ASBESTOS

1. Introduction

Asbestos is a generic term referring to six types of naturally occurring mineral fibers that are or have been commercially exploited. These fibers belong to two mineral groups: serpentines and amphiboles. The serpentine group contains a single asbestiform variety: chrysotile. There are five asbestiform varieties of amphiboles: anthophyllite asbestos, grunerite asbestos (amosite), riebeckite asbestos (crocidolite), tremolite asbestos, and actinolite asbestos. Usually, the term asbestos is applied only to those varieties that have been commercially exploited (1,2). That does not preclude the occurrence of other asbestos-like minerals, however. Magnesioriebeckite with an asbestiform habit was

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mined in Bolivia and potassian winchite with an asbestiform habit was found in western Texas. Additionally, richterite asbestos has been synthesized in the laboratory (3).

The asbestos varieties share several properties: (*1*) they occur as bundles of fibers that can be easily separated from the host matrix or cleaved into thinner fibers (1,4); (*2*) the fibers exhibit high tensile strengths (1); (*3*) they show high length: diameter (aspect) ratios, with a minimum of 20 and up to 1000 (1,4); (*4*) they are sufficiently flexible to be spun; and (*5*) macroscopically, they resemble organic fibers such as cellulose (2,4). Since asbestos fibers are all silicates, they exhibit several other common properties, such as incombustibility, thermal stability, resistance to biodegradation, chemical inertia toward most chemicals, and low electrical conductivity. The usual definition of asbestos fiber excludes numerous other fibrous minerals that may possess an asbestiform habit but do not exhibit all of the properties of asbestos. A few examples of these fibrous minerals are sepiolite, erionite (rod-like and fibrous habits), and nemolite. Other minerals also may occasionally crystallize with a fibrous habit (3,4).

The mineralogical designations of the various asbestos fibers, their most common alternative designations, and the main sources of these fibers are reported in Table 1. The fractional breakdown of the recent world production of the various fiber types shows that the industrial applications of asbestos fibers have now shifted almost exclusively to chrysotile. Amosite and crocidolite are no longer being mined although some probably is still being sold from stock. Current use of amosite and crocidolite is estimated to be less than a few hundred tons annually. Actinolite asbestos, anthophyllite asbestos, and tremolite asbestos may be still mined in small amounts for local use; production probably is <100 tons annually.

Table 1. **Asbestos Fiber Production**

Mineral species[a]	Other designations	Major sources[b]	World production, 2000, %
chrysotile	white asbestos	Russia, Canada, China, Brazil, Kazakhstan, and Zimbabwe	>99%
cummingtonite-grunerite	amosite (brown asbestos)	deposits in South Africa	none
riebeckite	crocidolite (blue asbestos)	deposites in South Africa	none
anthophyllite		deposits in Bulgaria, Finland, India, South Africa, United States	insignificant
actinolite		deposits in South Africa and Taiwan	insignificant
tremolite		deposits in India, Italy, Korea, Pakistan, South Africa	insignificant

[a] Chrysotile is in the serpentine mineral group; all others are amphiboles.
[b] In order of production only for chrysotile.

2. History

Early uses of asbestos exploited the reinforcement and thermal properties of asbestos fibers. The first recorded application can be traced to Finland (~2500 BC), where anthophyllite from a local deposit was used to reinforce clay utensils and pottery (5). Numerous early references also can be found describing the use of asbestos fibers for the fabrication of lamp wicks and crematory clothing. Other applications of asbestos fibers in heat- or flame-resistant materials have been sporadically reported. At the end of the seventeenth century, Peter the Great of Russia initiated the fabrication of asbestos paper, using chrysotile fibers extracted from deposits in the Ural mountains. The use of asbestos fibers on a true industrial scale began in Italy early in the nineteenth century with the development of asbestos textiles (4,6). By the end of the nineteenth century, significant asbestos deposits had been identified throughout the world and their exploitation had begun in Canada (1878), South Africa (1893, 1908–1916), and the USSR (1885) (7).

From the beginning of the twentieth century, the demand for asbestos fibers grew in a spectacular fashion for numerous applications, in particular for thermal insulation (8). The development of the Hatschek machine in 1900 for the continuous fabrication of sheets from an asbestos–cement composite also opened an important field of industrial application for asbestos fibers as did the development of the automobile industry for asbestos brakes, clutches, and gaskets.

World War II supported the growth of asbestos fiber production for military applications, typically in thermal insulation and fire protection. Such applications were later extended into residential or industrial constructions for several decades following the war.

During the late 1960s and 1970s, the finding of health problems associated with long-term heavy exposure to airborne asbestos fibers led to a large reduction in the use of asbestos fibers. In most of the current applications, asbestos fibers are contained within a matrix, typically cement or organic resins.

The world production of asbestos fibers reached a maximum in 1977 of 4.8×10^6 tons, decreasing to 1.9×10^6 tons in 2000. The major producing countries of chrysotile asbestos are Russia (39%), Canada (18%), China (14%), Brazil (9%), Kazakhstan (7%), and Zimbabwe (6%). In 2000, active mining operations of asbestos fibers are found in 21 countries (9).

3. Geology and Fiber Morphology

The genesis of asbestos fibers as mineral deposits required certain conditions with regard to chemical composition, nucleation, and fiber growth; such conditions must have prevailed over a period sufficiently long and perturbation-free to allow a continuous growth of the silicate chains into fibrous structures (10). Some of the important geological or mineralogical features of the industrially significant asbestos fibers are summarized in Table 2. More emphasis is given to chrysotile in the following section owing to its total dominance in the industry over the years.

Table 2. **Geological Occurence of Asbestos Fibers**

	Chrysotile [12001-29-5]	Amosite [19172-73-5]	Crocidolite [12001-28-4]	Tremolite [14567-73-8]
mineral species	chrysotile	cummingtonite-grunerite	riebeckite	tremolite
structure	as veins in serpentine and mass fiber deposits	lamellar, coarse to fine, fibrous and asbestiform	fibrous in ironstones	long, prismatic, and fibrous aggregates
origin	alteration and metamorphism of basic igneous rocks rich in magnesium silicates	metamorphic	regional metamorphism	metamorphic
essential composition	hydrous silicates of magnesia	hydroxy silicate of Fe and Mg	hydroxy silicate of Na, Mg, and Fe	hydroxy silicate of Ca and Mg

Only three varieties of amphibole fibers will be discussed because (*1*) crocidolite and amosite were the only amphiboles with significant industrial uses in recent years; and (*2*) tremolite, although having essentially no industrial application, may be found as a contaminant in other fibers or in other industrial minerals (e.g., chrysotile and talc).

3.1. Chrysotile. Chrysotile belongs to the serpentine group of minerals, varieties of which are found in ultra basic rock formations located in many places in the world (11). Chrysotile accounts for only a small percentage of the minerals found in these rock types. Chrysotile fibers are found as veins in serpentines, in serpentinized ultramafic rocks, and in serpentinized dolomitic marbles. It has been suggested that the ultrabasic rocks, containing olivine, Mg-rich pyroxenes, and amphiboles are first altered by hydrothermal processes to form the serpentine minerals; in a later metamorphic event, the serpentines are partially redissolved and crystallized as chrysotile fibers. Clearly, the genesis of each chrysotile deposit must have involved specific features related to the composition of the precursor minerals, the stress and deformations in the host matrix, the water content, the temperature cycles, etc. Nonetheless, it is generally observed that the chemical composition of the fibrous phase is closely related to that of the surrounding rock matrix (12).

Growth of chrysotile fibers at right angles to the walls of cracks (cross-vein) in massive serpentine formations led to the most common type of chrysotile deposit. Most of the industrial chrysotile fibers are extracted from deposits where fiber lengths can reach several centimeters, but most often do not exceed 1 cm (12). Figure 1 illustrates the typical aspect of cross-vein chrysotile fibers (also called cross-fiber) separated from the host serpentine rock; a non-fibrous variety of serpentine, antigorite [12135-86-3], having a chemical composition nearly identical to that of chrysotile, is also pictured in Figure 1. In some occurrences, the relative motions (slipping) of blocks in the host rock, during or after fiber growth, lead to veins in which the fibers are inclined or parallel

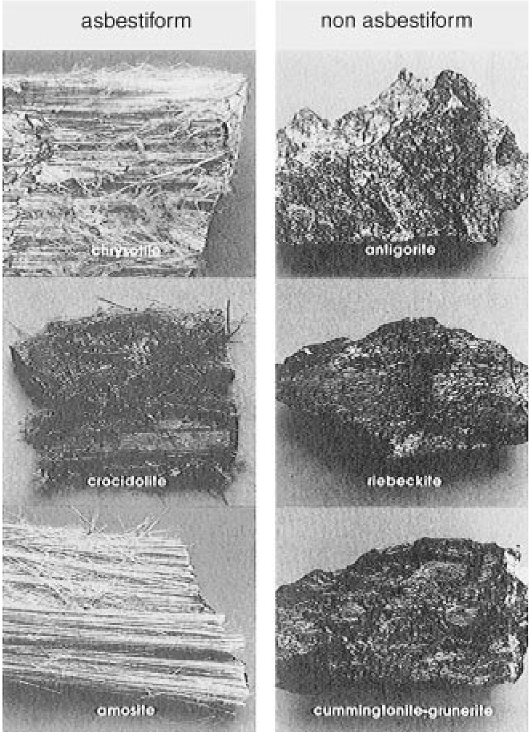


Fig. 1. Asbestos fibers (chrysotile, crocidolite, and amosite) as separated from host rock and their massive varieties (antigorite, riebeckite, cummingtonite- grunerite) (11). Courtesy of R. T. Vanderbilt Company, Inc.

to the vein axes (slip fibers). In still other local conditions, dispersed aggregates of short fibers are found with no preferential orientation; in such cases the fiber content of the rock can be very high, up to 50%. These are called mass-fiber deposits.

Chrysotile is a hydrated magnesium silicate and its stoichiometric chemical composition may be given as $Mg_3Si_2O_5(OH)_4$ [12001-29-5]. However, the geothermal processes that yield the chrysotile fiber formations usually involve the codeposition of various other minerals. These mineral contaminants comprise: brucite [$Mg(OH)_2$]; [1317-43-7], magnetite (Fe_3O_4); [1309-38-2], calcite ($CaCO_3$); [13397-26-7], dolomite [$(Mg,Ca)(CO_3)_2$]; [16389-88-1], chlorites [$(Mg,Al,Fe)_{12}Si_8O_{20}(OH)_{16}$], and talc [$Mg_6Si_8O_{20}(OH)_4$]; [14807-96-6]. Other iron-containing minerals may also be found in chrysotile, eg, pyroaurite, brugnatellite, and pyroxenes. In commercial fibers, dust particles from the host rock generated during the mining and milling processes are most inevitably present (3). Elemental analysis data for several chrysotiles and amphiboles are presented in Table 3.

Chrysotile fibers can be extremely thin, the unit fiber having an average diameter of $\sim$25 nm (0.025 μm). Industrial chrysotile fibers are aggregates of these unit fibers that usually exhibit diameters from 0.1 to 100 μm; their lengths range from a fraction of a millimeter to several centimeters, though most of the chrysotile fibers used are $<$1 cm.

Table 3. **Elemental Analysis of Asbestos Fibers**[a]

Variety and source	SiO_2 (silica)	FeO (ferrous oxide)	Fe_2O_3 (ferric oxide)	Al_2O_3 (alumina)	MgO (magnesia)	CaO (lime)	MnO (manganese oxide)	Na_2O (sodium oxide)	K_2O (potassium oxide)	H_2O, adsorbed	H_2O^+, combined
Chrysotile											
Quebec	40.2	1.0	0.5	2.9	39.9	1.1	0.1	0.1	0.1	0.8	13.4
Zimbabwe	39.7	0.7	0.3	3.2	40.3	1.1	0.3	0.1	0.1	0.6	12.2
Ural Mts.	38.1	1.3	1.4	5.0	37.7	2.2	0.1	0.1	0.1	0.8	11.1
Crocidolite											
Cape Province	50.9	20.5	16.9		1.1	1.5	0.1	6.2	0.2	0.2	2.2
Australia	52.8	14.9	18.6	0.2	4.6	1.1	trace	6.0	0.1	0.2	2.8
Bolivia	55.7	3.8	13.0	4.0	13.1	1.5	trace	6.9	0.4	trace	1.8
Amosite											
Transvaal	49.4	40.6	0.1		6.7	0.7	0.7	0.1	0.2	0.1	1.9
Tremolite											
Pakistan	55.1	2.0	0.3	1.1	25.7	11.5	0.1	0.3	0.2	3.5	0.2

[a] Ref. 13.

3.2. Amphiboles. The amphibole group of minerals is widely found throughout the earth's crust. Their chemical composition can vary widely. Of the amphiboles, only a few varieties have an asbestiform habit and the latter occur in relatively low quantities. The geological origin of amphibole asbestos fibers appears to be quite varied (3). In the case of the crocidolite deposit of South Africa (Transvaal), the amphibole fibers formed during secondary chemical reactions that took place as the banded ironstone host rock consolidated from a gel of iron hydroxide and colloidal silica. Crocidolite fiber veins formed, presumably with magnetite particles acting as nucleating agents. The presence of mechanical stress appears to be necessary for the formation of crocidolite. It appears that fibers form in places where there is shearing (slip fibers) or rock dialatium (cross fiber). One would not expect fibers to form in rock that is not mechanically disturbed. The amosite deposit found in similar rock formations is the result of a high temperature metamorphic process (3).

The chemical composition of amphiboles readily reflects the complexity of the environment in which they formed. The average chemical composition of amphibole minerals may be represented as

$$\begin{aligned} \mathrm{A_{0\text{-}1}, B_2C_5T_8O_{22}(OH, O, F, Cl)_2} \quad \text{where} \quad & \mathrm{A = Na, K} \\ & \mathrm{B = Na, Ca, Mg, Fe^{2+}, Mn, Li} \\ & \mathrm{C = Al, Fe^{2+}, Fe^{3+}, Ti, Mg, Mn, Cr} \\ & \mathrm{T = Si, Al} \end{aligned}$$

A, B, C each represent cationic sites within the crystal structure (2,4,10). From this generic representation, the chemical composition of the amphibole asbestos can be given as follows:.

Name	Composition	CAS Registry Number
grunerite (amosite)	$Na_2(Fe^{2+}, Mg)_3Fe^{3+}{}_2Si_8O_{22}(OH)_2$	[12172-73-5]
riebeckite (crocidolite)	$Na_2(Fe^{2+}, Mg)_3Fe^{3+}{}_2Si_8O_{22}(OH)_2$	[12001-28-4]
anthophyllite	$Mg_7Si_8O_{22}(OH)_2$	[17068-78-9]
tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	[14567-73-8]
actinolite	$Ca_2(Mg, Fe^{2+})_5Si_8O_{22}(OH)_2$	[12172-67-7]

From their respective compositions, the amphibole fibers can be viewed as a series of minerals in which one cation is progressively replaced by another at a given site. For example, tremolite and actinolite may be seen related; the magnesium in tremolite is partly replaced by divalent iron in the C position to yield actinolite. Similarly, in the cummingtonite–grunerite amphiboles, the substitution involves the replacement of magnesium in positions B and C by divalent iron (2,4). The change of designation from cummingtonite to grunerite is, by convention, at a Mg/Fe ratio of 0.5 (10).

The two most important amphibole asbestos minerals are amosite and crocidolite, and both are hydrated silicates of iron, magnesium, and sodium (crocidolite only). The appearance of these fibers and of the corresponding nonfibrous

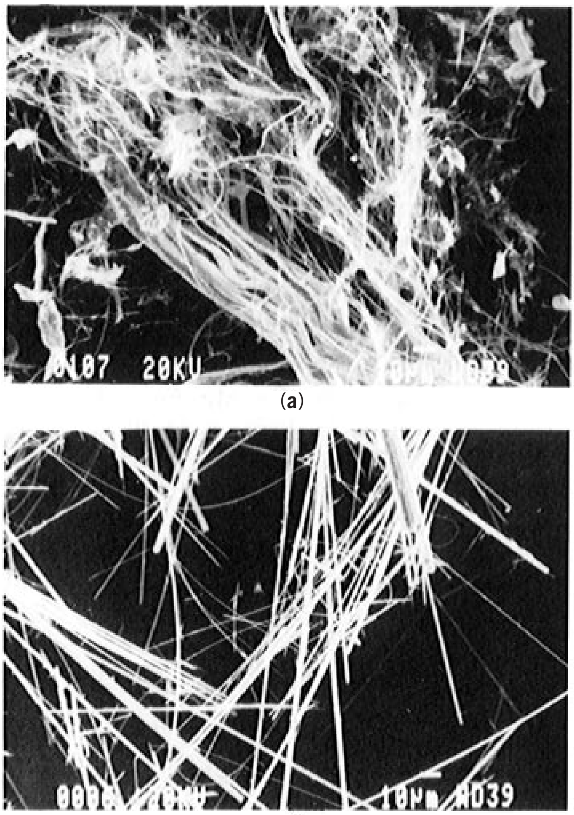


Fig. 2. Electron micrographs of asbestos fibers: (**a**) chrysotile; (**b**) crocidolite.

amphiboles is shown in Figure 1. Although the macroscopic visual aspect of clusters of various types of asbestos fibers is similar, significant differences between chrysotile and amphiboles appear at the microscopic level. Under the electron microscope, chrysotile fibers are seen as clusters of fibrils, often entangled, suggesting loosely bonded, flexible fibrils (Fig. 2a). Amphibole fibers, on the other hand, often appear individually, rather than in fiber bundles (Fig. 2b).

4. Crystal Structure of Asbestos Fibers

The microscopic and macroscopic properties of asbestos fibers stem from their intrinsic, and sometimes unique, crystalline features. As with all silicate minerals, the basic building blocks of asbestos fibers are the silicate tetrahedra that may occur as double chains $(Si_4O_{11})^{6-}$, as in the amphiboles, or in sheets $(Si_4O_{10})^{4-}$, as in chrysotile (4) (Fig. 3).

4.1. Chrysotile. In the case of chrysotile, an octahedral brucite layer having the formula $[Mg_6O_4(OH)_8]^{4-}$ is intercalated between each silicate tetrahedra sheet, as illustrated in Figure 4. The silicate and brucite layers share

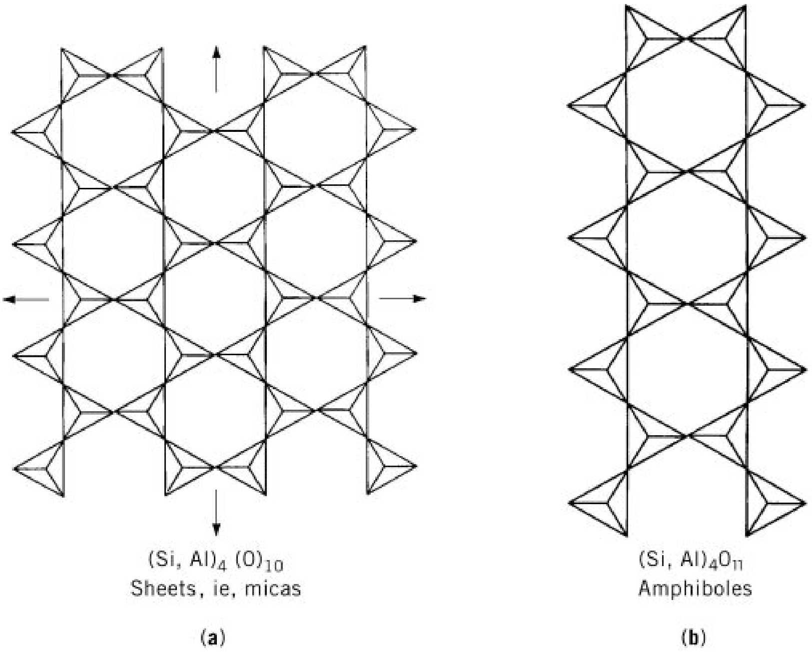


Fig. 3. Silicate backbones of chrysotile and amphiboles: (**a**) the sheet silicate structure of chrysotile, analogous to that of micas; (**b**) the double-chain silicate structure found in amphiboles (4). Courtesy of Oxford University Press.

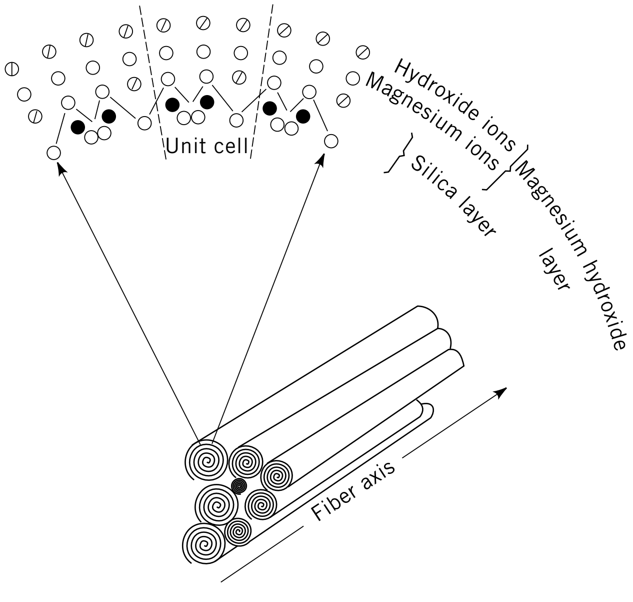


Fig. 4. Microscopic structure of chrysotile fibers (3). Reprinted with permission.

oxygen atoms that would normally be separated by distances of 0.305 nm in the silicate layer and 0.342 nm in the brucite layer (4). This mismatch of O–O distances induces a curvature of the sheets, the ideal radius of which has been calculated as 8.8 nm (14). The curvature of the sheets propagates along a preferred axis leading to the formation of the tubular structure found in chrysotile. The concentric sheets forming the fibers have a curvature radius from 2.5 to 3.0 nm for the internal layers up to ~25 nm for the external layers, yielding unit fibers (fibrils) with external diameters ranging between 20 and 50 nm (15). Electron microscopy studies (15) have also shown that, in the unit chrysotile fiber cross section, the layers may appear in a concentric or spiral arrangement.

The stacking of the tetrahedral and octahedral sheets in the chrysotile structure has been shown to yield three types of chrysotile fibers (3,4):

clino-chrysotile: monoclinic stacking of the layers, x parallel to fiber axis, most abundant form.

ortho-chrysotile: orthorhombic stacking of the layers, x parallel to fiber axis.

para-chrysotile: two layer structure, 180° rotation of two-layer structures, y parallel to fiber axis.

The extent of substitution of magnesium and silicon by other cations in the chrysotile structure is limited by the structural strain that would result from replacement with ions having inappropriate radii. In the octahedral layer (brucite), magnesium can be substituted by several divalent ions, Fe^{2+}, Mn^{2+}, or Ni^{2+}. In the tetrahedral layer, silicon may be replaced by or Al^{3+} or rarely Fe^{3+}. Most of the other elements that are rarely found in vein fiber samples, or in industrial asbestos fibers, are associated with interstitial mineral phases. Typical compositions of bulk chrysotile fibers from different locations are given in Table 3.

4.2. Amphiboles. The crystalline structure common to amphibole minerals consists of two ribbons of silicate tetrahedra placed back to back as shown in Figure 5. The plane of anionic valency sites created by this double ribbon arrangement is neutralized by the metal cations. The crystal structure has 16 cationic sites of four different types; these sites can host a large variety of metal cations without substantial disruption of the lattice (see Section 3.2 and Fig. 5).

In contrast to chrysotile fibers, the atomic crystal structure of amphiboles does not inherently lead to fiber formation. The formation of asbestiform amphiboles must result from multiple nucleation and specific growth conditions. The difference between asbestiform and massive amphibole minerals is obvious on the macroscopic scale, although the crystalline structures of the two varieties do not exhibit substantial differences. The asbestiform amphiboles tend to have a larger number of crystal defects (Wadsley defects and twinning and chain width disorder) than the nonasbestiform varieties. The frequency and width of these defects vary with amphibole type (3,10). Amphibole minerals, in general, are characterized by prismatic cleavage planes parallel to the c axis that intersect at an angle of ~56°. Hence, in the crushing of massive, nonfibrous amphiboles, microscopic fragments are found having the appearance of asbestos fibers. However, the statistical average of their aspect ratio is considerably lower than that of the asbestiform amphiboles.

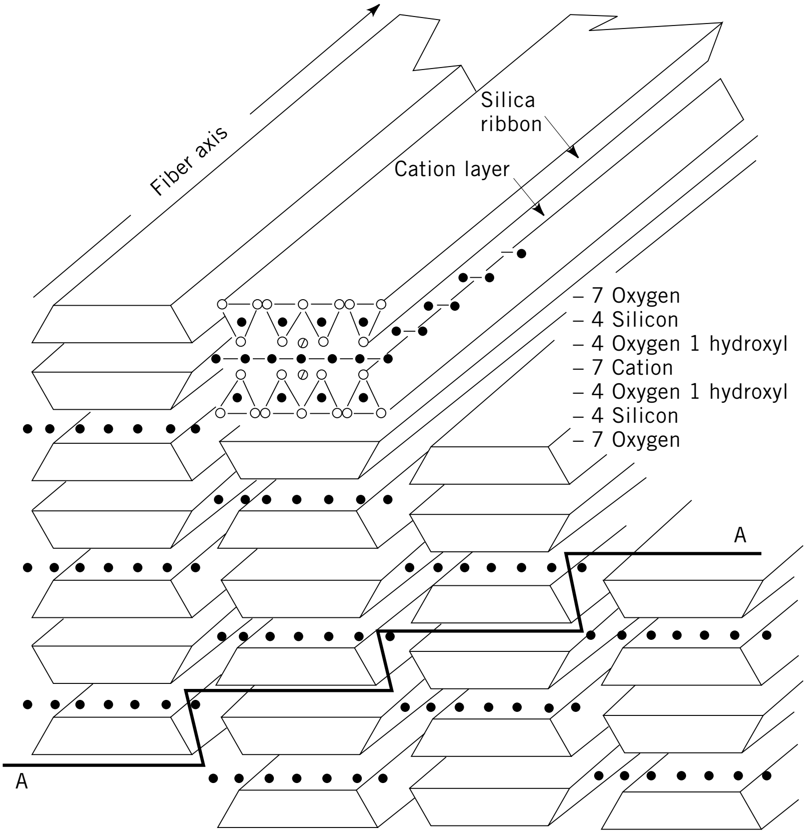


Fig. 5. Microscopic structure of amphibole fibers (22). Reprinted with permission.

5. Properties of Asbestos Fibers

Asbestos fibers used in most industrial applications consist of aggregates of smaller units (fibrils), which is most evident in chrysotile that exhibits an inherent, well-defined unit fiber. Diameters of fiber bundles in bulk industrial samples may be in the millimeter range in some cases; fiber bundle lengths may be several millimeters to 10 cm or more.

The mechanical processes employed to extract the fibers from the host matrix, or to further separate (defiberize, open) the aggregates, can impart significant morphological alterations to the resulting fibers. Typically, microscopic observations on mechanically opened fibers reveal fiber bends and kinks, partial separation of aggregates, fiber end-splitting, etc. The resulting product thus exhibits a wide variety of morphological features, some of which can be seen in Figure 2.

Morphological variances occur more frequently with chrysotile than amphiboles. The crystal structure of chrysotile, its higher flexibility, and interfibril adhesion (3) allow for a variety of intermediate shapes when fiber aggregates are subjected to mechanical shear. Amphibole fibers are generally more brittle and accommodate less morphological deformation during mechanical treatment.

5.1. Fiber Length Distribution. For industrial applications, the fiber length and length distribution are of primary importance because they are closely related to the performance of the fibers in matrix reinforcement. Various fiber classification methods have thus been devised. Representative distributions of fiber lengths and diameters can be obtained through measurement and statistical analysis of microphotographs (15); fiber length distributions have also been obtained from automated optical analyzers (16). Typical fiber length distributions obtained from these approaches are illustrated in Figure 6 for chrysotile fibers. As in the cases shown there, industrial asbestos fiber samples usually contain a rather broad distribution of fiber lengths.

5.2. Physicochemical Properties. The industrial applications of chrysotile fibers take advantage of a combination of properties: fibrous morphology, high tensile strength, resistance to heat and corrosion, low electrical

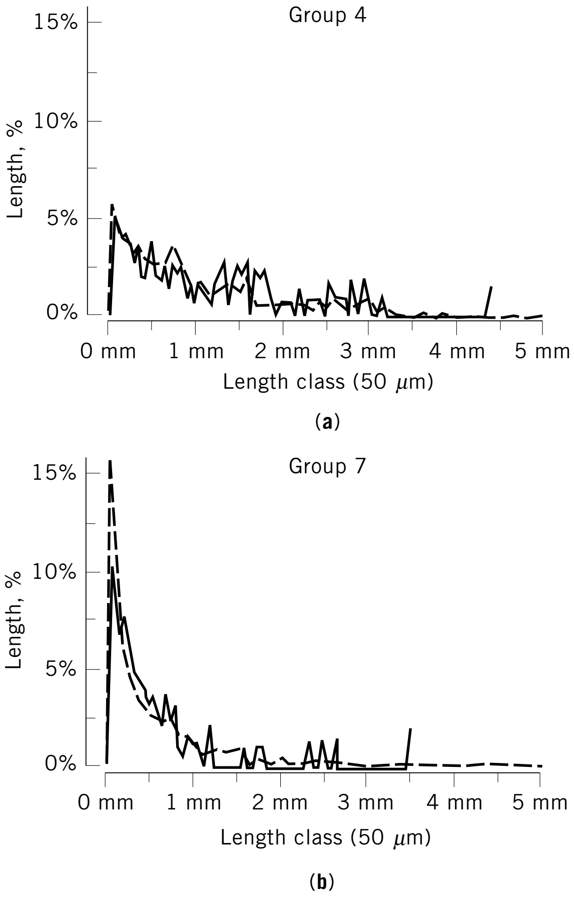


Fig. 6. Fiber length distribution for (**a**) a long sample (group 4) and (**b**) a short sample (group 7) of chrysotile; successive length classes separated by 50 μm. —, Automated measurement; —, microphotographic measurement.

Table 4. **Physical and Chemical Properties of Asbestos Fibers**

Property	Chrysotile	Amosite	Crocidolite	Tremolite
color	usually white to grayish green; may have tan coloration	yellowish gray to dark brown	cobalt blue to lavender blue	gray-white, green, yellow, blue
luster	silky	vitreous to pearly	silky to dull	silky
hardness, Mohs	2.5–4.0	5.5–6.0	4.0	5.5
specific gravity	2.4–2.6	3.1–3.25	3.2–3.3	2.9–3.2
optical properties	biaxial positive parallel extinction	biaxial positive parallel extinction	biaxial negative oblique extinction	biaxial negative oblique extinction
refractive index	1.53–1.56	1.63–1.73	1.65–1.72	1.60–1.64
flexibility	high	fair	fair to good	poor, generally brittle
texture	silky, soft to harsh	coarse but somewhat pliable	soft to harsh	generally harsh
spinnability	very good	fair	fair	poor
tensile strength, MPa[a]	1100–4400	1500–2600	1400–4600	<500
resistance to:				
acids	weak, undergoes fairly rapid attack	fair, slowly attacked	good	good
alkalies	very good	good	good	good
surface charge, mV (zeta potential)	+13.6 to +54[b]	−20 to −40	−32	
decomposition temperature, °C	600–850	600–900	400–900	950–1040
residual products	forsterite, silica, eventually enstatite	Fe and Mg pyroxenes, magnetite, hematite, silica	Na and Fe pyroxenes, hematite, silica	Ca, Mg, and Fe pyroxenes, silica

[a] To convert MPa to psi, multiply by 145.

[b] Chrysotile fibers tend to become negative after weathering and/or leaching.

conductivity, and high friction coefficient. In many applications, the surface properties of the fibers also play an important role; in such cases, a distinction between chrysotile and amphiboles can be observed because of differences in their chemical composition and surface microstructure. Technologically relevant physical and chemical properties of asbestos fibers are given in Table 4.

Thermal Behavior. Asbestos fiber minerals are hydrated silicates so their behavior as a function of temperature is related first to dehydration (or dehydroxylation) reactions. In the case of chrysotile, the crystalline structure is stable up to ∼550°C [depending on the heating period (17)], where the dehydroxylation of the brucite layer begins. This process is completed near 750°C and is characterized by a total weight loss of 13%. The resulting magnesium silicate recrystallizes to form forsterite and silica in the temperature range 800–850°C, as an exothermic process. The weight loss as a function of heating temperature [thermogravimetry (tga)] and the reaction heats [differential thermal analysis (dta)] are illustrated for chrysotile in Figure 7a. The strongly endothermic dehydration process enhances the high temperature thermal insulation properties of chrysotile asbestos.

The behavior of amphibole fibers under continuous heating is similar to that observed with chrysotile, although the temperatures of dehydroxylation and recrystallization processes are different. The amphiboles have a lower water (hydroxyl) content and their dehydroxylation reaction begins between 400 and 600°C, depending on the amphibole type; this reaction leads to a weight loss of ~2%. The latter is illustrated in Figure 7b, together with a dta recording of the associated thermal events. The products resulting from the thermal decomposition of the amphiboles are pyroxenes, magnetite, hematite, and silica.

In the presence of oxygen, the thermal decomposition of amphiboles is associated with an oxidation of divalent iron to trivalent iron, which may lead to an increase in the sample weight. The oxidation process also induces an obvious color alteration: The fibers acquire the characteristic ferric oxide color.

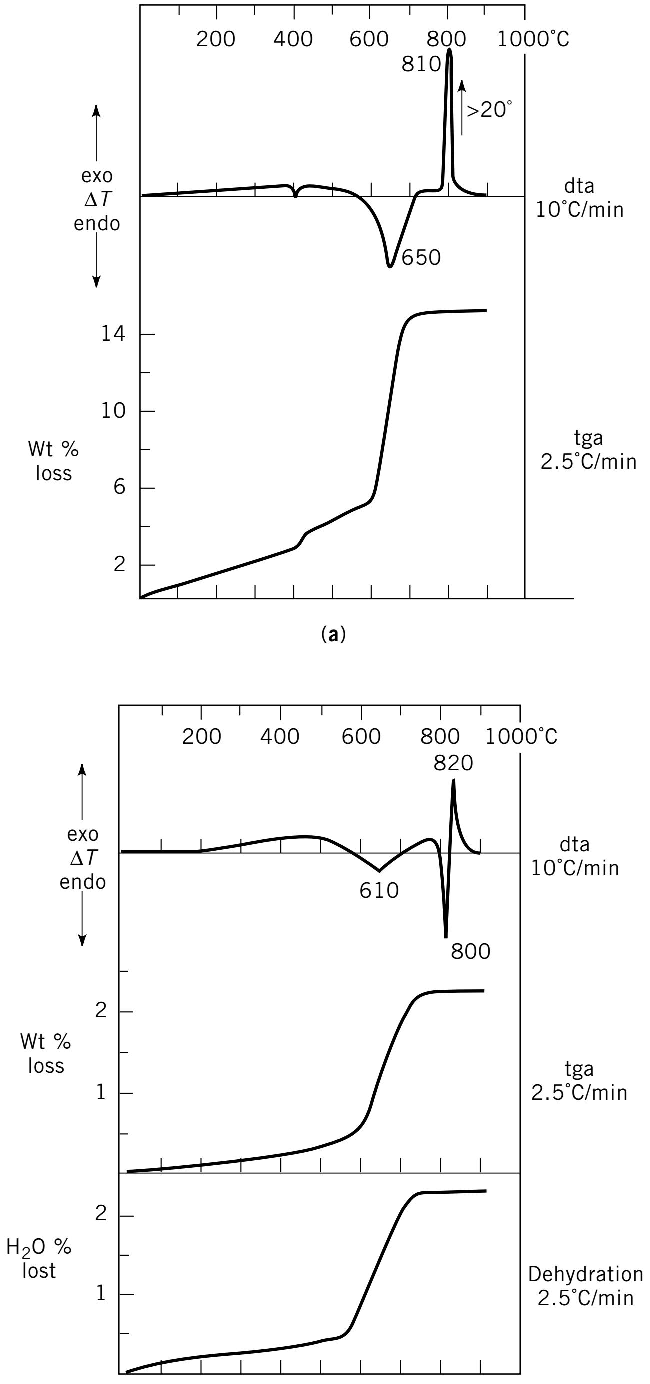
Asbestos fibers, in particular chrysotile fibers, can undergo substantial thermal degradation during mechanical grinding. In high energy attrition equipment, such as ball mills, the high localized impact energies can cause the crystalline structure to become amorphous, which is particularly true for dry milling or milling in organic solvents. However, milling in aqueous slurries is less detrimental, water offering some protection against high impact degradation (18).

Tensile Strength. The inherent tensile strength of a single asbestos fiber, based on the strength of Si–O–Si bonds in the silicate chain, should be near 10 GPa (1.45×10^6 psi) (19). However, industrial fibers exhibit substantially lower values, because of the presence of various types of structural or chemical defects.

The measured tensile strength of chrysotile fibers has been reported in the range 1.1–4.4 GPa (160,000–640,000 psi). The accurate determination of this parameter is difficult since the measurement performed on a fiber aggregate is influenced by interfibril adhesion, discontinuities in some of the unit fibers, mineral inclusions, etc. Consequently, higher tensile strength results are obtained for measurements done on short and thin fibers (20,21). The tensile strengths of amosite and crocidolite are comparable to that of chrysotile. With amphiboles, the tensile strength is highly influenced by the iron content since iron–oxygen bonds located in the fiber axes, particularly those involving trivalent Fe, are particularly strong. The trend observed of increasing tensile strength of amphiboles from tremolite, to amosite, to crocidolite is directly related to the iron content of these fibers (22).

The variation in tensile strength of asbestos fibers as a function of temperature also sharply distinguishes chrysotile and amphiboles. Chrysotile retains (and even slightly increases) its tensile strength up to 500°C, until the dehydroxylation reaction begins; it drops sharply at higher temperatures. Amphiboles, on the other hand, exhibit a decreasing tensile strength beginning at ~200°C. For example, at 350°C, crocidolite has lost 50% of its initial tensile strength (22).

Asbestos Fibers in Aqueous Media. Although asbestos fibers cannot be viewed as water-soluble silicates, prolonged exposure of chrysotile or amphiboles to water (especially at high temperature) leads to slow progressive leaching of



(**a**)

(**b**)

Fig. 7. Thermal analysis curves for asbestos: (**a**) chrysotile; (**b**) crocidolite (in inert atmosphere) (3). Reprinted with permission.

both their metal and silicate components (23). In the case of chrysotile fibers (in a given amount of water), the brucite layer will, fairly rapidly, dissolve in part, with concomitant increase in the pH of the solution. The equilibrium pH value for an aqueous chrysotile slurry reaches 10.0–10.5. Free brucite, present as contaminant in the fibers, also contributes to the pH increase.

In contact with solutions of mineral acids, organic acids, or magnesium complexing agents, the rate of dissolution of the brucite layers is increased. When carried out to the extreme, the leaching of magnesium leads to a weight loss of 58%. The residual silica is largely amorphous and, although the fibers retain an apparent fibrous morphology, their mechanical resistance is drastically reduced.

The dispersion of amphiboles in concentrated HCl solutions also leads to partial leaching, the rate of which depends on the metal cations present. With crocidolite, only small amounts of magnesium and sodium are extracted in these conditions, whereas amosite liberates substantial quantities of iron and magnesium. Overall, tremolite appears to exhibit the highest resistance to acid leaching (3).

On the other hand, both chrysotile and the amphiboles exhibit a high degree of chemical inertia toward strong alkalies over extended periods. At high temperatures, reactions with alkalies [NaOH, KOH, $Ca(OH)_2$] become significant over relatively short periods; eg, crocidolite was reported to be attacked by potassium hydroxide >100°C (23).

Other Bulk Physical Properties. The hardness of asbestos fibers is comparable to that of other crystalline or glassy silicates. Compared to glass fibers, amphiboles have similar hardness values, while chrysotile shows lower hardness values (22).

The friction coefficients of asbestos fibers are also different for chrysotile and amphiboles (when measured against the same material). Compared to glass fibers, the friction coefficients decrease in the order: chrysotile, amphiboles, glass fibers.

The high electrical resistivity of asbestos fibers is well known and has been widely exploited in electrical insulation applications. In general, the resistivity of chrysotile is lower than that of the amphiboles, particularly in high humidity environments because of the availability of soluble ions. For example, the electrical resistivity of chrysotile decreases from 1 to 2100 MΩ/cm in a dry environment to values of 0.01–0.4 MΩ/cm at 91% relative humidity. Amphiboles, on the other hand, exhibit resistivity between 8000 and 900,000 Ω/cm.

With respect to magnetic properties, the intrinsic magnetic susceptibility of pure chrysotile is very weak. However, the presence of associated minerals such as magnetite, as well as substitution ions (Fe, Mn), increases the magnetic susceptibility to values $\sim 1.9–3.5 \times 10^{-6}$/g Oe. With amphiboles, the magnetic susceptibility is much higher, mainly because of the high iron content; typically, amosite and crocidolite exhibit susceptibility values of $69–71 \times 10^{-6}$/g Oe (24).

5.3. Surface Properties. *Surface Area.* The specific surface area of industrial asbestos fibers obviously depends on the extent of their defiberization (opening), and is usually between 1 and 30 m^2/g. As measured by BET (Brunauer, Emmett, and Teller) nitrogen adsorption, chrysotile fibers exhibit surface areas between 15 and 30 m^2/g. With regard to amphibole fibers, surface areas of

1.8–9 m^2/g have been reported for crocidolite and 1.3–5.5 m^2/g for amosite (25). Such a difference originates, in part, in the relative sizes of the unit fibers of chrysotile and the amphiboles; however, the results also reflect the ability of nitrogen molecules to diffuse between the unit fibers of a larger aggregate. In relation to magnesium acid leaching of chrysotile discussed earlier, the surface area of an amorphous silica resulting from extensive acid leaching may reach 450 m^2/g (26).

Also, the adsorption of anionic or neutral surfactants on chrysotile fibers in aqueous dispersions enhances fiber separation, with a concomitant increase of surface area (27). Such effects have not been reported for amphibole fibers.

Surface Charge in Aqueous Media. Because of dissolution–ionization effects, the surface of asbestos fibers in aqueous dispersions adopts an electrostatic charge. In the case of chrysotile, partial dissolution of the brucite layer leads to a positive surface charge (or potential), which is strongly influenced by the solution pH. The isoelectric point of chrysotile (pH of zero surface charge) has been reported as 11.8. In the case of amphibole fibers, the surface charge seems dominated by the silica component, and is generally observed to be negative, increasing toward 0 as the pH is decreased. Since the progressive leaching of magnesium from the external brucite layer of chrysotile gradually exposes silica, the surface potential rapidly decreases early in the leaching reaction (3).

Adsorption and Surface Chemical Grafting. As with silica and many other silicate minerals, the surface of asbestos fibers exhibits a significant chemical reactivity. In particular, the highly polar surface of chrysotile fibers promotes adsorption (physi- or chemisorption) of various types of organic or inorganic substances (23). Moreover, specific chemical reactions can be performed with the surface functional groups (OH groups from brucite or exposed silica).

The chemical reaction of coupling agents, such as organosilane compounds, on chrysotile yields fibers with a highly hydrophobic surface. Through an adequate choice of coupling agents (organosilanes or others), the fiber matrix interactions in composite materials can thus be optimized (28). Surface chemical modifications can be carried out in fiber slurries or through gas–solid reactions; eg, the gas-phase reaction of $POCl_3$ with chrysotile, leads to a surface coverage with insoluble magnesium phosphate (29). The surface properties and reactivity of chrysotile fibers can also be modified by cationic substitution, eg, replacing magnesium by aluminum (30) or other metal cations (31).

6. Analytical Methods and Identification of Asbestos Fibers

The identification of asbestos fibers can be performed through morphological examination, together with specific analytical methods to obtain the mineral composition and structure. Morphological characterization in itself usually does not constitute a reliable identification criterion (1). Hence, microscopic examination methods and other analytical approaches are usually combined.

6.1. Microscopic Methods. The use of microscopic methods is preferred in cases where limited quantities of sample are available, typically in analyzing fibers recovered from sampling of airborne dust. With fibers having lengths in excess of 5 μm, optical microscopy with light polarization (polarizing light microscopy) has proven a very powerful technique. The optical properties of the different types of asbestos fibers, combined with information on fiber shapes, enable positive identification of all varieties of asbestos fibers. This identification can be carried out even when the fibers are mixed with their nonfibrous analogue or with various other materials (32). Often, refractive index, color, pleochroism, birefringence, orientation, etc cannot be measured accurately, thus other methods of analysis must be employed.

Asbestos fiber identification also can be achieved through transmission or scanning electron microscopy (TEM, SEM) techniques that are especially useful with very short fibers, or with extremely small samples (see MICROSCOPY). With appropriate peripheral instrumentation, these techniques can yield the elemental composition of the fibers using energy dispersive X-ray fluorescence, and the crystal structure from selected area electron diffraction (SAED). Both chemical composition and crystal structures are required for positive identification.

6.2. Instrumental Methods for Bulk Samples. With bulk fiber samples, or samples of materials containing significant amounts of asbestos fibers, a number of other instrumental analytical methods can be used to help in the identification of asbestos fibers. The elemental characterization of minerals can be accomplished using methods, such as X-ray fluorescence (XRF) and X-ray photoelectron spectroscopy (XPS). The X-ray diffraction technique (XRD) enables the analyst to identify the crystal structure of the various types of asbestos fibers, as well as the nature of other minerals associated with the fibers (12,33,34).

Thermoanalytical methods (DTA, TGA) often aid in the identification of the type of asbestos fibers (Fig. 7). For example, the strong exotherm observed with chrysotile at 830°C can be used as a routine indicator for determining the chrysotile content of talc (3,8). Thermal methods also are useful for determining certain mineral contaminants of asbestos fibers, eg, brucite and calcite in chrysotile.

Infrared (IR) spectroscopy also is used to analyze samples containing asbestos fibers. Absorption bands in the IR spectrum associated with asbestos fibers are in the 3600–3700-cm^{-1} range (specific hydroxyl bands) and the 600–800 and 900–1200-cm^{-1} ranges (specific absorption bands for various silicate minerals) (3). Because other minerals, including nonasbestiform amphiboles, also absorb within these wavelength bands, IR spectroscopy is not always definitive for identifying asbestos.

Each of these microscopic and bulk methods of analysis provide clues to resolve the identity of the asbestos type. As noted earlier, however, both crystallographic and elemental data are required for a positive identification.

7. Production

A breakout, by major producing countries, of the world asbestos production is shown from 1920 to 2000 in Table 5 and total world production from 1920 to 2000 shown in Figure 8. During the early 1930s, there was a brief period of stagnation in world asbestos production, much of which can be attributed to reduced consumption associated with the economic depression in the United States. At that time, Canada was the major producing country and was highly dependent on U.S. markets for sales. By 1935, production began to increase slowly until the

Table 5. **World Production of Asbestos by Principal Producing Countries, 1920–2000[a,b], tons**

Country	1920	1930	1940	1950	1960	1970	1980	1990	2000
Brazil	—	—	454	844	3,538	16,329	169,173	205,000	170,000
Canada	146,999	199,255	284,406	794,100	1,014,647	1,507,420	1,323,053	725,000	340,000
China	5	286	18,157	—	81,647	172,365	131,700	221,000	260,000
South Africa	5,853	15,868	22,543	79,300	159,544	290,318	277,734	146,000	18,909
U.S.S.R.[c]	—	49,063	—	217,725	598,743	1,065,943	2,070,000	2,400,000	875,000
United States (sold or used by producers)	1,356	3,491	16,509	38,496	41,026	113,683	80,079	W	5,260
Zimbabwe	15,491	31,080	46,093	64,888	121,529	79,832	250,949	161,000	110,000
Other	5,296	7,957	39,838	94,648	189,326	244,109	397,312	152,000	120,831
Total	175,000	307,000	428,000	1,290,000	2,210,000	3,490,000	4,7000,000	4,010,000	1,900,000

[a] World totals, U.S. data, and estimated data are rounded to three significant digits; may not add to totals shown.

[b] W. Withheld. — Zero.

[c] Soviet Republics combined, 1930 to 1990; Russia, 1920; Russia (750,000 tons) and Kazakhstan (125,000 tons), 2000.

Source: U.S. Geological Survey and U.S. Bureau of Mines Minerals Yearbook chapters on asbestos

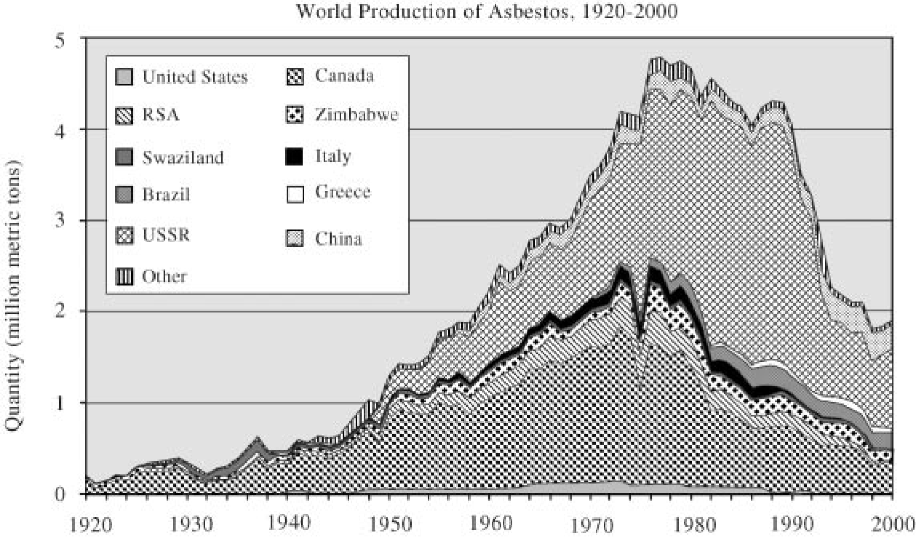


Fig. 8. World production of asbestos, 1920–2000.

onset of World War II. Canada accounted for the bulk of the increased production tonnage. During World War II, production declined in most regions of the world except Canada, and southern Africa. United States demands absorbed much of the increased production from these regions during the war. Following World War II, world production increased again, fueled by expanding economies, first in the United States and elsewhere later. However, growing opposition to the use of asbestos, which began in earnest in the early 1970s, soon brought this growth to a halt. After 1977, there was a downturn in world production and consumption. In the United States, asbestos regulations became increasingly strict with sizable reductions in permissible exposure limits being enacted. Liability also became a major issue. Companies that mined asbestos and those that manufactured asbestos products faced an increasing number of class-action lawsuits and had difficulties obtaining liability insurance. Compounding the problem was the slow shift to asbestos substitutes or alternative products [ie, ductile iron or poly(vinyl chloride) (PVC) pipe instead of asbestos-cement pipe] in response to public demand. As a result, U.S. consumption peaked in 1973 at ~801,000 tons. World production and consumption peaked at ~4.8×10^6 tons in 1977. In 2000, U.S. consumption was 14,600 tons and world production was 1.9×10^6 tons.

Shifts in production by the main producing countries occurred during this time. Canada was the dominant producer during the first half of the century. By 1980, the former Soviet Union had become, and still remains, the largest producing region. Brazil, China, South Africa, and Zimbabwe also rose from relatively obscurity to become major asbestos producers. Current production has declined in all major producing countries except China due to the opposition to the use of asbestos. Brazil, Canada, China, the former Soviet Union republics of Russia and Kazakhstan, and Zimbabwe now account for >90% of the world production (9). Most of China's production, as well as the limited production of many other countries, is used in local industrial applications. Essentially all production is now chrysotile. Production of amosite and crocidolite ceased in the mid-1990s. Small amounts of actinolite asbestos, anthophyllite asbestos, and tremolite asbestos probably are produced for local use in a few countries such as India, Pakistan, and Turkey.

8. Mining and Milling Technologies

The finding and mapping of chrysotile asbestos ore deposits usually relies on magnetometric surveys largely because magnetite is associated with asbestos deposits, except in the case of ore bodies located in sedimentary formations. As in other mining operations, core drilling is used for a precise evaluation of the grade and volume of the ore body (35).

The choice of a particular mining method depends on a number of parameters, typically the physical properties of the host matrix, the fiber content of the ore, the amount of sterile materials, the presence of contaminants, and the extent of potential fiber degradation during the various mining operations (36). Most of the asbestos mining operations are of the open pit type, using bench drilling techniques.

The fiber extraction (milling) process must be chosen so as to optimize recovery of the fibers in the ore, while minimizing reduction of fiber length. Since the asbestos fibers have a chemical composition similar to that of the host rock, the separation processes must rely on differences in the physical properties between the fibers and the host rock rather than on differences in their chemical properties (36).

In dry milling operations, which are currently the most widely used, the ore is first crushed to a nominal size and then dried (Fig. 9). Fiber extraction then begins through a series of crushing operations, each followed by a vacuum aspiration of the ore running on a vibrating screen. On the latter, the fibers released from the ore have a tendency to move to the surface and, because of their aerodynamic properties, they can be readily collected into a vacuum system. The fibers recovered from consecutive vibrating screens are brought to cyclone separators, and the air is filtered to remove the finer suspended fibers.

Generally, the consecutive crushing–aspiration steps liberate fibers that increasingly shorter. Longer fibers in wide veins are easier to release and thus are recovered in the early phases of the milling operation. In this way, a primary classification, or grading of the fibers can be achieved. Various secondary processing systems may be used to further separate the fiber aggregates and to remove nonfibrous mineral dust. All fiber extraction and classification operations are usually carried out under negative pressure to minimize airborne dust in the working environment.

Wet milling operations, where the asbestos is dispersed in water and not dried until after the final separation process is completed, offer advantages in dust control and the separation of mineral contaminants from the fiber product. However, wet process technology currently is used in only a few small-scale milling operations. With the decline of the asbestos market since the 1970s, the economics of constructing new wet processing facilities, or even dry milling facilities, was not favorable. For the most part, any new capacity that came on

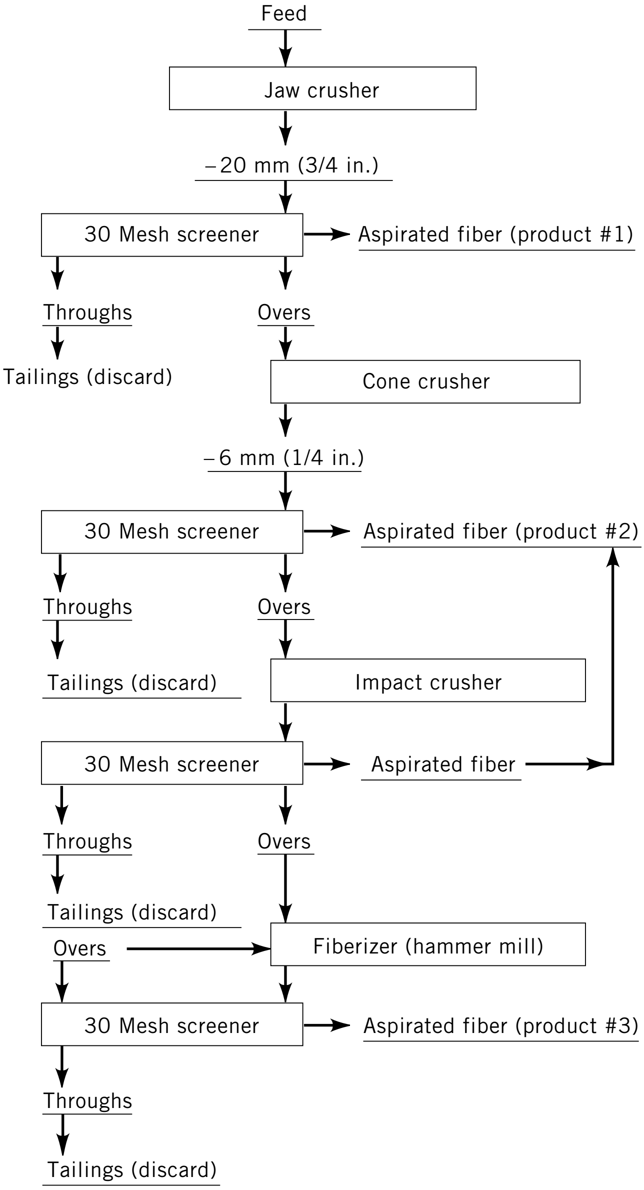


Fig. 9. Schematic of a typical asbestos milling flowline (30 mesh = 590 μm) (35).

line worldwide, with the possible exception of China, in the past 20 years has involved the reopening or expansion of old milling operations.

9. Fiber Classification and Standard Testing Methods

In the beneficiation of asbestos fibers, several parameters are considered critically important and are used as standard evaluation criteria (37): length (or length distribution), degree of opening and surface area, performance in cement reinforcement, and dust and granule content. The measurement of fiber length is important since the length determines the product category in which the fibers will be used and, to a large extent, their commercial value.

9.1. Dry Classification Method.

The most widely accepted method for chrysotile fiber length characterization in the industry is the Quebec Standard (QS), test, which is a dry sieving method (on vibrating screens) that enables the fractionation of an asbestos fiber sample into four fractions of decreasing sizes (>2 mesh, <2 and ≥4 mesh, <4 and ≥10 mesh, and <10 mesh, with mesh defined as the number of openings per linear inch). This standard test has been used as a basis for developing a grade system comprising nine main fiber grades. The grading system identifies the longest fibers as grade 1 and the shortest as grade 9. Grades 1 and 2 designate crude asbestos fibers that are hand picked and essentially contain large clusters or aggregates of fibers. Grade 1 fibers are those with lengths $\geq \frac{3}{4}$ in. (1.9 cm). Grade 2 fibers are those with lengths $\frac{3}{4}$ in. and $\geq \frac{3}{8}$ in. (0.95 cm).

Fiber grades between 3 and 9 (decreasing lengths) are known as milled asbestos fibers and represent most of the production. The fiber grades 3–7 are determined using the QS test, whereas grades 8 and 9, containing very short fibers, are usually determined according to their bulk densities.

Other fiber classification schemes have been devised for chrysotile fibers, but historically the QS grade system has been used as a reference; other classification schemes usually have correspondence scales for conversion to the QS values. Amosite can be classified according to the QS grade system, but crocidolite requires a different scheme mainly due to the harshness of these fibers.

9.2. Wet Classification Method.

A second industrially important fiber length evaluation technique is the Bauer–McNett (BMN) classification. In this method, a fiber slurry is circulated through a series of four grids with decreasing opening size (positioned vertically), thus yielding five fractions (+4, +14, +35, +200, and −200 mesh). A similar method, using smaller samples and horizontal grids has also been developed and referred to as the Turner–Newall classification.

Currently, the BMN classification and the QS test are the most widely used fiber classification techniques. Whereas there are qualitative relationships between QS and BMN, there is no quantitative correspondence. It is readily understood that these standard tests do not provide accurate definition of the fiber lengths; the classification also reflects the hydrodynamic behavior (volume) of the fibers, which, because of their complex shapes, is not readily predictable. Other classification techniques that provide some insight on fiber lengths are the Ro–Tap test, the Suter–Webb Comb, and the Wash test.

9.3. Other Fiber Evaluation Methods.

The extent of fiber separation (fiber openness) is an important evaluation criterion that is commonly measured by several techniques, viz, air permeability, adsorbent gas volume, bulk density, and resilience (compression and recovery). The adsorption and retention of kerosene is also used as a measure of fiber openness and fiber adsorption capacity (37).

The filtration behavior of asbestos fibers is evaluated through a drainage test using, generally, a saturated calcium sulfate solution. This test is designated as “freeness” and reflects the water drainage rate related to asbestos–cement fabrication processes (37).

The reinforcing capacity of asbestos fibers in a cement matrix constitutes another key criterion for the evaluation of asbestos fibers. Preparing samples of asbestos–cement composites that, after a standard curing period, are tested for flexural resistance assesses this property. The measured rupture moduli are converted into a parameter referred to as the fiber strength unit (37).

Finally, other properties of asbestos fibers may be evaluated depending on the potential application. Typically, the grits and spicule content, the magnetic susceptibility (magnetic rating), the content in soluble chlorides, and the humidity level may be of particular interest in specific applications.

10. Industrial Applications

Asbestos fibers have been used in a broad variety of industrial applications. In the peak period of asbestos consumption in industrialized countries, some 3000 applications, or types of products, have been listed. Because of recent restrictions and changes in end use-markets, most of these applications have been abandoned and the remainder is pursued under strictly regulated conditions.

The main properties of asbestos fibers that can be exploited in industrial applications (11) are their thermal, electrical, and sound insulation; nonflammability; matrix reinforcement (cement, plastic, and resins); adsorption capacity (filtration, liquid sterilization); wear and friction properties (friction materials); and chemical inertia (except in acids). These properties have led to several main classes of industrial products or applications (8).

Loose asbestos fibers, or formulations containing asbestos fibers for spray coatings, were widely used in the building industry for fire protection and heat or sound insulation during and following World War II. Such applications used mainly chrysotile or amosite, although crocidolite was commonly used in Europe, this practice was discontinued in the 1970s because of health concerns.

Asbestos fibers also have been widely used for the fabrication of papers and felts for flooring and roofing products, pipeline wrapping, electrical insulation, etc. Asbestos textiles, comprising yarn, thread, cloth, tape, or rope, also found wide application in thermal and electrical insulation and friction products in brake or clutch pads. In recent years, use of asbestos in these applications has decreased significantly. Production of asbestos roofing and flooring felts has been discontinued.

The reinforcing properties of asbestos fibers have been widely exploited in asbestos–cement products mostly by the construction and water industries. Asbestos–cement products such as board, pipe, and sheet represent by far the largest worldwide industrial consumption of asbestos fibers, an estimated 80% of the market in 1988 (38). With market changes since 1988, asbestos–cement products now probably account for >98% of fiber sales.

Asbestos fibers also have been used to reinforce plastic products made from PVC, phenolics, polypropylene, nylon, etc. Reinforcement of thermoset and thermoplastic resins by asbestos fibers was used to develop products for the automotive, electronic, and printing industries. Except for some specialty products, the use of asbestos in plastics has essentially ceased.

The combination of asbestos fibers with various types of natural or synthetic resins has led to the development of a variety of products and applications. Among those, the incorporation of asbestos fibers (mainly chrysotile) into rubber matrices yields materials that were widely used for fabrication of packings and gaskets. Complex formulations, comprising short asbestos fibers (usually chrysotile), resins, and other fillers and modifiers, have been developed as friction materials for brake linings and pads. Asbestos fibers also have found broad application as reinforcing agents in coatings, sealings, and adhesive formulations. Of these applications, brake linings and pads, gaskets, and roof coatings comprise the bulk of the consumption.

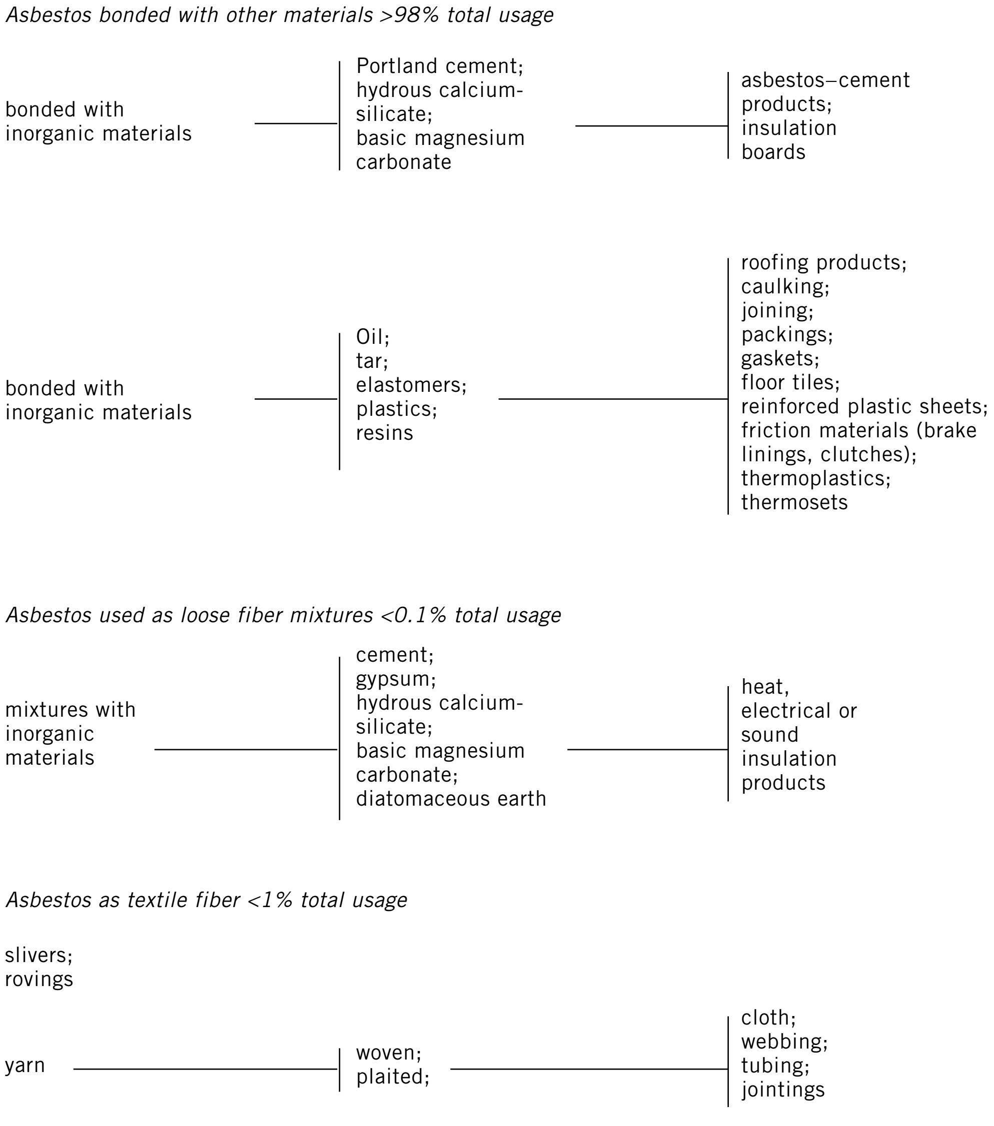


Fig. 10. Utilization of asbestos fibers by process. Percent, by category, in 2000. Product groups in bold represent major end uses within a process category (modified from 39).

Table 6. **Uses of Asbestos**[a]

Grade[b]	Length specifications, mm	Uses[c]
long fiber		
No. 1 crude	19	textiles
No. 2 crude	9.5–19	textiles, insulation
No. 3	6–9.5	textiles, packings, brake linings, clutch facings, electrical, high pressure and marine insulation
medium fiber		
No. 4	3–6	asbestos–cement pipe, brake linings, plastics
No. 5	3–6	asbestos–cement pipe and sheets, molded products, paper products, brake linings and gaskets
No. 6	3	asbestos–cement products, brake linings and gaskets, plaster, backing for vinyl sheets
short fiber		
No. 7	3	molded brake linings and clutch facings, plastics, filler in vinyl and asphalt floor tiles, asphalt compounds, caulking compounds, thermal insulation, gaskets, paints and drilling mud additive
No. 8	[d]	similar to No. 7

[a] Ref. 36.

[b] Quebec Standard.

[c] Many uses shown are discontinued; major use in 2000 in bold.

[d] Loose density specifications.

Finally, the combined reinforcing effect and high absorption capacity of asbestos fibers were exploited in a variety of applications to increase dimensional stability, typically in vinyl or asphalt tiles and asphalt road surfacing. Asbestos is no longer used in these applications.

Figure 10 summarizes the various classes of application for asbestos fibers in combination with other materials. The diagram shows that in recent years, most industrial applications involve asbestos fibers bonded within an organic or inorganic matrix. Asbestos–cement products account for the bulk of the world's asbestos usage. In the United States, the major use is in roofing compounds (62%), followed by gaskets (22%), and friction products (11%). Small amounts of asbestos also are used to manufacture some insulation products and woven and plastic products (9).

Each type or group of products usually requires a selected asbestos fiber grade (or range of grades). Table 6 lists various types of chrysotile applications in relation to QS fiber grades.

11. Alternative Industrial Fibers and Materials

Considerable effort has been devoted to finding alternative fibers or minerals to replace asbestos fibers in their applications. Such efforts have been motivated by various reasons, typically, availability and cost, and more recently, health and liability concerns. During World War II, some countries lost access to asbestos

Table 7. **Asbestos Substitutes and Relative Costs**[a]

Minerals	Synthetic mineral fibers	Synthetic organic fibers
	< 2 $/kg[b]	
attapulgite	mineral wool	
diatomite	glass wool	
mica		
perlite		
sepiolite		
talc		
vermiculite		
wollastonite		
asbestos, grades 3–7		
	2–10 $/kg	
	steel fibers	polypropylene (PP)
	continuous filament glass	poly(vinyl alcohol) (PVA)
	alkali-resistant glass	polyacrylonitrile (PAN)
	aluminosilicates	
	10–20 $/kg	
	continuous filament glass	polytetrafluoroethylene (PTFE)
	>20 $/kg	
	alumina fibers	polybenzimidazole (PBI)
	silica fibers	aramid fibers
	graphite fibers	pitch and PAN carbon fibers

[a] In U.S. $, 1989. Ref. 40.

[b] The natural organic fiber, cellulose (pulp), also falls in the < $2/kg range.

fiber supplies and had to develop substitute materials. Also, in the production of fiber-reinforced cement products, many developing countries focused on readily available, low-cost cellulose fibers as an alternative to asbestos fibers. Since the 1980s, however, systematic research has been pursued in several industrialized countries to replace asbestos fibers in many current applications because of perceived health risks.

The substitution of asbestos fibers by other types of fibers or minerals must, in principle, comply with three types of criteria (40): the technical feasibility of the substitution; the gain in the safety of the asbestos-free product relative to the asbestos-containing product; and the availability of the substitute and its comparative cost.

In some applications, particularly those that rely on several characteristic features of asbestos fibers, the substitution has presented a significant challenge. For example, in fiber–cement composites, the fibers must exhibit high tensile strength, good dispersibility in Portland cement pastes, and high resistance to alkaline environments. Likewise, in friction materials, several properties of the asbestos fibers are important: high affinity toward resins, good heat resistance, high friction coefficient, and low abrasion of the opposing surface. In such applications, the replacement of asbestos fibers has required a combination of several materials. Table 7 lists some of the materials and fibers that have been suggested or used in the development of asbestos-free products along with an estimate of the cost ranges of asbestos fibers and several types of substitution materials.

Various asbestos substitution strategies have been followed and a wide range of asbestos-free products have been developed. For example, in bulk thermal insulation and sprayed insulation coating applications, synthetic mineral fibers (glass or slag fibers) and cellulose fiber products have replaced natural asbestos fibers. Clothing made from aramid fibers or aluminized glass fibers has replaced asbestos in most textiles (see High performance fibers). Asbestos in floor tile has been replaced by a combination of synthetic fibers and nonfibrous fillers. Asbestos packings have been replaced by various materials including aramid and glass fiber, graphite mixtures, and cellulose fibers.

In fiber–cement construction materials, several alternatives are being practiced, either using cellulosic fibrous products or synthetic organic fibers such as polypropylene or polyacrylonitrile or alternative products such as cast iron, PVC, or PP pipe. The use of asbestos–cement products still is considerable owing to low cost, availability, low technology requirements, and performance.

For friction material applications, composite materials comprising glass or metallic fibers with other minerals have been developed. In these applications, aramid and graphite fibers are effective, although the cost of these materials restricts their use to heavy duty or high technology applications (see Carbon fibers). Substitution has been more successful in disk brake pads as compared with brake shoes (40).

Efforts to substitute for asbestos have been fairly successful as evidenced by the fact that peak world asbestos production was 4.8×10^6 tons in 1977, declining to 1.9×10^6 tons in 2000. This value represents a decline of 60% in the use of asbestos despite growth in every market in which asbestos was used during the 25-year period. The availability of adequate replacement materials, the cost-to-performance ratio of such materials, and the uncertainty of long-term health risks of these replacement materials have limited the extent of substitution of asbestos fibers by other fibers in some product applications.

12. Health and Safety Factors

The relationship between workplace exposure to airborne asbestos fibers and respiratory diseases is one of the most widely studied subjects of modern epidemiology (41–43). Asbestos-related health concerns were first raised at the beginning of the century in the United Kingdom, which appears to have been the first country to regulate the asbestos-user industry (44). It wasn't until the early 1960s, however, that, researchers firmly established a correlation between worker excess exposure to asbestos fibers and respiratory cancer diseases (45). This finding triggered a significant research effort to unravel important issues such as the influence of fiber size, shape, crystal structure, and chemical composition; the relationship between exposure levels and diseases; the consequence of exposure to asbestos fibers in different types of industries, or from different types of products; and the development of technologies to reduce worker exposure.

The research efforts resulted in a consensus in some areas, although controversy still remains in other areas. It is widely recognized that the inhalation of long (considered usually as >5 μm), thin, and durable fibers in high concentrations over a long period of time can induce or promote lung cancer. It is also widely accepted that asbestos fibers can be associated with three types of diseases (46): asbestosis: A lung fibrosis resulting from long-term, high level exposures to airborne fibers; lung cancer: Usually resulting from long-term high level exposures and often correlated with asbestosis; mesothelioma: A rare form of cancer of the lining (mesothelium) of the thoracic and abdominal cavities.

A further consensus developed within the scientific community regarding the relative carcinogenicity of the different types of asbestos fibers. There is strong evidence that the genotoxic and carcinogenic potentials of asbestos fibers are not identical; in particular mesothelial cancer is most strongly associated with amphibole fibers (47–51).

The replacement of asbestos fibers by other fibrous materials has raised similar health issues about substitute materials. However, lung cancer has a latency period of ~25 years and fiber exposure levels to substitutes are far lower than those that prevailed half a century ago with asbestos. Consequently, the epidemiological data on most substitutes is insufficient to establish statistically significant correlations between exposure and pulmonary disease (52). A possible exception is slag fibers for which several studies on worker populations are available over extended periods (53); some results show a substantial increase in lung cancer occurrence. Consequently, the toxicity of asbestos substitute fibers remains a subject of active investigation.

12.1. Regulation. The identification of health risks associated with long-term, high level exposure to asbestos fibers, together with the fact that large quantities of these minerals were used (several million tons annually) in a variety of applications, prompted the enactment of regulations to limit the maximum exposure of airborne fibers in workplace environments. The exposure limits may be defined as average or peak values, measured either as a weight or as a number of fibers-per-unit-volume. The International Labor Organization adopted the following definition (Convention 162, article 2d and R172): “the term respirable asbestos fibers means asbestos fibers having a diameter of less than 3 μm and a length-to-diameter ratio greater than 3:1. Only fibers of a length greater than 5 μm shall be taken into account for purposes of measurement.” In general, exposure limits vary considerably among countries with the range being from 0.1 fibers per cubic centimeter (f/cc) for 4- or 8-h time-weighted-average exposure to 2 f/cc.

In accordance with demonstrated differences between the various asbestos fiber types, workplace regulations in many countries specify different exposure limits for chrysotile and the amphiboles (54). Typically, exposure limits for amphibole asbestos are one-half to one-tenth that for chrysotile. Also, the European Union voted to ban the use of amphibole asbestos and its use has been discontinued. Moreover, to alleviate established, or apprehended, risk from substitute fibers, regulations often specify maximum exposure limits for synthetic fibers (55).

Some countries have opted for a broader approach and have adopted regulations that also minimize exposure of the general public to environmental asbestos fibers, ie, by banning or restricting asbestos imports and types of applications. Countries that have banned (either a complete bans or a ban with exemptions) or are phasing out the use of asbestos and in some cases, asbestos products, in the next few years include Argentina, Austria, Belgium, Chile, Denmark, Finland, France, German, Italy, Netherlands, Norway, Poland, Saudi Arabia, Sweden, Switzerland, and the United Kingdom. The European Union voted to ban asbestos use in most applications by its members by 2005.

The obvious trend with asbestos is toward stricter regulations or the banning of its use. Banning has occurred for the most part in developed countries where substitute materials or alternative products are readily available and it is economically feasible to use asbestos substitutes. In lesser developed countries where economics and the level of industrial development is a factor, asbestos substitutes are not yet considered to be a suitable option in many cases.

Despite the current bans and continued opposition to the use of asbestos, markets for asbestos probably will exist long into the future. Consumption can be expected to decline as substitutes and alternative products gain favor in the remaining world markets, which, however, is a process that probably will occur over a period of decades. Even then, there probably will remain specialized applications for asbestos, particularly for matrix-based products.

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Robert L. Virta
U.S. Geological Survey