

A COMPARATIVE STUDY OF THERMAL EFFECTS ON SURFACE AND STRUCTURAL PARAMETERS OF NATURAL CALIFORNIAN AND QUEBEC CHRYSOTILE ASBESTOS UP TO 700°C

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Abstract—The effect of heat treatment on surface area, pore volume, pore size distribution, physical and chemical structure up to 700°C have been studied on samples of naturally occurring chrysotile minerals from California and Quebec. Techniques used included thermogravimetric analysis, low-temperature nitrogen adsorption, electron microscopy, X-ray powder and electron diffraction. The materials behaved similarly on heating to 100°C showing a 0.5% weight loss attributable to desorption of physisorbed water. At 500°C, Quebec samples retained the chrysotile crystal structure while Californian samples were X-ray amorphous. Forsterite was formed by dehydration of both chrysotiles at 700°C; the greater stability of the Quebec samples to this process is explained by the presence of brucite as an impurity which enters into stray solid–solid interactions with the chrysotile.

INTRODUCTION

Structural changes caused by reactions associated with the thermal treatment of serpentine minerals in general, and of chrysotile in particular, have been examined by a number of workers (Van Biljon, 1960; Brindley *et al.*, 1967; Drobyshev and Govorova, 1971; Freund and Hainrich, 1971; Girgis, 1975). Few studies have been reported using gas adsorption techniques, but these have yielded important information in connection with the thermal decomposition of the minerals regarding the surface areas of component fibres and their surface chemistry (Addison *et al.*, 1962; Addison and Sharp, 1962). However, the effects of heat treatment on the pore nature and surface physical properties of natural chrysotile asbestos, both pure and impure, have not been reported in any detail.

The present communication describes the effects of heat treatment on the pore structure and surface of two types of natural chrysotile asbestos which differ significantly in terms of their purities and physical parameters. The effects have been investigated by thermogravimetric analyses, electron microscopy, X-ray powder and electron diffraction and by low-temperature gas adsorption/desorption techniques.

EXPERIMENTAL

Materials

Chrysotile samples were supplied by: (a) Lake Asbestos, Black Lake, Quebec (sample 7T/5, Quebec chrysotile) and (b) Union Carbide Corporation (Calidria asbestos sample HPO, Californian chrysotile). The raw materials were analyzed by X-ray

powder diffraction, X-ray fluorescence, thermogravimetry, and electron microscopy. The major impurities were brucite [$\text{Mg}(\text{OH})_2$], 10% in sample (a) and magnetite (Fe_3O_4), 3.75% in sample (a); 0.75% in sample (b). The manufacturers gave a surface area of $60 \text{ m}^2 \text{ g}^{-1}$ for the raw Californian chrysotile. Activation conditions for all samples treated at 150, 300, 500 and 700°C were 24 hr in air.

The comparison data on brucite were obtained with a mineral sample collected at Wakefield, Quebec. Magnesium hydroxide (NF grade) was supplied by the MacArthur Chemical Co., Montreal.

Apparatus and procedures

The surface area of the chrysotiles were determined by applying the BET method to nitrogen adsorption/desorption isotherms, at 77 K, and pore distribution data were calculated (Dollimore and Heal, 1964) using an IBM 360/50 computer. Adsorbents were out-gassed at 150°C for 24 hr at pressures $<10^{-4}$ Torr before commencing the isotherm determinations in order to remove physically adsorbed water (0.5% w/w).

The dynamic thermogravimetric analyses were performed in an air stream of 230 ml min^{-1} (NTP) at a heating rate of 7°C min^{-1} using a Stanton–Redcroft Thermobalance HT-5F. Buoyancy corrections were determined using dead-burned alumina. The differential plots ($\delta W/\delta T$ vs T) were computed from the primary weight loss data.

Electron micrographs and associated SAED patterns were taken with a Philips EM300 instrument using 100 kV energy and 0° tilt. The X-ray powder diffraction measurements were carried out with a Philips PW 1050/65 diffractometer.

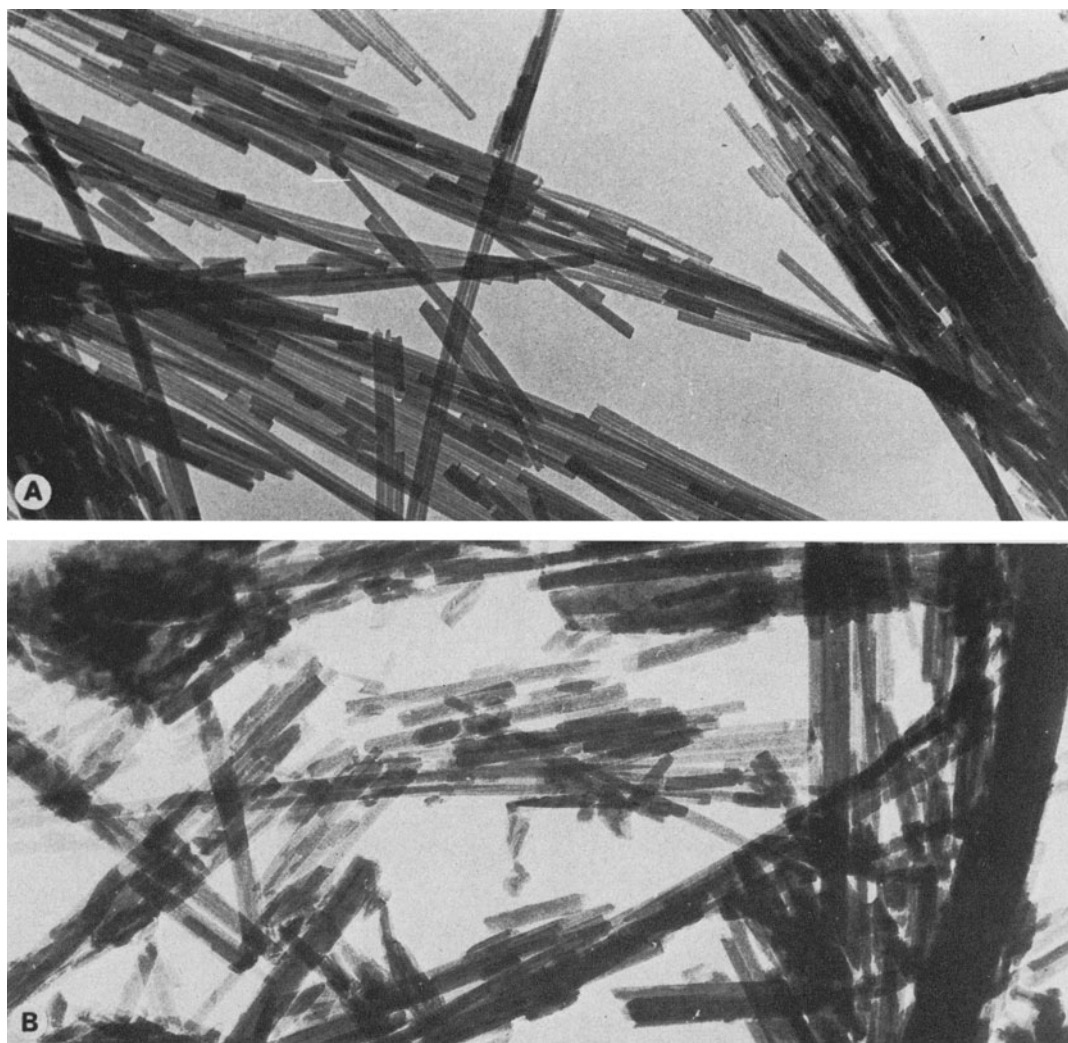


Figure 1. Electron micrographs of chrysotile asbestos ($\times 85,000$): (A) Californian chrysotile; (B) Quebec chrysotile.

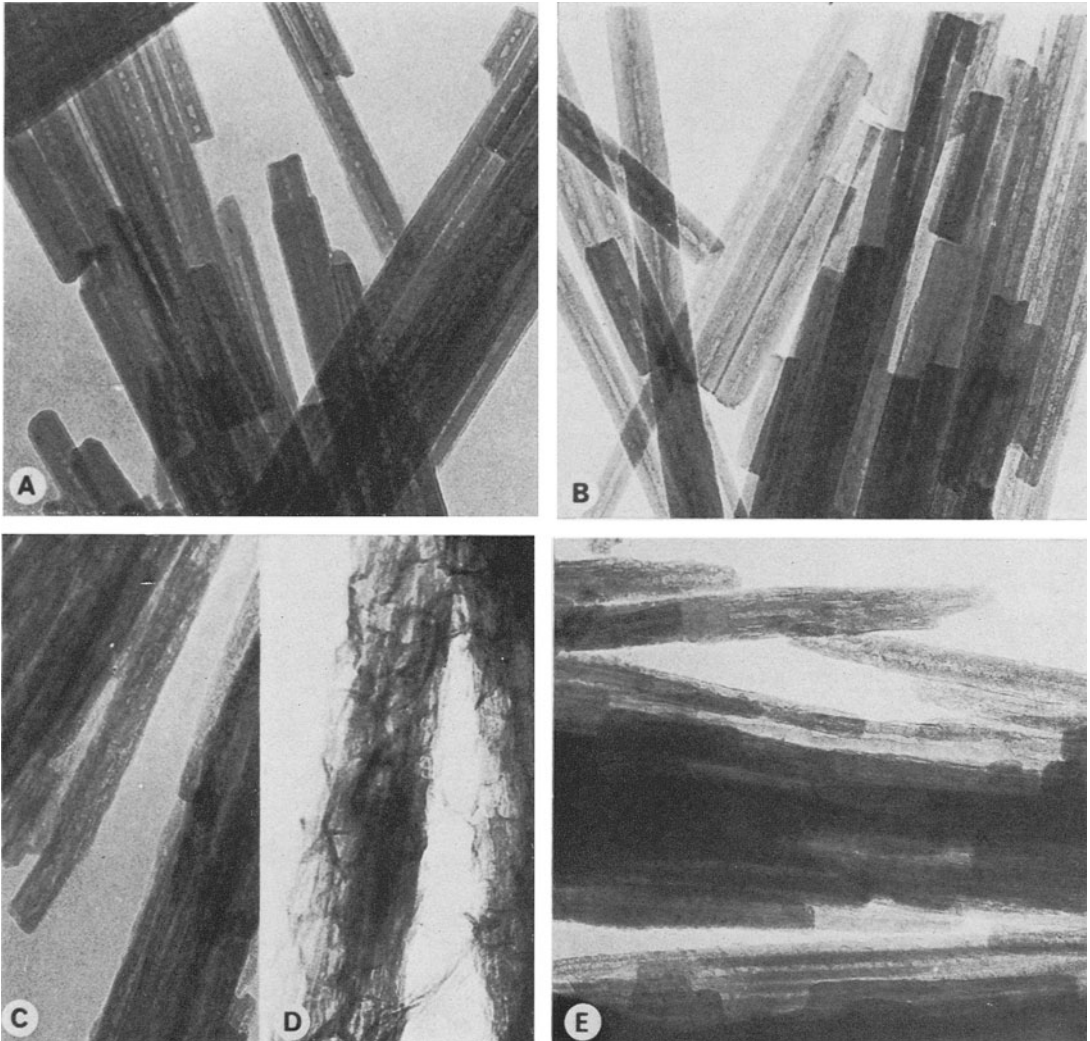


Figure 2. Effect of heat treatment on Californian chrysotile at: (A) 150°C; (B) 300°C; (C) and (D) 500°C; and (E) 700°C ($\times 200,000$).

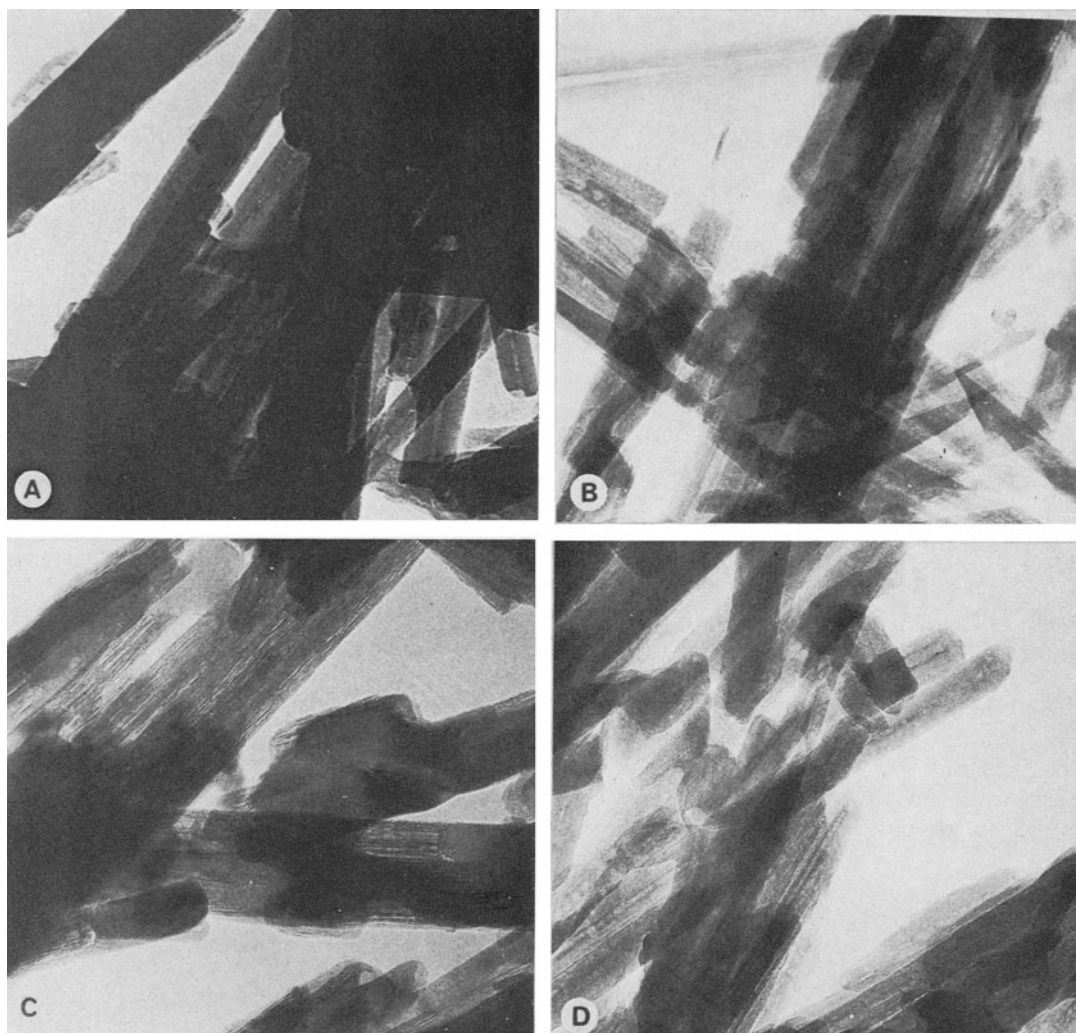


Figure 3. Effect of heat treatment on Quebec chrysotile at: (A) 150°C; (B) 300°C; (C) 500°C; and (D) 700°C ($\times 200,000$).

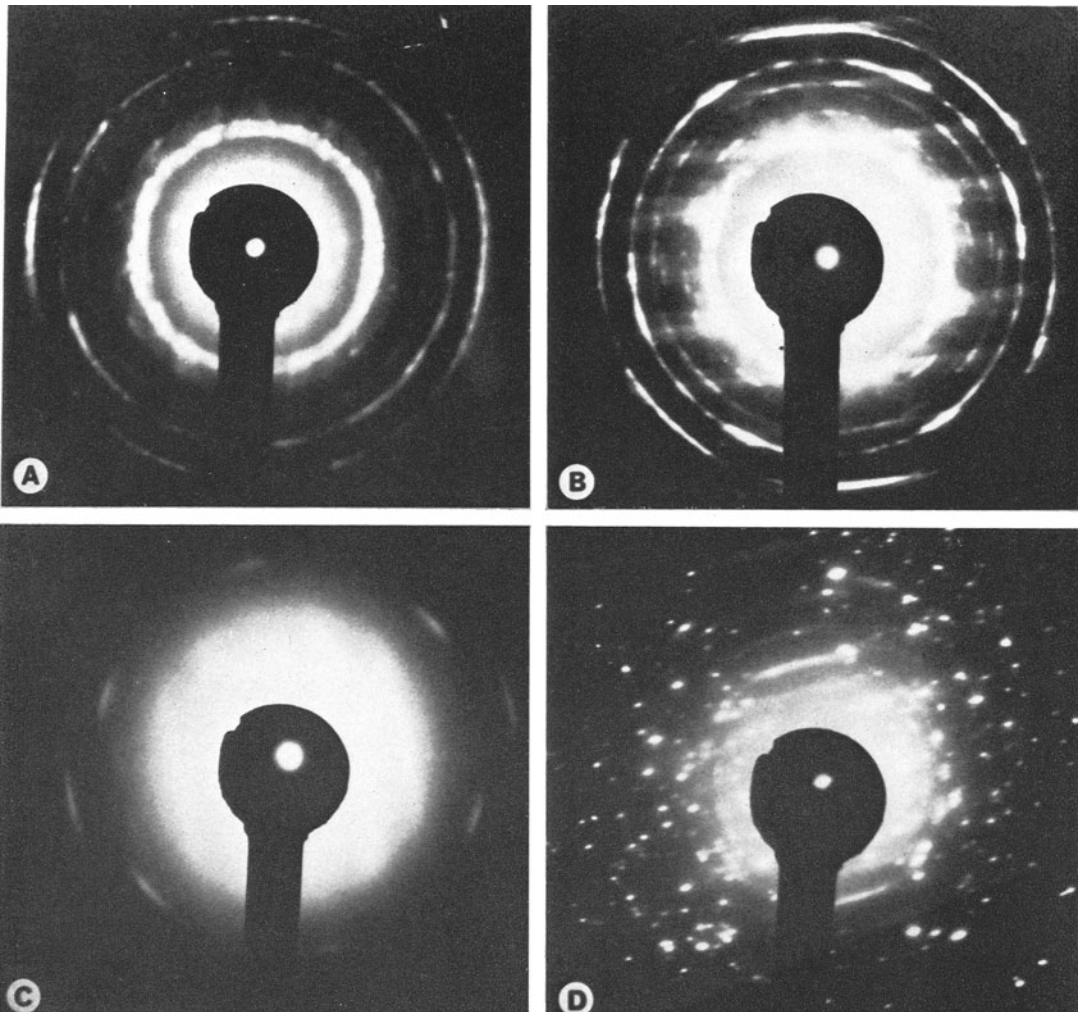


Figure 4. Selected area electron diffraction patterns of Californian chrysotile after heat treatment at: (A) 150°C; (B) 300°C; (C) 500°C; and (D) 700°C.

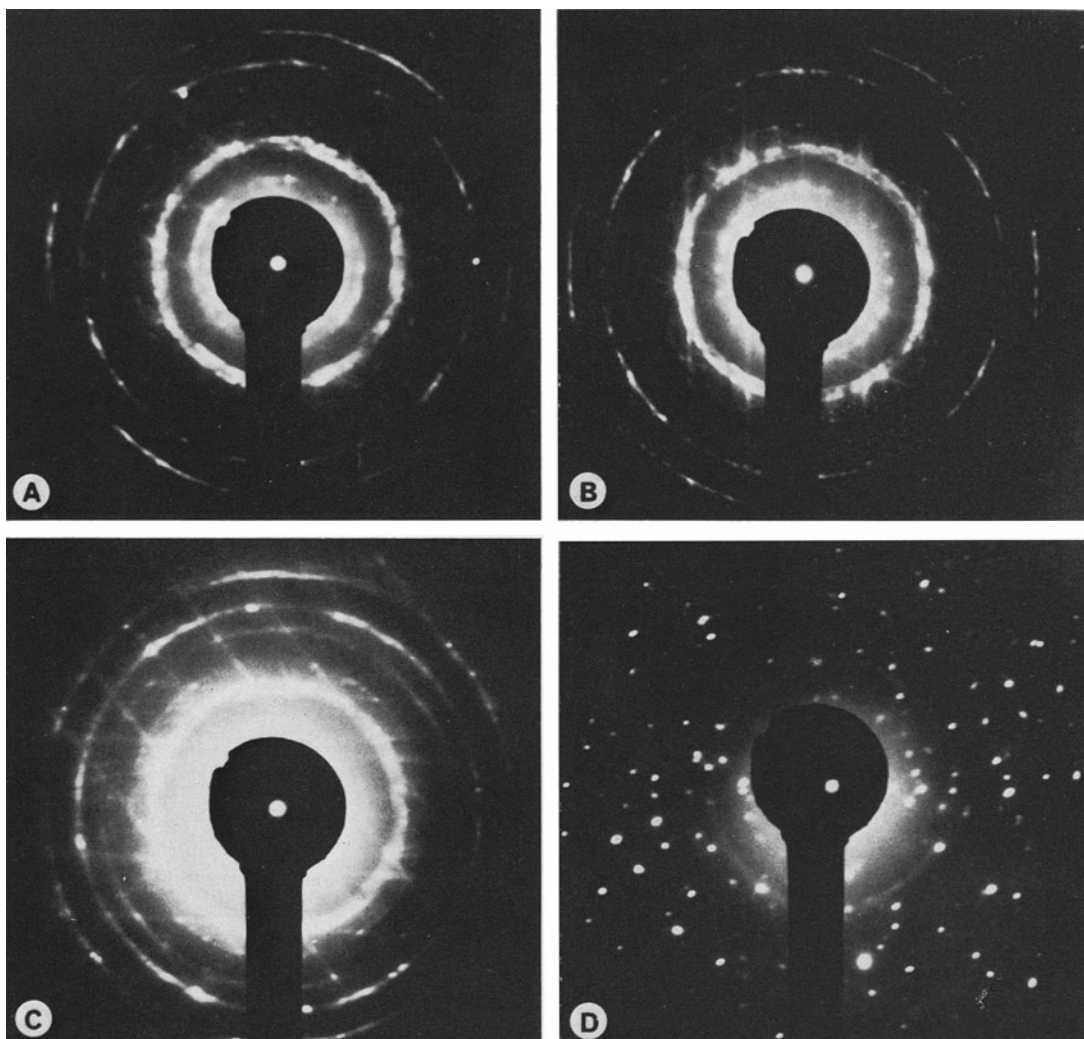


Figure 5. Selected area electron diffraction patterns of Quebec chrysotile after heat treatment at: (A) 150 °C; (B) 300 °C; (C) 500 °C; and (D) 700 °C.

RESULTS

Electron microscopy and selected area electron diffraction

Electron microscopy showed that both chrysotiles (Figure 1) were fibrous in nature with many of the individual fibers, especially in the Californian sample, in the form of hollow cylindrical tubes in agreement with current literature data (Eitel, 1964). The Quebec sample existed largely as fiber bundles, whereas the Californian chrysotile tended towards a conglomeration of discrete fibers. Figures 2 and 3 show that with increase in temperature of heat treatment, the basic fibrous appearance of the chrysotiles was maintained although structural changes were occurring. The regular profile of the fibers became somewhat diffuse with heating and it was also observed that at 500°C, some Californian chrysotile fibers cracked and appeared to flake (Figure 2D). This may be due to the onset of dehydration which could cause rupture of the fiber structure. There was no indication, however, that the fibers broke up into smaller pieces.

Figure 4 shows that, on increasing the temperature of heat treatment of the Californian sample, the chrysotile structure which was evident at both 150 and 300°C was destroyed at 500°C, the sample becoming amorphous. However, on increasing the temperature of heat treatment of Quebec samples (Figure 5), the chrysotile structure was retained on activating at 500°C. Figures 4 and 5 further show that no distinct SAED pattern could be obtained for either Californian or Quebec samples after activation at 700°C.

Dynamic thermogravimetric analyses

Figures 6 and 7 show the pyrolyses curves for both chrysotiles. The Californian sample (Figure 6) lost 0.5% weight when heated to 100°C due to a loss of physically adsorbed water from the surface and a further 0.5% weight loss occurred on heating the material from 225 to 500°C. This loss may be attributed to removal of water from within pores, as has been suggested previously (Young and Healey, 1954). An additional 12.5% weight loss, the rate of which maximized at 680°C, was observed on heating the

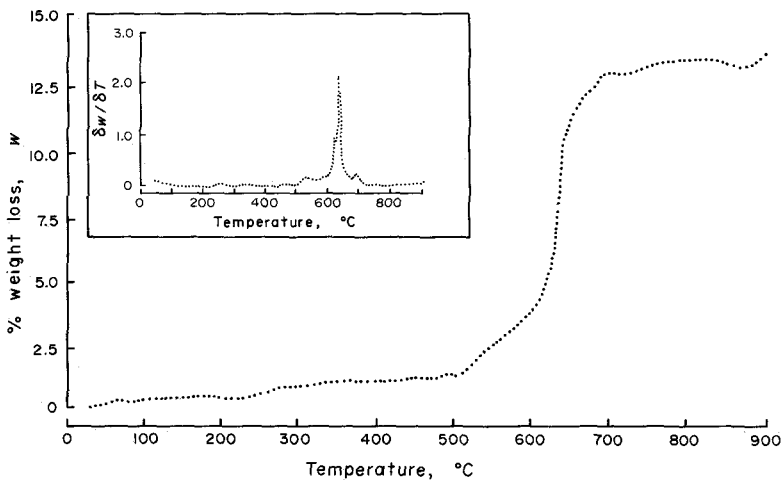


Figure 6. Dynamic thermogravimetric analyses of Californian chrysotile. Insert: differential thermogravimetric analyses of Californian chrysotile.

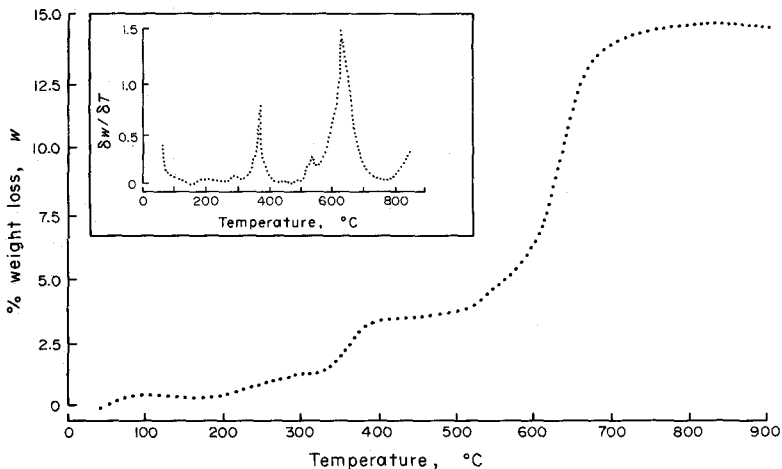


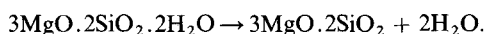
Figure 7. Dynamic thermogravimetric analyses of Quebec chrysotile. Insert: differential thermogravimetric analyses of Quebec chrysotile.

Table 1. X-ray powder diffraction data of some standards and products of the thermal activation of chrysotile

2θ degrees	15.4	22.0	23.0	23.5	29.0	30.5	30.9	32.5	37.5	41.1	45.4	46.5
Californian chrysotile (°C)												
150	S	—	—	—	—	—	S	—	—	—	—	—
300	S	—	—	—	—	—	S	—	—	—	—	—
500	—	—	—	—	—	—	—	—	—	—	—	—
700	—	W	—	—	S	W	—	W	W	W	S	S
Quebec chrysotile (°C)												
150	S	—	—	S	—	—	S	—	W	W	W	—
300	S	—	—	—	—	—	S	—	W	W	W	—
500	S	—	—	—	—	—	S	—	W	W	W	—
700	—	W	—	S	W	W	—	W	W	W	S	S
Brucite	—	—	—	S	—	—	—	—	—	—	—	—
Forsterite	—	—	—	—	S	—	—	—	—	M	S	S
Magnetite	—	—	W	—	—	—	—	—	M	—	S	—

Peak intensity: S = strong, M = medium and W = weak.

chrysotile from 500 to 700°C. This loss can be attributed (Woodroffe, 1956; Hodgson, 1975) to dehydration of chrysotile to serpentine anhydride:



Quebec chrysotile (Figure 7) gave a 0.5% weight loss on heating to 100°C similar to that observed for the Californian material. Further heat treatment resulted in an additional 3% weight loss from 200 to 500°C, which maximized at 360°C in agreement with the dehydration temperature region of brucite (Hodgson, 1965). Treatment of Quebec chrysotile from 500 to 700°C resulted in a further 11% weight loss with a maximum rate at 625°C. This loss, when allowance was made for the brucite and magnetite impurities, corresponded to 12.8% based on the chrysotile component.

In separate experiments it was shown that the mineral brucite underwent dehydration between 300 and 500°C with a maximum at 425°C and that magnesium hydroxide on dehydration between 300 and 500°C showed a maximum weight loss at 390°C.

Scanning X-ray powder diffraction

X-ray powder diffraction, Table 1, showed that no change in the structure of Californian chrysotile occurred on heating to 300°C. Further heating to 500°C produced an X-ray amorphous phase and still further heating to 700°C produced forsterite, Mg_2SiO_4 , in agreement with published data (Brindley

and Zussman, 1956; Wittaker and Zussman, 1956). The X-ray amorphous phase observed at 500°C corresponds closely to that in the Brindley/Hayami reaction scheme (Brindley and Hayami, 1965).

X-ray powder diffraction (Table 1) clearly showed the presence of brucite in the Quebec chrysotile. Heat treatment to 300°C destroyed the crystal structure of the brucite but did not appear to affect the chrysotile pattern. Further heating to 500°C appeared to have no effect on the chrysotile structure and no X-ray amorphous phase was observed. Forsterite was formed at 700°C.

Low-temperature nitrogen adsorption studies

Table 2 shows that, apart from the 700°C samples, Californian chrysotile exhibited larger surface areas and larger pore volumes than the Quebec materials. Figures 8 and 10 show the nitrogen adsorption/desorption isotherms determined at 77 K for each set of samples after heat treatment at 150, 300, 500 and 700°C. Figures 9 and 11 show the corresponding pore distribution patterns determined from the desorption branch of the isotherms (Dollimore and Heal, 1964).

With the Californian chrysotile samples, heat treatment from 150 to 300°C increased the per cent number of 'small' pores (19–22 Å) with a corresponding decrease in pores of radius > 30 Å (Figure 9). This trend was accompanied by a decrease in pore volume and an increase in surface area (Table 2). Further tempera-

Table 2. Surface area and pore volume for Californian and Quebec chrysotile samples activated at 150, 300, 500 and 700°C

	Activation temperature of Californian chrysotile samples (°C)				Activation temperature of Quebec chrysotile samples (°C)			
	150	300	500	700	150	300	500	700
Surface area ($\text{m}^2 \text{g}^{-1}$)	60	65	65	60	40	40	40	65
Pore volume (ml g^{-1} ; NTP)	75	71	74	60	44	44	43	72

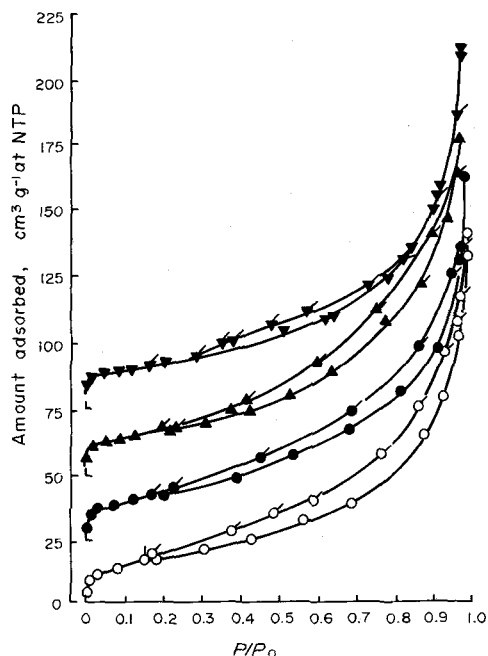


Figure 8. Nitrogen adsorption/desorption isotherms at 77 K on Californian chrysotile heat treated at 150°C (—○—), 300°C (—●—, origin displaced to 25 cm³ g⁻¹), 500°C (—▲—, origin displaced to 50 cm³ g⁻¹) and 700°C (—▼—, origin displaced to 75 cm³ g⁻¹). "Tailed" symbols denote desorption points.

ture increase to 500°C resulted in the collapse of the smallest pores and an increase in the per cent number of pores between 30 and 45 Å radius. There was a corresponding increase in pore volume at this temperature. Heating to 700°C resulted in the reformation of very small pores (<19 Å) and a corresponding decrease in the amount of larger pores. A large decrease in pore volume accompanied this change but the surface area did not change appreciably.

Heat treatment of the Quebec samples from 150 to 500°C (Figure 11) resulted in a progressive decrease in the number of the smallest pores and little or no change in pore volume. The surface areas remained constant. At 700°C a decrease in the per cent number of pores >21 Å radius was apparently accompanied by a very large increase in both surface area and pore volume.

DISCUSSION

The effects of heat treatment on both chrysotiles can be discussed conveniently by division into the three temperature regions; namely, 150–300, 300–500 and 500–700°C.

Californian chrysotile. Figure 6 shows that heating Californian chrysotile from 150 to 300°C resulted in a 0.5% weight loss while Figure 9 shows that the ratio of the percentage of 'small' pores to 'larger' pores increased over this temperature range. These observations may be explained by the Young and Healey water plug removal proposal (Young and Healey, 1954). However, it was also observed (Table 2) that pore volume decreased and surface area increased over these temperatures. This suggests that the process involved is not only a freeing of pores, e.g. the hollow fiber centers, by removal of water plugs, which would tend to result in an overall pore volume increase, but also includes a contribution from the dissociation of the fiber conglomerates into more discrete fibers. This implies that the original contributions to the pore volumes came from both the hollow fiber centers (intra-fiber volume) and pores formed within the fiber packs (inter-fiber volume).

Further heat treatment to 500°C coincided with the initial stages of the main dehydration step for the chrysotile. X-ray powder diffraction data (Table 1) indicated that the X-ray amorphous stage had been reached at this temperature which has been attributed

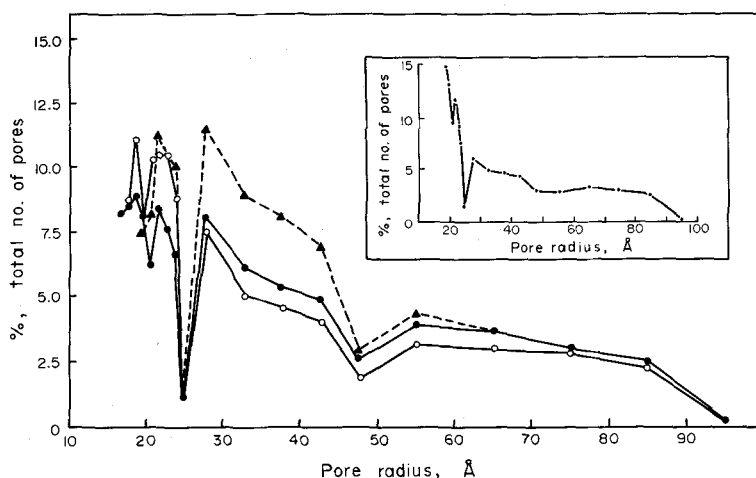


Figure 9. Pore size distribution based on nitrogen desorption at 77 K on Californian chrysotile heat treated at 150°C (—●—), 300°C (—○—) and 500°C (---▲---). Insert: pore size distribution for Californian chrysotile heat treated at 700°C.

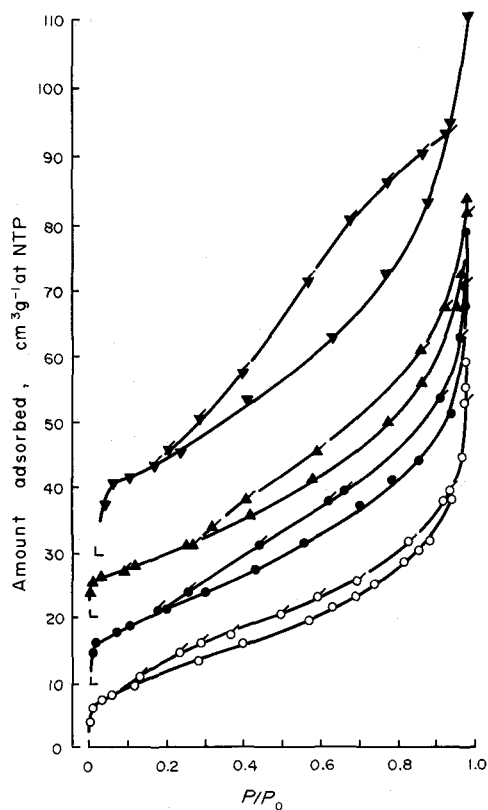


Figure 10. Nitrogen adsorption/desorption isotherms at 77 K on Quebec chrysotile heat treated at 150°C (—○—), 300°C (—●—, origin displaced to 10 cm³ g⁻¹), 500°C (—▲—, origin displaced to 20 cm³ g⁻¹) and 700°C (—▼—, origin displaced to 30 cm³ g⁻¹), "Tailed" symbols denote desorption points.

to the formation of a partially disordered serpentine anhydride (Brindley and Hayami, 1965). However, isothermal gravimetric analyses of Californian chrysotile at 500°C resulted in 1% weight loss only, i.e. no weight change over that at 300°C. Thus, bulk serpentine anhydride does not appear to have been formed.

Certainly, water had not then been desorbed from the chrysotile lattice. It may be postulated that this 'labile' water can cause the reversible disruption of the crystal at a temperature just below that necessary for its desorption from the lattice consistent with the amorphous region observed by X-ray powder diffraction and selected area electron diffraction. Electron microscopy (Figure 2D) of the 500°C sample showed that a large percentage of the fibers had started to flake or fibrillate which may also be caused by lattice disruption through water removal. Figure 9 and Table 2 indicate a decrease in the number of pores of radius <20 Å with respect to the number of pores of radius 30–45 Å which has the observed effect of increasing the total pore volume whilst the surface area remains unchanged, probably corresponding to the formation of fissures and/or pores by the 'flaking' process.

Heating Californian chrysotile from 500 to 700°C resulted in the dehydration of chrysotile (Table 1) and in the formation of forsterite, as expected from the literature (Brindley and Zussman, 1956). Selected area electron diffraction (Figure 4) further showed that the forsterite formed had little ordered arrangement since no clear electron diffraction pattern was obtained (Figure 4D). The formation of forsterite was accompanied by a considerable decrease in pore volume and surface area (Table 2). These results are consistent with the recent works of Girgis (1975) who concluded that the formation of forsterite should coincide with collapse of the MgO(OH) segment of the serpentine layer on dehydration thus causing a corresponding collapse of the layer structure to yield the three-dimensionally co-ordinated forsterite structure.

Quebec chrysotile

Figure 7 indicates that on heating Quebec chrysotile from 150 to 300°C, similar behaviour to Californian chrysotile over the same temperatures was

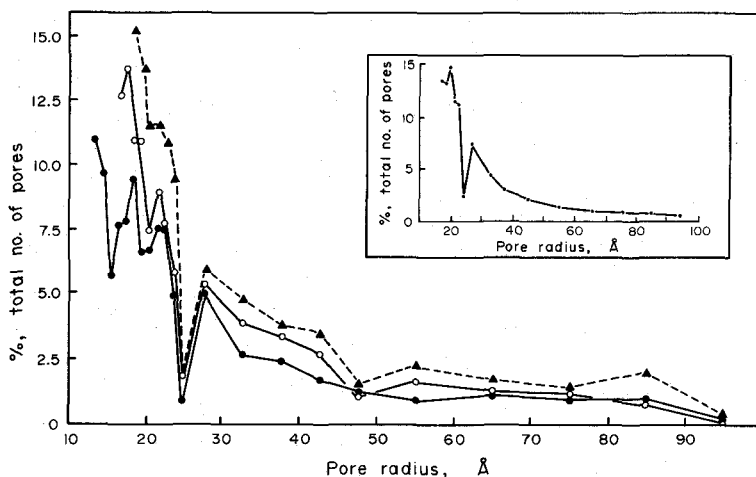


Figure 11. Pore size distribution based on nitrogen desorption isotherm at 77 K on Quebec chrysotile heat treated at 150°C (—●—), 300°C (—○—) and 500°C (---▲---). Insert: pore size distribution for Quebec chrysotile heat treated at 700°C.

observed, i.e. a 0.5% weight loss. Isothermal gravimetric analyses at 300°C over a 24 hr period showed that the Quebec samples lost 2.5% weight due to brucite dehydrating to magnesium oxide in agreement with the diffraction results which showed that the brucite crystal structure was destroyed. Over this temperature range the percentage of $\sim 20 \text{ \AA}$ radius pores increased (Figure 11), the pore volume increased and the surface area remained constant (Table 2). The results may be explained by the unplugging of pores of radius $\sim 20 \text{ \AA}$, an increase in the size of very small pores $< 20 \text{ \AA}$ to $\sim 20 \text{ \AA}$, or the formation of further pores around 20 \AA radius due to water loss in brucite dehydration. Since no increase in surface area was observed, probably little or no dissociation of the fiber bundles had occurred at these temperatures.

X-ray powder diffraction (Table 1) showed that the chrysotile crystal structure was retained at 500°C, cf. Californian chrysotile which was X-ray amorphous at this temperature, indicating that the Quebec sample was stabilized towards dehydration. A further increase in the number of pores of $\sim 20 \text{ \AA}$ radius and a corresponding increase in pore volume was also observed (Figure 11 and Table 2). Table 2 also shows that the surface area remained constant indicating that no dissociation of the fiber bundles took place at 500°C.

The stability of this chrysotile to dehydration and its fiber bundles towards separation may be due to the presence of MgO formed as a result of the dehydration of brucite. A comparison for the dehydration temperatures of brucite (425°C), magnesium hydroxide (395°C) and the brucite impurity present in the Quebec chrysotiles (365°C), indicates that the brucite impurity is strongly destabilized to dehydration compared to pure brucite or even magnesium hydroxide. This suggests that very strong interactions take place between brucite and the chrysotile. Further, dehydration of chrysotile in the X-ray amorphous regions observed at 500°C for Californian samples was not evident for the Quebec chrysotile which tends to confirm that strong solid-solid interactions are involved between brucite and the Quebec material.

Temperature increase to 700°C resulted in a very large pore volume and surface area increase (Table

2), in accord with the splitting up of the fiber bundles. The chrysotile had, in fact, been converted to forsterite (Table 1), and the disorder of the forsterite thus formed was demonstrated by the absence of a clear electron diffraction pattern (Figure 5D).

It is hoped that the above observations will contribute to current studies concerned with an understanding of the properties of these asbestos minerals in both scientific and medical areas of research. In a continuation of this work the possible relationship between these structural and surface properties and chemisorption phenomena will be explored in the hope that we may be able to assess a range of gas/solid reaction parameters and thus perhaps contribute to an evaluation of the likelihood of the occurrence of synergetic effects.

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