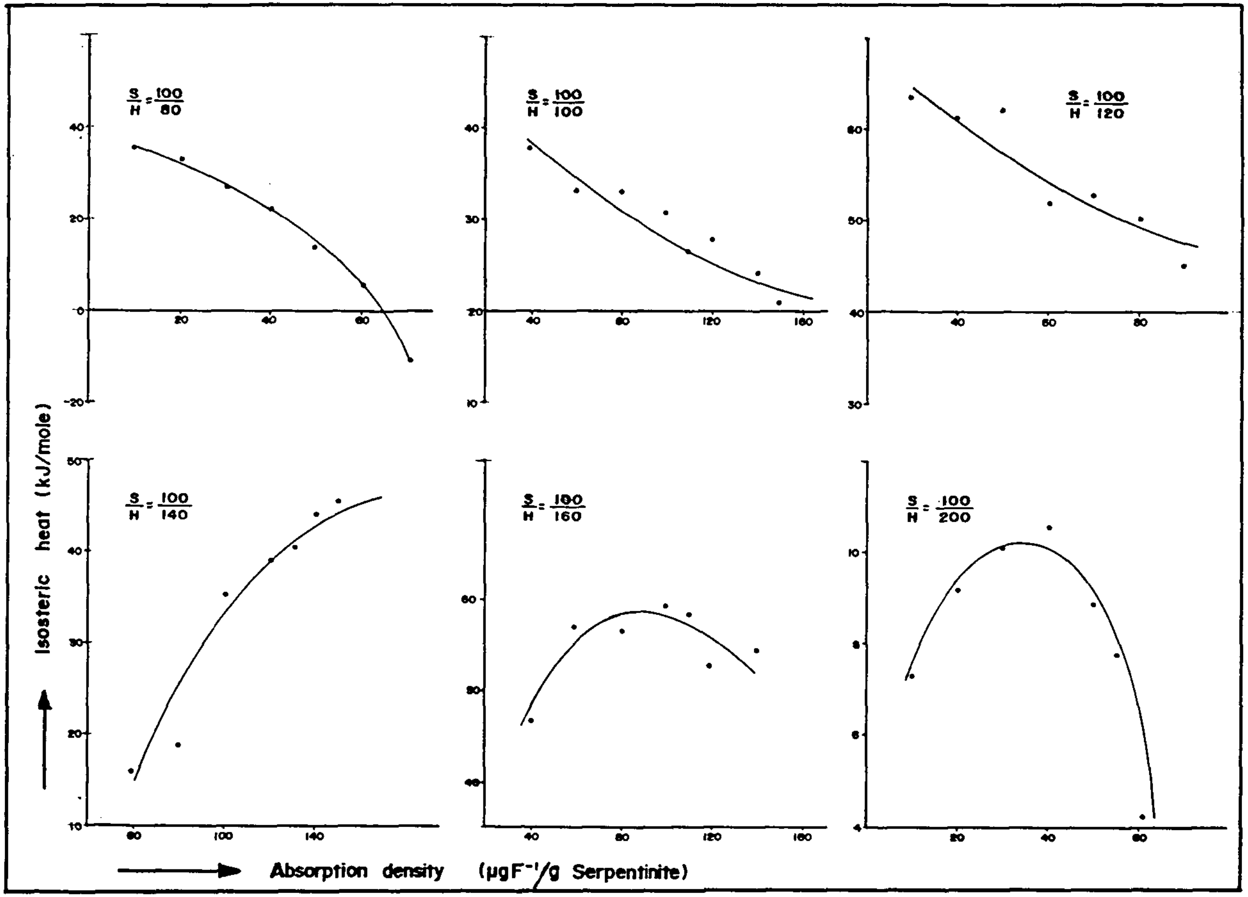

Figure 12 Isosteric heats for serpentinite at 25°C and 50°C.

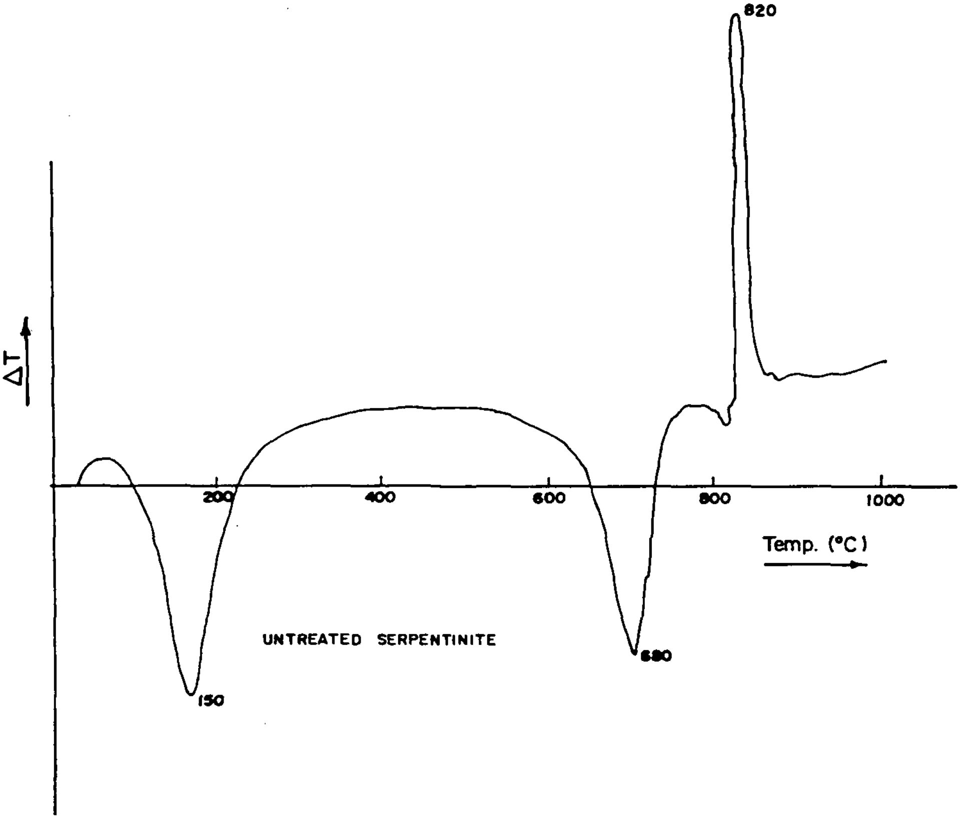

Figure 13 DTA pattern for raw serpentinite.

The large exothermic peak at 820°C is due to recrystallization to enstatite. However, the identification of serpentine minerals individually as antigorite, chrysotile or lizardite proved difficult.

Figure 14 shows the DTA curves for acid treated serpentinite and acid treated (2 mM NaF) fluoride contact serpentinite. As shown in Figure 14, with increasing acid volume, the endothermic peak height increases first followed by the endothermic peak height increases first followed by the endothermic peak heights which decrease significantly. At the S : H ratio of 50 : 100 endothermic and exothermic peaks are absent. In this case it appears likely that with increasing acid volume, structural changes take place. At the S : H ratio of 50 : 100, significant change of the structure is distinctly observed. Schreier *et al.*[10] showed that serpentinite minerals such as chrysotile or lizardite which were treated with acetic or citric acid resulted in structural changes due to leaching of structural elements such as Mg. When considering acid treated and fluoride contact serpentinite, increase of exothermic peak height at temperature (820°C) and endothermic peak height at temperature (150°C) were also observed.

From XRD data it can be deduced that the major structural formulae for acid treated (S : H = 50 : 50) serpentinite was $Mg_3Si_2O_5(OH)_4$ and [S : H = 50 : 50] acid treated, 2 mM NaF contact serpentinite was $K_2(Fe, Mn, Mg)_3 Si_8O_{20}(F,OH)$. According to the above formulae, F^- ion substitution for OH^- ions has taken place.

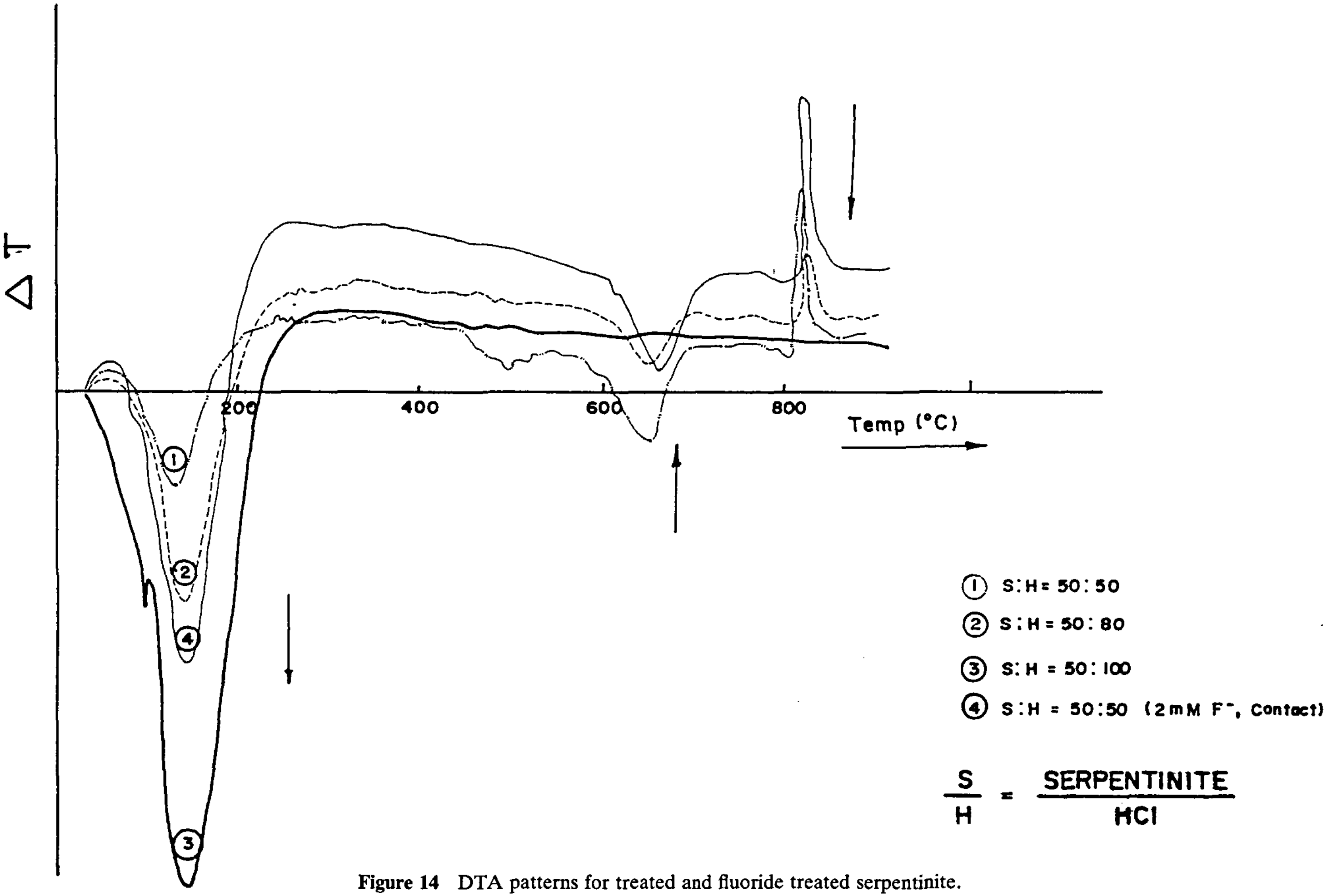

Figure 14 DTA patterns for treated and fluoride treated serpentinite.

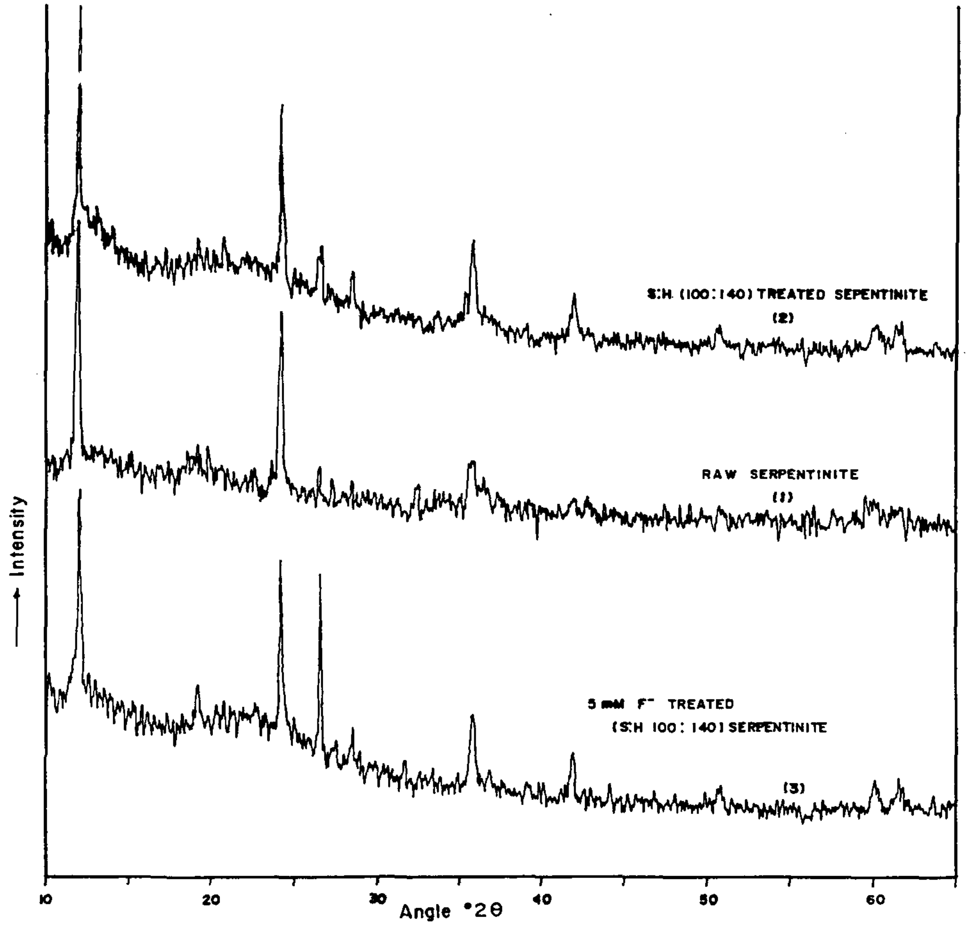

Figure 15 XRD patterns for raw, acid treated and acid treated fluoride adsorbed serpentinite.

Figure 15 shows the XRD patterns for raw, acid treated (S : H = 10 : 140) and acid treated (S : H = 100 : 140) with 5 mM NaF treated serpentinite. The strongest peaks observed for raw serpentinite were 20 (11.9, 24.2 and 67.5) and d (7.43, 3.68 and 1.39) and for treated serpentinite they were 20 (11.9, 24.1 and 35.7) and d (7.43, 3.68 and 2.51). The change of 20 and intensity may be caused by a change of the serpentinite structure. In acid treated (S : H = 100 : 140) 5 mm NaF treated serpentinite, it was noted that major peaks were at 20 (11.9, 24.2 and 26.5) and d (7.42, 3.67 and 3.36). In treated serpentinite, at 20 (24.2), the height was significantly smaller than in fluoride contacted sample. The compositions of these serpentinites as observed were raw $Mh_sSI_2O_5(OH)_4$, acid treated $Mh_3SI_2O_5(OH)_4$ and acid treated fluoride contact K_2 (Fe, Mn, Mg)$_3$ Si_8O_{20}(F,OH).

Figure 16 shows the variation of XRD patterns for treated serpentinites. The intensity of the peaks were reduced significantly with increasing acid volume. Shewry and Peterson;[17] Proctor and Woodell,[18] reported that trace elements are readily removed from the structure of the serpentine minerals in acid media.

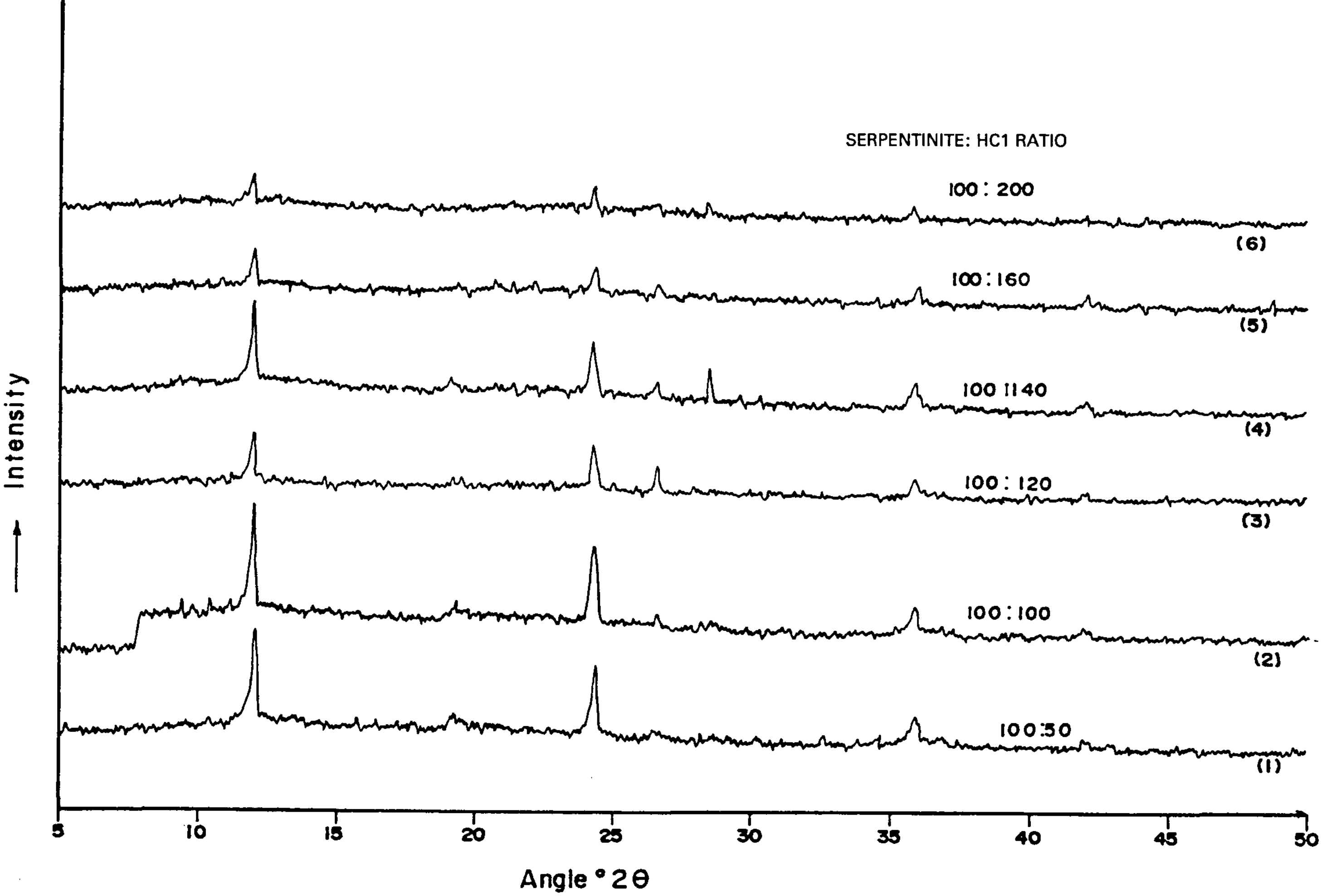

Figure 16 XRD patterns for acid treated serpentinite.

CONCLUSIONS

The maximum fluoride adsorption was observed at a serpentinite to acid ratio of 100 g : 120 ml. In this material 1.1 meq/100 g positive surface charge was observed, while raw serpentinite showed 2.6 meq/100 g negative surface charge. This clearly showed that the surface charge influenced the fluoride adsorption process. Desorption studies have shown the need for more energy to loosen the surface bound fluoride. This may be due to the strong adsorption between negative fluoride ions and positively charges treated serpentinite that many have taken place. However, 1% (W/V) NaOH showed good desorption capacity. According to thermodynamic properties (such as isosteric heat of adsorption) this treated serpentinite (S : H = 100 g : 120 ml) surface behaves as a heterogenous surface. Thus sites are available in excess at low adsorption densities and the surface behaves as though it was homogeneous. Results also showed that 16.6 kg of treated serpentinite (S : H = 100 g : 120 ml) is needed to bring a 5 mg/l, 1 m^3 fluoride solution down to 1.3 mg/l F^-.

Considering the XRD and DTA patterns for raw and treated serpentinite, it is clearly seen that there are structural changes in the treated sample, caused perhaps by the leaching of ions such as Mg, Fe and Al with conc. HCl treatment. The present results clearly indicate that the serpentinite (treated) prepared in our laboratory can be used in the defluoridation of fluoride from community water supplies. Thus an inexpensive fluoride decontamination plant can be designed to suit the requirements of a developing country. However the technical details involved in these plants should be studied further.

Acknowledgements

Thanks are due to the World Health Organization for providing the necessary funds for this research. We thank Dr. H. Hillmer of the University of Hamburg, West Germany, for his help in obtaining the XRF data, and Miss Avanthi Wickramasinghe for her assistance in drafting the figures.

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