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FIBROUS SILICATES

by A. A. HODGSON



LECTURE SERIES 1965
NUMBER 4

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FIBROUS SILICATES

BY

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FIBROUS SILICATES

By A. A. HODGSON, B.SC., PH.D., F.R.I.C.

There are two kinds of distinctly fibrous silicates, one man-made, the other occurring naturally. Glass fibres, silica and aluminosilicate fibres and those mineral fibres known as rock-wool and slag wool constitute the group of artificial fibrous silicates, all of which, with the possible exception of certain highly-developed quartz fibres, have a random non-crystalline structure. In contradistinction to glass fibres, the naturally occurring inorganic fibres possess true crystallinity of structure, which in turn predetermines and contributes to their range of unusual chemical and physical properties. They consist exclusively of several remarkable minerals, recognized as fibres of considerable technical and economic value, and known collectively as asbestos. These are the fibrous silicates which we shall be considering here.

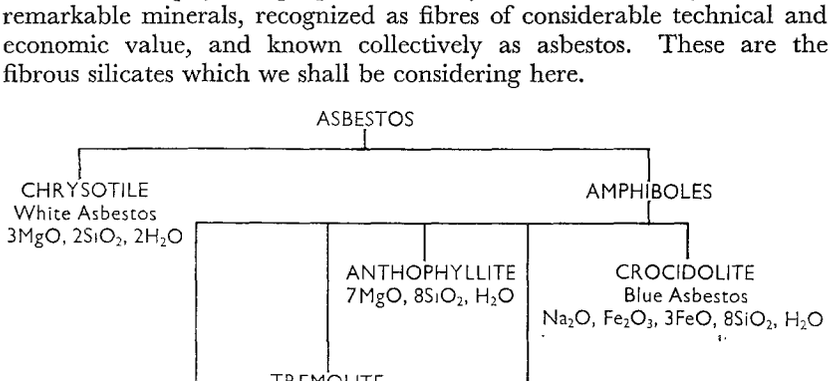

FIG. 1. Varieties of asbestos.

Six species of asbestiform minerals are known, these being derived from two large groups of rock-forming minerals, the serpentines and the amphiboles. Chrysotile or white asbestos is the sole species classified in the serpentine group, but it is by far the most abundant kind of asbestos. The amphibole group includes asbestiform types, namely crocidolite, amosite, anthophyllite, tremolite and actinolite. While the names anthophyllite, tremolite and actinolite apply equally to the fibre and crystal forms of these minerals, the name crocidolite is given to the fibrous form of riebeckite, and amosite to the fibrous form of grunerite. Fig. 1 shows a classification of these minerals, together with their approximate chemical composition. The bulk of the world's asbestos has developed as cross-fibre seams or veins in their host rocks, although this is not the only form of development. The seams contain fibres in an extremely tightly packed parallel formation (Plate I), their width, which of course determines the fibre length, generally being between $\frac{1}{32}$ and $\frac{3}{4}$ in. Longer fibres are less abundant, but it is not uncommon to find chrysotile, crocidolite and tremolite fibres up to 4 in long, and amosite

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fibres up to 12 in long. Anthophyllite (Plate I) and certain forms of crocidolite do not occur in cross-fibre development, but rather as fibrous masses containing randomly orientated cubic blocks of fibre up to 1 in in length. Within each block the fibres lie parallel as in a seam.

The nature and texture of asbestos fibres are matters of considerable technical importance. Those kinds containing a high proportion of magnesium, such as chrysotile, anthophyllite and tremolite, generally form white silky fibres, the smallest diameters of which may be less than 0·01 μ. At the other extreme, amosite, an ash-grey fibre with a high proportion of iron in its composition, has a harsh, spiky texture, its fibres being springy and often brittle. Crocidolite, or blue asbestos, has a texture intermediate between these two extremes, but neither amosite nor crocidolite can be split down to individual fibres much smaller than 0·1 μ in diameter. Within each species there is a relatively wide variation in texture, chrysotiles from some localities being considered harsh and brittle, while a variety of amosite known as montasite has a distinctly soft, silky nature. Differences in texture and flexibility, and indeed in the fundamental property of fibrosity itself, can be explained from structural considerations. In crystallographic terms, chrysotile is described as a sheet silicate, but the two-dimensional layer structure is rolled about an axis to form a narrow tube, possessing both strength and flexibility. This constitutes the ultimate fibre and its form can be clearly demonstrated by electron micrographs (*see* Plate IV*a* and *b*). The amphiboles are chain silicates; their unit of structure comprises two bands of silica tetrahedra separated by a band of cations, the whole having a rigid lath-like appearance (*see* Plate IV*d* and *e*). In this structure, cleavage between the laths becomes more difficult as one approaches the ultimate crystallite.

As a mineral of practical value to mankind, asbestos has a long history, evidence for its early existence and application being found in the writings of Plutarch in 438 B.C. The ancient Romans worked the chrysotile deposits in the Italian Alps and made asbestos cremation cloths from the fibre, which was known during the first century B.C. to the Greeks, who probably obtained supplies from Cyprus and Turkey. The anthophyllite deposits of Finland have an even longer history of application, and the Finns may claim to be the first to make use of the reinforcing properties of asbestos. Since immemorial times local inhabitants have made a fireproof mortar of clay and asbestos rock, and evidence of its use has been proved in fragments of stone-age utensils. Marco Polo recorded that his explorations in 1250 had led him to asbestos mines which were probably those known to have been operating in the Russia of Peter the Great. In more recent times asbestos came into its own as a material of commercial importance with the discovery of chrysotile deposits in Canada during the last century. Sir William Logan, first Director of the Geological Survey in Canada, 'noted' these as early as 1847, but it was not until some 30 years later that mining operations began at the principal deposits at Thetford in Eastern Quebec Province. Asbestos has been recognized in the Bjanova area of the Urals in Russia since the time of Peter the Great, having been discovered

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about the year 1725. The first mining started in 1885. Mines are located in Asbest, which is 80 km east of Sverdlovsk. The deposits there are comparable in size with those of Eastern Quebec.

The discovery of blue asbestos is attributed to a German geologist, Lichtenstein, who, at some time between 1803 and 1806, was travelling near Prieska in the Orange River Valley in South Africa, and came upon a mass of heavy asbestos which was lavender blue in colour. The discovery appears to have been forgotten for many years, to be revived in 1891 by a diamond prospector whose attention had been drawn to the 'blue ground' at Prieska. Diamonds there were none, but it was through De Beers Consolidated Mines, whose main interest lay in diamond mining, that a company was formed in 1893 to exploit these new deposits of blue asbestos. The only known deposits of amosite asbestos, which occur in a fairly small area in the Eastern Transvaal, were discovered in 1907, and were mined some years later.

TABLE I

WORLD PRODUCTION OF ASBESTOS, 1964 (SHORT TONS*)

Data compiled from Bureau of Mines *Minerals Yearbook, 1964* (United States Dept. of the Interior)

	Chrysotile	Crocidolite	Amosite	Anthophyllite
Canada ..	1,416,650			
U.S.S.R. ..	1,300,000			
S. Rhodesia ..	153,450			
China	130,000			
U.S.A... ..	101,100			
Italy	75,570			
Swaziland ..	39,860			
S. Africa ..	35,920	102,400	77,270	
France.. ..	24,250			
Japan	17,980			
Cyprus ..	13,040			
Australia ..	—	16,200		
Finland ..	—			11,610
Others† ..	21,700			
	3,330,000	118,600	77,270	11,610

* 1 Short Ton = 2000 lb; † includes 12 countries.

These, then, were the pioneer mines of a world-wide industry which now produces more than 3 million tons of asbestos of all values, ranging from £20 to £500 per ton, according to quality (Table I). The great deposits of chrysotile asbestos in Eastern Quebec and in the Russian Urals contribute the lion's share of this production, but there are several other important sources of chrysotile which need to be mentioned. The Shabani mines in Southern Rhodesia and the smaller Cassiar mine in Northern British Columbia produce substantial quantities of high-quality long-fibred chrysotile. Smaller deposits are located in Italy, Corsica, Greece, Turkey, India, Transvaal, Swaziland, Brazil and in Vermont and Arizona. China is coming forward as a significant producer with chrysotile deposits in Szechwan province and other areas. Small

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occurrences of chrysotile can be found in many serpentine emplacements throughout the world, and in the United Kingdom small veins and patches of the fibre can be found in the serpentines at the Lizard, at Portsoy, Banffshire, and Glen Urqhart, Inverness-shire, though of course these are of academic interest only.

While chrysotile is a ubiquitous and abundant mineral, the same is not true of the amphibole asbestos fibres. The largest source of blue asbestos remains in South Africa, where a number of underground mines operate along a line of hills stretching northwards for some 300 miles from the original locations on the Orange River and as far as the Bechuanaland Border. Crocidolite from these mines is known as 'Cape Blue' to distinguish it from 'Transvaal Blue' taken from the mines in the Malips River area near Pietersburg (*see* Map, Fig. 2). In the Hammersely Range in Western Australia, there is an important crocidolite deposit in rocks that are remarkably similar in geological formation to those of the crocidolite fields of South Africa. Two further occurrences of crocidolite are known, one at Cochabamba in Bolivia and the other at Lusaka in Northern Rhodesia. The Bolivian deposit produces less than 300 tons of fibre per year, but Lusaka is not mined. Both these deposits are interesting because fibre formation has an igneous origin, unlike that of South Africa, which has a sedimentary origin.

As we have already mentioned, the only known amosite deposits in the world are in the Eastern Transvaal; they occur in geological formations similar to those of the Cape Province crocidolites. Of the other amphiboles, anthophyllite is mined on a fairly large scale in the Paakkila area in Finland, commercial operations having commenced there about 1918; tremolite has little economic importance but is available in Italy, Pakistan and one or two other countries; and fibrous actinolite is no more than a curiosity, though a reef of such material has been uncovered at the blue asbestos mine at Koegas in Cape Province.

Mining

All forms of asbestos are metamorphic minerals developed through several stages of paragenesis from their parent rocks. Most chrysotiles have formed in metamorphic rocks of an igneous origin, namely ultra-basics such as peridotite, dunite and pyroxenite, in which the olivines and pyroxenes have been altered by hydrothermal action to serpentine. Part of this serpentine has recrystallized as fibrous material in fissures and cracks which developed during emplacement and cooling of the original magma. Since chrysotile veins form an irregular lattice work in serpentine, the winning of the fibre necessitates removal of the whole mass of its host rocks for crushing and extraction at the refinery. Modern methods of refining allow for the economical extraction of serpentine with yields of fibre as low as 2 per cent.

Such serpentine masses which contain chrysotile are usually extensive both in plan and depth. Consequently open-cast methods have proved to be the most economical way of working chrysotile deposits, and the immense quarries in the asbestos fields of Quebec Province are typical

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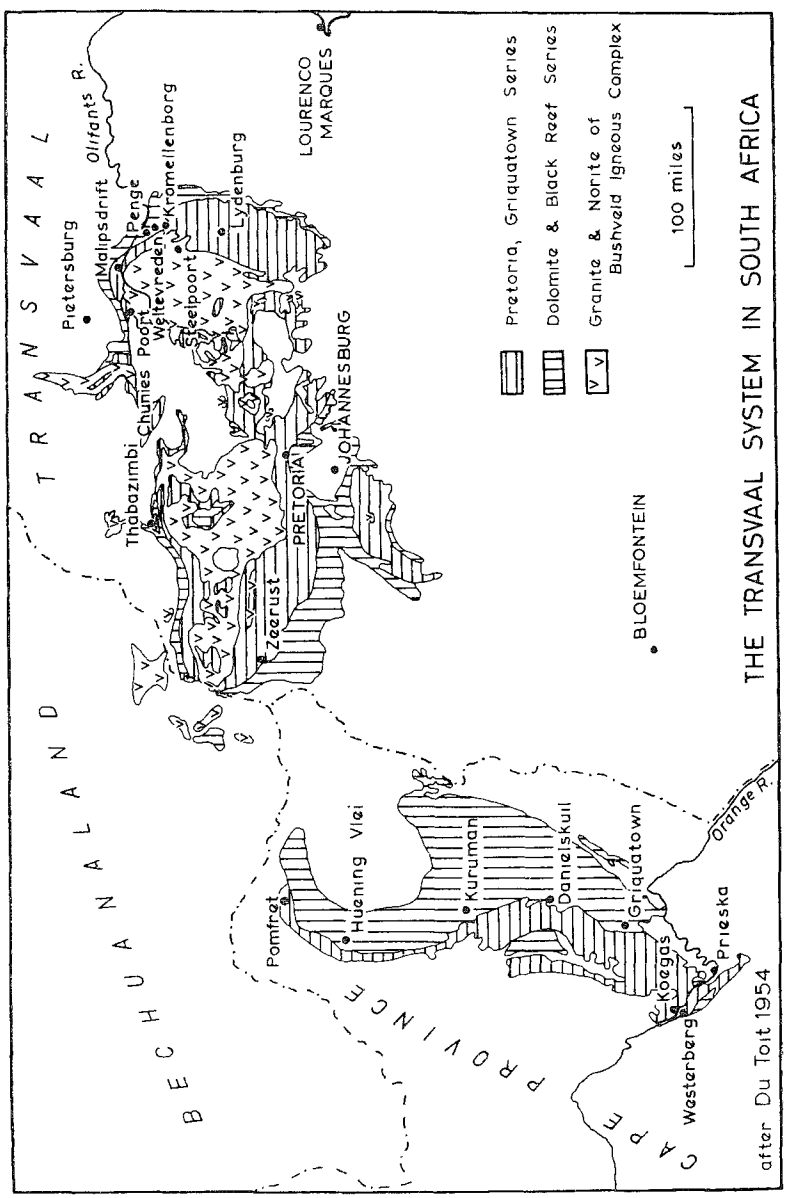

FIG. 2. Geological map of the Transvaal system in South Africa.

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of this development. However, in Southern Rhodesia and South Africa most of the exploitation is underground. There the ore bodies are generally tabular in shape with a pronounced dip. Mining operations follow the dip of the ore body and horizontal galleries are cut along the strike. The ore bodies at Shabani are extensive and underground development has been carried for 3 miles along the strike and to sub-surface depths of over 1000 ft.

Underground development accounts for most of the amphibole asbestos workings in South Africa, but for rather different reasons from those applying to the chrysotile deposits. Crocidolite and amosite asbestos occur in metamorphosed sedimentary strata, known as the Banded Ironstones. These are included in the upper part of the Transvaal System of rocks, which form a broad front from the Orange River in Cape Province to the Eastern Transvaal (Fig. 2). Similar formations occur in Western Australia in association with crocidolite asbestos. These, essentially, are stratified rocks of which typical horizons can be traced for hundreds of miles. The asbestos horizons consist of a number of reefs up to 10 ft in thickness. The deposits are worked by the systematic cutting of galleries at various sub-surface levels along the strike of the reefs and the galleries are connected by inclined or vertical main shafts to the ground surface. The Penge amosite mine is the largest asbestos mine in the Union and the development there is at a maximum depth of 1300 ft. Plates II and III show a typical underground ore face at Penge, compared with that in a chrysotile deposit at Thetford.

The list of references, p. 45, contains some useful papers dealing with the geology and origin of asbestos deposits.

Applications

The widest use of asbestos fibre lies in the manufacture of asbestos–cement products. These include flat sheets or sidings, tiles and corrugated sheets for roofing, rain-water pipes and guttering, and pressure pipes capable of working at hydraulic pressures up to 200 p.s.i. These products usually contain 10–16 per cent of asbestos fibres, the main function of which is to act as fibrous reinforcement in the cement. The bulk of asbestos fibre going into the products is of the chrysotile type, but up to 40 per cent of amphibole fibres may be incorporated to enhance reinforcement, dispersion of fibre and the drainage properties of the asbestos–cement mix. The most widely used of these processes is based on conventional practice for making board, in which an endless conveyor felt picks up the solid materials from an aqueous asbestos–cement slurry. The felt passes over vacuum filter boxes through which excess water drains away, leaving a thin laminate of the solids on the felt. A making roller or mandrel riding on the felt picks up the laminate, winding it on continuously until a sheet or pipe section of the desired thickness is built up. The green product is air-cured for up to 28 days, or may be cured in autoclaves in less than 24 hr, provided that silica is included in the mix of raw materials to complete the reaction. There are alternative methods of manufacture based on asbestos–cement pastes from which

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excess water is squeezed out in the forming of the product, or on dry asbestos–cement mixes which are spread out on a conveyor belt and wetted out by a water spray. Chrysotile cement pastes modified with a cellulose-based extender can be extruded to enable square sections or more complicated shapes to be formed.

Asbestos–cement products have densities in the range 1·6 to 2·0. They are suitable for exterior panelling and roofing, but are not resistant to thermal shock at temperatures in excess of 800°C; asbestos–cement products also have a relatively high thermal conductivity. Improved thermal properties can be obtained with materials at densities of 0·8 or less. These include insulating wall or ceiling boards for interior applications, containing up to 35 per cent amosite in an autoclaved calcium silicate matrix. These products are manufactured on similar machinery to that employed in the asbestos–cement industry.

Other thermal insulating materials incorporating amosite fibres include lightweight magnesia, autoclaved calcium silicate products and materials containing high proportions of fibre bonded with sodium silicate.

The longer and more valuable grades of chrysotile and blue asbestos are directed to the manufacture of asbestos textiles for inclusion in asbestos clothing, safety curtains and conveyor belting. Blue asbestos has considerable resistance to chemical attack and finds special application in filtration cloths for use in acid media, in diaphragms in electrolytic cells and in fume-exhaust dampers.

Second only to its use in building materials, asbestos has a large range of applications in conjunction with organic resins and similar matrices. Considerable quantities of chrysotile are incorporated in asphalt floorings and vinyl floor tiles, and various types of asbestos–asphalt mixes are proposed for pavings and road-surfacings.

Chrysotile asbestos is a crucial, almost irreplaceable raw material in vital automotive products. Combinations of up to 60 per cent chrysotile with phenolic resins go into the making of brake linings and clutch facings as well as heavy-duty friction materials for other purposes. The frictional properties of these materials are largely dependent on the physical and chemical characteristics of the fibre, though the composition may include small amounts of other minerals and even metals to modify the finished product.*

Amphibole fibres have a specific role in reinforced plastic materials for structural applications, since they are superior to chrysotile and glass fibres in reinforcing properties and chemical resistance. For similar reasons there are other important combinations of the amphibole fibres with resins and rubber in gaskets and jointing materials and with bitumen in lead–acid battery casings. Chrysotile fibre is widely employed in the manufacture of engine gaskets and flange jointings where the conditions are not likely to be corrosive.

It should be briefly mentioned here that refined asbestos fibre as produced at the mines for shipment elsewhere is not necessarily in a form suitable for direct use in many of its applications. Further

* Readers may be interested in *Practical Motorist*, November, 1965, p. 288.

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processing of the fibre may be required and this is usually done at the manufacturing site. This involves milling the raw fibre to increase its degree of fiberization, or in other words to reduce and split the coarser fibres to finer ones. A variety of methods are used, ranging from edge-runners and rod mills to hammer-mills and attritors. While certain mechanical principles dictate which mills make the most suitable fiberizers of the different types of asbestos, it is also true that particular techniques produce changes in texture and surface properties of specific types of asbestos fibre, and such changes are of profound technical importance.

STRUCTURAL AND CHEMICAL PROPERTIES OF ASBESTOS FIBRES

Structures

The principal minerals of the serpentine group—chrysotile, lizardite and antigorite—all have the approximate compositional formula $Mg_3(Si_2O_5)(OH)_4$. Warren and Hering (1941) were the first to investigate the structure, which is essentially a layered type analogous to that of the clay mineral, kaolin[1–3], based on a pseudo-hexagonal network of SiO_4 tetrahedra forming a sheet in which all the tetrahedra

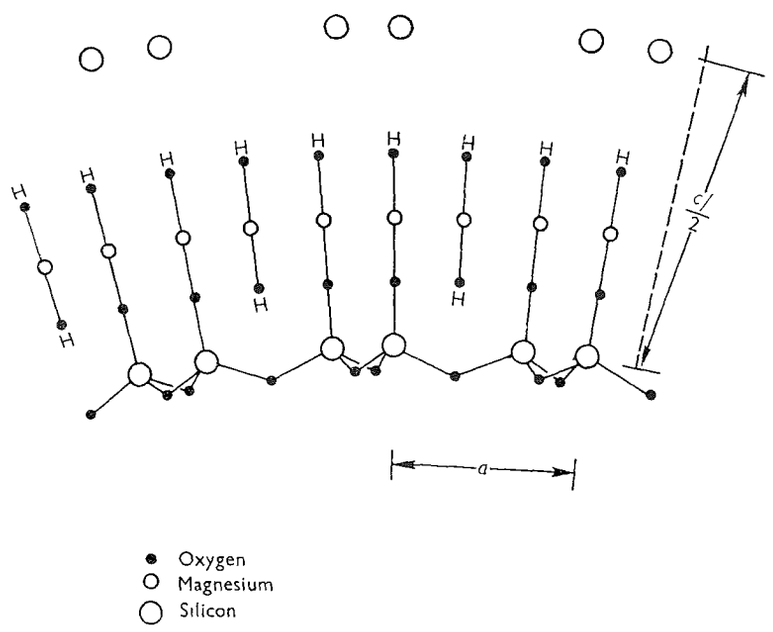

Fig. 3*a*. Schematic structure of clino-chrysotile on (010). Sheets are continuous in direction of curvature and normal to plane of section. Fibre axis is also normal to plane of section.

point one way. A brucite layer, $Mg(OH)_2$, is joined to the SiO_4 network in such a way that on one side two out of every three hydroxyls are replaced by oxygens at the apices of the tetrahedra. A cross-section of the layer structure is shown schematically in Fig. 3*a* in which only

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the essential bonds appear. The macromolecule consists of parallel sheets of the brucite–silica layers. Consideration of the dimensions of the two layers taken separately shows that they cannot be joined together without mismatching, the corresponding parameters being slightly larger for the brucite layer than for silica sheets. In lizardite such mismatching is accommodated with considerable limitation on crystal growth, resulting in an extremely fine grained, but platy form. In antigorite and chrysotile the layers fit together by a bending of the brucite layers over the silica layers, along the *b* axis, in such a way as to form a curvilinear composite layer. Antigorite, which has a brittle lath-like form, does not possess complete curvature of structure because the composite layers reverse polarity at regular intervals, thus giving rise to a series of shallow corrugations.[3,4] But with chrysotile the curvature of the layers is complete, and Whittaker[2,5] has described cylindrical lattices involving closed concentric cylinders, spirals and sometimes a helical arrangement.

Evidence for the cylindrical structure of chrysotile has been obtained from X-ray and electron-diffraction studies, and from numerous electron micrographs. Detailed study of the latter certainly indicates a tubular structure, and often shows tubes projecting from the ends of larger tubes (*see* Plate IV*a*). Under these conditions of observation, the most frequently occurring fibril has an inner diameter of 110 Å and an outer diameter of 260 Å. Pundsack[6] in 1955 pointed out that the tubular structure was not compatible with experimentally determined density values for sealed solid blocks of the fibre, and suggested that fundamental fibres existed as distorted ribbon-like structures with a limited curvature. There was considerable controversy over this for some time and various theories were put forward suggesting that the tubes themselves were not hollow but filled with fragmented cylinders[7]; that the ends of the fibres were plugged with water thus preventing entry of gases which in absorptiometric work would have solved the problem[8]; and that the tubes were filled with amorphous material[9]. Maser, Rice and Klug[10] however, in 1960, obtained what appears to be undisputed evidence from electron micrographs of end-on cross-sections of chrysotile fibres which clearly show concentric and spiral structures (Plate IV*b*). It now seems certain that these structures and the voids between them are filled with an amorphous material, probably with the composition of a magnesium silicate gel. The proposition of a gel has been suggested by the appearance in electron micrographs of cellular forms along the inner axis of the chrysotile fibres, such cells being the result of partial dehydration of the gel. Cleavage of the macro-fibres into finer forms must obviously take place along the longitudinal weaknesses represented by the in-filled voids between the fibrils.

One other aspect of the structure of chrysotile concerns its crystallographic classification. Whittaker and Zussman[11] found three varieties, ortho-chrysotile, clino-chrysotile and para-chrysotile. The ortho and clino varieties have similar cell parameters, with the exception of the differences in β (*see* Table II, cell data for asbestos fibres). The structure of para-chrysotile is analogous to that of ortho-chrysotile except

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that the 9·2 Å axis, instead of the normal 5·3 Å axis, becomes the fibre axis. Clino-chrysotile is the most abundant of the three varieties, but the range of ortho-chrysotile contents of fibre samples varies markedly from source to source. The maximum values observed by Whittaker and Zussman are for Thetford 7 per cent, Shabani 35 per cent and Cuddapah (India) 81 per cent.

TABLE II

CELL PARAMETERS OF ASBESTOS MINERALS

Type of fibre	*a* (Å)	*b* (Å)	*c* (Å)	*β*
1. Chrysotile, clino- ..	5·34	9·25	14·65	93° 16′
2. Chrysotile, ortho- ..	5·34	9·2	14·63	90°
3. Anthophyllite ..	18·5–18·6	17·7–18·1	5·27–5·32	90°
4. Anthophyllite ..	18·50	17·96	5·28	90°
5. Amosite	9·89	18·26	5·30	110°
6. Amosite	9·56	18·30	5·34	101° 50′
7. Crocidolite	9·89	17·95	5·31	107° 30′
8. Crocidolite	9·6	18·3	5·3	110°
9. Crocidolite	9·8	17·85	5·3	103° 50′
10. Tremolite	9·78	17·8	5·26	106°
11. Actinolite	9·85	18·1	5·3	104° 50′

1, 2. Thetford, Shabani, Transvaal etc. Whittaker, 1956.[11]
3, 11. Standard data from Deer, Howie and Zussman.[3]
4. Finland. Freeman, 1962.[12]
5. Transvaal. Garrod, Rann, 1952.[13]
6. Penge, Transvaal. Hodgson, Freeman, Taylor, 1965.[14]
7. Bolivia. Whittaker, 1949.[15]
8. West Australia. Garrod, Rann, 1952.[13]
9. Koegas, Cape Province. Hodgson, Freeman, Taylor, 1965.[16]
10. St. Gotthard, Switzerland. Warren, 1929.[17]

Note: Cell parameters for fibrous tremolite and actinolite have not been recorded in the literature. The specimen 10 above was a crystal form.

No definite correlation of texture with structure has been recorded, but while on the one hand brittleness has been associated with structures having a high degree of three-dimensional order, it is also possible that the proportion of the ortho and clino varieties at any one source may be important. For example, the Shabani chrysotile has a recognizably silkier and finer texture than the Thetford material, and the proportion of ortho-chrysotile in the two specimens may have some bearing on this.

The most significant fact arising out of the interpretation of the structure of chrysotile is that the surface chemistry of chrysotile is clearly defined. Since the brucite layer forms the outer layer of the curved composite structure, the external surfaces of all chrysotile fibrils, assuming the cylindrical form to be complete, are composed exclusively of hydroxyl ions. Chrysotile thus possesses strongly basic properties, exerts a relatively high surface potential in water and has marked hydrophilic tendencies.

The first structural analysis of an amphibole was made by Warren[17] in 1929 on crystal specimens of the St Gotthard tremolite. He determined the structure which serves as a model for all the amphiboles and

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which is shown schematically as basal section in Fig. 3*b*. Essentially this structure consists of two chains or ribbons based on Si_4O_{11} units, separated by a band of cations, seven cations forming the basal unit. Two hydroxyl groups are attached at the central cation of each unit cell

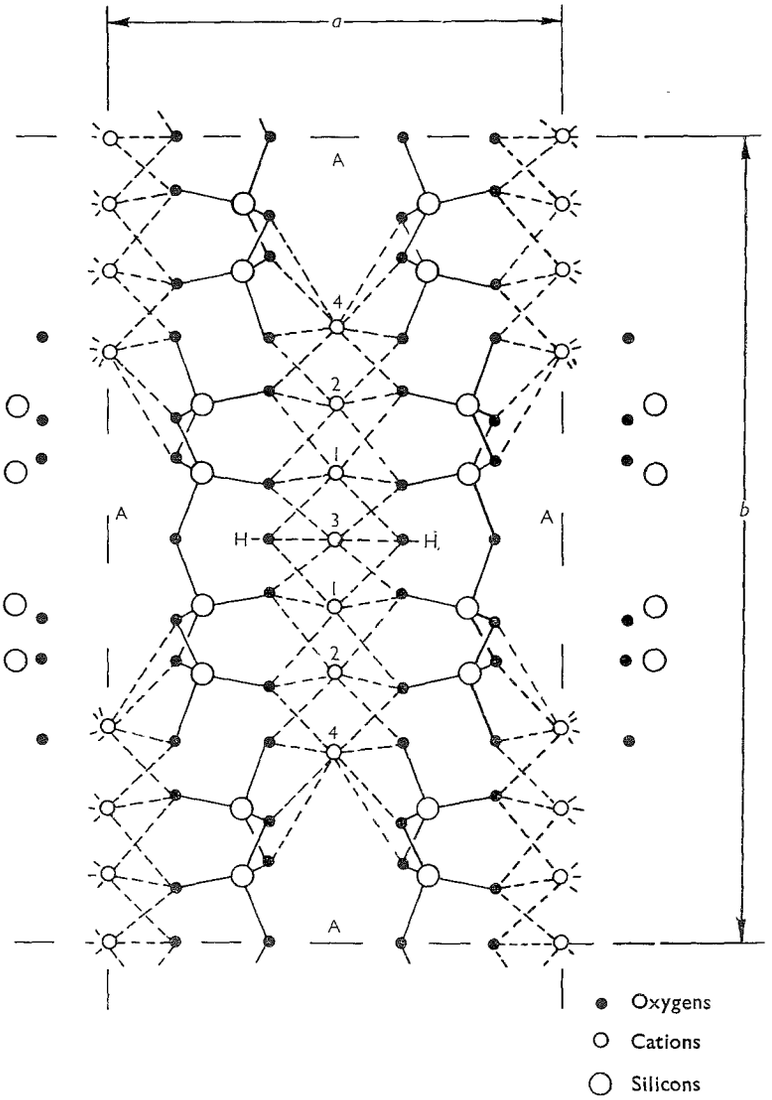

FIG. 3*b*. Schematic amphibole structure on (001). The unit cell is based on 48 oxygens and the fibre axis is normal to the plane of the paper.

and are contained wholly within the structure. In the *b* direction the basal units form a step-wise continuum, while in the *a* direction they are separated by a gap, known as the A site. These dispositions determine the perfect (210) cleavage of the amphibole structure, which can be

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seen in basal sections of amphibole crystals under the microscope and which is assumed to apply equally to fibrous varieties. The extended plan of the basal section in Fig. 4 shows how this comes about. Of the five amphiboles which concern us here, only anthophyllite has an orthorhombic cell; the others have a monoclinic cell, in which *c*, the fibre axis, is inclined to *a* (Table II). This inclination can occasionally be discerned in very high magnification electron micrographs of amosite and crocidolite fibres, in which striations inclined to the fibre wall appear.

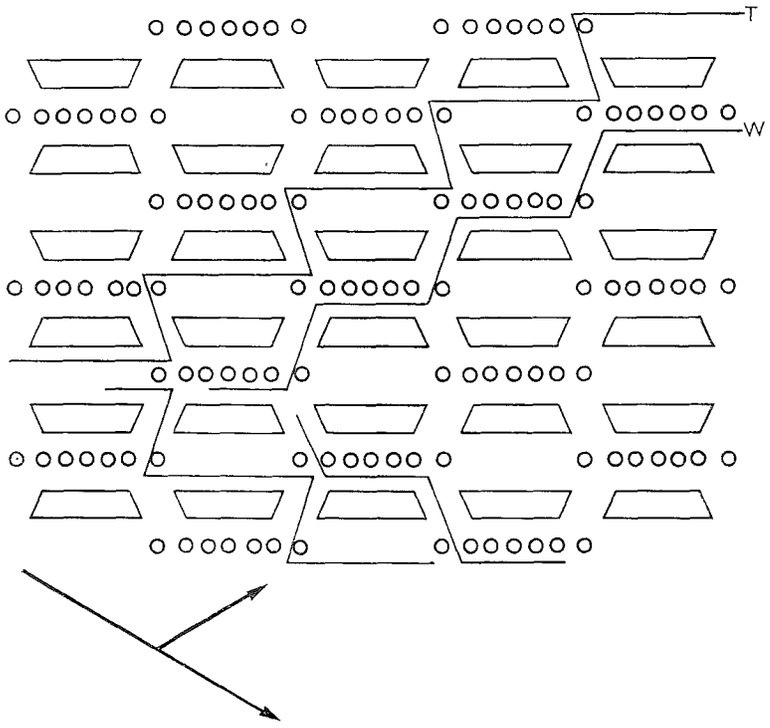

Fig. 4. Extended plan of basal section of amphibole structure showing possible cleavage lines: W as suggested by Warren[12], T by Taylor.[14] Both account for observed cleavage directions but T breaks many fewer cation–oxygen bonds.

Plate IV, *d* and *e*, shows typical electron micrographs of crocidolite fibre. The end-on views are by no means as definitive as those of chrysotile, but their form has some relationship with the basal sections of the amphibole structure.

Referring to Fig. 1, the dominant cations in amphibole asbestos comprise Mg^{2+}, Fe^{2+}, Fe^{3+}, Na^{+} and Ca^{2+}, but substitution of minor amounts of Mg^{2+}, Al^{3+}, Ti^{4+}, K^{+} and Li^{+} may occur. The extensive amphibole group of minerals contains 27 type-species in three groups (the anthophyllite-cummingtonite series, the calcic amphiboles and the soda amphiboles). Obviously considerable variations of ionic substitution are possible, and Whittaker[18] has shown that this follows a systematic course. The following essential rules, due to Whittaker[18]

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and Taylor[19], are of considerable help in clarifying the order of the cation sites, in so far as is necessary here.

1. The fundamental formula is $X_{2-3}Y_5Z_8O_{22}(OH,F)_2$ and the cation sites are labelled in order (*see* Fig. 3*b*).

   $$M_4\ M_2\ M_1\ M_3\ M_1\ M_2\ M_4$$

   their size decreasing from M_4 through to M_3.
2. X sites (M_4): any one- or two-valent cation with radius from Mg^{2+} (0·78 Å) to K^+ (1·33 Å); preferably occupied by the largest cations (Na^+, K^+, Ca^{2+}).
3. Y sites ($2M_2$, $2M_1$ and M_3): any two- or three-valent cation of radius from Al^{3+} (0·57 Å) to Mn^{2+} (0·91 Å).
4. Z sites: mainly Si^{4+}, but can be replaced by 25 per cent of three-valent ions of small radius (Fe^{3+}, Al^{3+}).
5. Orthorhombic amphiboles (anthophyllite): all X and Y sites are occupied by Mg^{2+}, but up to $3Fe^{2+}$ can go into the internal positions ($2M_1 + M_3$) without disturbing the edgewise packing.
6. Monoclinic amphiboles: transition from the orthorhombic to the clino-form occurs with $4Fe^{2+}$, which being the larger cations occupy the $2M_4 + 2M_2$ sites with Mg^{2+} in the internal positions. Fe^{2+} occupies M_1 sites in preference to Mg^{2+} as in amosite. When a large cation such as Na^+ occupies M_4, then a correspondingly smaller cation, Fe^{3+}, must occupy M_2, the order of decreasing size being taken up again with M_1 (Fe^{2+}) and M_3 (Mg^{2+}) as in crocidolite. Similarly tremolite has Ca^{2+} at M_4 and Mg^{2+} at the remaining sites; actinolite has Ca^{2+} at M_4, Fe^{2+} at M_2 and Mg^{2+} at M_1 and M_3.
7. There is no crystallographic evidence for occupancy of A sites, but from analytical evidence it seems certain that any cations in excess of seven must be sited there. The A sites are partially occupied in any event by large cations at M_4 sites.

Two points arise from these structural considerations. Firstly, while all the cations in the Y sites are 6-coordinated, the two cations at X (M_4) are 8-coordinated, mainly to the next adjacent unit cells (*see* Fig. 3*b*). Individual bonds are therefore weak, and it is not difficult to see that cleavages would pass through these rather than along cation bands as originally postulated by Warren (*see* Fig. 4). Secondly, the order of cation sites in crocidolite is such that Fe^{3+} and Fe^{2+} come into juxtaposition. It is strongly believed that the distinctive blue colour of crocidolite is due to resonance, $Fe^{3+} \rightleftharpoons Fe^{2+}$, between the M_2 and M_3 sites. Characteristically, the Koegas crocidolite is intensely dark blue and contains a minimum of Mg^{2+} in the M_3 sites only, while paler blue crocidolites, such as those from the Transvaal and Bolivia, are known to contain sufficient Mg^{2+} such that a proportion of the M_1 sites must be so occupied, thus reducing the amount of resonance.

Finally, on structure it is almost impossible to visualize the chrysotile and amphibole frameworks without the aid of three-dimensional crystal

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models in colour. However, these structures can be simplified to tetrahedra and octahedra only, and models on this scheme portraying the main differences between the two types are shown in Plate IV, *c* and *f*.

Composition

Although chrysotile occurs in a number of countries, many of the published analyses[3,20,21] of the mineral refer to the source at Thetford, Canada. With regard to analyses of amphibole asbestos of South Africa, many of which were gathered together by du Toit[22] in a 1945 paper, it is known that before the 1950s the South African amosites and crocidolites were mined from partially weathered zones of strata. Not until 1961 were analyses available[23] of examples of these kinds of asbestos that could be considered fresh and unaltered by natural weathering.

TABLE III

COMPOSITIONS AND CELL-CONTENTS FOR SOME TYPICAL CHRYSOTILES

(Analyst: D. G. Hiscock, Cape Asbestos Fibres Ltd)

	Thetford, King Beaver Mine	British Columbia, Cassiar	Russia, Asbest	Rhodesia, Shabani	Swaziland, Havelock Mine
SiO_2	38·75	40·75	39·00	39·70	39·93
FeO	2·03	0·28	1·53	0·70	0·45
Fe_2O_3 ..	1·59	0·44	0·54	0·27	0·10
Al_2O_3 ..	3·09	3·37	4·66	3·17	3·92
CaO	0·89	0·35	2·03	1·08	1·02
MgO	39·78	41·28	38·22	40·30	40·25
MnO	0·08	0·03	0·11	0·26	0·05
Na_2O ..	0·10	0·07	0·07	0·04	0·09
K_2O	0·18	0·04	0·07	0·05	0·09
H_2O^+	12·22	12·86	11·37	12·17	12·36
H_2O^-	0·60	0·78	0·77	0·64	0·92
CO_2	0·48	0·44	1·83	2·13	1·04
TOTAL ..	99·63	100·37	100·20	100·51	100·24
Mg	5·79	5·70	5·60	5·68	5·70
Fe^{2+}, Mn ..	0·12	0·01	0·12	0·07	0·04
Na, K ..	0·04	0·02	0·02	0·02	0·02
Al	0·05	0·23	0·26	0·23	0·28
TOTAL ..	6·00	5·96	6·00	6·00	6·00
Si	3·80	3·85	3·86	3·88	3·84
Al	0·30	0·15	0·28	0·13	0·31
TOTAL ..	4·1	4·00	4·14	4·01	4·15
O	10·07	9·91	10·49	8·65	10·53
$(OH)_6$ ..	5·92	7·07	5·93	6·49	6·66
$(OH)_2$ ..	2·01	1·02	1·58	1·43	0·80

Table III contains some new analyses of typical chrysotiles from various sources together with their cell contents, and Table IV contains similar data from the more recent analyses of amphibole fibres. The hydroxyl ions contained in the cell have been determined from thermal

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gravimetric analysis data, an important analytical departure, which is discussed further in a later section.

Regardless of source there is a marked uniformity among the compositions of chrysotiles, and one has to look hard for differences which might explain variations in other chemical or physical properties. The analyses disclose the presence of two impurities, CO_2 being linked with calcium–magnesium carbonates, while FeO and Fe_2O_3 arise from a magnetite impurity. The magnetite impurity in the Cassiar and Shabani chrysotiles is low and as a result these materials are particularly valued in certain electrical applications. These impurities are discounted in the breakdown of cell contents.

Referring back to the structure of chrysotile, of the eight OH groups per unit cell, six are exposed externally and two are associated with the internal oxygen layer. From the content of water determined by thermal gravimetric methods, it can be shown that the combined water

TABLE IV

COMPOSITIONS AND CELL-CONTENTS OF SOME TYPICAL AMPHIBOLE ASBESTOS VARIETIES
(Analysts: D. G. Hiscock and staff of Cape Asbestos Fibres Ltd)

	Koegas, Cape Prov.	Kuruman, Cape Prov.	Pomfret, Cape Prov.	Malips-drift, Transvaal	Cocha-bamba, Bolivia	Hammers-ley Range, W. Australia
SiO_2 ..	50·90	50·70	52·00	59·41	55·65	52·85
FeO ..	20·50	17·50	17·65	15·11	3·84	14·94
Fe_2O_3 ..	16·85	18·30	16·05	14·03	13·01	18·55
Al_2O_3 ..	nil	0·70	nil	nil	4·00	0·18
CaO ..	1·45	1·30	1·20	0·49	1·45	1·07
MgO ..	1·06	3·05	4·28	3·53	13·09	4·64
MnO ..	0·05	0·06	tr.	tr.	tr.	tr.
Na_2O ..	6·20	5·30	6·21	4·63	6·91	5·97
K_2O ..	0·20	tr.	0·06	0·28	0·39	0·05
H_2O^+ ..	2·37	2·53	2·43	2·07	1·78	2·77
H_2O^- ..	0·22	0·29	0·26	0·14	tr.	0·22
CO_2 ..	0·20	0·45	0·09	0·09	tr.	0·23
TOTAL ..	100·1	100·18	100·23	99·78	100·35	101·47
Na, K ..	1·92	1·59	1·86			1·91
Ca, Mn ..	0·21	0·13	0·12			0·13
TOTAL $2M_4$	2·13	1·72	1·98			2·04
Fe^{3+} ..	1·98	2·13	1·85			2·00
TOTAL $2M_2$	1·98	2·13	1·85			2·00
Fe^{2+} ..	2·68	2·27	2·26			1·90
Mg.. ..	0·25	0·69	0·93			1·06
TOTAL $2M_1 + M_3$	2·95	2·96	3·19			2·96
Si, Al ..	7·97	8·00	7·96			7·98
22(O) ..	22·05	22·03	22·06			21·82
2(OH) ..	1·95	1·97	1·94			2·18

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TABLE IV (*continued*)

	Amosite Penge, Transvaal	Amosite Welte-vreden, Transvaal	Antho-phyllite Paakkila, Finland	Tremolite, Pakistan	Prieskaite Koegas, Cape Prov.
SiO_2	49·70	51·30	57·20	55·10	53·80
FeO	39·70	35·50	10·12	2·00	25·30
Fe_2O_3	0·03	0·90	0·13	0·32	1·90
Al_2O_3	0·40	nil	—	1·14	1·20
CaO	1·04	0·95	1·02	11·45	10·20
MgO	6·44	6·90	29·21	25·65	4·30
MnO	0·22	1·76	—	0·10	0·40
Na_2O	0·09	0·05	—	0·14	0·10
K_2O	0·63	0·51	—	0·29	0·40
H_2O^+	1·83	2·31	2·18	3·52	2·60
H_2O^-	0·09	0·05	0·28	0·16	nil
CO_2	0·09	0·25	—	0·06	0·20
TOTAL	100·53	100·54	100·48	99·93	100·40
Fe^{2+}	1·78	1·28	—	0·23	—
Ca, Mn	0·23	0·33	0·16	1·71	1·71
Mg	—	—	2·08	0·31	—
Na, K	0·07	0·12	—	0·11	0·13
TOTAL $2M_4$ ..	2·08	1·73	2·24	2·36	1·84
Fe^{2+} (Fe^{3+}, Al) ..	1·39	1·35	—	—	1·72
Mg	0·61	0·65	2·00	2·00	—
TOTAL $2M_2$ ..	2·00	2·00	2·00	2·00	1·72
Fe^{2+}	2·09	2·03	1·15	—	2·00
Mg	0·91	0·97	1·85	3·00	1·00
TOTAL $2M_1 + M_3$	3·00	3·00	3·00	3·00	3·00
Si, Al, Fe^{3+} ..	7·99	8·17	7·79	8·00	8·26
22(O)	21·98	21·96	22·00	22·05	22·46
2(OH)	2·02	2·04	2·00	1·95	1·54
H·	—	—	0·68	—	0·45

in chrysotile is evolved in two stages which, for specimens of the kind of mineral obtained from Thetford, can be closely equated to 2OH and 6OH. (This is discussed more fully on p. 39.) For chrysotiles from other sources this differentiation is by no means so clear, as the data in Fig. 5 indicate. Not only may the total number of hydroxyl groups be less than eight, but also those falling into the 'exposed' category may be up to or over seven. This technique of analysis is adequate enough to distinguish between chrysotiles from large regional sources (*e.g.* Thetford, Transvaal or Urals) but in addition there are obvious implications here of structural, chemical, physico-chemical and possibly textural importance.

Given a sufficiently wide range of analyses it is not difficult to distinguish between the various kinds of amphibole asbestos. For example, among the crocidolites the most useful marker elements are Na and Mg (Table IV). The mineral from Koegas has about 6·20 per cent Na_2O and 1 per cent MgO, while crocidolite from the Kuruman Hills

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some 150 miles north of Koegas has 5 to 5·5 per cent Na_2O and up to 3 per cent MgO. Australian crocidolite has a lower total iron content than the Cape Province specimens, although in other respects it is similar to the Pomfret, C.P., variety. The Malipsdrift and Cochabamba crocidolites are problem minerals, as their analyses immediately indicate. Other methods of investigation by differential thermal analysis and by microscopic examination suggest strongly that these are mixed amphiboles.[24] Apart from containing a fibrous silica intergrowth (hence the high SiO_2 content by analysis) the Malipsdrift crocidolite is in fact a mixture of crocidolite and amosite. The Bolivian material appears to be a mixture of crocidolite and anthophyllite, though it is also referred to as a magnesio-riebeckite, having close similarities to a crocidolite from Lusaka, N. Rhodesia.[25]

Amosites have a high ferrous-iron content, approaching 40 per cent FeO, but within their sole environment there is a variation to types with lower FeO contents, this being associated with diminishing harshness. A variety of amosite known as montasite from Pietersburg has 31 per cent FeO and is described as a silky fibre.[22] Anthophyllites have high magnesium contents (30–35 per cent MgO) associated with 5–10 per cent FeO, and tremolites a similar MgO content, with 10–15 per cent CaO. The 'prieskaite' discovered by Cilliers in a horizon in the Koegas mine[26] may well be described as a ferro-actinolite, having the Ca–Mg–Fe make-up necessary for actinolite, but with excess iron. It is one of the few known actinolites that is truly fibrous.

Chemical analysis will give some indication of the degree of natural weathering to which an amphibole asbestos has been exposed, a question which particularly applies to amosite and crocidolite. Amosite should contain ferrous iron only, and ground surface weathering or sub-surface leaching shows up in the increasing amounts of ferric iron on analysis. Fresh crocidolite has a distinct excess of FeO over Fe_2O_3 in analysis, and otherwise, when FeO is equal to or less than the Fe_2O_3 content, the crocidolite cannot be considered to be fresh.

The hydroxyl components of the amphiboles have special significance in the deduction of the cell contents. Thermal gravimetric and dehydration studies (*see* p. 36) show that only part of the total H_2O liberated at 105°C by the amphiboles is correctly defined as chemically combined water which can be allotted to the two hydroxyl sites.

The cell contents given in Table IV have been compiled from these data. The values are shown here in a simplified form, in which cations have been allocated to their positions according to literal interpretation of the substitution rules. In fact there must be some overlapping, and in detailed breakdown small amounts of appropriate ions must be moved to fill up the inner cation sites. Excesses of large ions in M_4 go into the A sites. Anthophyllites and actinolites usually contain more combined water than can be allocated to the two hydroxyl sites, a problem which has been the subject of several mineralogical papers.[27–29] The current view is that extra hydrogen as hydroxyl may replace some of the oxygen in the Si_4O_{11} bands. In the cell analysis for the anthophyllite and the actinolite, extra hydrogen is shown as H·.

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Chemical reactions

All forms of asbestos progressively break down to simpler components, such as pyroxenes and silica, when heated to temperatures in the range 600–1000°C. Reactions of asbestos, as such, with other materials at high temperature do not therefore exist. In any reactions involving high-melting-point metals or fused salts, such as the sodium carbonate fusion in the preliminary step of chemical analysis, it can be assumed that primary breakdown of the mineral at the temperature of fusion will be followed by reaction of the products with the fusion material. At lower temperatures asbestos fibres appear to be resistant to attack by molten materials. Attempts have been made to incorporate these fibres in low-melting-point metals such as tin, zinc and lead, and there is no apparent reaction with the metal. It is however suspected that molten sodium and potassium will attack asbestos fibres through reactions involving both dehydration and extraction of silica.

In connexion with the above, asbestos fibres as such do not have melting points. It is the products of decomposition which melt. In general, if these contain iron pyroxenes, fusion occurs between 1000 and 1100°C, such being typical of the high-iron asbestos minerals, amosite and crocidolite. The high-magnesium varieties, such as chrysotile and anthophyllite, decompose to give magnesium-pyroxenes in the products which melt about 1450°C.

The reactivity of the asbestos minerals towards acids and alkalis is fairly well known and has been summarized by Badollet.[30] Strong acids rapidly decompose chrysotile with removal of all its MgO and H_2O content, amounting to about 58 per cent by weight, but amphibole fibres show various degrees of resistance to reaction with acids. All varieties of asbestos will resist prolonged attack by strong alkalis, such as 5·0N NaOH, at least up to 100°C.

The relative weight losses of anthophyllite, crocidolite and chrysotile after reflux in acid and alkali solutions have been reported in connexion with the inclusion of these fibres in chemically resistant reinforced plastic materials.[31] Several important points arise in elaboration of investigations such as these.[32] Fig. 5 shows some typical acid-resistance curves for asbestos fibres refluxed in 4·0N HCl for periods up to 8 hr. These differentiate clearly between chrysotile and the amphibole fibres, though the range of reactivity of the latter fibres to hydrochloric acid is wide. Moreover different types and strengths of acid produce varied results. Hydrofluoric acid will completely decompose all asbestos fibres; sulphuric and nitric acids both have much the same effects on amosite and crocidolite regardless of concentration above 1·0N, but phosphoric and hydrochloric acids at 4–5N decompose these two fibres to a far greater degree than the same acids at 1·0N. Chrysotile possesses such little resistance to acids that it may be decomposed by strong acetic acid.

Referring to Fig. 5, the early stages of acid attack on the amphibole fibres indicate rapid reaction, due partly to the removal of impurities such as alkali and iron carbonates, but mainly to the decomposition of extremely finely divided fibres and the stripping of imperfect surfaces on coarser fibres. In the later stages of the reactions, the rate of weight

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loss becomes steady, and is then considered indicative of the true acid-resistance of the fibre. It should be added that the rate of decomposition is also a direct function of the surface area of the asbestos fibres, and all the curves of Fig. 5 have been produced by fibres of similar surface area to make their comparison valid.

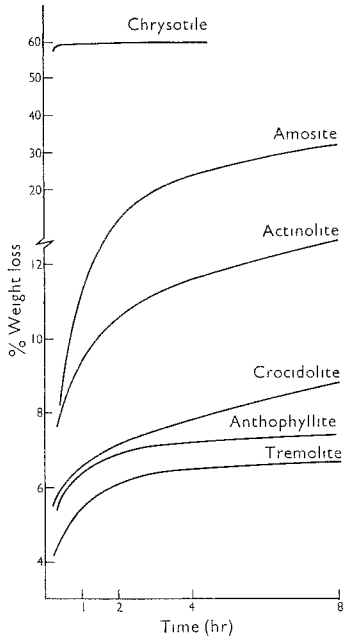

FIG. 5. Typical acid-resistance curves for asbestos fibres refluxed in 4·0N HCl.

There are obvious structural differences between the two major groups of asbestos fibres, which account for the rapid decomposition of chrysotile by acids, and the relatively slow breakdown of the amphiboles. When chrysotile reacts with strong acids the whole of its (MgOH) layer is stripped, leaving a silica skeleton. However there does not appear to be any immediate reason why acid-resistance of the amphiboles themselves varies so markedly. By examining the solutions from acid extractions of amphibole fibres it is possible to obtain some further information about the relative rates of cation extraction. Table V shows some typical results which can be correlated with the curves of Fig. 5.

Two possible mechanisms may account for the decomposition of amphiboles in strong acids. Firstly, cations may be continuously extracted from the nucleus leaving behind a silica skeleton that has the elements of the original structure. Secondly the whole nucleus may break down to cations and hydrated silica, which may coat unattacked fibrils and thereby make it more difficult for the acid to reach fresh surfaces. The information in Table V indicates that all constituent cations are continuously extracted from amosite, crocidolite and

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prieskaite, with the exception that little Na^+ is removed from crocidolite. Some of the Ca ion is removed from tremolite in the early stages only; while extraction of Mg^{2+} occurs in the later stages. In anthophyllite, there is little change in the cations removed between $\frac{1}{2}$ and 8 hr. Close comparison of the results suggests that certain cations are selectively extracted at a somewhat greater rate than others, an observation which is not entirely compatible with the breakdown of the whole nucleus.

TABLE V

CATIONS EXTRACTED FROM AMPHIBOLE FIBRES BY HYDROCHLORIC ACID AFTER $\frac{1}{2}$ AND 8 HR REFLUXES

Fibre	Cation	Cations extracted by reflux with 4·0N HCl	
		after $\frac{1}{2}$ hr	after 8 hr
Anthophyllite	Mg^{2+}	0·46	0·46
	Fe^{2+}	0·15	0·18
Tremolite	Ca^{2+}	0·38	0·38
	Mg^{2+}	0·02	0·41
Prieskaite	Ca^{2+}	0·25	0·40
(Actinolite)	Fe^{2+}	0·55	0·92
	Mg^{2+}	0·20	0·32
Crocidolite	Na^+	tr.	tr.
	Fe^{3+}	0·32	0·55
	Fe^{2+}	0·33	0·58
	Mg^{2+}	0·01	0·10
Amosite	Fe^{3+}	1·48	2·81
	Mg^{2+}	0·36	1·00

The rate of decomposition of amphibole fibres by a strong acid clearly depends on the disposition of cations in the unit-cell structure, and may also depend on the sequence of these cations. With refinements involving the continuous record of the rate of extraction of each type of cation, including those present in trace amounts, it may be possible to throw some further light on the chemistry of these materials.

Such is the pronounced basicity of chrysotile that suspensions of the fibre can be titrated against 0·1N hydrochloric acid at 100°C. According to Pundsack[33] the complete reaction proceeds in three distinct steps: (i) the reaction of some surface hydroxyl groups corresponding to the decomposition of less than 5 per cent of the fibre; the observed reaction here was more likely due to the removal of the brucite, $Mg(OH)_2$, impurity commonly found in chrysotile; (ii) reaction of structural hydroxyl groups amounting to two-thirds of the total present, that is, stripping of the surface layer of (Mg–OH); (iii) completion of the reaction to form hydrated silica. The last step corresponds to reaction of hydroxyl groups associated with the silica layer.

The total reaction differs slightly from the reaction of chrysotile with strong acids. The solubility of 58 per cent of the chrysotile in such circumstances corresponds to removal of all cations and all hydroxyls in the composition leaving an unhydrated silica skeleton.

Chrysotile is vulnerable to alternating acid and alkaline conditions.[34] Dilute (0·1N) hydrochloric acid reacts with chrysotile to give orthosilicic

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acid and magnesium ions in solution. But while sodium hydroxide does not attack chrysotile, it will react with a chrysotile washed in acid to form a sodium silicate, though little magnesium passes into solution.

Suspensions of chrysotile in water possess alkalinity in the pH range 10–11. Part of this alkalinity can of course be attributed to the solution of brucite impurities, but the continuous extraction of the chrysotile in hot water shows that the fibre itself is decomposed.[34] The extracts contain orthosilicic acid and magnesium, the latter accumulating with time (approx. 1 mg per 100 ml extract after 5 days). The breakdown of the chrysotile appears to follow a course in which Mg ions are leached out, leaving fragments of the Si–O lattice. These fragments are probably of a colloidal form, since they can be hydrolysed to orthosilicic acid by heating the extract after the fibre has been removed.

In connexion with its inclusion in asbestos–cement and in autoclaved calcium silicate products, Ball and Taylor have investigated the hydrothermal reactions of chrysotile with such materials as magnesium oxide, silica, lime, alumina, ferric oxide, tricalcium silicate and β-dicalcium silicate.[35] All these occur in the chemical and phase compositions of cement. The reactions between chrysotile and MgO, SiO_2, Al_2O_3 or Fe_2O_3 gave products such as forsterite (Mg_2SiO_4), talc ($Mg_3Si_4O_{12}H_2$) and brucite, all with a definite crystallographic orientation relative to the chrysotile. Reactions of this type come into the category termed topotactic, and occur where there is a three-dimensional similarity between the crystal structures of the starting material and the product. Reactions between chrysotile and Al_2O_3 or Fe_2O_3 gave, in addition, a mica-like product with a high thermal stability. In other reactions, products containing calcium, such as $CaMgSiO_4$ (monticellite), were unorientated.

The hydrothermal conditions used in these investigations require temperatures of 300–570°C, pressures between 80 and 330 kg/cm² and times up to 84 days. These considerably exceed the autoclaving temperatures and pressures of industrial practice where 200°C, 10–12 kg/cm² and times of 24 hr are reckoned as upper practical and economic limits. Nevertheless the reactions may occur at these lower temperatures and pressures, though to a much smaller extent. They thus have a bearing on the type of bond that may be formed between chrysotile and cement and associated compounds. There is no available evidence that amphibole fibres take part in similar reactions, at least in normal manufacturing processes, but at the same time investigations at higher temperatures and pressures have not been attempted. It is believed that the amphiboles, having an inherently better chemical stability than chrysotile, will only react to a very limited extent.

Synthesis of the asbestos minerals

It is relevant to this section that having described the structure, composition and stability of asbestos, note should be taken of the many attempts that have been made to synthesize it. Perhaps the earlier work in this subject during the 1920s and 1930s was of academic interest only, but more recently the purpose of synthesis has been sharpened by

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research in the allied field of metal whiskers. This research has demonstrated that metal-whisker crystals of a strength similar to that predicted by theory can be made. It is supposed that their phenomenal strength arises from their perfection in surface and structural details, and similar materials are being sought among the fibrous silicates in an attempt to improve on the naturally occurring product.

Chrysotile has been synthesized hydrothermally from silica gel and a magnesium salt solution[36], from silica gel and magnesium hydroxide solution[37], from sodium silicate and magnesium carbonate[38] and as a result of fundamental studies on the MgO–SiO_2–H_2O system[39], to quote a few earlier attempts. The fibres produced were generally in the form of matted fibrils, about 1 μ in length and recognizable only under the electron microscope. More recently, following on further studies of the MgO–SiO_2–H_2O system, Yang[40] has synthesized chrysotile, mainly of the clino-variety, in bundles of 100 μ lengths, with individual fibres 15–20 μ in length. The synthesis required a mixture of MgO and a bulky silicic acid in a molecular ratio of 1·5, and hydrothermal conditions of 300–350°C, 85–130 kg/cm^2 maintained over 5–10 days. The pH of the system was maintained at 10·3–10·7 by means of Na_2CO_3, and 1–2 per cent of F^- as NH_4F was added as a mineralizer. The synthetic fibres had all the characteristics of the naturally occurring mineral, despite their diminutive size.

The synthesis of minerals of the amphibole group has been done by fusion of suitable batch compositions in which the OH ion has been substituted by fluorine.[41–43] The fusion technique has evolved as a result of studies into the formation of amphibole crystals in igneous magma. Such fluor-amphiboles, crystallized from melts, form as crystals, needles and fibres all of a microscopic size. Apart from the necessity of substituting F for OH, these syntheses have also been limited to the production of soda-amphiboles of the riebeckite-crocidolite and soda-tremolite varieties. Saito[43] found that by crystallizing a mass of fluor-amphibole from a suitable alkaline melt, and then subjecting it to hydrothermal treatment in strong NaOH or Na_2CO_3 solution at 350°C for 8–16 hr, he could produce fine needles of a fluor-riebeckite up to 15 mm long and 15 μ thick. This appears to be the closest attempt to form an asbestiform amphibole. Probably the hydroxyl ion is an essential factor in the formation of amphibole asbestos, and its synthesis may require a combination of hydrothermal and fusion techniques under great pressure, or alternatively the hydrothermal treatment of mixed metal silicate gels, again under considerable pressure.

It is possible that the synthesis of chrysotile may at some time be turned to commercial application, particularly if the demand for chrysotile fibre continues to increase at its present rate. This does not seem to be so likely to happen with amphibole fibres as the synthesis particularly is so much more difficult. On the other hand, as a source of new materials, routes via synthetic amphiboles have excited some interest. One possibility lies in the modification of the properties of natural amphiboles by the substitution of other cations and the substitution of fluorine for hydroxyl groups.

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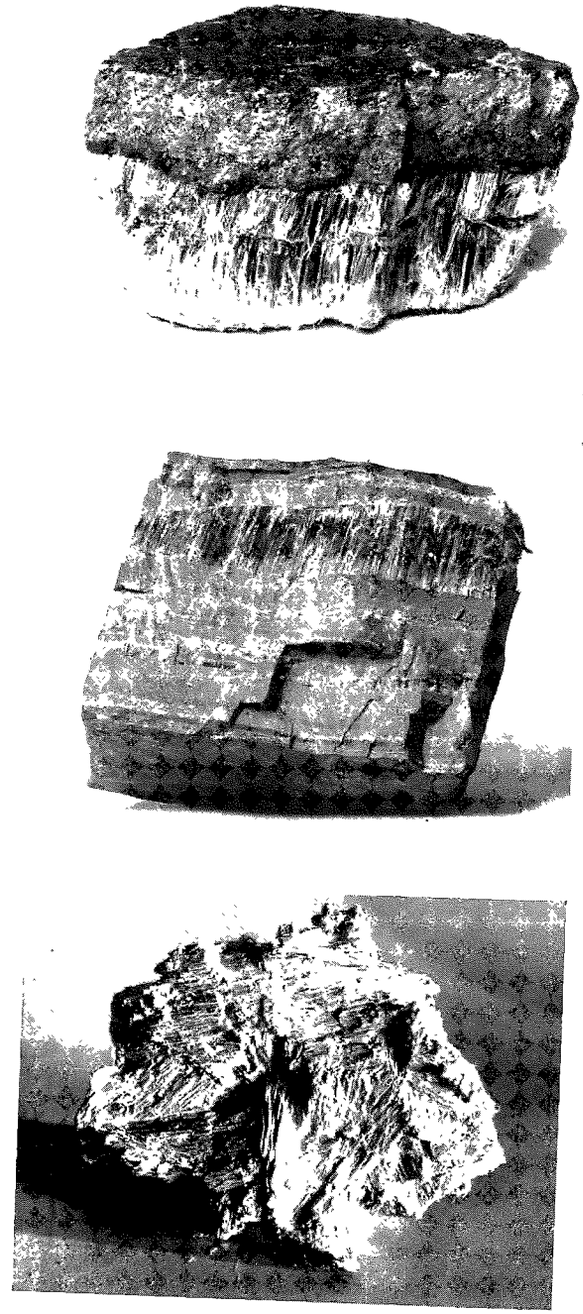

PLATE I. Asbestos ore; chrysotile (upper); crocidolite (middle); anthophyllite (lower).

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PLATE II. Underground workings at Thetford Mine, Quebec (Asbestos Corporation Ltd).

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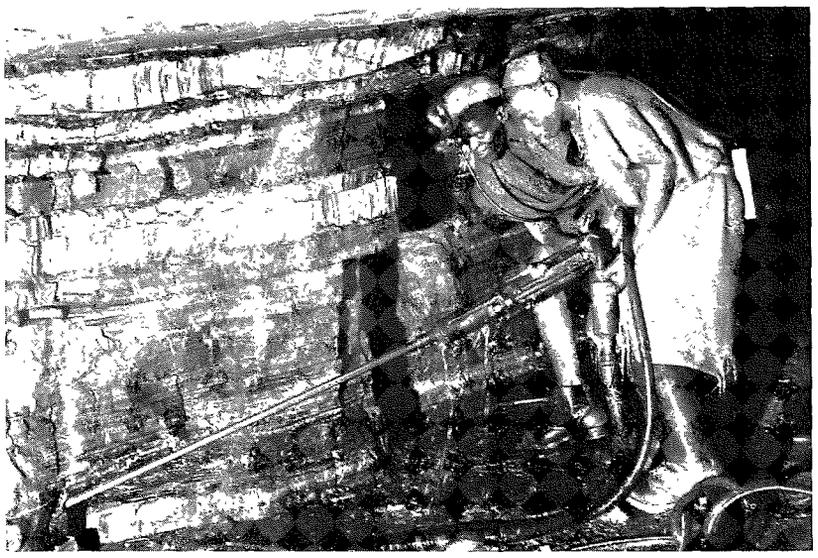

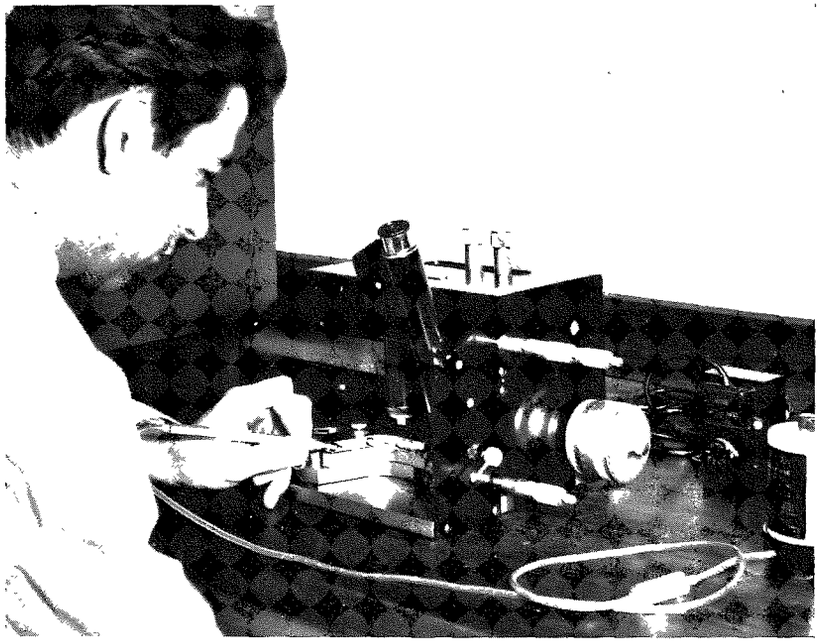

PLATE III. (*Above*) Underground workings at Penge Mine, Transvaal (Cape Asbestos South Africa (Pty) Limited).

(*Below*) Micro-tensile testing machine (Techne Ltd, Duxford) used to determine strength of asbestos fibres.

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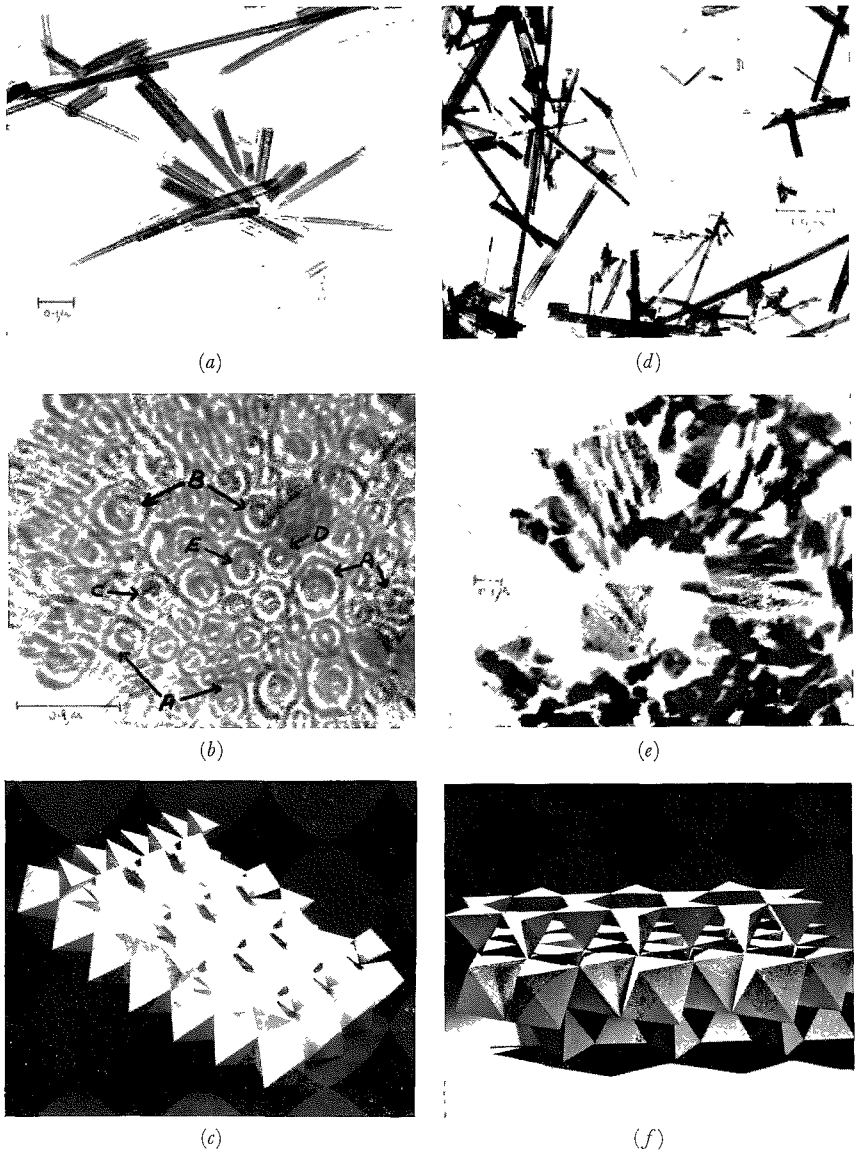

(*a*) (*d*)

(*b*) (*e*)

(*c*) (*f*)

PLATE IV. Electron micrographs.

CHRYSOTILE

(*a*) axial view.

(*b*) end-on view; photograph taken from Maser, Rice and Klug, 1960.[10]

(*c*) schematic model of cell structure.

AMPHIBOLES

(*d*) axial view (crocidolite).

(*e*) end-on view (crocidolite).

(*f*) schematic model of cell structure of amphiboles.

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PHYSICAL PROPERTIES OF ASBESTOS FIBRES

These are compounded in Table VI.

Tensile Strength

This is the most important and most commonly quoted physical property of asbestos fibres. There is, however, considerable diversity in the published values for the tensile strength of the various fibres. In 1951 Badollet[44] gave 5500–7000 kg/cm² for chrysotile, 1100–6500 kg/cm² for amosite, 700–21,000 kg/cm² for crocidolite and less than 600 kg/cm² for anthophyllite and tremolite. Some later work by Zukowski and Gaze[45] produced very much higher values, particularly for crocidolite and chrysotile, the measured maxima for which were 61,500 kg/cm² and 58,000 kg/cm² respectively. These authors were able to show that the observed tensile strengths were dependent on the length of the specimens tested, the shortest lengths of fibre in the experimental range 35–2 mm giving the highest strengths. The coefficients of variation on all sets of results lay between 20 and 57 per cent. By taking a high-speed cine film of fibres in the act of breaking, it was possible to see that the mechanism of failure was far from simple. Failure begins at a surface flaw, proceeds by the rupture of relatively weak interfibrillar bonds, thus producing broken fibrils, and exposing fresh surfaces which may fail at a different place. Each handlable fibre, however minute, can of course always be reduced to smaller fibres, ending up with fibrils of diameters of less than 0·1 μ.

Recent investigations in this subject have taken advantage of two of the conclusions arising from the earlier work. Firstly, the relationships between tensile strengths and length of fibre specimens fall into shallow but smooth curves, and it is reasonable to assume from this that flaws along the length of asbestos fibres occur at relatively regular intervals. Comparative measurements must therefore be made on specimens of a standardized minimum length, compatible with their handlability, on the assumption that these will contain similar numbers of flaws. Secondly, the tendency is to work towards fibres of the smallest diameter, composed of the minimum number of fibrils. It has been possible to refine the technique of measurement of these tensile strengths since Marsh's invention of the micro-tensile testing machine developed primarily for the investigation of metal and crystal 'whiskers'.[46] With this equipment (Plate III) it is possible to measure the tensile strengths of fibres with average diameters in the range 10–20 μ. To obtain the mean cross-sectional areas of the fibres, it is necessary to weigh each specimen on a deci-micro balance and thence compute from the measured length and known specific gravity. The operator handles the fibres with a vacuum hypodermic needle and seals them in position in quartz anvils in the tensile-testing machine. He then proceeds to take a series of load and extension measurements up to the breaking-point of the fibre.

Table VI includes the average tensile strength and Young's Modulus value for chrysotile, amosite and crocidolite as determined by this technique.[47] These are mean values on several hundred specimens of fibre, all of a standard length (4 mm) and 10–20 μ in diameter. The

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TABLE VI

PHYSICAL AND OPTICAL PROPERTIES

Property	Chrysotile	Anthophyllite	Amosite	Crocidolite	Tremolite	Actinolite
Tensile Strength kg/cm² ..	31,000	<5000	25,000	35,000	<5000	<5000
Young's Modulus kg/cm² ..	$1{\cdot}65 \times 10^6$	—	$1{\cdot}65 \times 10^6$	$1{\cdot}9 \times 10^6$	—	—
Flexibility	Good	Fair to Brittle	Fair	Good	Fair to Brittle	Fair
Specific Gravity	2·55	2·85–3·1	3·43	3·37	2·9–3·2	3·0–3·2
*Hardness, Mohs	2·5–4·0	5·5–6·0	5·5–6·0	4	5·5	6
*Specific Heat kcal/g/°C ..	0·266	0·210	0·193	0·201	0·212	0·217
*Volume Resistivity megohm-cm	0·003–0·15	2·5–7·5	up to 500	0·2–0·5	—	—
Colour	Colourless	Colourless	Colourless to pale fawn	Blue	Colourless	Green
Refractive Index n_α ..	1·493–1·553	1·578–1·652	1·657–1·688	1·685–1·698	1·599–1·628	1·600–1·628
Refractive Index n_γ ..	1·517–1·557	1·591–1·676	1·675–1·717	1·689–1·703	1·622–1·655	1·625–1·655
Pleochroism	Nil	Nil	Nil	Pale grey blue to dark blue	Nil	Pale green to deep green
Birefringence	Moderate first-order	Moderate low second-order	Strong second-order	Weak (masked)	Moderate low second-order	Moderate low second-order
Orientation	Length slow	Length slow	Length slow	Length fast	Length slow	Length slow
Extinction	Parallel	Parallel	Parallel	Parallel	Oblique (Max. 20°)	Parallel

Data marked * from Badollet (Refs. 44 and 54). Remaining Information from Cape Asbestos Fibres Ltd.

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coefficient of variation on the results is 10–15 per cent. The figures for anthophyllite, tremolite and actinolite are provisional estimates. In comparison, the tensile strength of steel piano wire is usually given as 25,000 kg/cm² and of typical glass fibres as 14,000 kg/cm². The results for chrysotile in Table VI agree closely with those for a normal chrysotile given by Professor P. N. Sokolov in his book on Asbestos-Cement Technology (in Russian).

Very high values may be predicted for tensile strength of silicates particularly from consideration of the strengths of the stable silicon–oxygen chains or sheets which characterize these minerals. Orowan[48] has suggested a value above 100,000 kg/cm² and tensile strengths approaching 60 per cent of this figure have been obtained with very short crocidolite fibres. The values given in Table VI are interesting because they show a narrowing of the overall range of tensile strengths of the three major kinds of asbestos fibre in comparison with the earlier figures given by Badollet. This is to be expected if, fundamentally, tensile strengths depend on continuous and linear silicon–oxygen structures. In glass and silica fibres such structures are normally discontinuous and randomly orientated, with the result that tensile strengths have low values. It is, however, known that silica fibres can now be made with highly orientated structures and these have tensile strengths above 75 per cent of the theoretical figure.

Under the influence of heat, the onset of detectable decomposition of asbestos fibres begins above 500°C. Between 200 and 500°C their tensile strength diminishes without any chemical changes necessarily taking place. It is true that an oxidation change occurs with crocidolite at 400°C, but if this is precluded by heating the fibre in an inert atmosphere, the change in tensile strength still takes place. In Table VII the

TABLE VII

EFFECT OF TEMPERATURE ON THE TENSILE STRENGTH OF ASBESTOS

Temperature °C	Percentage of original tensile strength		
	Chrysotile	Crocidolite	Amosite
200	—	~100	100
320	91·6	70	58
430	73·3	32	32
550	59·5	20	15
670	32·0	—	—
Period of heat soak ..	3 min	4 hr	4 hr
Reference	44	47	47

effect of temperature is expressed by the percentage change in tensile strength for three typical fibres. The results are not strictly comparable as they are given from different sources and obtained under different conditions. Since this destruction of the tensile properties of asbestos cannot be linked with the breakdown of the crystal structure, an explanation has to be sought in the following way. Certain evidence from electron micrographs suggests tube-in-tube structures in chrysotile

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and a lath-on-lath appearance in some amphibole fibres. It seems possible that asbestos fibres are built up from a series of overlapping crystallites of various lengths, held together by intramolecular cohesive forces and also by co-ordinate linkages via –H–O–H– bridges. The amphibole fibres give up a small amount (0·25 per cent) of water when heated in the range 200–500°C (*see* p. 32) and since this is not associated with any chemical change in the fibre, it is termed 'physically combined water'. Thus if by heating the fibre this water is expelled and the co-ordinate linkages broken down, then the longitudinal adhesion between crystallites weakens and in the axial direction the whole fibre is weakened. The conception of fibres built up of crystallites both overlapping and end-to-end is consistent with suggestions that fibres contain repetitive flaws which may well arise from imperfections in the imbricate structure.

The importance of these physical properties lies in the reinforcing effect of asbestos fibres in asbestos cement, reinforced plastics and similar products. Reinforcement in terms of a tensile measurement is a function of the tensile strength of the reinforcing filaments and the volume fraction which these occupy in the matrix. While the high tensile strength *per se* of asbestos fibres plays a big part in the reinforcement of cements and organic resins, the full effect is of course complicated by the compatibility of the fibre and the matrix. In a moulded structure the stiffness of asbestos fibres also ensures excellent rigidity. The Young's Modulus of crocidolite is nearly three times that of glass fibres. In practical terms this means that a reinforced plastic laminate such as might be used in the construction of a storage vessel or a car body will be considerably stiffer when reinforced with crocidolite fibres rather than with glass fibres.

Bond Strengths

This term concerns the forces of adhesion between asbestos fibres and the matrices containing them. Bond strengths of asbestos–cement and asbestos–resin systems have been measured by embedding straight macro-fibres, 0·1–1 mm in mean diameter, in the matrix leaving part

TABLE VIII

BOND STRENGTHS BETWEEN FIBRES, POLYESTER RESIN AND PORTLAND CEMENT

Matrix	Chrysotile Thetford kg/cm²	Crocidolite Koegas kg/cm²	Amosite Penge kg/cm²	Glass surface treated kg/cm²
Polyester resin* ..	—	81·5	—	37·5
Portland cement† ..	8·4	32·5	33·5	—

* Bennett (ref. 31); † Burman (ref. 47)

of the fibre projecting; the composite is then subjected to a straight tensile pull between the end of the fibre and the block of matrix. Some results of these tests are shown in Table VIII.

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Although the amount of work in this subject has been limited, it is possible to formulate a few observations on the question of bonds involving the surfaces of asbestos fibres. Adhesion between asbestos and organic polymers would appear to depend largely on the relative polarities of the two component surfaces. It is generally accepted that materials with similar polarities and those classified as non-polar attract each other, but that polar substances repel non-polar substances.[49] Organic polymers exhibit substantially non-polar surfaces, with perhaps the exception of residual hydroxyl groups which may be spaced at relatively large intervals. Such materials adhere satisfactorily to non-polar surfaces only.

A glass fibre under atmospheric conditions presents a hydroxylated surface arising from –SiOH nuclei, and this strongly polar surface is incompatible with organic resins. Bond strengths are typically poor. The problem can be overcome by placing a coupling agent, such as an organic chromium complex or a chlorosilane between the glass and the resin. Such compounds displace the hydroxylated surface and couple a non-polar surface to (SiO–) groups at the glass surface. The amphibole fibres, on the other hand, have substantially non-polar surfaces and their compatibility with organic polymers is good. Thus glass and crocidolite exemplify differing degrees of bond strength with polyester resin according to their surface characteristics (Table VIII). Comparative figures for chrysotile are not available but initial investigations suggest that the chrysotile polyester bond has a strength comparable to that for the crocidolite given in Table VIII. Evidence from industrial applications of chrysotile and crocidolite in organic resin systems indicates that the reinforcement strengths attributable to the two types of fibre are similar. There is a confliction between theory and practice since chrysotile has a highly hydroxylated, strongly polar surface to which one would not expect organic resins to adhere. In such a system it seems highly probable that some chemical bonding occurs between the alkaline surface of the fibre and suitable residues in the organic matrix.

Another anomaly arises in considering bonds between asbestos fibres and cementitious materials such as Portland cement. On the accepted basis that polar surfaces attract each other, we would expect chrysotile and cement, both of a highly reactive alkaline nature, to form a good bond. Conversely highly polar cement particles would not be expected to be compatible with non-polar surfaces of amphibole fibres. The possibility of chemical reactions between chrysotile and the phases of cement cannot be ruled out, but it is arguable whether these are advantageous or not.[35] If chrysotile reacts with cement phases, then this might lead to a stripping of the Mg–OH layer and a breaking of the chemical bonds between this layer and the essential silica core of the structure. The net bond strength may then be reduced. While the amphibole fibres do not participate in chemical reactions of this nature, it seems possible that their silica surfaces may provide nucleating points to which cement particles attach themselves in the process of hydration. The crystalline phases so formed grow normal to the fibre axis[50,51], an observation which has been amply supported by electron micrographs of

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platy crystals of tobermorite ($Ca_5Si_6O_{22}H_{10}$) attached to amosite fibres. (The name tobermorite is given to the synthetic calcium silicate produced by autoclaving mixtures of lime and silica.)

There are reasons then for supposing that the bond strengths between Portland cement phases and any type of asbestos fibre would at least be comparable. On the industrial scale it is recognized that good quality chrysotiles and amphibole fibres provide similar reinforcing strengths in asbestos–cement products. The results given in Table VIII do not however support this, the amphibole fibres having much higher bond strengths than chrysotile. The reason here appears to be mechanical. The amphibole fibres, rigid in all directions, have been literally clamped in position by the expansion of the cement particles in the course of their hydration. Chrysotile fibres, being softer and more flexible, probably take up the form of distorted tubes, under the same influences, with the result that they are not clamped so tightly. Fine chrysotile fibres will of course distort even more in a cement matrix and may bend around cement particles, anchoring themselves in position. Under certain conditions, therefore, we may expect chrysotile fibres to display the same or even better mechanical reinforcement than amphibole fibres. Indeed the fractured edge of a piece of asbestos cement containing both kinds of fibres invariably shows amphibole fibres which have pulled out of the matrix, while chrysotile fibres have broken, indicating their stronger adherence to the matrix.

It now seems clear that the bonds between asbestos fibres and various matrices cannot be described solely in terms of interfacial adhesion effects. Depending on the kind of matrix involved, the influence of both chemical and mechanical bonds has to be taken into account and, in the final analysis, these may have an overriding effect.

Surface Area

While tensile strength is the most important intrinsic physical property of asbestos fibres, their surface area is the most important parameter in all their industrial applications. In industrial parlance, surface area becomes degree of openness or degree of fiberization. Each process involving asbestos fibre requires a degree of fiberization which within limits is critical for that process. For example, chrysotile fibres prepared for inclusion in moulded brake linings will have a different degree of fiberization from those prepared for carding in the first stage of textile manufacture. The correct degree of fiberization is achieved by milling the raw asbestos in a hammer mill, pin disc mill, rod mill or similar types of machine. In multistage manufacturing processes, account must also be taken of the further fiberization which may occur through mechanical handling or wet-mixing stages.

The ability of asbestos fibres to open or split into finer fibres through suitable treatment is one of their most valuable properties. Ideally the best fiberizing technique should open a fibre without damaging it by disintegration into shorter lengths. In practice this is hardly possible, though laboratory-scale ultrasonic treatment of asbestos fibres shows that ideal fiberization can be achieved.

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The term degree of fiberization can be explained by saying that if a fibre of cross-sectional area a splits down to n fibres having average cross-sectional area a/n, then its degree of fiberization has been increased by n times. If the mean radius of cross-section of the n fibres is r, then it can be shown simply that their absolute surface area is proportional to $1/r$. Degree of fiberization can therefore be expressed directly in terms of the measured surface area of the fibres. Theoretically of course the ultimate limit to this value is enormous. The absolute surface area of typical asbestos fibres used in manufacturing processes lies between 30,000 and 90,000 cm^2/g, as measured by the nitrogen absorption method at room temperature. Measurements on the same fibres after out-gassing at higher temperatures (100 and 400°C) may raise the upper limit of surface area to 140,000 cm^2/g.[52] Raw amphibole asbestos as shipped from refineries at the mines may have an absolute surface area of 6000–20,000 cm^2/g and for similar unprocessed chrysotile fibres the value may be up to 30,000 cm^2/g. It will be appreciated from these figures that while the mean surface area of commercial asbestos fibres is several thousand times greater than that of the massive ore, the amount of milling that the fibres receive in manufacturing processes will only increase the degree of fiberization by a factor of perhaps five or six at the most.

In practice the nitrogen absorption method of measurement of surface area cannot be used, and the usual technique on the industrial scale involves an air-permeability measurement based on the method of Rigden.[53] This technique is widely used in the cement and clay-mineral industries where it gives reasonably accurate results, but it gives low results for asbestos fibres—some three to four times lower than the absolute figures. The theoretical background to the air-permeability method is only true for small spherical particles which can be packed into a volume of low porosity. Asbestos fibres satisfy neither of these conditions and, in fact, an empirical factor must be introduced into calculations to account for their rod-like shape. Nevertheless the method is sufficiently useful for rapid practical purposes. It is usual to state such measurements on asbestos fibres as 'apparent surface area'.

Other Physical Properties

Specific gravities have been determined by weighing in water prepared blocks of fibre approximately 1 cm cube taken from ore specimens. Before weighing the specimens, it is essential that they are outgassed under water by placing them under high vacuum for several hours. Occluded gases, probably of primitive origin, may account for up to 5 per cent of pore space in fresh specimens, and air in weathered specimens may account for up to 20 per cent of pore space. No attempts have yet been made to identify the gases of supposed primitive origin.

The only available electrical data on asbestos concerns volume resistivity, which is low for chrysotile and very variable for amphibole fibres.[54] Some new information on the resistive and magnetic properties of asbestos is required, particularly in terms of the resistivity and magnetic susceptibility parallel to and normal to the fibre axes.

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The optical data in Table VI have been compiled recently and refer to fresh specimens of fibres.[55] The refractive indices correspond to changes in cation composition and as a general rule are related directly to the Fe/Mg ratio. Thus crocidolite and amosite with highest Fe-contents have the highest refractive indices, while chrysotile with high Mg-content has the lowest refractive index. The values for crocidolite shown in the table apply to the typical mineral from Koegas. Bolivian crocidolite has n_α 1·659 and n_γ 1·673, the indices being lower than those of the Koegas mineral because of its much higher Mg-content.

THERMAL DECOMPOSITION OF ASBESTOS

It could be said that up to the early 1950s asbestos fibre was always regarded as a thermally resistant, fire-proof material. Except for statements that the fusion point of asbestos lay above 1000°C and that the products of decomposition at high temperature were known, no precise limitations were placed on the supposed high degree of heat-resistance of asbestos fibres. In fact all varieties of asbestos fibres break down progressively through a series of internal reactions which may begin as low as 200°C. This does not mean that their properties as heat insulators are diminished. Whether compounded partially or wholly into heat-insulating materials, asbestos fibres possess ablative properties in that the products of decomposition at a hot surface form a poorly conductive layer which provides protection to the succeeding layers of insulation. The insulating properties of asbestos depend much more on its fibrous nature and on the poor thermal conductivity of individual fibres than on limitations arising from its thermal decomposition.

The study of the thermal decomposition of asbestos has been aided considerably in recent years through the development of thermal analysis techniques, namely differential thermal analysis (d.t.a.) and thermal gravimetric analysis (t.g.a., *see* ref. 56 for reviews of these techniques). It is usual to couple these techniques with X-ray diffraction studies and, in more recent work in this subject, investigations by all three methods have been made in conditions of both oxidizing and inert atmospheres. A further valuable method of investigation is that of dynamic dehydration. Since dehydroxylation is one of the most important stages in the decomposition of the asbestos minerals, it is necessary to devise a technique whereby the amount of water evolved from samples under investigation is measured at all stages of decomposition over a wide temperature range. This is important, since dynamic dehydration determinations such as these do not necessarily coincide with dynamic weight losses.

Amphibole asbestos

Wittels[57] and Vermaas[58] were the first to use thermal analysis methods to investigate the decomposition of amphiboles, amphibole asbestos and certain associated minerals such as goethite, magnetite and hematite. Vermaas proposed some empirical equations for the complete decomposition reactions and showed that amosite broke down to magnetite,

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cristobalite and water, while crocidolite, anthophyllite and tremolite gave a pyroxene with cristobalite and water, and an iron oxide. He also pointed out a significant exothermic reaction of crocidolite at 400°C in oxidizing conditions, due to the oxidation of some of its ferrous iron to ferric iron. This reaction was amplified later[59] to a dual process in which OH^- was replaced by O^{2-} and Fe^{2+} by Fe^{3+}. More recent investigations have thrown further light on this process which is repeated to a smaller extent in some of the other amphiboles.[12,16,60,61]

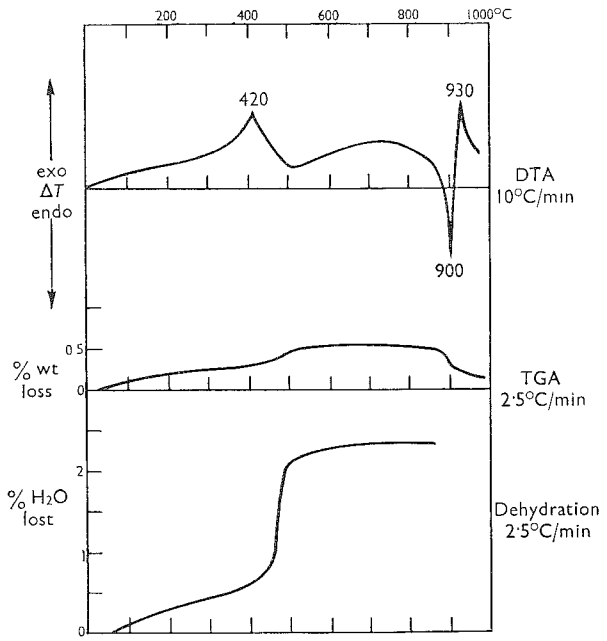

FIG. 6*a*. Thermal analyses of crocidolite in oxygen.

Typical complete thermal analysis curves for crocidolite are shown in detail in Fig. 6, *a* and *b*. The d.t.a. curve of crocidolite in an inert atmosphere has a dehydroxylation endotherm at about 600°C, which coincides with distinct steps on curves of weight loss and dynamic dehydration. The loss of water from dehydroxylation amounts to about 1·9 per cent in fresh crocidolite, and agrees with the theoretical quantity. The endothermic–exothermic pattern about 800°C on the d.t.a. curve corresponds to breakdown of the amphibole anhydride to simpler molecules, in this example a NaFe–pyroxene (probably acmite), magnetite, silica and a glass phase. These products fuse and melt between 850 and 1000°C.

Decomposition of crocidolite in an oxidizing atmosphere proceeds somewhat differently. An oxidation process occurs at 400°C, and although dehydration curves point to the loss of water, curves for weight loss do not. Condensation of OH^- groups does not take place, but an oxyamphibole is formed with protons—the hydrogen ions of the hydroxyl

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groups—migrating to the surface of crystallites to combine with atmospheric oxygen to form water, again 1·9 per cent. There is a corresponding movement of electrons and some Fe^{2+} changes to Fe^{3+}. Addison[62] has studied the same reaction by gas-absorptiometric methods and has postulated the following redox equation for the combined process of dehydrogenation and oxidation.

$$4Fe^{2+} + 4OH^- + O_2 \rightarrow 4Fe^{3+} + 4O^{2-} + 2H_2O$$

No structural changes accompany this process, and none in fact are detected until the temperature of the oxycrocidolite has reached 850°C. Decomposition takes place completely at 900°C, giving the pyroxene, magnetite, hematite and silica.

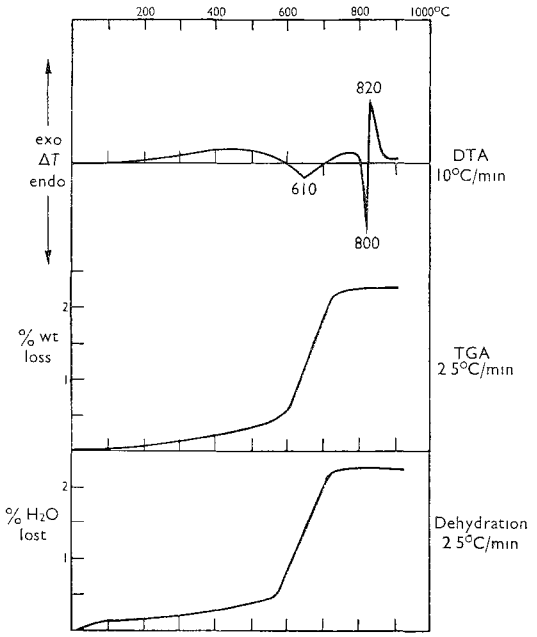

FIG. 6*b*. Thermal analyses of crocidolite in an inert atmosphere (argon).

In addition to the true chemically-combined water, crocidolite loses about 0·5 per cent or less of water in the range 100–500°C, independently of the surrounding atmosphere. Similar amounts are attributed to the other amphibole fibres. The sole change with which this loss of water can be associated is in the loss of tensile strength of the fibre, and consequently this particular quantity of water is referred to as 'physically combined'. It appears to be associated with the phenomenon of fibrosity in the amphiboles; water molecules form cross-links between individual crystallites which thus bond into a strong fibrous structure. The distribution in fresh crocidolite amounts to one molecule of water, or one cross-link, to every four unit cells.

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TABLE IX

SUMMARY OF DECOMPOSITION REACTIONS OF AMPHIBOLES

	Oxidizing Conditions			Neutral Conditions		
	Dehydrogenation	Dehydroxylation	Breakdown	Dehydroxylation	Dehydrogenation	Breakdown
Crocidolite ..	R 400–600°C P 420°C 1·9% H_2O		P 900°C NaFe–py. hem. sil.	R 550–700°C P 610°C 1·9% H_2O		P 800°C NaFe–py. mag. sil. glass-phase
Prieskaite .. .. (fibrous actinolite)	R 450–670°C 1·9% H_2O		R 900–110°C CaMgFe–py. sil.	R 400–850°C (2) P 700°C 1·9% H_2O		P 1040°C CaMgFe–py. sil.
Amosite	R 600–800°C 0·9% H_2O	R 800–900°C 1% H_2O	R 600–900°C FeMg–py. mag. hem. sil.	R 600–800°C P 780°C 1·5% H_2O	R 600–800°C 0·4% $H_2\uparrow$	R 600–900°C FeMg–py. sil.
Anthophyllite ..	R 600–850°C 1% H_2O	R 850–1000°C P 950°C 2% H_2O	P 950°C MgFe–py. sil. mag. (?)	R 800–1050°C P 950°C 2·7% H_2O	R 800–1050°C 0·3% $H_2\uparrow$	P 950°C MgFe–py. sil. mag. (?)
Actinolite .. .. (semi-fibrous)	R 620–960°C 1·1% H_2O	R 960–1080°C P 1040°C 1·5% H_2O	P 1040°C CaMgFe–py. sil.	R 620–1080°C (2) P 1040°C 2·4% H_2O	R 620–1080°C 0·2% $H_2\uparrow$	P 1040°C CaMgFe–py. sil.
Tremolite		R 950–1040°C P 1040°C 2% H_2O	P 1040°C CaMg–py. sil.	R 950–1050°C P 1040°C 2% H_2O		1040°C CaMg–py. sil.

R, temperature range; P, typical peak temperature (d.t.a.); (2) indicates two steps in dehydration; py. = pyroxene; hem. = hematite; mag. = magnetite; sil. = silica.

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Addison and Sharp[63] have studied the reduction of fresh dehydroxylated and oxidized crocidolite in a hydrogen atmosphere at temperatures of 450 and 615°C. The reductions follow different mechanisms—both water and zero-valent iron are formed in each. A pyroxene is formed together with silica at temperatures of 600–850°C.[16]

The decomposition reactions of the fibrous amphiboles are summarized in Table IX, together with typical d.t.a. curves in Fig. 7, *a* and *b*.[12,60] The outstanding feature of these reactions is the ability of the amphiboles to lose the elements of chemically combined water by dehydroxylation, dehydrogenation and oxidation, or by dehydrogenation and expulsion of free hydrogen, depending on the external conditions.

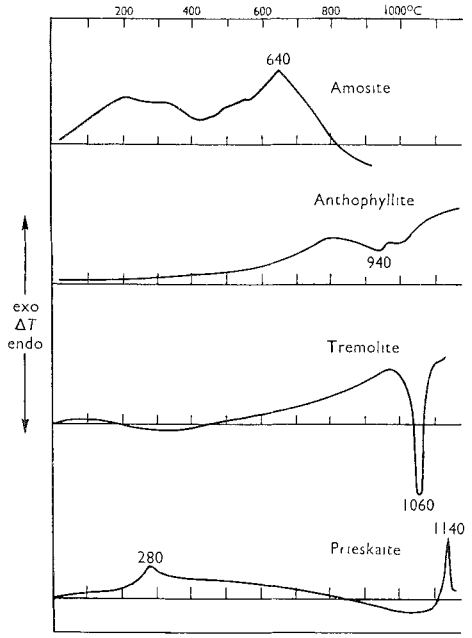

FIG. 7*a*. Typical d.t.a. curves for amphibole fibres in oxygen (10°C/min).

Straightforward dehydroxylation, as for crocidolite in an inert atmosphere, can be expressed by $2OH^- = H_2O + O^{2-}$. The dehydroxylation of amosite in an inert atmosphere is however complicated by an auto-oxidation of some of the ferrous-iron content, coupled with the expulsion of an equivalent amount of free hydrogen:

$$4Fe^{2+} + 6OH^- = 2Fe_2O_3 + 3H_2$$

About one quarter of the total hydrogen content of amosite is lost in this way. The remainder is lost as water in the condensation of OH^- groups. Anthophyllite and non-fibrous actinolite apparently behave similarly, though the amount of free hydrogen expelled will be small, being dependent on the presence of available ferrous iron. Tremolite

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loses water solely through a dehydroxylation reaction in both inert and oxidizing atmospheres.

When amosite is heated in oxygen, water forms partly by oxidation of protons and partly by dehydroxylation, in that order, and with some overlapping of the reactions. The oxidation of protons accounts for one quarter to one half of the hydrogen present. Anthophyllite and non-fibrous actinolite also lose some water via proton oxidation, though considerably less than does amosite. The fibrous actinolite, prieskaite, behaves similarly to crocidolite and loses all its proton content to external oxidation.

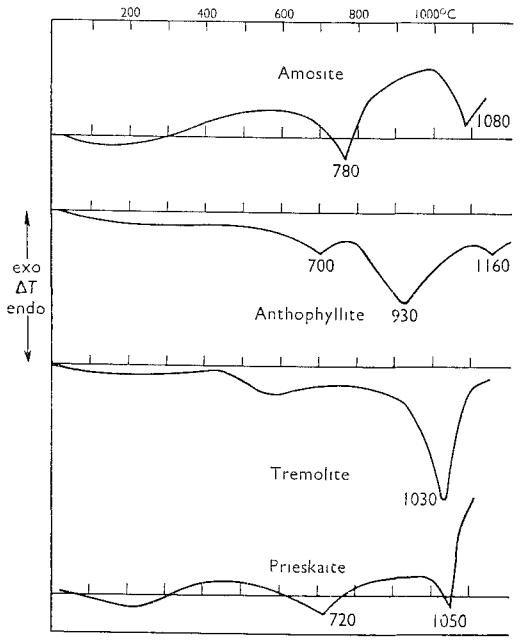

FIG. 7*b*. Typical d.t.a. curves for amphibole fibres in an inert atmosphere (argon, 10°C/min).

The amount of water formed from proton oxidation seems to depend on proton mobility. All the protons in crocidolite (and prieskaite) may be oxidized, up to half of them in amosite, small amounts only in anthophyllite and non-fibrous actinolite and none at all in tremolite. The series crocidolite, amosite, anthophyllite (actinolite), tremolite is loosely linked by these several factors: decreasing proton mobility; increasing temperature of dehydroxylation both in inert and oxidizing atmospheres; increasing temperature of structural breakdown; and increasing magnesium content at M_1 and M_3 sites. Addison[62] in comparing the slow oxidation of amosite with the rapid oxidation of crocidolite suggested that magnesium-blocking at M_1 and M_3 sites must interfere with the redox reaction. This is not the complete explanation because crocidolites with various magnesium contents oxidize at similar

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temperatures (near 400°C by d.t.a.) and always indicate complete proton mobility with no tendency to a dehydroxylation reaction. Nevertheless the magnesium content of the amphiboles appears to be the most important factor in determining their thermal stability.

In summary, the decompositions of these amphiboles comprises three fundamental stages: loss of physically combined water, loss of chemically combined water, and breakdown into simpler products, the main one of which is a pyroxene. The loss of chemically combined water is associated with proton mobility, a phenomenon which cannot be confined solely to reactions in oxidizing atmospheres. While dehydroxylation can be over-simplified as a condensation of OH^- groups, this reaction seems to proceed through migration of protons to reaction zones where they unite with oxygen. In the absence of oxidizing conditions at structural surfaces, these reaction zones must be structural parts. Freeman and Taylor[64] and Taylor[65] explain the whole process of decomposition in terms of the formation of donor and acceptor regions in the crystalline structure. The donor region is destroyed and supplies not only oxygen, which will react with protons which migrate towards it, but cations which migrate to the otherwise undisturbed acceptor regions. The main products of decomposition form in the acceptor regions, and the products as well as the starting materials have structures based on nearly close-packed oxygen layers, with cations at interstices. The crystalline products are always formed topotactically, that is with definite preferred orientations. The smallest changes in cation positions and disturbance of the oxygen layers occur in the formation of the pyroxenes, which in consequence are always highly orientated.

The way in which these amphiboles lose combined water is of considerable importance in the interpretation of chemical analyses. The question of allocation of the water liberated from the amphiboles has been the subject of several mineralogical papers in the past, particularly with respect to anthophyllite and actinolite where an excess of combined water is found.[27–29] It is now clear that one cannot assume that water lost above 105–110°C is chemically combined and that an understanding of the dehydration processes involved is necessary before determinations of combined water can be made. The true content of hydroxyl water in crocidolite (and prieskaite) can be found most conveniently from t.g.a. or dynamic-dehydration curves in a neutral atmosphere, but for the other amphiboles dynamic dehydration in an oxidizing atmosphere would be necessary to ensure complete oxidation of protons.[16,60] By such methods it is possible to separate physically combined water from chemically combined water which is normally evolved in a sharp loss over a narrow range of temperature. Fresh amosite, crocidolite and tremolite give losses which on calculation of the contents of the cell agree closely with the $2OH^-$ requirement. Anthophyllite and actinolite may have an excess of OH^- groups, and since not more than two can be allocated to the normal structure, it is assumed that extra hydroxyls may replace some of the oxygens in Si_4O_{11} bands.

This general outline of the thermal decomposition of the amphibole fibres applies to the typical minerals. Obviously a number of variants

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exist. For example weathered amosites and crocidolites may have losses of chemically combined water corresponding to $1\frac{1}{2}$ OH^- per unit cell, the loss of up to $\frac{1}{2}OH^-$ being associated with naturation oxidation processes. These processes appear to be limited by the disposition of Fe^{2+} ions in M_1 and M_3 sites.[60] Other than this, the complete decomposition of such materials is not affected by weathering. The detailed pattern of breakdown of crocidolites from the Transvaal, Bolivia and Australia varies somewhat from the general scheme. In particular, the Transvaal and Bolivian crocidolites behave as mixed amphiboles. The Transvaal material is known to be an intimate physical mixture of crocidolite and amosite, and the Bolivian material has been classified as a magnesio-riebeckite[25] and has characteristics of both anthophyllite and crocidolite on the evidence of thermal decomposition[24]. The compositions of both tremolites and anthophyllites include pure magnesium varieties as well as ferro-magnesium varieties, and the proportion of iron present will influence the thermal decomposition of these minerals. Usually the effect of a high iron-content is to produce two distinct steps in the loss of chemically combined water and a lowering of the temperature of final decomposition.

Finally in discussing the amphiboles, further reference should be made to the influence of magnesium on their decomposition reactions. In general the greater the magnesium content, the higher the temperatures at which dehydroxylation and breakdown occur. While magnesium-blocking at M_1 and M_3 sites can affect the rate of oxidation of certain types of amphiboles, this appears to be subsidiary to the control of ultimate decomposition temperatures. This has been shown to be true for crocidolite itself. By correlating d.t.a. evidence with chemical compositions for 21 crocidolites from South Africa and Australia, it is possible to show that the temperature of breakdown is influenced by the Fe^+/Mg^{2+} ratio.[24] These cations fill the M_1 and M_3 sites. Where this ratio is high, *i.e.* 8–11, ultimate decomposition occurs at 890–900°C in oxidizing conditions and at 800°C in inert conditions. Progressive lowering of the ratio to 2 coincides with a rise in the temperature of breakdown by some 80°C, in both oxidizing and inert conditions. Some similar evidence from tremolites has shown that for a number of specimens having FeO-contents between 7 and 0·3 per cent, the endothermic temperature of decomposition increases from 980 to 1080°C as Fe^{2+} diminishes. All the evidence points to magnesium as the key to the control of the upper temperature limit of decomposition for these amphiboles and to control of proton mobility except in crocidolite where the separate redox mechanism operates. In this sense crocidolites are unique among the amphiboles.

Chrysotile asbestos

The thermal decomposition of chrysotile follows a two-stage sequence of dehydroxylation and breakdown. The mechanism of decomposition of serpentine, the mother-rock of chrysotile, has been studied by a number of authors[66–68] and the same mechanism applies to chrysotile[68,69]. The dehydroxylation of chrysotile takes place in the range 600–780°C, and

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at 800–850°C the anhydride breaks down in a sharp transformation to forsterite and silica. The total decomposition corresponds to:

$$Mg_6Si_4O(O_{10}H)_8 = 3Mg_2SiO_4 + SiO_2 + 4H_2O$$

The forsterite is well crystallized and persists together with the silica up to 1000°C, but above this temperature some enstatite is formed:

$$3Mg_2SiO_4 + SiO_2 = 2Mg_2SiO_4 + Mg_2Si_2O_6$$

The reactions take place independently of surrounding atmospheres. Typical thermal analysis curves (Fig. 8) show on d.t.a. a dehydroxylation endotherm and a sharp exotherm corresponding to the forsterite recrystallization; and on t.g.a., a gradual weight loss between 100 and 600°C and a sharp loss above 600°C, the total dehydration amounting to about 13 per cent H_2O.

A 'donor–acceptor' mechanism of decomposition has been applied to the transformation of the serpentine minerals, based initially on a similar mechanism for the dehydration of brucite.[68] In Ball and Taylor's mechanism,[68] donor regions, corresponding to two-ninths of the whole, supply cations to acceptor regions and oxygens to react with protons which migrate from acceptor regions and form water. The scheme can be represented by:

$$\begin{array}{lcc} & 7Mg_3Si_2O_5(OH)_4 & \underset{6Mg,4Si}{\overset{28H}{\rightleftharpoons}} \quad 2Mg_3Si_2O_5(OH)_4 \\ 600°C & \text{Acceptor region} & \qquad\qquad \text{Donor region} \\ & \downarrow & \qquad\qquad \downarrow \\ & \text{Serpentine Anhydride} & \qquad\qquad 18H_2O \\ & \downarrow & \\ 800°C & Mg_2SiO_4 + SiO_2 & \end{array}$$

The donor regions are completely destroyed and form pores. In Brindley and Hayami's interpretation[69] one-third of the whole becomes a donor region and residual silica remains there after its destruction. A highly disorganized forsterite forms in the acceptor region which transforms to a well crystallized material at 800°C. The forsterite always forms topotactically and the energy of its recrystallization is well exemplified by d.t.a. which can give a sudden recrystallization exotherm of 50–100°C amplitude. Under static heating conditions the transformation is more gradual, beginning in small nuclei and spreading as cation migrations and packing changes occur. Further information on the dehydration of chrysotile has been obtained by thermal-gravimetric methods. Woodrooffe examined a number of Canadian chrysotiles, using a Chevenard thermobalance operating at a heating rate of less than 1°C per minute.[70] He found three stages of dehydration; 100–500°C, giving up to 1 per cent H_2O; 500–700°C, 10–13 per cent H_2O; and 700–900°C and above, 1 per cent H_2O. The total dehydration ranged from 12 to 15·5 per cent for 16 specimens. The extent and temperature range of the main part of the dehydration fits in well with the proposed decomposition mechanisms.

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However some recent investigations of chrysotile by thermal analysis have brought to light a further aspect of these mechanisms.[71] In this work 15 specimens of the type mineral from the Thetford and Asbestos areas of Quebec province have been examined along with a further 15 specimens from world-wide sources. D.t.a.s show that the endothermic peak temperature of dehydroxylation is, with few exceptions, 650 ± 20°C, and the exothermic peak temperature of recrystallization is almost invariable at 810 ± 10°C. T.g.a. and dehydration measurements agree approximately with those of Woodrooffe, but the main loss of water appears between 600 and 700°C (±20°C) and amounts to 9–11·3 per cent according to specimen; the loss between 100 and 600°C is up to 2·5 per cent. T.g.a. results alone can be misleading since part of the weight loss may be due to the decomposition of brucite and carbonate impurities, but provided these are accounted for the loss due to water alone agrees well with dehydration measurements.

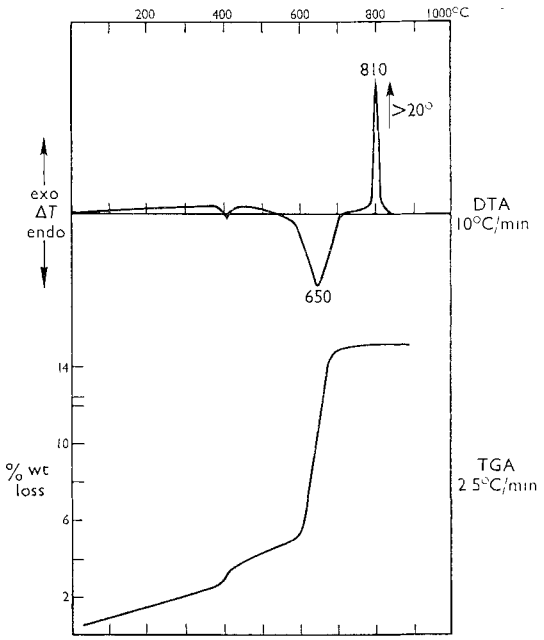

FIG. 8. Typical thermal analyses of chrysotile. The small peak near 400°C corresponds to the dehydration of the brucite impurity.

A theoretical composition of chrysotile based on structural considerations will show that 9·75 per cent H_2O, equivalent to $6OH^-$, rests in the external hydroxyl layer with 3·25 per cent H_2O, equivalent to $2OH^-$, in the internal hydroxyl layer (*see* Fig. 3*a*). There are reasons, therefore, for associating the main dehydration loss of chrysotile with disruption of the external hydroxyl layer, while the sum of losses below 600°C and above 700°C appears to be associated with the remaining

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hydroxyl groups. On this basis, calculation of the disposition of OH^- groups in cell contents gives the following results (Table X).

TABLE X

Source	$(OH)_6$	$(OH)_2$	Total
Quebec, Thetford (*a*)	5·9–6·4	1·7–2·0	7·9–8·0
Quebec, Thetford (*b*)	6·4–6·8	1·6–2·3	7·9–8·7
Quebec, Asbestos	6·3	2·1	8·4
Russia, Asbest (*a*)	5·9	1·6	7·5
Russia, Asbest (*b*)	6·7	0·8	7·5
Transvaal, Barberton	6·5	1·4–1·9	7·9–8·4
S. Rhodesia, Shabani	6·5	1·4	7·9
British Columbia, Cassiar ..	7·1	1·0	8·1
Arizona	6·2	1·2	7·4
Greece	6·2	1·6	7·8
Turkey	6·4	1·5	7·9

The total number of OH^- groups does not often exceed eight, and more often than not shows deficiencies. Since the measurements commence at 100°C, it seems unlikely that chrysotile contains inter-fibril –H–O–H– links in the same way that the amphiboles do. All H_2O (+100°C) can be attributed to chemically combined water. Hydroxyl in the $(OH)_6$ layer approaches a minimum of six, while there are often deficiencies in the $(OH)_2$ layer.

The evidence points to proton movement beginning at about 150°C and to the $(OH)_6$ layer remaining virtually intact up to 600°C. Initially, proton migration may take place in the $(OH)_2$ layers alone to incipient donor regions where the protons will react with hydroxyl groups to form water. When brucite itself is subjected to thermal decomposition, it dehydrates under static conditions at 250°C and under dynamic conditions at 350–400°C. Thus although a similar mechanism can be used to explain the dehydration of brucite and chrysotile, proton migration in the latter appears to take place in two distinct modes. One of these is delayed until the chrysotile reaches a temperature of 600°C, and then produces a large and rapid dehydration; the other commences at low temperatures and produces a continuous small dehydration which may not be completed up to 900°C.

Although chrysotiles contain small amounts of Fe^{2+}, Mn^{2+} and Al^{3+} in their composition, no conclusive relationship exists between these and the disposition of OH^- groups, as derived from dehydration evidence. It is possible that the natural conditions of temperature and pressure and availability of water pertaining to the formation of chrysotile may have been the deciding factor here. It is believed that hydroxyl-content may have an influence on the texture of the fibre which may be silky, harsh, brittle or splintery. Many difficulties arise in attempting to correlate texture and the disposition of OH^- groups, but there are some common factors in the quantitative dehydration evidence of chrysotiles from the same regional source. For example, some distinction exists between chrysotiles from the Thetford massif, from the

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Russian Urals and from Southern Rhodesia, and subjectively these chrysotiles can be distinguished from each other on textural grounds.

SURFACE PROPERTIES OF ASBESTOS

A consideration of the elements of the chrysotile and amphibole structures leads immediately to the conclusion that the two groups of fibres must have totally different surface properties. Chrysotile has a predominant surface layer of hydroxyl sites connected to an adjacent inner layer of magnesium sites. These alkaline sites would be expected to exert a strong surface activity either by partial solution or by attraction of ions of opposite charge. In contrast amphibole asbestos has external bands of silica sites which are recognized as having a weakly acidic nature. Such sites, being highly insoluble, would be expected to exert a weak surface charge solely by attraction of suitable ions, comparable to the effect obtained with ordered silica surfaces, such as in quartz.

Fundamental studies of this subject have provided some valuable though limited information. The influence of electrolytes on the surface charge of asbestos fibre has been investigated in two ways. Pundsack[72] determined the isoelectric point of chrysotile by sedimentation methods, by increasing the alkalinity of suspensions of fine fibres until a floc formed and the suspension clarified. Later Martinez and Zucker applied a streaming potential technique to the measurement of the zeta potential of chrysotile.[73] They obtained values of about +100 mV for the zeta potential of chrysotile in neutral solutions, the isoelectric point being at pH 11·8, somewhat higher than the value obtained by Pundsack. Independent studies on amphibole fibres have given values of −10 mV for crocidolite and −20 mV for amosite in neutral solution. Isoelectric points have not been determined, but the zeta potential of these two fibres tends towards zero with increasing alkalinity of the solutions. There are considerable technical difficulties in measuring streaming potentials at high and low values of pH, since the high conductivities of the solutions cause a virtual short between the points at which potential is measured. Nevertheless the technique provides sufficient evidence to confirm theoretical suggestions about the surface charges of asbestos fibres.

The sedimentation behaviour of particles in aqueous suspension depends largely on their surface charge. The effect is paradoxical in that large sedimentation volumes occur where there is small repulsion of individual particles, while small volumes are due to the relatively large repulsion of particles. Where particles bear a strong charge, mutual repulsion prevents their coalescence and provides a virtual lubricating effect whereby particles slide over one another. Gravitational force causes the particles to move over each other until all available voids in the volume occupied by them have been filled. Sedimentation volume is then small and also dense. On the other hand where repulsive forces between particles are small, the particles will tend to touch at a limited number of points and form an open latticework with many voids. The sedimentation volume will be determined by the compactness or otherwise of the mechanical structure.

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With respect to asbestos fibres these observations are of considerable practical importance. For example the drainage properties of the asbestos–cement–water system depend on the type of asbestos incorporated. Chrysotiles, having typical small and dense sedimentation volumes, form with cement sediments which possess poor permeability to water, while the amphibole fibres in similar conditions form open networks of fibres, giving a relatively high porosity. The hydrophylic nature of chrysotile brings about a further complication, in that its hydroxylated surfaces undoubtedly form contiguous phases with the gels formed in the early stages of the hydration of cement particles. The drainage rates of asbestos–cement–water systems based on amphibole asbestos are some three to four times better than those based on chrysotile, a fact which has bearing on the speed of production of most types of asbestos–cement manufacturing machinery. It is a widespread practice to blend amphibole and chrysotile fibres in the manufacture of asbestos–cement products to ameliorate drainage problems. However it is not practical to use more than about 40 per cent of amphibole fibres in such blends, so that only a limited improvement in drainage can be achieved with these materials alone. If excessive amounts of amphibole fibres are incorporated in asbestos cement, the high wet bulk of the fibre leads to undesirable low densities in the product and a corresponding diminution in strength. Moreover in the manufacturing process each laminate wound on to the making roll would be insufficiently wet, since the asbestos–cement mix would be over-drained. This in turn would lead to lack of adhesion between the laminates.

Numerous attempts have been made to modify the surface properties of chrysotile asbestos, by surface-active agents and other organic absorbates. Generally, these are not as successful as might first appear. The density of hydroxyl groups at the surface of chrysotile is high and no more than a limited number of links with the relatively large molecules of typical surface-active agents, such as quarternary compounds and sulphonates, can be expected. The residue of unlinked hydroxyl groups must still exert a considerable anionic influence. Polyacrylamides have been suggested as being among the best flocculating agents for asbestos–cement slurries.[74] High-molecular-weight linear polymers that have two amide groups per carboxylic group are recommended. They act through absorption of amide groups at the surfaces of chrysotile fibres, and here the coverage of the surface by a relatively non-polar layer will be considerable.

From zeta-potential studies, Martinez has shown that inorganic polyvalent ions, such as are present in sodium silicate solutions, may be specific in altering the surface charge on chrysotile.[75] Sodium silicate solutions at concentrations of 10^{-3}–10^{-2} mole/litre produced a reversal from positive to negative at a pH of 10·9. This is taken to indicate that $(SiO_3)^{2-}$ is a surface-active ion for chrysotile since the reversal of polarity occurs at a pH below the normal isoelectric point. Sodium phosphate and sodium carbonate solutions bring about a reduction in the positive surface charge of chrysotile through absorption of the anions but do not produce a reversal of polarity. These findings have been applied to the

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treatment of chrysotile asbestos for manufacturing purposes. By milling the fibre in the presence of limited amounts of dilute sodium silicate solution, the drainage properties of this form of asbestos in asbestos–cement slurry can be improved. However, the presence of sodium silicate in such a system can introduce undesirable side-effects by accelerating the rate of hydration of the cement in the initial stages of manufacture and before the asbestos–cement product is formed.

Another obvious means of modifying the surface properties of chrysotile is to subject the fibre to a limited degree of heat treatment and drive off part of its chemically combined water. The aim is to reduce the constitutional water content by amounts up to 30 per cent, preferably by flash heating at 500–600°C.[76,77] The drainage properties of chrysotile in water are improved considerably by this treatment, but these must be offset against losses in tensile strength and reinforcement properties.

Although surface-active agents are not satisfactory modifiers for chrysotile in manufacturing processes, they have a use in another way. A piece of chrysotile ore immersed in a strong household detergent solution, and without any other disturbance, will in the course of time completely fiberize of its own volition to a mass of extremely finely divided fibres. Amphibole fibres do not respond to this treatment at all. The effect has been adapted to industrial use where it is desirable to produce aqueous dispersions of chrysotile of a 'fibro-colloidal' character from the relatively coarse commercial fibre. By wet milling the chrysotile fibre with surface-active agents, such as straight sodium soaps, fatty-acid sulphonates and more complex derivatives of these, extensive reduction of fibre diameters to values between 200 and 500 Å can be achieved.[78,79] Fine fibres such as these have applications in the manufacture of asbestos papers and felts.

While it could be said that fundamentally the surface characteristics of asbestos fibres are recognized and understood, there are many gaps in knowledge here. Most of the relevant physico-chemical studies have been orientated towards the properties of chrysotile in the asbestos–cement system, and a general study of the surface properties of all types and varieties of asbestos fibres is still wanting. With the increasing inclusion of asbestos in reinforced plastics, more information is needed about its interfacial effects in organic systems. Although chrysotile is widely used in conjunction with organic resins, it is said that these are not compatible with the highly polar surface of the fibre, while on the other hand they are compatible with the non-polar amphibole surface. The term compatibility, and the borderline between physico-chemical and chemical effects (which might destroy the fibre surface) remain to be defined.

Some aspects of the surface chemistry of asbestos fibres have already been discussed. Gas absorptiometric studies have yielded much information connected with the oxidation and thermal decomposition of asbestos, with the surface area of fibres and with their surface chemistry in gaseous systems.[61–63] The surface properties of both chrysotile and amphibole asbestos, referred to ammonia or nitrogen atmospheres, show many similarities. Generally the apparent surface area to ammonia is greater

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than that to nitrogen at normal temperatures. It is possible that NH_3 links to excess of OH^- sites at fibre surfaces with more than one ammonia molecule per site. At higher temperatures (400°C) the surface areas determined by either NH_3 or N_2 absorption are similar for each individual sample of fibre. This implies that the surface properties of all asbestos fibres may be modified by out-gassing at higher temperatures, although the mechanisms involved are different. By out-gassing crocidolite in oxygen all surface-absorbed water and chemically combined water (by proton ejection) is removed. Partial oxidation and removal of protons occur in amosite, and partial dehydroxylation occurs in chrysotile. Young and Healey[8] suggested that hollow tubes of chrysotile contained plugs of water which when removed at higher temperatures allowed equal absorption of both NH_3 and N_2. It would therefore appear that regardless of residual hydroxyl sites, profound modifications to the surface properties of asbestos fibres can be achieved by the removal of absorbed water at fibre surfaces. Such desorption is not necessarily irreversible.

An interesting outcome of gas-absorptiometric studies on crocidolite concerns its potential as a catalyst. Addison found that after oxidizing crocidolite at 450 or 650°C it could in turn be reduced with conversion to its Fe^{3+} content to Fe^{2+} or Fe^0 together with the expulsion of water :[63]

$$\text{at } 450°C,\quad 4Fe^{3+} + 2O^{2-} + 2H_2 \rightarrow 4Fe^{2+} + 2H_2O$$
$$\text{at } 615°C,\quad 2Fe^{3+} + 3O^{2-} + 3H_2 \rightarrow 2Fe^{0} + 3H_2O$$

Both these reactions involve removal of oxygen from the lattice, but if an oxygen atmosphere can be maintained around the crocidolite then the forward oxidation reaction (p. 32) and the reverse reduction can be maintained in equilibrium. Some independent experiments along these lines have shown that carbon monoxide and methane in mixtures with oxygen can be smoothly oxidized at temperatures of 500–600°C. Crocidolite does not however offer any advantage over other types of catalysts, such as platinized asbestos or transition-metal oxides, mainly because its threshold temperature for oxidation is too high. As a laboratory reagent, oxidized crocidolite may be more valuable than the conventional cupric oxide as a high surface-area oxidant. It has been used to detect the evolution of hydrogen from amosite and other amphiboles during their thermal decomposition in inert atmospheres.[60]

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I am indebted to the Directors of the Cape Asbestos Co. Ltd for permission to make use of unpublished work in the Company's records, and to Dr R. Gaze and Mr W. Benns for their comments on the construction of this monograph. Plate II, underground working at Thetford, is reproduced by kind permission of Asbestos Corporation Ltd. Plate IV*e*, end-on view of crocidolite, is reproduced by kind permission of Professor Dr O. E. Radczewski, Rhein-Westf. Technische Hochschule, Aachen. Plate IV*b*, end-on view of chrysotile, is taken from Maser, Rice and Klug (ref. 10), and is reproduced by kind permission of Dr Maser. Fig. 2, map of the Transvaal System in South Africa, is taken from *The Geology of South Africa*, by Alex. L. du Toit, third edition, 1954.

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