

## GRINDING OF CHRYSOTILE IN HYDROCARBONS, ALCOHOL, AND WATER

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**Abstract**—The change of the properties of chrysotile after ball milling in organic liquids (aromatics, alcohols, silicone oils) or water was studied by gas adsorption, electron microscopy, X-ray powder diffraction, infrared spectroscopy, differential thermal analysis, zeta potential measurements, and chemical analysis. Grinding in low viscosity organic solvents leads initially to a rapid defiberization of the asbestos bundles and to a fragmentation of the isolated fibrils. Finally, amorphization and agglomeration occur causing a drastic decrease of the specific surface area of the ground material. Grinding in water brings about a defiberization, but much more slowly than in organic solvents. Moreover, prolonged grinding in water does not significantly alter the structure of chrysotile. The efficiencies of the organic solvents, considered as grinding aids that induce fracture of the fibrils, are related to the environmental stress cracking of brittle solids (Rehbinder theory). Hence, the pertinent properties of the organic liquids are their viscosity and their cohesion energy (solubility parameter). Solvents chemisorbed on the surface of the ground chrysotile reduce the surface energy of the fracture surface and prevent aggregation. Water does not react according to Rehbinder's theory, but appears to form a protective layer around the fibrils. This hypothesis was verified by dry grinding defiberized asbestos (rapid amorphization) or by disturbing the stability of the water coating by coadsorbing alcohol on the solid surface. Alternatively, the resistance of the fibrils to fracture may be explained by Westwood's theory that grinding in water is equivalent to grinding in an alkali medium, wherein the surface charge of the chrysotile becomes negligible, and the mechanical stability of the fiber reaches a maximum.

**Key Words**—Amorphization, Asbestos, Chrysotile, Defiberization, Grinding, Morphology.

### INTRODUCTION

Many asbestos composite materials, e.g., brake linings, asbestos cement, owe their mechanical performance to the physical-chemical characteristics of chrysotile. For these materials, optimum properties are obtained by maximizing the interfacial area between the reinforcing fiber and the matrix, i.e., by increasing the specific surface area of the chrysotile, usually by grinding. Although grinding is a common operation, it is in fact a complex process. The aim of this paper is to elucidate the primary parameters of the grinding of chrysotile and to show the role of the liquid environment. Several processes will be examined: grinding in the dry state, grinding in organic solvents, and grinding in water.

### EXPERIMENTAL

Chrysotile from Black Lake, Quebec (grade 5R) was heated at 150°C for 24 hr before ball milling. The ball mill consisted of two, 600-cm<sup>3</sup> stainless steel jars animated by a periodic movement (25 Hz) with an amplitude of 2 cm. The jars contained 1.8 kg of stainless steel spheres, 12 cm in diameter. In a typical run, 30 g of asbestos was dispersed in 300 cm<sup>3</sup> of liquid. The grinding was monitored by measuring the change in specific surface area and by observing the morphology and evaluating the structure of the ground material.

The specific surface area (m<sup>2</sup>/g) of chrysotile samples

was measured by nitrogen adsorption at liquid nitrogen temperature, after a 24-hr outgassing at 150°C. Generally, well-defined relations (BET equation) were recorded from which the specific surface areas were calculated. Electron microscopy was performed in the transmission (TEM) and scanning (SEM) modes using a JEOL, JEM 100B instrument. For TEM examination, the fibers were first opened using an ultrasonic technique applied to a water suspension of the chrysotile. For SEM examination, it was necessary to coat the fibers with a thin layer of gold to avoid surface charging. X-ray powder diffraction (XRD) was carried out using CuK $\alpha$  radiation. The measured d-values, close to those in the literature (Whittaker, 1956), indicated that the asbestos is mainly clinochrysotile. The thermal behavior was examined with a Mettler thermo-microgravimetric balance. About 250 mg of chrysotile was heated from 20° to 1000°C at a heating rate of 8°C/min. Differential thermal analyses (DTA) were made using the same equipment, at the same heating rate.

Transmission infrared spectroscopy (IR) was performed with a Beckman IR 20 instrument using KBr pellets containing 5% asbestos. The kinetics of Mg-extraction from the treated chrysotile was established using a technique described earlier (Papirer *et al.*, 1976). The extraction of Mg from the surface of chrysotile, using an aqueous solution of EDTA, obeys first order kinetics. When the outer brucite-like layer of the chrys-

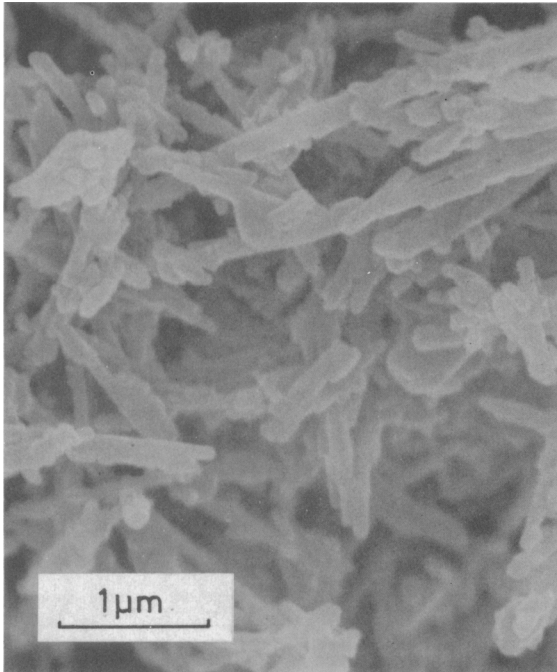


Figure 1. Scanning electron micrograph of chrysotile ground in toluene for 24 hr.

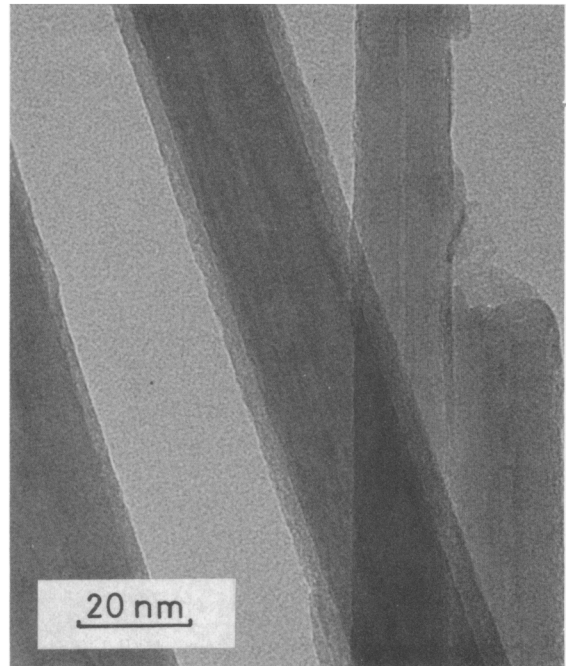


Figure 2. High resolution transmission electron micrograph of chrysotile ground in toluene for 24 hr.

otile is totally eliminated, the rate of reaction decreases because further attack is diffusion controlled. Consequently, the Mg that passes into solution immediately corresponds to the Mg of the surface layer. Eventually, Mg from the amorphous material produced during grinding dissolves. By monitoring the amount of Mg entering solution, it is possible to follow the amorphization of chrysotile produced by grinding. The surface charge of chrysotile in aqueous medium was evaluated by zeta potential measurements (see Nardin, 1980) according to the streaming potential method. Asbestos samples (8 g) were dispersed in 2 liters of demineralized water. After stabilization, pH, either in the presence or absence of 30 ppm methanol, was  $9.0 \pm 0.1$ , whereas the resistivity of the solution was close to  $42 \mu\text{S}$ .

Table 1. Grinding of chrysotile in the presence of organic liquids.<sup>1</sup>

Liquid	Initial grinding rate (m <sup>2</sup> /g/hr)	$\gamma_L$ (mJ/m <sup>2</sup> )	$\gamma_L^D$ (mJ/m <sup>2</sup> )	$\delta$
Benzene	18	28.4	26.7	9.5
Toluene	20	28.4	26.1	8.9
O-Xylene	20	28.9		9.0
Methanol	5	22.6	15.2	14.5
Ethanol	5	22.8	17.0	12.7
Water	2	72.4	22.0	23.4

<sup>1</sup>  $\gamma_L$  = surface energy; ( $\gamma_L^D$ ) = dispersive component;  $\delta$  = solubility parameter of the liquids.

## RESULTS AND DISCUSSION

### Dry grinding of chrysotile

Dry grinding of chrysotile has been used to increase its surface area. However, in the present experiment, dry grinding for 24 hr produced no significant increase in surface area over the initial value of  $15 \text{ m}^2/\text{g}$ . Furthermore, TEM and SEM examination of the dry-ground product showed no change in the morphology of the fiber bundles, and the grinding treatment appeared to have no effect. This observation raises the question of the mechanical energy dissipation. Clearly, there must exist a specific energy-dissipative process that consumes energy and preserves the integrity of the fiber bundle.

Possibly, asbestos fibers, even temporarily separated at atomic distances, reagglomerated, thereby expending energy. Alternatively, the bundles acted as a composite material made of individual fibers held together by interfibrillar forces. Upon deformation, the microfibrils were able to move somewhat; stress was then more uniformly distributed resulting in an apparent improved strength of the asbestos bundles. With increasing grinding time, the specific surface of chrysotile increased, but at a lower rate than in the presence of liquids, especially toluene.

### Grinding in organic solvents

Grinding in toluene led to a rapid increase of the specific surface area ( $70 \text{ m}^2/\text{g}$ , 24 hr) compared to dry grind-

Table 2. Variation of the specific surface area of chrysotile after grinding in toluene.

Grinding time (hr)	0	3	8	16	24	30
S (m <sup>2</sup> /g)	15	39	49	58	66	20

ing under identical conditions. SEM examination (Figure 1) showed extensive defiberization of the asbestos bundles. Moreover, the individual microfibrils appeared to fracture. To test the generality of this result, chrysotile was ground in different organic liquids, including benzene, xylene, and alcohols. After 24 hr, the specific surface areas of the ground samples were comparable and about 70 m<sup>2</sup>/g for all liquids. However, significant differences were noted in the specific surface areas during the initial hour of grinding (Table 1). The initial grinding rates are mean values of at least three runs. Toluene parent liquids behave similarly, whereas more polar liquids are less effective as grinding aids. The surface energy ( $\gamma_L$ ) differences of the two classes of liquids are not directly related to their grinding efficiencies. The surface tension of a liquid is a combination of different forces: inductive or dispersive forces ( $\gamma_L^D$ ) (e.g., London, van der Waals), polar forces (e.g., permanent dipoles), and acid-base-like forces (e.g., H-bonding). Thus, it is highly probable that a chrysotile surface will favor a given type of interaction. The different surface energy components of the liquids were therefore considered (Fowkes, 1971); no direct relationship was apparent when, for example, the dispersive component ( $\gamma_L^D$ ) of the surface energy of the liquid was taken into account.

The surface area increased monotonously for grinding times between 0 and 30 hr, following a complex law. For example, a linear relationship was established between time (t) of grinding and 1/S, where S is the specific surface area of the ground sample at time t. For grinding times exceeding 24 hr, a dramatic decrease in surface area occurred corresponding to the agglomeration stage of a grinding operation.<sup>1</sup> Possibly, the solid grinding residues became cemented together by highly reactive amorphous material. Snow and Luckie (1979) reported that severe grinding induced irreversible

<sup>1</sup> See Table 2.

Table 3. State of chrysotile after grinding, as estimated from X-ray powder diffraction patterns. (Debye-Scherrer method.)

Grinding time (hr)	Toluene	Water
1	Fiber	Fiber
8	Powder	Fiber
24	Powder	Fiber
30	Amorphous	Fiber
48	Amorphous	Fiber
120	Amorphous	Powder

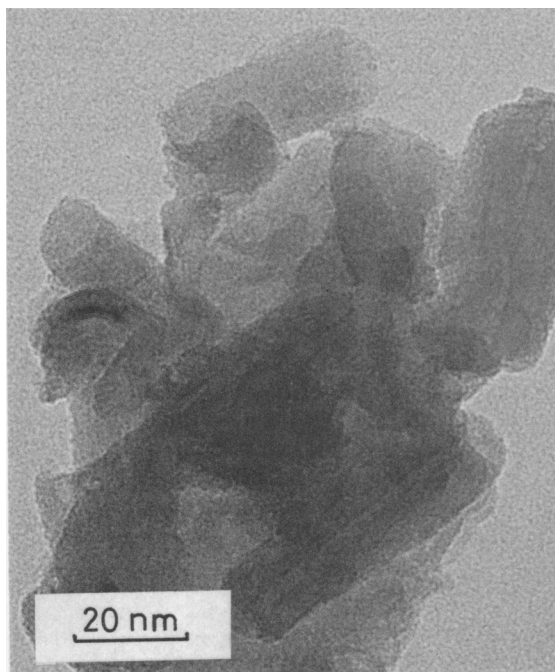


Figure 3. High resolution transmission electron micrograph of chrysotile ground in toluene for 30 hr.

transformations in solids. In addition, a spontaneous reduction of surface free energy by coarsening, changes in atomic structure of the surface and polymorphic transformations were observed. Clay materials show a similar behavior; e.g., Juhasz (1974) found that lattice defects are created and an amorphous material is formed when kaolinite is ground in the presence of halides. Montmorillonite, upon prolonged crushing, breaks down and releases alumina and magnesia (Block, 1950).

Chrysotile ground in toluene for long durations underwent an irreversible transformation as indicated qualitatively by the XRD data in Table 3. High resolution (phase contrast) electron microscopy illustrated the abrupt change in morphology when the grinding was extended from 24 to 30 hr. Figure 2 shows fibrils, apparently having only disturbed surface layers, whereas Figure 3 shows the marked change of the morphology after a few additional hours of treatment. The highly distorted fragments appear to be agglomerated through solid bridges of possibly amorphous material. Consequently, an increase in amorphous material should have been found when the treatment was extended from 20 to 30 hr.

The formation of amorphous material can be quantitatively followed by measuring  $(Mg)_a$  as defined above. Figure 4 illustrates the first order kinetics of the Mg extraction from chrysotile samples ground in toluene. From the ordinate at the origin,  $(Mg)_a$  values were computed (Table 4). Up to an 8-hr treatment,

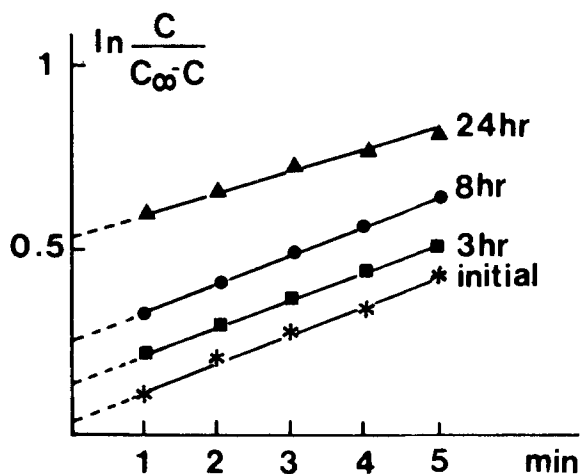


Figure 4. First order kinetics of EDTA extraction of Mg, from different samples of chrysotile ground in toluene. C = concentration of Mg at time t; C<sub>∞</sub> = total extractable Mg.

(Mg)<sub>a</sub> did not increase significantly. Moreover, when referred to the specific surface areas of the ground samples, (Mg)<sub>a</sub> seemed to decrease. This is not entirely unexpected because usually due to weathering, the outer surfaces of the chrysotile bundles probably contained more (Mg)<sub>a</sub> than the inner fibrils; hence, during the opening of the bundles, the mean value of (Mg)<sub>a</sub> should have decreased. It is important to stress the sudden increase of (Mg)<sub>a</sub> after a 30-hr treatment. It is precisely this amorphous reactive matter that will cause the agglomeration of the residual fragments as seen by electron microscopy.

Because (Mg)<sub>a</sub> per unit surface remains almost constant up to 24 hr of grinding, it can be concluded that the main grinding mechanism is the fragmentation of the individual fibers and not a progressive accumulation of (Mg)<sub>a</sub> on the fiber surface. Indeed, Figure 2 shows that the external layer thickness of chrysotile, disturbed during grinding, is rather restricted. A different way of expressing this result is to calculate the degradation yield, τ, of the asbestos, which is the ratio between the amount of (Mg)<sub>a</sub> and the initial amount of Mg. Even after a 24-hr treatment (Table 4) τ was relatively small whereas after 30 hr almost half of the crystalline material was destroyed. The rupture of the crystalline network and the formation of (Mg)<sub>a</sub> increased the number of free hydroxyl groups which belong no longer to

Table 4. Amount of "amorphous" (Mg)<sub>a</sub> and chrysotile degradation (τ) as a function of grinding time in toluene.

Grinding time (hr)	0	3	8	24	30
(Mg) <sub>a</sub> (10 <sup>-3</sup> mole/g)	0.30	0.35	0.55	0.80	4.80
(Mg) <sub>a</sub> (10 <sup>-5</sup> mole/m <sup>2</sup> )	2.0	1.8	1.35	1.30	24.0
τ (%)	2.8	3.2	4.8	6.9	42.5

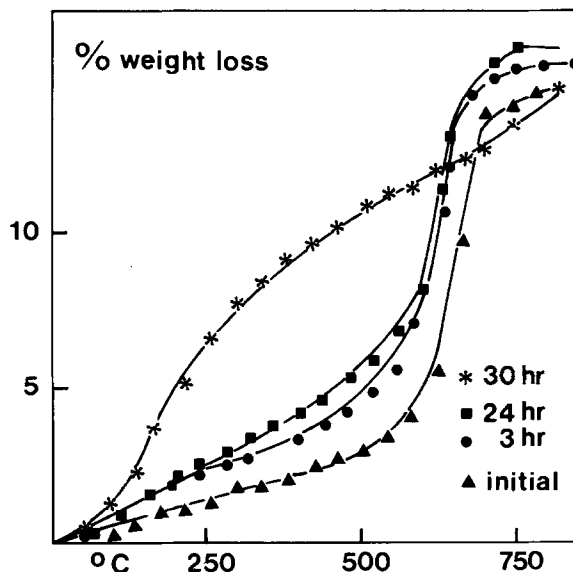


Figure 5. Percentage weight loss vs. temperature of chrysotile samples ground in toluene. Heating rate = 8°C/min.

the structure. Thus, the dehydration of asbestos should have been facilitated, a prediction that was verified by thermogravimetric analysis.

Figure 5 shows the weight loss of samples after various times of grinding as a function of temperature. As expected, water was lost at lower temperature with ground samples. Moreover, the highly amorphous sample behaved like MgO, exhibiting a totally different behavior upon heat treatment. Table 5 indicates the weight loss (Δw) after heating at 150° and 800°C. The total weight loss at 800°C due to loss of water closely approached the theoretical value for pure chrysotile (12.95%), whereas the weight loss at 150°C traced the amount of physically adsorbed water. Even though the specific surface area of chrysotile decreased after a 30-hr treatment, more water was retained on the ground sample.

Further indications of the structural breakdown of chrysotile upon prolonged grinding are given by IR spectroscopy. Narrow absorption bands, vanished particularly those at 3670 cm<sup>-1</sup> (external -Mg-OH) and 3655 cm<sup>-1</sup> (internal -Mg-OH), vanished from the spectrogram of chrysotile ground for 30 hr. Bands at 1080

Table 5. Weight loss at 150° and 800°C of chrysotile ground in toluene.

Grinding duration (hr)	0	3	8	24	30
Weight loss at 150°C (%)	0.8	1.0	1.5	1.9	3.0
Weight loss at 800°C (%)	14.6	14.7	15.8	15.4	14.8

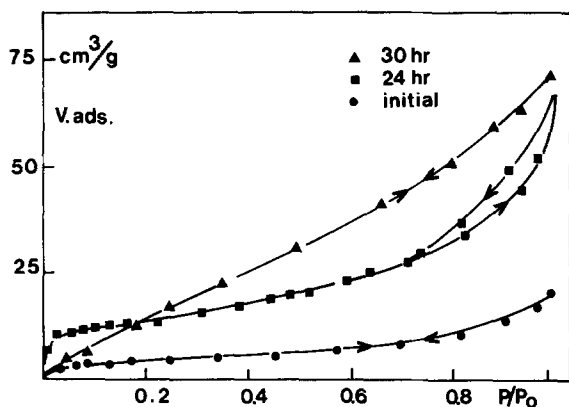


Figure 6. Nitrogen adsorption isotherms of chrysotile samples ground in toluene.

and  $965\text{ cm}^{-1}$  assigned to the stretching of  $\text{-Si-O}$  bonds also disappeared as did those due the vibrations of  $\text{Si-O}$  bonds at  $610$  and  $438\text{ cm}^{-1}$  (Hodgson, 1979). Additional evidence of the structural breakdown comes from an analysis of nitrogen adsorption and desorption isotherms (at liquid nitrogen temperature) (Figure 6). Generally, initial fiber bundles do not present mesopores, i.e., pores in which capillary condensation can take place; comminuted fibers behave like a mattress in which interfibrillar capillary condensation is possible; and agglomerated fibers probably possess no mesopores (according to TEM). Only the isotherms relat-

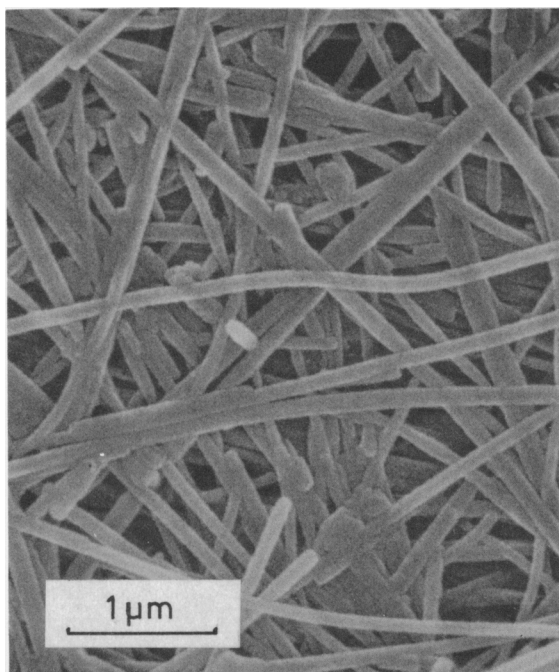


Figure 7. Scanning electron micrograph of chrysotile ground in water for 24 hr.

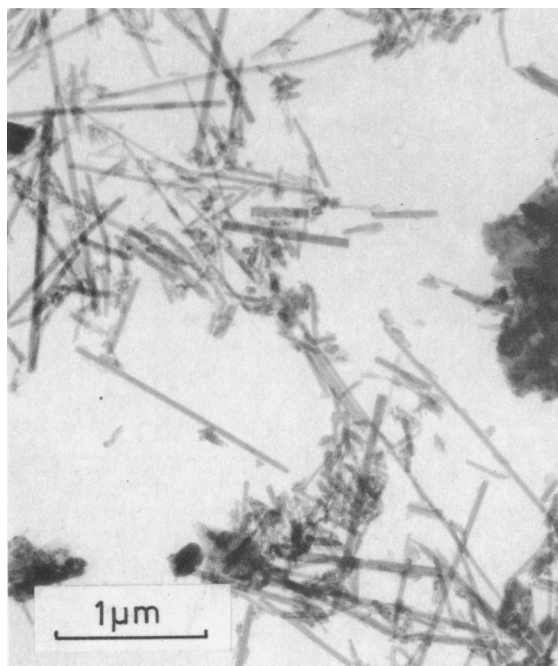


Figure 8. Transmission electron microscopy of chrysotile ground in water for 5 days.

ed to comminuted fibers show a hysteresis cycle which is caused by capillary condensation. However, a true calculation of the pore volume is not possible since it

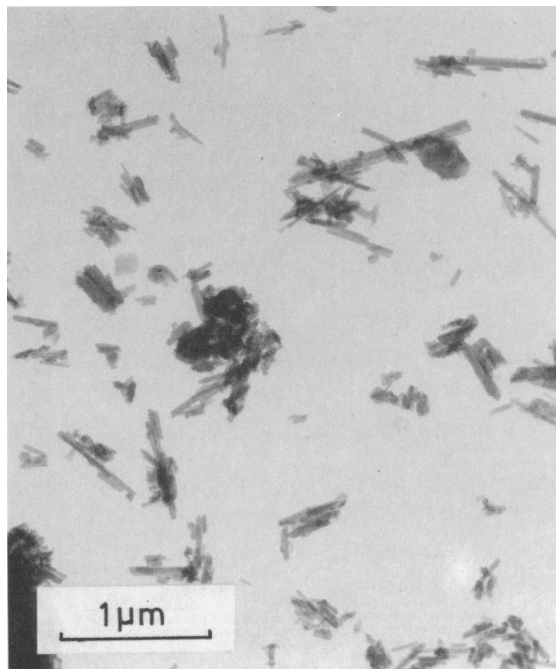


Figure 9. Transmission electron microscopy of chrysotile ground in toluene for 24 hr, illustrating the difference between grinding in toluene and water.

Table 6. Variation of the specific surface area of chrysotile after grinding in water.

Grinding duration (hr)	0	20	40	60	80	100	120
S (m <sup>2</sup> /g)	15	35	76	84	87	87.5	89

requires a precise knowledge of the shape of the pores. Nevertheless, the results of the gas adsorption measurements are in qualitative agreement with the expectations.

#### Grinding in water

Tables 1 and 3 indicate that grinding of chrysotile in water leads to different results; the initial grinding rate in water is ten times smaller than in toluene, whereas the resistance of chrysotile amorphization is surprisingly high in aqueous medium. Figures 7 and 8 show the morphology of chrysotile ground in water for 24 hr or  $5 \times 24$  hr. Even after prolonged grinding, TEM shows the persistence of rather long microfibers compared to those resulting from a 24-hr grinding in toluene, observed also by TEM (Figure 9). The grinding of chrysotile in water possibly obeys a different mechanism; no agglomeration stage took place, at least not after a 5-day treatment. Table 6 indicates the variation of the specific surface area of chrysotile with increasing grinding times in water. The specific surface area increased up to 87 m<sup>2</sup>/g after an 80-hr treatment and then remained almost constant. This increase followed apparent first order kinetics, indicating a different grinding mechanism compared to that encountered with toluene.

### DISCUSSION

The above results raise two questions. First, why do organic solvents present different efficiencies when used as grinding aids of chrysotile? Second, what distinguishes the behavior of chrysotile in water? To answer these questions, it is useful to recall modern grinding theories. Grinding is the fracture of a solid caused by a stress of a critical intensity. Upsetting the order of the crystal lattice structure, for instance, is induced by deformation starting at existing defects. The size of the defects increases to a critical value (c) at which the

Table 7. Viscosity, surface energy of the siloxanes, and initial grinding rate of chrysotile in various siloxanes.

	Hexamethyl- disiloxane	Poly(dimethylsiloxane)			
Viscosity (cP)	0.5	19	96	490	12,160
Surface energy (mJ/m <sup>2</sup> )	15.9	20.6	20.9	21.1	21.5
Grinding rate (m <sup>2</sup> /g/hr)	2.5	0	0	0	0

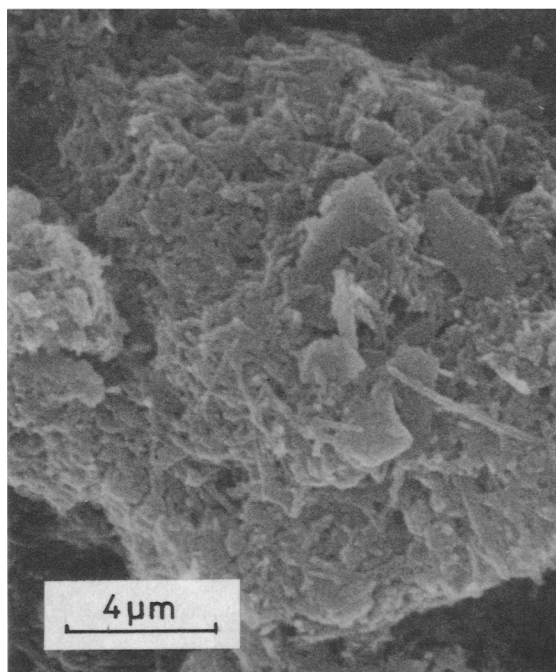


Figure 10. Scanning electron micrograph of chrysotile ground in hexamethyl disiloxane for 24 hr.

propagation of defects and, finally, fracture occurs. In pure elastic deformation (in the absence of plastic flow which can be considered as one of the most important energy dissipation mechanisms), the critical stress value, according to Griffith (1920), is proportional to  $(E\gamma/c)^{1/2}$ , where E is Young's modulus and  $\gamma$  the surface energy of the newly created surface. When a liquid is present and able to follow the fracture front, it will adsorb on the fracture surface and consequently reduce the value of  $\gamma$ . Rehbinder's theory (Rehbinder *et al.*, 1948) corresponds to adsorption-induced softening and strength reduction as a result of the lowering of the specific surface free energy of the solid (work of formation of new surfaces during deformation and fracture). An efficient grinding aid will therefore be a liquid that adsorbs readily on fracture surface of asbestos. To the first approximation, since asbestos is a high surface energy solid, almost all liquids should perform similarly. However, the reality is somehow different.

Westwood's concept (Westwood and Latanison, 1976) applies perhaps more specifically to grinding in ionic media, i.e., water or aqueous solutions. According to these authors, the adsorption of the grinding aid onto a solid changes its surface or zeta potential, which in turn brings about a redistribution of the charge carriers emerging at the surface. A rearrangement of the charge carriers inside the solid is finally induced. In other terms, the generation, motion, and mutual interactions of the near-surface dislocations will depend on the zeta potential: a change in zeta potential can be ac-

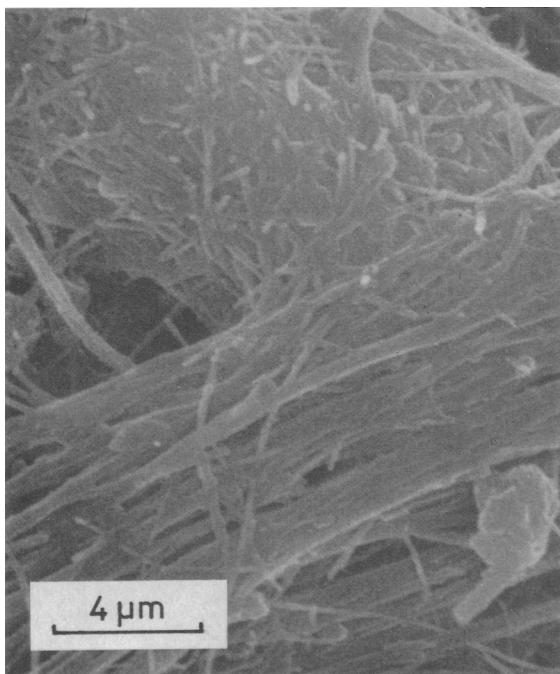


Figure 11. Scanning electron micrograph of chrysotile ground in poly(dimethylsiloxane) for 24 hr.



Figure 12. Transmission electron micrograph of chrysotile opened in water and reground in the dry state for 0.5 hr.

accompanied by an increase of the repulsion of the charge carriers or a weakening of the solid itself.

Thus, two criteria are essential: one is of a kinetic nature because the liquid must be present at the fracture front; the other is of an energetic nature because the liquid must be able to reduce significantly the surface energy of the newly created fracture surface. Thus, viscous liquids should not be able to intervene in the grinding mechanism. This prediction was verified using siloxanes of similar chemistry and comparable surface energies (16–21 mJ/m<sup>2</sup>) but whose viscosities vary widely (0.5–12,160 cP). Table 7 summarizes the properties of the siloxanes and the results of the grinding experiments. It can be seen that low viscosity hexamethyl disiloxane was indeed an efficient grinding aid, somewhat more active than water, but that polydimethylsiloxanes having relatively higher viscosities were inoperative. Figures 10 and 11 illustrate the aspects of chrysotile ground either in hexamethyl disiloxane or in poly(dimethylsiloxane). Clearly, a defiberization occurred in the first case, whereas fiber bundles remained after grinding for 24 hr in the viscous liquids.

Rehbinder's theory also states that effective stress-corrosion cracking liquids possess adsorption capacity or special surface energy properties. However, (cf. Table 1), no direct relationship between the surface energy parameters of the liquids and grinding efficiencies was apparent. The ability of a liquid to spread over a solid surface is further described by a spreading coefficient, i.e., the difference between the adhesion energy

of the liquid on the solid surface and its cohesion energy; the higher the cohesion energy ( $C_1$ ), the lower the spreading coefficient. The cohesion energy density of a liquid is represented by its solubility parameter ( $\delta_1$ ) which is the square root of the cohesion energy  $\delta_1 = C_1^{1/2}$ , where  $C_1 = (L_1 - RT)/V_1$ .  $L_1$  is the latent heat of vaporization of the liquid, and  $V_1$  is its molar volume. If the solubility parameter of the liquids is considered, the liquids can be ranked according to their grinding efficiency (cf. Table 1).

This conclusion is understandable when the value of the adhesion energy of the liquid on to the solid is of the same order of magnitude as the cohesion energy of the liquid itself, which is the case for low energy solid surfaces. Electron microscopy shows that the fracture of the fibrils occurred perpendicular to their main axis. The fracture surface thus contained hydrophobic Si-O-Si bonds; i.e., the fracture surface had a much lower surface energy than the outer burcrite-like surface layer of chrysotile. Hence, it appeared reasonable to employ the theory of Rehbinder.

Fracture of the chrysotile fibril implies a rupture of atomic bonds leading to a highly reactive surface, which possibly reacts with the solvent. Chemisorption is the most effective way to reduce surface energy and explains why fractured material remains separated. A possible chemisorption of organic derivatives, derived from the chemical activation of the solvents, was explored after grinding in toluene or in alcohol. Moreover, to distinguish between physisorption and chemisorp-

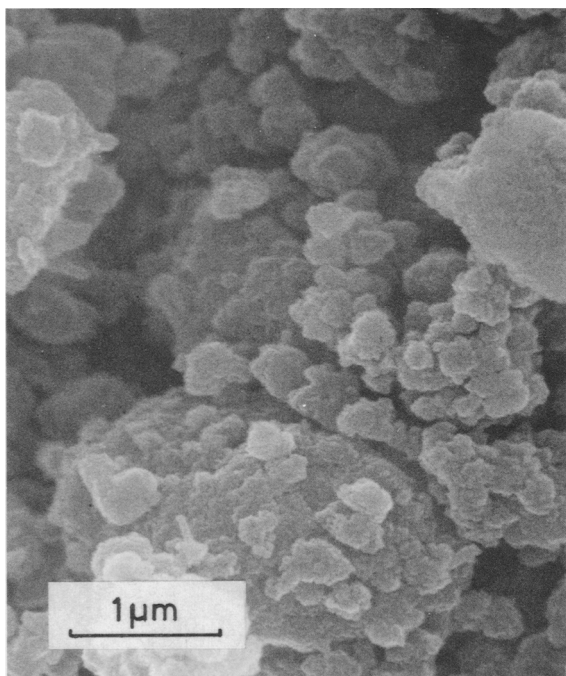


Figure 13. Scanning electron micrograph of chrysotile opened in water and reground in the dry state for 0.5 hr.

tion, chrysotile was outgassed at 150°C prior to analysis. Chemical analysis indicated significant increase of the carbon content of the ground asbestos (3.2% on a 70 m<sup>2</sup>/g chrysotile sample). A rough calculation, assuming that the packing of the chemisorbed species is close to that of toluene (Clellan and Harnsberger, 1967) indicates that the carbon uptake was close to the amount required for a monolayer formation. The more reliable technique of radiochemistry was used to assess the irreversible fixation of a derivative of alcohol during comminution of chrysotile in methanol. A 24-hr grinding experiment was performed using <sup>14</sup>C labeled methanol. After elimination of physisorbed methanol by drying at 150°C, the organic material retained on ground asbestos was oxidized to <sup>14</sup>CO<sub>2</sub> which was analyzed by liquid scintillation β spectrometry. About 5 × 10<sup>-3</sup> mole of a carbon derivative was fixed onto the ground chrysotile which had a specific surface area of ~60 m<sup>2</sup>/g. Assuming the packing of the alcohol molecule as a mean value for the chemisorbed compound, it follows that one monolayer was deposited onto the chrysotile during grinding. The role of the solvent during the grinding of chrysotile is clear: it facilitates fracture under stress by decreasing the surface energy of the fracture surface, and it prevents reagglomeration by chemisorbing onto the ground asbestos. The rate of grinding of chrysotile in water is significantly lower than in toluene, a not unexpected behavior because water has the highest cohesion energy (Ostrovskii and Kharitonov, 1974).

Table 8. Zeta potential of chrysotile (mV).

	In water	In water + 30 ppm CH <sub>3</sub> OH
After 30 min	+7.0 ± 0.5	+6.6 ± 0.5
After 240 min	+6.9 ± 0.3	+7.7 ± 0.3
After 480 min	+6.8 ± 0.3	+12.8 ± 0.5
After 720 min	+6.7 ± 0.3	+14.0 ± 0.5

Water, however, plays a supplementary role by preventing a severe degradation of chrysotile during prolonged grinding. The high resistance of isolated fibrils towards amorphization in water is explained by postulating the existence of a protective water film covering the entire surface of the chrysotile. Indeed, the organization of the water molecules near surface interfaces has been recognized (Drost-Hansen, 1971). In the present study, indirect tests were made to probe the eventual intervention of a water film by grinding in the absence of the water film and by trying to destabilize the protective coating. In the first experiment, chrysotile was "opened" by grinding in the presence of water for 24 hr. Its specific surface area increased from 15 to 35 m<sup>2</sup>/g. The sample was then dried at 150°C and reground repeatedly in the dry state for short times. A 30-min treatment caused a dramatic change in the chrysotile properties. Instead of increasing the surface area, the treatment brought about a significant decrease, from 35 to 20 m<sup>2</sup>/g. Moreover, the ground material resembled a powder. XRD peaks were also attenuated, suggesting the formation of amorphous material. This possibility was substantiated by electron microscopy (Figures 12, 13) which shows fibrils embedded in shapeless material.

The alternative verification of the role of a protective water coating consisted of the addition of molecules that preferentially adsorb on or displace water from chrysotile and thereby affect the strength of the supposed water film. In water solution, 30 ppm methanol was found to be as effective in reducing the grinding efficiency as pure alcohol—5 m<sup>2</sup>/g/hr. In addition, electron microscopy indicated a fragmentation of the individual fibrils, but only if alcohol was present at the fracture front, i.e., close to the surface of the solid. Alcohol in the liquid surface layer modified the composition and possibly also the thickness of the water coating. As a consequence, the surface potential of chrysotile in the

Table 9. Variation of the specific surface area of chrysotile after grinding in an aqueous solution of bis(2ethylhexyl) sodium sulfosuccinate.

Grinding duration (hr)	0	8	16	24	31	48
S (m <sup>2</sup> /g)	15	27	30	35	48	58



presence of minor amounts of alcohols should be modified. Zeta potential measurements in pure water and after the addition of 30 ppm methanol gave the results listed in Table 8.

The equilibrium value of the zeta potential in water was reached only after several hours, a result which is accounted for by the slow establishment of the chemical equilibrium (Mg extraction) in the nearly static conditions of the measurements. During prolonged grinding, however, the chemical equilibrium was attained more rapidly because the diffusion process near the solid interface was highly facilitated. Table 7 shows the significant variation of the zeta potential of chrysotile upon addition of minor amounts of alcohol, supporting the previous hypothesis.

Grinding in the presence of water was, in fact, equivalent to grinding in an alkali medium, due to the formation of  $Mg(OH)_2$ . For example, the pH of the grinding solution, after a 24-hr run, was 10.5. The zeta potential of chrysotile varies with pH and approaches zero when it reaches 11–12 (Light and Wei, 1977). Hence, grinding in water was equivalent to grinding at zero surface potential charge. According to the Westwood theory, it is the situation where the solid manifests its highest mechanical strength!

The existence of a protective water film further accounts for the remarkable state of dispersion of the chrysotile fibers ground in water. Water acted as a stabilizing agent opposing the aggregation of individual fibrils in a way similar to many surface active agents. This supplementary hypothesis was assessed experimentally by grinding chrysotile in an aqueous solution of bis(2ethylhexyl) sodium sulfosuccinate. The adsorption of this substance from a water solution was studied by Otouma and Take (1975) who showed that, first, a monolayer is adsorbed onto the chrysotile surface. Then, with increasing concentration of the surface active agent, a second layer is deposited and orders with the lyophilic portion of the agent in contact with the first adsorbed layer and the polar part directed towards the aqueous solution. Similar results were obtained in the present study. Indeed, the adsorption isotherms showed two plateaus; one corresponding to monolayer coverage (the surface area calculated from the monolayer corresponds to that determined by gas adsorption), and another related to the second adsorption layer. The formation of this surface layer can be taken as evidence for the existence of a protective film. Grinding experiments were performed in a 1% aqueous solution of the sulfosuccinate. The specific surface areas of the ground samples are reported in Table 9. Thus, the grinding efficiency ( $1.5 \text{ m}^2/\text{g/hr}$ ) expressed as the ratio of increase of the initial specific surface is comparable to that obtained in pure water ( $2 \text{ m}^2/\text{g/hr}$ ), and prolonged grinding does not cause agglomeration. Moreover, SEM shows that grinding products look like those ground in pure water; the chrysotile underwent essentially a defiberization process.

## CONCLUSIONS

The behavior of the chrysotile used in this study can not, without further experimental support, be generalized to all chrysotiles; however, work is in progress with a totally different clay mineral (mica), and the preliminary results support the grinding mechanisms reported here for chrysotile. Finally, the grinding medium strongly affects the morphology of the ground chrysotile; a conclusion which has obvious practical applications when ground asbestos is used as a filler in mineral or organic matrices.

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**Резюме**—Изменение свойств хризотила после шарообразного перемала в органических жидкостях (ароматических, алкоголях, силиконовых маслах) либо в воде исследовались при помощи газовой адсорбции, электронного микроскопа, рентгеновской порошковой дифракции, инфракрасной спектроскопии, дифференциального термоанализа, измерения зета-потенциала, и химического анализа. Растирание в органических жидкостях с низкой вязкостью сначала приводит к быстрому отделению волокон асбестовых пакетов и к фрагментации отделённых волокон. Окончательно появляются аморфизация и аггломерация, вызывая решительное уменьшение величины удельной площади поверхности порошкового материала. Растирание в воде тоже приводит к отделению волокон, но более медленно, чем в органических жидкостях. Кроме того, длительное растирание в воде не изменяет значительно структуры хризотила. Эффективности органических растворителей, рассматриваемых в качестве помощников растирания, которые приводят к раздроблению волокон, связаны с вызванными окружающей средой напряжениями разрыва хрупких тел (теории Ребиндера). Отсюда, основные свойства органических жидкостей—это вязкость и параметр энергии сцепления (растворяемость). Растворители, химически адсорбированные на поверхности порошкового хризотила, уменьшают поверхностную энергию поверхности излома и предохраняют от агрегации. Согласно теории Ребиндера вода не реагирует, но вызывает образование предохранительного слоя вокруг волокон. Эта гипотеза была проверена путем сухого растирания асбеста с отделёнными волокнами (быстрая аморфизация) либо путем распределения стабильности воды при помощи коадсорбции алкоголя на поверхности. С другой стороны сопротивление волокон к разрыву может быть объяснено теорией Вествуда, что растирание в воде соответствует растиранию в щелочной среде, в которой поверхностным зарядом хризотила можно пренебречь и механическая стабильность волокон достигает максимума. [E.C.]

**Resümee**—Die Veränderung der Eigenschaften von Chrysotil durch das Mahlen in der Kugelmühle mit organischen Flüssigkeiten (Aromaten, Alkoholen, Silicon-Ölen) oder Wasser wurde mittels Gasadsorption, Elektronenmikroskopie, Röntgenpulverdiffraktometrie, Infrarotspektroskopie, Differentialthermoanalyse, Zeta-Potentialmessungen, und chemischer Analyse untersucht. Das Mahlen in niedrig viskosen organischen Lösungsmitteln führt zu Beginn zu einer schnellen Entfaserung der Asbestbündel und zum Zerbrechen einzelner Fasern. Am Ende tritt eine Amorphisierung und eine Agglomeratbildung auf, die eine drastische Abnahme der spezifischen Oberfläche des gemahlten Materials verursachen. Das Mahlen in Wasser ist mit einer Entfaserung verbunden, die jedoch viel langsamer vor sich geht als in organischen Lösungsmitteln. Darüberhinaus ändert ein längeres Mahlen in Wasser die Struktur von Chrysotil nicht wesentlich. Die Wirksamkeit der organischen Lösungsmitteln, die als Mahlhilfen betrachtet werden, indem sie ein Brechen der Fasern bewirken, werden mit der Umgebungsbeanspruchung, die spröde Feststoffe zerbricht, in Beziehung gebracht (Rehbinder-Theorie). Daher sind die hervorstechenden Eigenschaften von organischen Flüssigkeiten ihre Viskosität und ihre Kohäsionsenergie (Löslichkeitsparameter). Lösungsmittel, die an die Oberfläche des gemahlten Chrysotil chemisorbiert sind, verringern die Oberflächenenergie der Bruchstückoberfläche und verhindern die Agglomeratbildung. Für Wasser gilt die Theorie von Rehbinder nicht, da es um die Fasern eine Schutzschicht zu bilden scheint. Diese Hypothese bewährte sich durch trockenes Mahlen von entfaserter Asbesten (schnelle Amorphisierung) oder indem die Stabilität der Wasserhülle durch Mitadsorption von Alkohol an die Festkörperoberfläche zerstört wurde. Auf der anderen Seite kann die Widerstandsfähigkeit der Fasern gegen Brechen durch die Westwood'sche Theorie erklärt werden, wonach das Mahlen in Wasser dem Mahlen in einem alkalischen Medium entspricht, wodurch die Oberflächenladung des Chrysotil vernachlässigbar wird, und die mechanische Stabilität der Fasern ein Maximum erreicht. [U.W.]

**Résumé**—La variation des propriétés du chrysotile, traité dans un broyeur à boulets en présence de liquides organiques (aromatiques, alcools, huile de silicone) ou d'eau, a été étudiée par adsorption gazeuse, microscopie électronique, diffraction des rayons X, spectroscopie infra-rouge, analyse thermique différentielle, mesure de potentiel zeta, et analyse chimique. Le broyage dans des solvants organiques de faible viscosité cause initialement une défibrillation des microfibrilles et une segmentation des microfibrilles. Finalement, il se produit une amorphisation et une agglomération se traduisant par une chute considérable de la surface spécifique du matériau broyé. Le broyage en milieu aqueux entraîne une défibrillation, mais beaucoup plus lentement qu'en milieu organique. De plus, le broyage prolongé, dans l'eau, n'affecte pas sensiblement la structure du chrysotile. L'efficacité des solvants organiques en tant qu'adjuvants de broyage ou d'initiateurs de la fracture des microfibrilles, s'explique par la théorie de Rehbinder (rupture fragile, sous contrainte et en milieu corrosif). Aussi, convient-il de considérer comme importante la viscosité et l'énergie de cohésion des liquides (paramètre de solubilité). Par ailleurs, les solvants se chimisorbent sur les surfaces de fracture réduisant ainsi leur énergie superficielle et prévenant l'aggrégation des fibres séparées. L'eau ne répond pas exactement à la théorie de Rehbinder, mais semble former une gaine protectrice autour des fibrilles. Pour vérifier cette hypothèse, les microfibrilles ont été rebroyées à sec (amorphisation rapide) et de plus, des essais de destabilisation du film d'eau, par coadsorption d'alcool, ont été entrepris. La résistance à la segmentation des fibrilles en présence d'eau, pourrait aussi s'expliquer en remarquant que le milieu de broyage devient alcalin; par suite leur potentiel zeta devient négligeable et leur stabilité mécanique optimale.