name "Kalahaweirina Groove" was by Williams (1973, 1975).

THE BOTTOM PROFILE

The positions of the Warburton and Kalaweirina Grooves, and the Neales and Cooper Depressions are illustrated in the locality map, Fig. 1A, together with the profile section line X-Y and river systems entering Lake Eyre.

Soundings were made from the sailing craft Ibis, with a graduated pole at points fixed by log line and compass course along the true west bearing of the section line X-Y. Where it was necessary to deviate from the true west bearing, sounding values were transferred from actual sounding points to the line X-Y, along north-south perpendiculars as illustrated in Fig. 1B. This was acceptable as deviation distances were relatively very small, and the significant depth changes under investigation were those in an east-west direction.

The detail plan of sounding points along the profile section X-Y is shown in Fig. 1B, together with the exact positions and widths of the Warburton and Kalaweirina Grooves, and the general areas of the Neales and Cooper Depressions, as determined by aerial photointerpretation. Immediately beneath this plan in Fig. 1B, is the profile section placed with shoreline points and sounding points directly beneath corresponding points in the plan. The profile was constructed by plotting measured depths, at sounding points, in relation to mean lake level of -11.1 m A.M.D.in August 1975. Extrapolation of the profile to the shorelines beyond closely spaced soundings, is indicated by broken lines.

RESULTS AND CONCLUSIONS

The profile constructed from soundings shows definite groove-like features corresponding closely in position and width with the Warburton and Kalaweirina Grooves plotted in plan from aerial photography. The Warburton Groove is the deeper and wider of the two. They stand out very clearly in profile, but their actual depths of 54 and 13 cm in relation to widths of 4.6 and 2.7 km respectively, indicate the extremely shallow nature of the grooves, and the "flatness" or remarkably low relief across the lake bed. There is a slope of 4 cm per km to the west, between the Cooper Depression and the Kalaweirina Groove, then a slight rise to a low ridge between the two grooves. Overall, the bed of the lake exhibits a slight average fall of about 8 mm per km from east to west, in the vicinity of the profile section.

The general areas of the Neales and Cooper Depressions, near the western and eastern shores are shown in plan by broken lines in Figs. 1A and 1B and appear in the profile section in Fig. 1B. They are visible in aerial photography of the dry lake bed, but differ considerably in appearance from the two grooves. They have ill-defined sides, are vague in shape and form, and lack definite orientation. From low altitude aerial observation of both areas in 1974-75, and examination of the Cooper Depression by boat in 1974, there appeared to be offshore silt or sand banks and inshore channels in the areas of the depressions. As they may be due to outwash sand and silt from the Cooper and Neales Estuaries, and inshore scouring by water flowing south along the shores, the term "depression" is used in this paper so as not to infer tectonic significance as in the case of the "grooves" in the profile.

The profile shows the eastern sides of the Warburton and Kalaweirina Grooves steeper than their western sides. When considered in relation to their widths of 4.6 and 2.7 km, this feature would seem to be of some significance, although uncertain in meaning. If the grooves are related to faulting it may mean similar elements of movement beneath each of the grooves. The long narrow nature of the grooves, and their well-defined sides, would seem to indicate sharp fault displacement rather than warping or flexing.

Floodwaters from the Warburton River and Kalaweirina Creek, flow south west across the lake bed, then into and south along their respective grooves (Fig. 1A). Aerial photography (South Australian Department of Lands 1961-64 photography) indicates continuation of the grooves to the north from the places where the floodwaters flow into them, as illustrated by broken lines in Fig. 1A. This strongly supports previous opinions that they originated as tectonic features. It also indicates that floodwaters flow along the grooves as pre-determined channels, and have not been able to develop meanders owing to continued or contemporary tectonic influences or controls. There is no evidence of antiquity of the grooves, and absence of any significant modification by flowing water may mean that they have developed very recently, or are at present developing as a result of contemporary tectonism evidence of which, at Lake Eyre, has been previously recorded by Wopfner and Twidale (1967), and Williams (1973, 1975).

ACKNOWLEDGEMENTS

It is wished to acknowledge (i) the co-operation of Messrs. R. Clark and M. and A. Atkinson, and use of their boat Ibis, in obtaining soundings across Lake Eyre North as described in the text, (ii) assistance of Mulorina Station in field investigations, (iii) funds provided by the Australian Research Grants Committee, and (iv) research facilities of the Department of Geology and Geophysics, University of Sydney.

REFERENCES


sequence of green rocks have been studied for more than a century, there exists only one geological study of the Balangero deposit (Riccio, 1969). Riccio concludes that an original Iherzolite has been serpentinised as well as antigorised. These phenomena as well as the fibre formation are attributed to alpine tectonics. The chrysotile asbestos from Zidani (CZM) belongs to the slip fibre type. The deposit is located in Thessalia, northern Greece and is mined by extensive underground operations. The ultrabasic body is an outlier of the large ophiolitic sequence of rocks forming Vourinos mountain. Macroscopic examination of the fibre bearing rocks shows considerable shearing. The country rocks are considered to be Jurassic. No geological study of Zidani is known. The fibre containing rocks were processed in the mining company's mills as follows: Separation of the fibres by crushing in mills; successive milling for opening and classification of the fibres according to their length and quality. Fibres with a specific surface area of about 20,500 cm$^2$ g$^{-1}$ (determined by N$_2$-absorption) which did not differ more than 7% from each other, were used. In a wet cleaning process in the company's labs particles smaller than 100 μm, i.e. the dust-fraction were removed. The remaining cleaned fibres were opened again to the above mentioned specific surface area and named AMC, BMC, ZMC. Synthetic material, which we obtained through the kindness of Prof. de Vynck/Gent, was synthesized from gels in 15 days according to a method similar to that of Bowen and Tuttle (1949). The synthesized material showed DTA and X-ray diffraction peaks characteristic of chrysotile, but no fibrous texture could be observed under the microscope. Electron microscopic examination, however, showed fibrils of 700 to 12,000 μm in length with 40 to 70 μm inner and 140 to 240 μm outer diameters, together with relics of starting gels.

A hundred runs of aqueous suspensions of unground cleaned and uncleaned chrysotile fibres from Advocate, Balangero and Zidani were carried out in an oilbath and in 2 litre and 10 litre autoclaves. Pressures were varied from 1 to 300 atm and temperatures from 2 to 250°C, and the length of runs from 2 hours to 120 days.
Influence of Hydrothermal Treatment on Physical and Chemical Properties of Chrysotile Asbestos*

P. HAHN-WINHEIMER AND A. HIRNER

ABSTRACT. Aqueous suspensions of natural chrysotile fibres of equivalent specific surface area, originating from Advocate, Balangero and Zidani, and synthetic chrysotile were treated hydrothermally at pressures ranging from 1 to 300 kp cm⁻² and temperatures from 20 to 250°C for 2 hours to 120 days. The resulting solid and liquid phases were investigated by physical and chemical methods.

The influence of a second mechanical cleaning process and of hydrothermal treatment on structural, chemical and technical properties of the fibres and on the dissolved phase of chrysotile in water are presented. It can be demonstrated that the technical qualities of the fibres depend mainly on the constitution of the fibre surface, and to a lesser degree on the amounts of accessory minerals.

Thermodynamic data, as activation energies, activity product constants and Gibbs free energies are calculated and compared with those reported in literature.

INTRODUCTION

Of all asbestos minerals, chrysotile is the fibre most used in industry and accounts for more than 90% of the demand for asbestos fibres. The production of fibre has increased from the fifty tons at Thetford, Canada in 1877 to the world annual output of 4.5 million tons in 1975, an indication of the still growing economic significance of chrysotile (Lincoln, 1975). Compared with the quality of man-made fibres (glass filament, steel, carbon etc.) chrysotile has an important advantage in terms of basic material properties per unit cost. Chrysotile plays an essential role in the asbestos cement industry, and is used in a wide range of friction materials for transmitting power or converting kinetic energy into heat energy. All known substitutes fail on the grounds of efficiency, consistency, or cost effectiveness. Unfortunately the average extrapolated life for economical exploitation of chrysotile does not exceed forty years.

This study on chrysotile was stimulated by industry, on the one hand, and by unsolved problems in fundamental research, on the other. It differs from synthetic experiments (Bowen and Tuttle 1949, Yang 1960, 1961, and Kuczynski et al 1975) in that aqueous suspensions of fibrous chrysotile were used, instead of highly concentrated gels, with the aim to improve or modify the qualities of the fibres.

We exposed chrysotile fibres of equivalent specific surface areas to various hydrothermal conditions, and investigated the physical and chemical properties of the treated fibres. As the quantities of treated fibres were in the range of a few grams up to 50 g per run we were able to perform all analytical work on the same material.

Investigations on the properties of ground chrysotile in water are described by Holt and Clark (1960), Hostetler and Christ (1968), and Choi and Smith (1972). Ball and Taylor (1963) carried out similar experiments, but on a more amplied basis by adding several oxides and hydroxides to the aqueous suspensions of chrysotile. In our study, however, the hydrothermal treatment was performed with unground chrysotile fibres under such conditions that, in most instances, the conversion of chrysotile into forsterite, talc, enstatite and antigorite did not take place. Our results are in agreement with recently developed model of Evans et al (1976) which was derived from field observation.

MATERIALS AND METHODS

The starting materials for the experiments consisted of chrysotile fibres of grade 4D from three different localities, Newfoundland, Italy and Greece.

Advocate asbestos (AM) originates from the Advocate deposit situated in the Burlington Peninsula, 5 km north of the small town of Baie Verte. The main body is a harzburgite with dunite enclaves; it covers an area 3 to 5 km wide and 75 km long. The ultrabasics are mainly near the western contact, where the eruptives of Baie Verte are exposed. The fibre bearing rock (exploited area 1200m x 500m) is wrapped in dark chloritized schists of volcanic origin. The cross fibre is mined by open pit operation. Geological studies were published by Church (1969). The Balangero (BM) open pit mine is located in northern Italy, 50 km northwest of Turin in the hills of San Vittore. This slip fibre deposit occurs in northeastern digitation of the large pre-Triassic peridotitic massif of Lanzo. Although the Lanzo massif and the associated

* An extract from this publication was presented at the 25th International Geological Congress 1976 in Sydney entitled "Investigation of the Behaviour of Chrysotile under Hydrothermal Conditions".
sequence of green rocks have been studied for more than a century, there exists only one geological study of the Balangero deposit (Riccio, 1969). Riccio concludes that an original lherzolite has been serpentinised as well as antigorised. These phenomena as well as the fibre formation are attributed to alpine tectonics. The chrysotile asbestos from Zidani (ZM) belongs to the slip fibre type. The deposit is located in Thessalia, northern Greece and is mined by extensive underground operations. The ultrabasic body is an outlier of the large ophiolitic sequence of rocks forming Vourinos mountain. Macroscopic examination of the fibre bearing rocks shows consideration shearing. The country rocks are considered to be Jurassic. No geological study of Zidani is known.

The fibre containing rocks were processed in the mining company’s mills as follows: Separation of the fibres by crushing in mills; successive milling for opening and classification of the fibres according to their length and quality. Fibres with a specific surface area of about 20,500 cm² g⁻¹ (determined by N₂ -absorption) which did not differ more than 7% from each other, were used. In a wet cleaning process in the Company’s labs particles smaller than 100 µm, i.e. the dust-fraction were removed. The remaining cleaned fibres were opened again to the above mentioned specific surface area and named AMC, BMC, ZMC.

Synthetic material, which we obtained through the kindness of Prof. de Vynck/Gent, was synthesised from gels in 15 days according to a method similar to that of Bowen and Tuttle (1949). The synthesised material showed DTA and X-ray diffraction peaks characteristic of chrysotile, but no fibrous texture could be observed under the microscope. Electron microscopic examination, however, showed fibrils of 700 to 12,000 Å in length with 40 to 70 Å inner and 140 to 240 Å outer diameters, together with relics of starting gels.

A hundred runs of aqueous suspensions of unground cleaned and uncleared chrysotile fibres from Advocate, Balangero and Zidani were carried out in an oilbath and in 2 litre and 10 litre autoclaves. Pressures were varied from 1 to 300 atms. and temperatures from 250°C to 250°C, and the length of runs from 2 hours to 120 days. Pressures

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Figure 1. Bleeding Device in 2L-Autoclave after Dickson et al. (1963)
Characterisation of Starting Material

Influence of Mechanical Cleaning

Orthochrysotile was found in ZM and the synthetic chrysotile in AM. Our fibres to be mainly clinochrysotile; in AM and AMC. In the Zidani fibre, however, orthochrysotile is present as intergrown fibres. The inner and outer diameters of the three types of natural fibres range from 50 to 90 Å and 100 to 200 Å, respectively. These fibres may be well shaped, straight, and not very flexible, and show geometric shapes: the Advocate fibres are well shaped and soft; those from Balangero are straight and soft; those from Zidani are not well shaped, scaly, with adhering particles which were identified as platy particles (Fig. 3). Fig. 4 shows mineral reflections (002) and (004) are increased by 25% in the Advocate fibre, by 17% in Balangero fibre, and 10% in Zidani. The different surface potentials affect the mechanical properties: the transition from single fibrils to aggregated bundles of fibres could be observed by electron microscopy and single fibres could not be removed, a fact which indicated that the fibres are the only minerals of the Balangero and Zidani fibres increased simultaneously which clearly indicates that the fibres are the only minerals.

Table 2. In addition, analogous runs were tried between serpentine minerals and made possible the minerals. Chemical compositions of the solid products were tested with respect to filtrability of hydrated magnesium and silicon in the liquid state were determined by wet-chemical methods. The contents of contaminating elements were analysed by physical and chemical methods: the transition from single chemical methods to aggregated bundles of fibres could be observed by electron microscopy and single fibres could not be removed, a fact which indicated that the fibres are the only minerals.

Table 1

<table>
<thead>
<tr>
<th>pressure P(kPa cm(^{-2}))</th>
<th>1</th>
<th>10</th>
<th>50</th>
<th>100</th>
<th>200</th>
<th>100</th>
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<td>temperature T(°C)</td>
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<td>100</td>
<td>100</td>
<td>100</td>
<td>200</td>
<td>200</td>
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</tbody>
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TABLE 1

CONDITIONS OF HYDROTHERMAL EXPERIMENTS IN OILBATH AND 2 LITRE AUTOCLAVE

<table>
<thead>
<tr>
<th>fibre</th>
<th>P(kPa cm(^{-2}))/T(°C)</th>
<th>conc. of chrysotile (%)</th>
<th>duration</th>
<th>additives +)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM</td>
<td>50/150</td>
<td>2.9</td>
<td>80 hrs</td>
<td>B, S, A</td>
</tr>
<tr>
<td></td>
<td>100/150</td>
<td>2.9</td>
<td>80 hrs</td>
<td>B, S, A</td>
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<tr>
<td></td>
<td>200/150</td>
<td>2.9</td>
<td>80 hrs</td>
<td>B, S, A</td>
</tr>
<tr>
<td></td>
<td>100/100</td>
<td>9</td>
<td>50 hrs</td>
<td>B, S</td>
</tr>
<tr>
<td>BM</td>
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<td>100 hrs</td>
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<td></td>
<td>200/100</td>
<td>9</td>
<td>100 hrs</td>
<td>B, S</td>
</tr>
<tr>
<td></td>
<td>100/200</td>
<td>9</td>
<td>100 hrs</td>
<td>B, S</td>
</tr>
<tr>
<td></td>
<td>200/200</td>
<td>9</td>
<td>100 hrs</td>
<td>B, S</td>
</tr>
<tr>
<td>ZM</td>
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<td>9</td>
<td>50 hrs</td>
<td>B, S</td>
</tr>
<tr>
<td>AMC</td>
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<td>100 hrs</td>
<td>B, S</td>
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<tr>
<td></td>
<td>200/200</td>
<td>9</td>
<td>120 d</td>
<td></td>
</tr>
<tr>
<td>BMC</td>
<td>100/200</td>
<td>9</td>
<td>100 hrs</td>
<td>B, S</td>
</tr>
<tr>
<td></td>
<td>200/200</td>
<td>9</td>
<td>120 d</td>
<td>S</td>
</tr>
<tr>
<td>ZMC</td>
<td>100/200</td>
<td>9</td>
<td>100 hrs</td>
<td>B, S</td>
</tr>
<tr>
<td></td>
<td>200/200</td>
<td>9</td>
<td>120 d</td>
<td>B</td>
</tr>
</tbody>
</table>

TABLE 2

HYDROTHERMAL EXPERIMENTS IN 10 LITRE AUTOCLAVE

*+) weight % of fibre
B = brucite
S = SiO\(_2\)
A = Al\(_2\)O\(_3\)
SZ = SiO\(_2\) (liquid and solid, resp.) + 20% and 40%
ZMC, resp.
Figure 2. Aggregated chrysotile fibres from Balangero (mode: SEM).

Figure 3. Chrysotile fibres from Zidani (mode: SEM).

Figure 4. Aggregated particles in chrysotile (mode: SEM).
and temperatures were monitored and recorded by a ten-channel printer during the runs. The precision of the pressure and temperature regulation devices was 1% and 0.3%, respectively. Immediately after the termination of the runs the suspensions were filtered through 0.45 μm pore-size filters, and the solid and liquid phases were analysed separately.

The reaction vessel and the 2 litre autoclaves were constructed in such a manner that enabled samples to be bled off during the runs (Fig. 1). The various hydrothermal conditions of the runs in the ollibath and the 2 litre autoclaves are compiled in Table 1. These experiments may be regarded as fundamental research, whereas those in closed 500 ml teflon vessels in the 10 litre autoclave are of a more applied character. The conditions of these experiments are listed in Table 2. In addition, analogous runs were tried in 0.01 normal ammonia. Of course, blanks were carried out for each run.

The solid phase was analysed by physical and chemical methods: the transition from single fibrils to aggregated bundles of fibres could be observed by electron microscopy and single fibres were identified by electron diffraction; X-ray diffraction revealed structural differences between serpentine minerals and made possible the determination of the contents of contaminating minerals. Chemical compositions of the solid state were determined by wet-chemical methods, X-ray fluorescence spectrometry, instrumental neutron activation analysis and electronprobe microanalysis. The surface properties of the different kinds of fibres were investigated by zetapotential measurements. The mechanical properties of chrysotile asbestos in cement products were tested with respect to filtrability and strength (Hirner, 1976). The concentrations of hydrated magnesium and silicon in the liquid phase were analysed by atomic absorption and spectrophotometry, respectively.

For the various physical and chemical analyses the fibres were prepared in non-destructive manner by suspension methods; for X-ray fluorescence analyses, the diluted samples were fused with lithium metaborate.

**RESULTS**

**Characterisation of Starting Material**

The inner and outer diameters of the three types of natural fibres range from 50 to 90 Å and from 200 to 500 Å, respectively, which is in general agreement with diameters observed by Yada (1971). Uncleaned Advocate fibres are well shaped and soft; those from Balangero are straight and not very flexible, and show geometric shapes in aggregates (Fig. 2). Uncleaned fibres from Zidani are not well shaped, scaly, with adhering particles (Fig. 3). Fig. 4 shows mineral particles which were identified as platy aggregates of lizardite and antigorite. These minerals were found in all kinds of fibres on a microscopic scale. Diffraction patterns proved our fibres to be in a similar mineralogical state. In addition, antigorite was identified in BM, and orthohysotile was found in 2M and the synthetic matrix. The contents of accessory minerals are presented in Table 3. The highest amounts of dolomite and magnetite were found in Zidani and Balangero fibres, respectively. The chemical compositions of the untreated fibres are illustrated on Figure 5. The groups of major, minor and trace elements including extreme traces are clearly separated. In spite of the small variations in the major elements a relatively high amount of magnesium is characteristic of the Advocate fibre and a relatively high amount of silica of the Zidani fibre. The surface charge differs between the three fibres; the following zetapotentials were determined: +54 mV for Advocate, +24 mV for Balangero and +18 mV for Zidani. The different surface potentials affect the different mechanical properties. Asbestos cement cakes with fibres from Advocate have a lower density, but higher strength (340 kp cm⁻²) than those from Zidani (245 kp cm⁻²).

**Table 3**

<table>
<thead>
<tr>
<th>Accessory Minerals Associated with Chrysotile Fibres (%) Determined by X-Ray Diffraction Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
</tr>
<tr>
<td>Advocate</td>
</tr>
<tr>
<td>Balangero</td>
</tr>
<tr>
<td>Zidani</td>
</tr>
</tbody>
</table>

**Influence of Mechanical Cleaning**

Residual amounts of orthorychotile in AM and antigorite in BM were almost quantitatively removed; in the Zidani fibre, however, orthochryosotile could not be removed, a fact which indicated that orthochryosotile is present as intergrown fibres. As the amounts of accessory minerals are reduced the integral intensities of the principal reflections (002) and (004) are increased by 25% in the Advocate fibre, by 17% in Balangero fibre, and by 9% in the Zidani fibre.

In the Balangero fibre the appreciable amounts of contaminating minerals could be removed down to the limits of detection, i.e. 0.1% for brucite, 0.1% for dolomite, 0.2% for calcite and 0.2% for magnetite. This holds true for magnetite in the Advocate fibre. Brucite in this fibre and dolomite and magnetite in the Zidani fibre, however, are so intimately intergrown that they still remained after mechanical processing. This procedure proved to be efficient in reducing the chromium content in the Advocate and Zidani fibres by a factor of 2.5 to 3.5. In the Balangero fibre the nickel, manganese and titanium contents were lowered by a factor of about 2. Because of the removal of interfering and specifically heavier contaminants the density of asbestos cement decreased, as if the fibre material had passed a cleaning process. Filtrability and strength of the Balangero and Zidani fibres increased simultaneously which clearly indicates that the fibres are the only
Figure 6. Filtrability and strength of asbestos cement cakes Advocate fibre after treatment.
reinforcing material in asbestos cement products. The soft cleaned fibres from Advocate have a lower filtrability and a slightly better strength than the uncleaned material, because the platy lumps of lizardite were removed.

Influence of Hydrothermal Treatment

In principle, the mineralogy was not influenced except for a small portion of Zidani chrysotile - perhaps the orthotype - which was converted into antigorite. This conversion was prevented by the addition of 1% brucite.

The integral intensities of the main reflections and therefore the concentrations of natural and synthetic chrysotile were not increased by hydrothermal treatment (detection limit 2%). In dust-fractions (particles smaller than 100 μm), however, the amounts of chrysotile could be increased by about 22%. Two explanations may be valid for this effect; either an appreciable amount of amorphous substances was dissolved, and/or additional chrysotile was formed. As relatively high contents of accessory minerals were unexpectedly resistant to dissolution, the above mentioned increase of chrysotile concentrations cannot be correlated with this fact. Concerning the accessory minerals, dolomite in Zidani fibre was hydrothermally reduced by a factor >6 (0.3% still remained). By simple exposure to water brucite can be removed from the cleaned Advocate fibre. 25% to 35% of the contaminating calcium present was dissolved, from all kinds of fibres, when treated hydrothermally.

THERMODYNAMIC DATA

In principle there are two possible mechanisms responsible for dissolution of serpentine: solid state diffusion and/or dissociation of the mineral surface. Luce et al. (1972) showed for lizardite that dissolution is a function of time squared; strong acid causes a linear relationship. Dissolution of ground chrysotile is affected only by dissociation of the large "brucite-like" surface of the fibres. After the first minutes of contact with water hydroxyl groups of chrysotile are already dissolved and final pH is reached. The dissolution of Mg\(^{2+}\) is proportional to the temperature and is terminated within the first hour at T>45°C. In the following the reactions on the surface of chrysotile equilibrate by readsorption of MgOH\(^{+}\) and Mg(H\(_2\)O)\(_6\)^{2+} (Choi and Smith 1972).

Dissolution of ground chrysotile in water is incongruent for short periods (minutes to hours) and congruent for long periods (days to months). The simplified description given above cannot be fully accepted for the dissolution processes of unground fibres. The latter showed solubility equilibria of the major elements only at 1/20 for BMC and P = 1 kp cm\(^{-2}\) and T<100°C for ZMC for one to twenty days. Within the first day no equilibria were detected for any kind of fibre. A stationary dissolution process under hydrothermal conditions could not be observed in any run. In order to get data suitable for thermodynamic calculations the above mentioned fluctuations and trends were averaged or extrapolated.

Activation energies of dissolution for the main constituents of unground chrysotile in water were calculated from the time-dependent solubility plots, assuming a first order reaction. By plotting log [Rate (=slope/ax)/T] versus 1/T, as it is shown on Figure 7, the energy of activation for the magnesium ions and the silica complexes in water were determined by the slopes of the graphs. For magnesium dissolution from AMC 6.4 kcal/mole (Choi and Smith (1972) found 5.5 kcal/mole), and for silica dissolution from BMC and ZMC 11.25 and 8.5 cal/mole were calculated, respectively. If these values are compared with that of 5.3 kcal/mole for self-diffusion of water molecules in water (Glasstone et al. 1941), it is clear that the dominant process of dissolution of unground chrysotile is the diffusion of magnesium and silicon from the surface of the fibre into the suspending medium.

| TABLE 4 |
| ZETA-POTENTIALS OF CHRYSOTILES (mV) |

<table>
<thead>
<tr>
<th>origin</th>
<th>no cleaning</th>
<th>special cleaning</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>blank</td>
<td>blank treated in H(_2)O normal hydrothermal conditions</td>
</tr>
<tr>
<td>Advocate</td>
<td>+54</td>
<td>+48</td>
</tr>
<tr>
<td>Balangero + 1% SiO(_2)</td>
<td>+24</td>
<td>+26</td>
</tr>
<tr>
<td>Zidani + 1% brucite</td>
<td>+18</td>
<td>+17</td>
</tr>
<tr>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Table 4 illustrates the influence of hydrothermal treatment on the electrical potentials of the fibre surfaces. It is surprising that the surface charge of the Advocate fibres could not be changed. A complex hydrated magnesium layer surrounding the fibres may be the explanation; this layer seems to be much more resistant to hydrothermal influence than brucite. The surface of Balangero fibres with medium zeta-potentials is more sensitive to hydrothermal conditions, whereas the surface charge of Zidani fibres with low zeta-potentials changes its sign even in water under normal conditions. A reversal of the sign of the surface charge can be produced with the Balangero fibres when silica is added (Table 4).

As a result of our experiments concerning adsorption of brucite on Zidani fibres, we suggest that experiments concerning the chemical adsorption of organic polymers on unsaturated silanol groups of chrysotile, as described by Cossette and Lalancette (1975) would be particularly successful with hydrothermally treated Zidani fibres.

The behaviour of the surface as already described is most important in regard to the contact of the various fibres with the basic medium of the cement slurry and, therefore, the mechanical qualities can be correlated with out observations of the zeta-potentials. By hydrothermal treatment filtrability and strength (determined in the Company's labs according to a modified F.V.T. test) were improved for the Advocate fibre, but not for Balangero or Zidani fibres. The results of the more detailed investigation of the Advocate fibre with respect to filtrability and strength are compiled in the diagram of Figure 6. Filtrability is strongly enhanced by additives (1% of silicic, brucite and alumina at higher temperatures (200°C), whereas the strength was remarkably reduced if fibres were treated in diluted ammonia.

Liquid Phase

The behaviour of magnesium in solution under hydrothermal conditions is described in the following: under normal conditions (at 1 kp cm\(^{-2}\) and 20°C, abbreviated 1/20) 7.7 · 10\(^{-5}\) mole/1 Mg\(_2\)O from AMC, 2.9 · 10\(^{-5}\) mole/1 from BMC, and 5.0 · 10\(^{-5}\) mole/1 from ZMC were dissolved after one day. Equilibrium was already reached in this time and maintained until the 20th day. At the higher temperature of 80°C the dissolution of magnesium was strongly enhanced; after 20 days the amounts had increased by factors of 2.9, 9.0, and 5.5 for AMC, BMC and ZMC, respectively. Contaminating minerals containing magnesium, such as brucite were increasingly dissolved at higher temperatures. The amount of dissolved magnesium decreased with increasing pressure. Magnesium ions are prevented from moving from the fibre surface into solution at pressures >50 kp cm\(^{-2}\) and temperatures >100°C.

The dissolved silica in aqueous phase behaved differently for the three types of chrysotile fibres: 5.7 · 10\(^{-5}\) mole/1 (SiO\(_2\))\(_{aq}\) were dissolved in suspensions of ZMC reaching solubility equilibrium at 1/20 after one day. Increasing temperature caused higher solubility of (SiO\(_2\))\(_{aq}\) whereas pressure had almost no influence. As the silicon layers cover a great area of the surface of the Zidani fibre, continuous dissolution of silicon from the surface is guaranteed; it cannot be excluded, however, that amorphous silica originating from the inner space of the tubular fibres is being dissolved, too. 2 · 10\(^{-5}\) mole/1 dissolved silica were determined in the suspensions of BMC under normal conditions; equilibrium was reached after one day. At 100°C the solubility increased by a factor of 4. Further
1) 100/100 in H₂O
2) 100/200 in H₂O
3) 50/100 in 0.01 nNH₄OH
4) 50/200 in 0.01 nNH₄OH

- without additives
X + 1% SiO₂
○ + 1% brucite
△ + 1% Al₂O₃

mean and standard deviation of approx. 10 sample tests.

Figure 6. Filtrability and strength of asbestos cement cakes Advocate fibre after treatment.
In principle there are two possible mechanisms responsible for dissolution of serpentine: solid state diffusion and/or dissociation of the mineral surface. Luce et al. (1972) showed for lizardite that dissolution is a function of time squared; strong acid causes a linear relationship. Dissolution of ground chrysotile is affected only by dissociation of the large "brucite-like" surface of the fibres. After the first minutes of contact with water hydroxyl groups of chrysotile are already dissolved and final pH is reached. The dissolution of Mg$^{2+}$ is proportional to the temperature and is terminated within the first hour at T = 45°C. In the following the reactions on the surface of chrysotile equilibrate by readsoption of MgOH$^+$ and Mg(H$_2$O)$_2$$^+$ (Choi and Smith 1972). Dissolution of ground chrysotile in water is incongruent for short periods (minutes to hours) and congruent for long periods (days to months).

The simplified description given above cannot be fully accepted for the dissolution processes of unground fibres. The latter showed solubility equilibria of the major elements only at 1/20 for BMC and P = 1 kPa cm$^{-2}$ and T = 100°C for ZMC for one to twenty days. Within the first day no equilibria were detected for any kind of fibre. A stationary dissolution process under hydrothermal conditions could not be observed in any run. In order to get data suitable for thermodynamic calculations the above mentioned fluctuations and trends were averaged or extrapolated.

**Activation energies** of dissolution for the main constituents of unground chrysotile in water were calculated from the time-dependent solubility plots, assuming a first order reaction. By plotting log [Rate vs $\text{slope}_{\text{max}}/T$] versus 1/T, as it is shown on Figure 7, the energy of activation for the magnesium ions and the silica complexes in water were determined by the slopes of the graphs. For magnesium dissolution from AMC 6.4 kcal/mole (Choi and Smith 1972) found 5.5 kcal/mole, and for silica dissolution from BMC and ZMC 11.25 and 8.5 kcal/mole were calculated, respectively. If these values are compared with that of 5.3 kcal/mole for self-diffusion of water molecules in water (Glassstone et al. 1941), it is clear that the dominant process of dissolution of unground chrysotile is the diffusion of magnesium and silicon from the surface of the fibre into the suspending medium.

**Figure 7. Activation Energy Plot**

<table>
<thead>
<tr>
<th>Rate</th>
<th>$\text{slope}_{\text{max}}$</th>
<th>$1/T$</th>
<th>Activation Energy (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1)</td>
<td>ZMC, (SiO$_2$)$_aq$ dissolution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2)</td>
<td>BMC, (SiO$_2$)$_aq$ dissolution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3)</td>
<td>AMC, Mg$^{2+}$ dissolution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4)</td>
<td>Chrysotile from Quebec, Mg$^{2+}$ dissolution</td>
<td>Choi and Smith (1972)</td>
<td></td>
</tr>
</tbody>
</table>

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Chernosky, J. V., 1973. The stability of magnesium and silicon demonstrate that these minerals are removed by mechanical cleaning and surface charge, such as Advocate, are suitable for the manufacture of asbestos cement products; fibres of low surface potentials, such as Zidani, should be more advantageous for the development of composite materials.


Dickson, F.W., Blount, C.W., and Tunell, G., 1963. Use of hydrothermal solution equipment to determine the solubility of anhydrite in water from 100°C to 275°C and from 1 bar to 1000 bars pressure. Amer. J. Sci., 261, 349-373.


Klapdor, K., 1973. The stability of magnesium and silicon demonstrate that these minerals are removed by mechanical cleaning and surface charge, such as Advocate, are suitable for the manufacture of asbestos cement products; fibres of low surface potentials, such as Zidani, should be more advantageous for the development of composite materials.

Mg$^{2+}$ dissociation

**ACKNOWLEDGEMENTS**

We are grateful to Eternit S.A., Belgium, and its director A. Gosseye for financial support and instrumental help.
### Table 5

Gibbs Free Energy $-\Delta G^\circ_F$ (kcal/mole) for Chrysotile at 25°C, 1 ATM.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>New Idria</td>
<td>synth. chrys.</td>
<td>New Idria</td>
<td>New Idria Hennake</td>
<td>New Idria chrys.</td>
<td>synth. chrys.</td>
<td>AMC</td>
</tr>
<tr>
<td>Sample preparation</td>
<td>grinding</td>
<td>grinding</td>
<td>crushed serpentine</td>
<td>grinding</td>
<td>&quot;free of amorphous material&quot;</td>
<td>manufactured fibres &gt;100 µm</td>
<td></td>
</tr>
<tr>
<td>Method</td>
<td>equilibrium in H$_2$O</td>
<td>calorimetry</td>
<td>equilibrium in H$_2$O</td>
<td>stability conditions</td>
<td>equilibrium in H$_2$O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temp. of exp.</td>
<td>25°C</td>
<td>25°C</td>
<td>90°C</td>
<td>25°C</td>
<td>80°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$-\Delta G^\circ_F$ (25°C)</td>
<td>963,5±0,5</td>
<td>957</td>
<td>964,75</td>
<td>962,9±3</td>
<td>962,6±8</td>
<td>963,69±0,31</td>
<td>965,48±0,44</td>
</tr>
<tr>
<td></td>
<td>964,92</td>
<td>962,9±3</td>
<td>962,6±8</td>
<td>963,69±0,31</td>
<td>964,99±0,29</td>
<td>962,97±0,57</td>
<td>965,48±0,44</td>
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</table>
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