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Correlation between chemical corrosion and structural variations in fibrous tremolite

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An understanding of the correlation between the durability under different corroding conditions and the corresponding structural variations of silicates, is highly essential for their proper utilization in modern technology. To achieve this, a sample of fibrous chain silicate (tremolite) was subjected to various mechanical and chemical treatments and the resulting samples were analysed by X-ray diffraction, differential thermal analysis, scanning electron microscopy, and infrared spectroscopy. Several interesting results on chemical corrosion have been obtained. Attempts have been made to establish a correlation between these results with the X-ray diffraction data.

1. Introduction

In modern technology, use of silicate-based materials spans from sheet glass for windows, thin films in microelectronics, core and cladding of optical fibres [1] and hosts for radioactive waste fixation [2], to chemical implants [3], slow-release synthetic fertilizers [4], and even to non-durable silicate glass beads containing short-lived radioactive elements which are injected into malignant tumors to be destroyed by radiation [5]. To have practical viability, the former class of silicates must possess a very high chemical resistance towards exposed environments, whereas in the latter cases, the silicate structures must be modulated so as to impart controlled durability/non-durability to the materials. Thus tailor-made silicates having exact chemical resistance under a predetermined weathering condition are in great demand in modern technology. No doubt this can only be satisfactorily achieved if the "structure" of silicate can be correlated with durability under different corroding conditions.

Silicates, either crystalline or glassy, weather mainly through chemical reaction followed by mass transfer, and to some extent through mechanical abrasion. These two factors often operate simultaneously and separation of individual influences on silicate weathering becomes complicated, if not impossible. Although most of the above-mentioned materials are used in the glassy form, the detailed structure and the true thermodynamic state of a glass, even of simple composition, are yet to be firmly established. During conventional study of chemical resistance of silicate materials, the exposed surface area accessible to the attacking medium is one of the important factors [6]. Measurement of the true surface area of a glassy silicate surface, particularly during chemical attack is extremely difficult and uncertain. For laboratory studies, often test samples are made by grinding the material to fine powder, and the size of the crystallites in the powder thus produced is estimated from X-ray line broadening or other suitable techniques.

In the present investigation we have taken a natural tremolite sample (general formula $Ca_2Mg_5Si_8O_{22}(OH)_2$), prepared the powder by mechanical grinding, and chemically corroded the powder in different acidic and alkaline aqueous solutions. The powders, before and after chemical treatment, were studied with X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDAX), infrared spectroscopy and thermal analysis. The amount of powder constituents (CaO, MgO and SiO_2) leached out into the solution after chemical treatment was estimated by atomic absorption (calcium, magnesium) and the molybdate calorimetric method (SiO_2).

Tremolite has a fibrous structure, and during powder making by grinding, the XRD pattern changes markedly [7]. The objective of the present investigation was to determine if there is any correlation between the change in the XRD pattern with chemical corrosion of the tremolite powders.

2. Experimental procedure

The tremolite sample was pulverized and then ground in an all-agate mechanical mortar for various lengths

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[†] This paper is dedicated to the memory of Professor A. Paul who passed away on 29 November 1990.

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of time under dry conditions. The grinding time was increased step-wise from 1 to 24 h. The XRD patterns and scanning electron micrographs of a few selected samples are shown in Figs 1 and 2. Portions of 500 mg of each powder were treated with HCl (concentrated 11 N, and diluted 1 N), HNO_3 (concentrated 16 N), aqua regia (3 volume parts concentrated HCl + 1 volume part concentrated HNO_3), and 1 N NaOH solution for times ranging from 7–48 h at room temperature (30 ± 2 °C). After the desired period of leaching, the powders were separated from the solution, washed with deionized water followed by dry ethyl alcohol and finally dried in an air oven at 110 °C for 24 h. The dried powder was then used for further studies with various physical and chemical techniques. As a typical example, the amount of CaO, MgO and SiO_2 leached out in different times in 1 N HCl and 1 N NaOH solutions by two sets of powder are given in Table I. The EDAX results (CaO, MgO and SiO_2) of a typical powder after leaching with different solutions are given in Table II; the powders used in these experiments were ground for 7 h, and 500 mg samples were treated with 50 ml leach solution. Typical thermograms (differential thermal analysis, DTA, and thermogravimetry, TG) of some chosen samples are shown in Fig. 3.

3. Discussion

Tremolite is a double-chain silicate mineral belonging to the amphibole group of asbestos with ideal formula $Ca_2Mg_5Si_8O_2(OH)_2$. In the fibrous (asbestos) tremolite, the double chain is formed when two pyroxene-type chains ($CaMgSi_2O_6$) are joined by sharing suitable oxygens. This complex fibrous structure is responsible for its several important physical properties. During processing for commercial uses, these minerals are often ground to fine powders. It is possible that during grinding the material undergoes some transformation which is more than mere morphological. These transformations are expected to affect the chemical reactivity/rate of chemical corrosion.

3.1. Scanning electron microscopy

Typical scanning electron micrographs, as shown in Fig. 2, clearly indicate the tremolite sample to be fibrous, and during grinding the long fibres break down to smaller pieces. After 24 h grinding, the average fibre length reduces to about 2–5 μm.

3.2. Thermal analysis and infrared spectroscopy

Thermograms of powdered tremolite samples treated under different conditions are shown in Fig. 3. Tremolite of theoretical composition contains 4.14 wt % constitutional water. The chemically untreated sample (Fig. 3a) shows a cumulative weight loss of 5.44 wt % up to 1200 °C; this slight excess weight loss of 1.3 wt % is probably due to the presence of some low-temperature volatiles and/or chemisorbed moisture on the powdered sample.

However, the thermogram clearly shows the thermal stability of the sample up to about 860 °C, where a weak endothermic shoulder, which becomes more prominent on acid treatment (Fig. 3b), is developed. This is followed by a relatively well-defined endothermic peak around 1025 °C. This feature indicates that the loss of structural water takes place in two stages, the final one being at 1025 °C accompanied by structural breakdown of tremolite into pyroxenes and silica as is usual in any untreated tremolite sample [8]. Thus the broad features of the thermogram conform with the usual thermal behaviour of tremolite sample

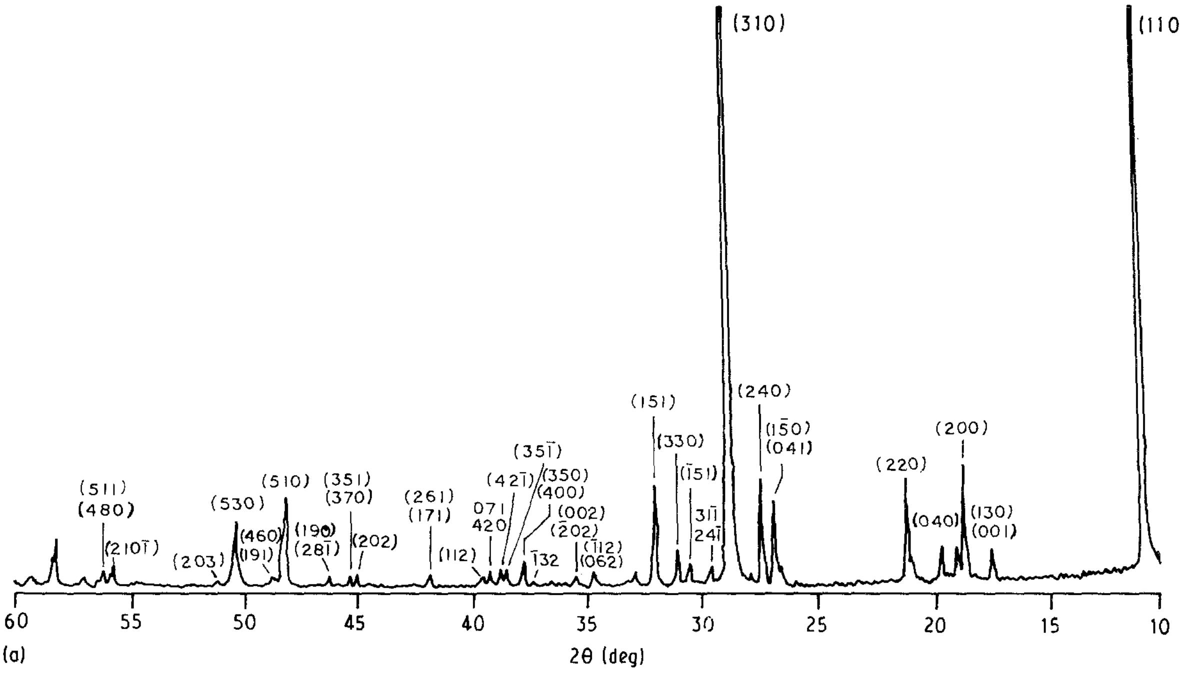


Figure 1 (a) X-ray diffractogram of the untreated tremolite sample. The peaks have been indexed by assuming a monoclinic cell.

without any iron content which is confirmed by the EDAX results [8].

In the case of the HCl-treated sample (Fig. 3b) the endothermic peak around 100 °C is stronger, indicating some hydration of silica; and the endothermic peak around 1050 °C has become sharper. The remaining part of the thermogram appears virtually the same as that of the untreated sample. The cumulative weight loss from this sample is 3.17 wt % indicating some further preferential loss of constitutional water during acid treatment as is indicated by the sharper endothermal peak around 1050 °C.

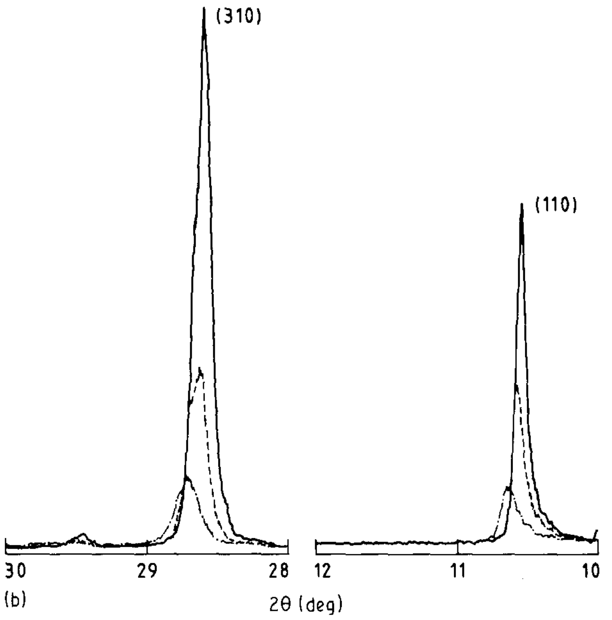
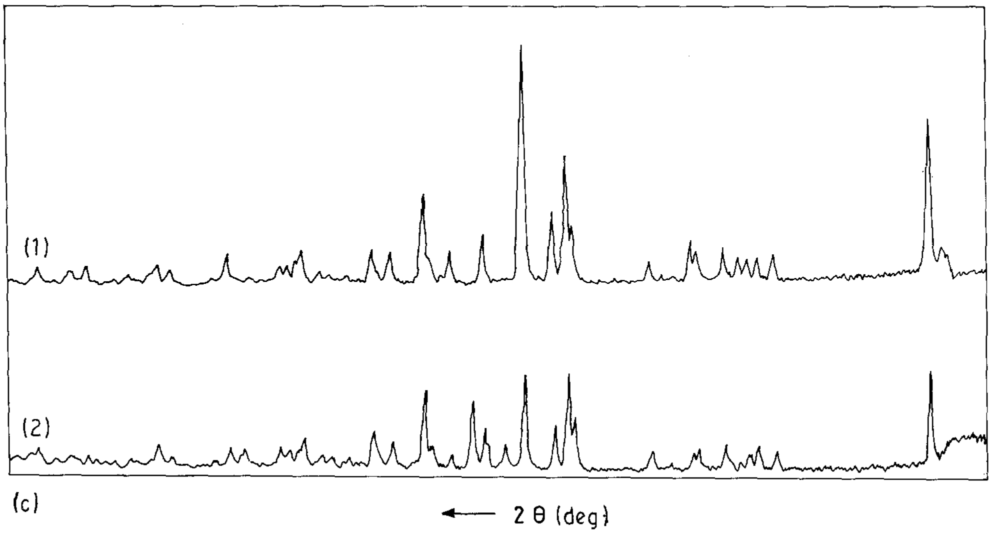
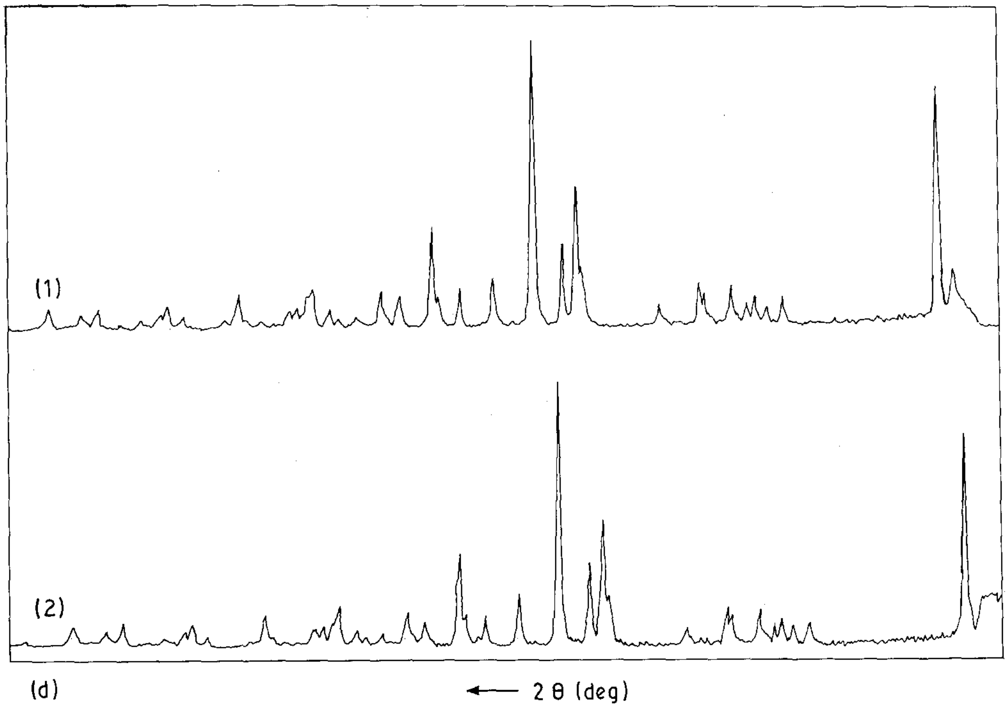


Figure 1 Continued. (b) (1 1 0) and (3 1 0) diffraction peaks of the tremolite samples (——), roughly ground, and machine ground for (– – –) 2 h, (—·—) 24 h. (c) X-ray diffractograms of tremolite treated with (1) HCl (concentrated) and (2) NaOH. (d) X-ray diffractograms of tremolite treated with (1) HNO_3 (concentrated) and (2) HNO_3 + HCl (concentrated).





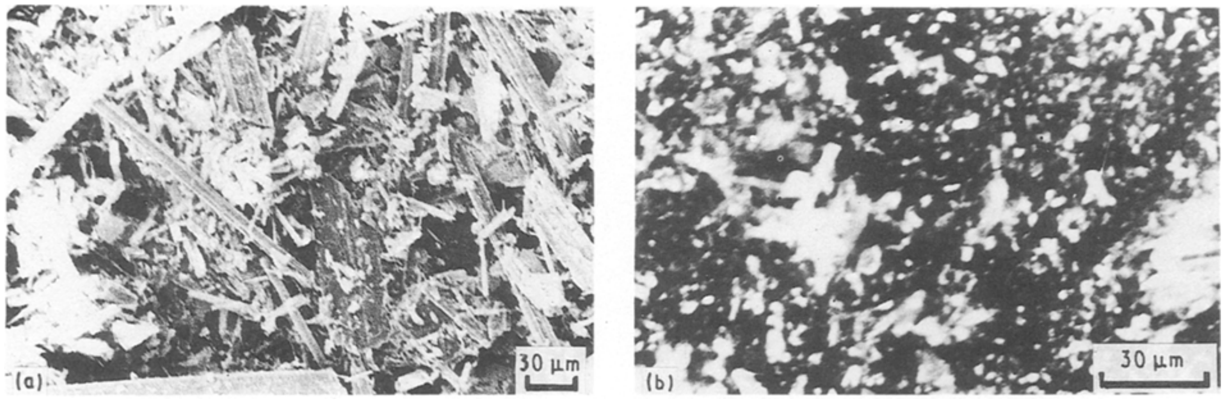


Figure 2 Scanning electron micrographs of (a) an untreated sample, (b) a machine-ground sample.

TABLE I Extraction of CaO, MgO and SiO_2 from two grades of tremolite powder

Time of leaching (h)	Powder I (ground for 4 h)						Powder II (ground for 24 h)					
	CaO[a]		MgO[a]		SiO_2[a]		CaO[a]		MgO[a]		SiO_2[a]	
	1N HCl	1N NaOH	1N HCl	1N NaOH	1N HCl	1N NaOH	1N HCl	1N NaOH	1N HCl	1N NaOH	1N HCl	1N NaOH
7	11.02	–	6.12	–	–	4.06	16.51	–	9.21	–	–	6.10
24	13.44	–	6.46	–	–	4.26	20.12	–	9.70	–	–	6.40
48	19.04	–	6.80	–	–	5.31	28.63	–	10.19	–	–	7.96

[a] Wt % solid in the leaching solution.

TABLE II EDAX analysis of tremolite powder[a] before and after chemical treatment[b]

Sample type	Normalized wt %		
	CaO	MgO	SiO_2
Untreated	17.59	23.57	58.84
Treated with conc. HCl	16.04	17.01	66.95
Treated with conc. HNO_3	17.06	15.83	67.12
Aqua regia	13.90	18.04	68.07
1N NaOH solution	21.25	21.04	57.71

[a] Ground for 4 h.
[b] 500 mg powder treated with 50 ml solution for 24 h.

In the case of aqua regia treatment (Fig. 3c) the thermogram shows a small but sharp exothermic peak around 230 °C; the origin of this peak could not be definitely established, although this could be due to formation of some alkaline earth metal oxychloride/nitrate.

The thermogram of the 1N NaOH-treated sample (Fig. 3d) is distinctly different from the others. Well defined and sharp exothermic peaks occur around 290, 340 and 450 °C followed by a strong endothermic doublet at 760 and 773 °C; the later two peaks are similar to the decomposition of $MgCO_3$. Formation of alkaline earth carbonates during alkaline treatment of the powder is also corroborated from infrared results, as shown in Fig. 4 where strong and distinct absorption band could be seen around 1450 cm^{-1}. For easy comparison, Fig. 4 also contains infrared spectra of pure $CaCO_3$ and $MgCO_3$.

3.2. X-ray diffraction

For proper identification of the sample, the d values of all the peaks in the diffractogram of the untreated sample (Fig. 1a) were measured from their θ values. The three strongest peaks corresponding to $d = 0.835$, 0.310 and 0.279 nm characterize the sample as tremolite [9]. For further confirmation, all the d values were measured and indexed by assuming the usual monoclinic structure of tremolite with lattice parameters $a = 0.989$ nm, $b = 1.802$ nm, $c = 0.527$ nm and $\theta = 105°$, as given in the literature [9]. The results agree well with the ASTM powder diffraction data of tremolite (13–437).

The highly preferred orientation of the fibrils parallel to the fibre axis is revealed by the two peaks at 0.835 and 0.309 nm which are several times stronger than the other peaks. These peaks are due to reflections from (1 1 0) and (3 1 0) planes parallel to the cleavage faces which are parallel to the fibre axis.

The diffractograms of the machine-ground samples (Fig. 1b) show some very interesting features, while the two strongest peaks, (1 1 0) and (3 1 0), are found to decrease progressively in height, without any appreciable variation in width. All other peaks are found to remain virtually unaffected with gradual increase in grinding time. This behaviour is suggestive of gradual destruction of the preferred orientations of the fibrils due to grinding which is responsible for the decrease in peak heights with marginal change in their widths, that is related to the size of the crystallite. It may be pointed out that the crystallite size measured from the width of an XRD peak is a measure of the thickness of the crystallite perpendicular to the reflecting planes

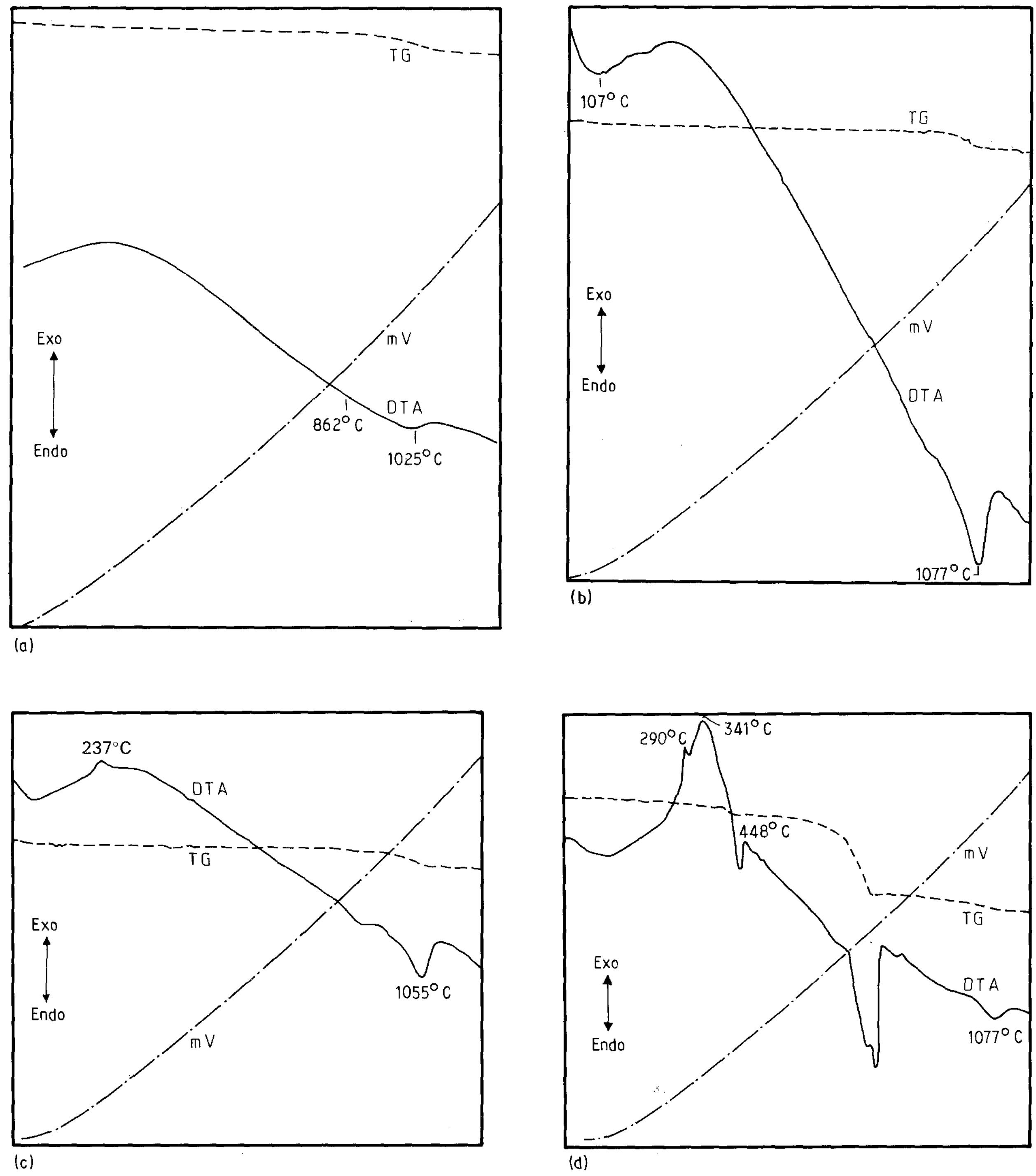


Figure 3 Thermograms of tremolite sample under different treatment: (a) chemically untreated sample, (b) acid-treated (HCl), (c) Aqua regia-treated, (d) NaOH-treated.

producing the peak. Hence, unlike the morphological shape and size as revealed by microscopic observation, crystallite size measured by XRD, depends on the indices of reflection and the shape of the particle. This explains why the XRD peaks indicate only marginal variation in crystallite sizes, while the scanning electron micrographs clearly show the gradual breakdown of the fibrils into minute pieces with progressive grinding of the sample.

The diffraction patterns of the samples treated chemically (Fig. 1c) are modified in almost the same fashion as in the case of grinding when compared with the untreated sample. However, the peak heights of the two principal maxima are found to decrease successively as the reagent varies from HNO_3, (HCl and HNO_3) to HCl and finally to NaOH with the appearance of a number of new lines most likely due to formation of various decomposition products, as discussed in the following section.

3.3. Chemical corrosion

Silicates (crystalline or glassy) become unstable in aqueous alkaline solution due to hydration of silica followed by ionization of the silicic acid thus formed. In aqueous solution at 298 K, the first and second ionizations of H_2SiO_3 ($SiO_2 + H_2O$) occur around pH 10 and 12, respectively [10]. In less alkaline or

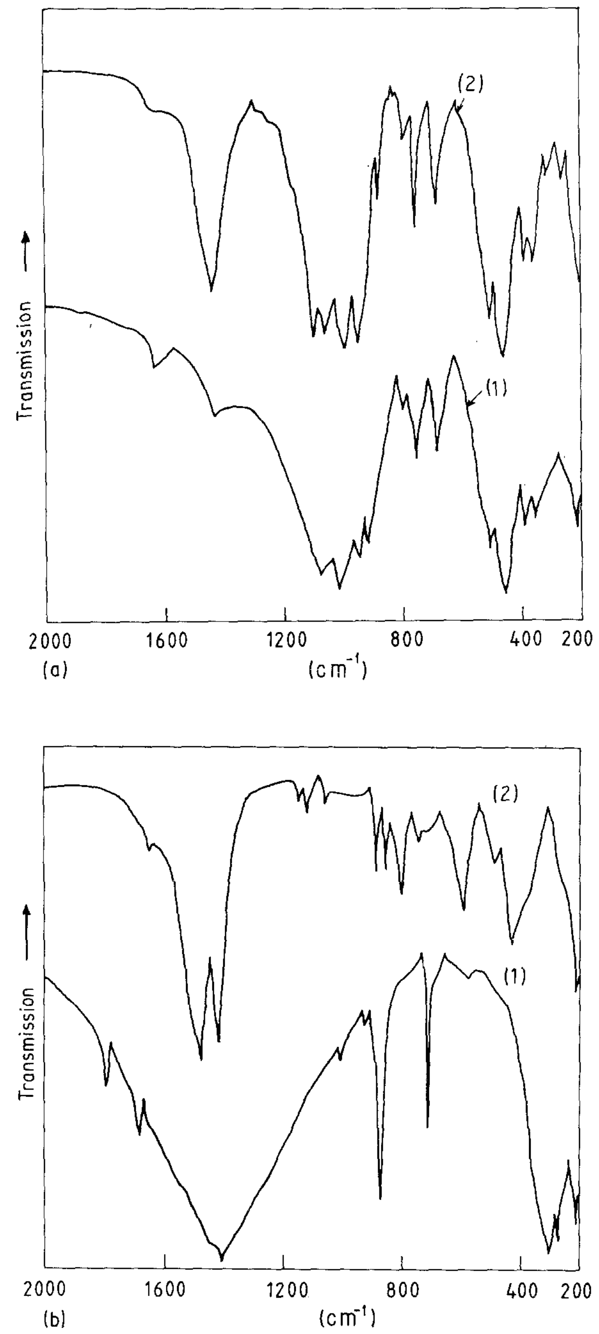


Figure 4 Infrared absorption spectra of (a) the tremolite (1) and alkali-treated tremolite (2) sample, (b) pure $CaCO_3$ (1) and $MgCO_3$ (2).

acidic media (pH 9) although the hydrated silicate surface is stable (equilibrium solubility is 1–10 p.p.m.), ion exchange takes place between mobile alkali or alkaline earth metal ions of the silicate structure and hydronium ion (H_3O^+) of the aqueous solution [11, 12]. In the present investigation, four types of acidic solutions were used: concentrated HCl (11N), dilute HCl (1N), concentrated HNO_3 (16N) and aqua regia. All these solutions are highly acidic, the last two also being oxidizing. The extra oxidizing power of aqua regia is due to formation of nascent chlorine in this mixture. A typical set of results of EDAX analysis of a particular grade of powder after leaching for 7 h is given in Table II. It is clear that in acid solutions, calcium and magnesium were extracted from the surface of the sample leaving a silica-rich surface layer. The larger retention of magnesium relative to calcium by the tremolite surface can be accounted for by considering the larger hydration energy of Ca^{2+} (-132.18 kcal mol^{-1}) relative to Mg^{2+} (-108.99 kcal mol^{-1}). It may be pointed out that in the case of binary alkali silicates, the rate of alkali extraction also decreases with decreasing size of the alkali ion, i.e. for equimolar composition, less lithium is extracted relative to sodium from binary alkali silicate glasses under identical condition of leaching. However, in this case the hydration energy of Li^+ (-70.22 kcal mol^{-1}) is larger than that of Na^+ (-62.589 kcal mol^{-1}). This apparent anomaly can be accounted for by considering the total hydration energies of the binary silicates as given in Table III.

In aqua regia, extraction of both magnesium and calcium increased; this is most probably due to the oxidative action of nascent chlorine in enhancing the kinetics of the leaching process. In none of the acid solutions could any measurable amount of silica (0.10 p.p.m.) be detected. This may be either due to non-extraction of hydrated silica in these highly acidic solutions, or to the extracted silicic acid polymerizing in the acid solution, and thus being undetectable by the molybdate method presently in use.

In 1N NaOH solution, as expected, silica was preferentially extracted, the rate of silica extraction is more than that of CaO and MgO considering the base composition of the untreated tremolite sample. Thus in 1N NaOH solution something more than pure dissolution of the silicate surface occurs. It is possible, as in the case of "setting" of Portland cement, silicic acid, $Ca(OH)_2$ and $Mg(OH)_2$ were all formed during the initial stage of the reaction, followed by formation of some amorphous calcium magnesium silicate hydrate on the surface (leached layer); this layer might have further preferentially retained $Ca(OH)_2$ and $Mg(OH)_2$ within it.

Finally, from Table I it is clear that the rate of leaching of the components in all these solutions increased with increasing time of mechanical grinding, i.e. exposed surface area of the sample. However, in any particular leach solution, the relative amounts of different components that have been extracted do

TABLE III Hydration energies of some binary silicates in water at 25 °C

Reaction	ΔG° (cal mol^{-1})[a]
Li_2SiO_3 (cryst) + $2H^+$ (aq) = H_2SiO_3 + $2Li^+$ (aq)	− 22 740
Na_2SiO_3 (cryst) + $2H^+$ (aq) = H_2SiO_3 + $2Na^+$ (aq)	− 28 815
$MgSiO_3$ (cryst) + $2H^+$ (aq) = H_2SiO_3 + Mg^{2+} (aq)	− 13 888
$CaSiO_3$ (cryst) + $2H^+$ (aq) = H_2SiO_3 + Ca^{2+} (aq)	− 16 116

[a] 1 cal = 4.1868 J.

not change significantly although the XRD pattern changes markedly.

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