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THE MORPHOLOGY OF CHRYSOTILE ASBESTOS AS INFERRED FROM NITROGEN ADSORPTION DATA

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ABSTRACT

The examination of samples of chrysotile asbestos from areas other than the usual Canadian sources has aided in the determination of the morphology of the mineral chrysotile. Chromatographic and gravimetric nitrogen adsorption data confirm the view that naturally occurring chrysotile consists of an assemblage of sub-microscopic tubular crystals. Some specimens have solid matter filling the voids between fibrils, and have surface areas and porosities considerably smaller than would be expected from the geometry of the fibrils. Others have little (if any) interstitial material, and have surface areas that correspond to adsorption on essentially all external fibril surfaces. The adsorption data indicate further that the central pores of chrysotile fibrils are not available for adsorption, and that the pore structures frequently observed in chrysotile specimens are associated with voids between, rather than channels within, fibrils.

INTRODUCTION

The layer structure and tubular morphology of chrysotile asbestos are well established (Warren and Hering, 1941) (Whittaker, 1957) (Turkevich and Hillier, 1949) (Maser *et al.* 1960). Points that remain to be resolved are (a) whether the central pores of chrysotile fibrils are filled or empty, and (b) the extent to which solid matter fills the voids between fibrils in a massive specimen. An assemblage of tubes like that depicted in Fig. 1 should be of high surface area and high porosity. Taking 150 Å as a typical external fibril radius (R_0), 75 Å as a typical internal radius (R_i), and the *x*-ray density of chrysotile (2.56) for the density of the tube walls, the surface area should be approximately 100 m^2/g and the porosity (pore volume) approximately 30% of the total volume. Neglecting the area lost where tubes are in contact, the individual contributions for the pores within and between cylindrical fibrils in a close-packed, hexagonal array, would be as follows:

Surface Area	69 m^2/g for external fibril surfaces
	35 m^2/g for internal fibril surfaces
	104 m^2/g Total
Porosity	9% for voids between fibrils
	23% for the central pores of fibrils
	32% Total

The observed bulk properties of chrysotile seldom approach these values. Surface areas generally range from 10 to 20 m^2/g and porosities from 1 to

10% (Young and Healey, 1954) (Pundsack, 1955) (Pundsack, 1961) (Kalousek and Muttart, 1957).

The most reasonable explanation for the discrepancies between the potential and the observed bulk properties is that at least part of the potential void spaces are filled. Convincing evidence has been obtained for the presence of solid matter between fibrils, particularly the electron microscope replicas of Bates and Comer (1959), which show troughs with

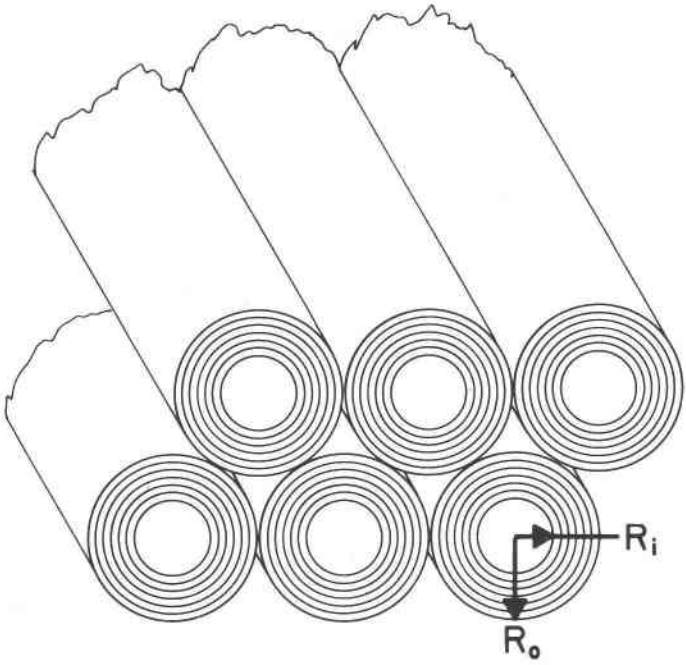

FIG. 1. Idealized representation of fibril packing in chrysotile.

sharp cusps between them on fracture surfaces. These may be identified as regions where asbestos fibrils have been pulled from a solid matrix. The question of the presence of solid material in the central pores of chrysotile fibrils is less well resolved. Electron micrographs show that the centers of fibrils are of lower electron density than the fibril walls, but it is also observed that the density is greater in some regions than in others. Thus, some regions may have a solid filling and others have none. On the other hand, the fibrils may be completely filled and the differences result from variations in the density of the filling. Density data for massive chrysotile specimens favor the latter interpretation (Kalousek and Muttart, 1956)

(Pundsack, 1956). Gas adsorption data have been interpreted in terms of the availability of at least a portion of the central pores for adsorption (Young and Healey, 1954) (Pundsack, 1961), but these results do not preclude a partial blocking.

Aside from the probable existence of solid material within and between the fibrils, little can be said about its composition or structure. Presumably, it can range from an amorphous phase as favored by some authors (Maser *et al.*, 1960) (Bates and Comer, 1959) (Martinez and Comer, 1964) to crystalline cylindrical segments of chrysotile as suggested by Whittaker (1957). There can also be a variation in the amount of the extra-fibril solid matter. It is the purpose of this communication to show that the amount of extra-fibril matter differs for chrysotile from different localities, and that for the materials studied, the central pores of chrysotile fibrils were not available for adsorption.

Experimental

Nitrogen adsorption data were obtained for chrysotile specimens from California, Yugoslavia, and two Canadian localities.

Specimen Designation	*Source*
Quebec Long Fiber	Wards Natural Science Establishment
Cassiar AC	Cassiar Asbestos Corporation, Ltd.
Commercial Grade 7TF	Johns-Manville Corporation
Commercial Grade 7R	Philip Carey Manufacturing Corp.
New Idria Chrysotile	Union Carbide Corp.
Stragari Chrysotile	American Museum of Natural History

The first two materials were essentially pure chrysotile. The first was a long-fiber asbestos from the Thetford Mines, Quebec area. The adsorption data were obtained for filaments pulled from a cross-fiber block specimen. The second was a mechanically purified product from Cassiar, British Columbia. This was also a long-fiber material and was in the form of tangled filaments. The third and fourth specimens were powdery, commercial asbestos products prepared by conventional dry-processing methods. They were probably also from the Thetford Mines, Quebec area. Both contained appreciable brucite and magnetite and lesser amounts of other impurities. Of the two, 7TF had the greater gangue content. The fifth and sixth materials were essentially pure chrysotile in the form of thin, tough, leathery flakes. The fifth was from a massive asbestos deposit discovered recently in the New Idria serpentinite formation of central California (Munro and Reim, 1962), and the sixth from a similar deposit near Stragari, Yugoslavia.

Surface-area data were obtained for chrysotile specimens in the form in which they were received and, in most cases, for portions of the samples

after having mechanical-opening and/or chemical-dispersion treatments performed upon them. The chemical-dispersion treatments consisted of thrashing the samples in a Waring Blendor with a solution of an appropriate dispersing reagent such as acetic acid (Naumann and Dresher) or aluminum chloride (Barbaras, 1953). The resultant suspensions were centrifuged for five minutes at 1000 rpm in an International Model SBV centrifuge to remove gangue particles and partially opened fiber bundles. The materials remaining in suspension were collected and dried, providing a source of defibrillated chrysotile, *i.e.*, samples in which essentially all of the ultimate crystalline fibrils were separated from one another. Purely mechanical opening was achieved either by thrashing a suspension of the materials in a Waring Blendor without dispersing reagents, or by dry-grinding to minus 200 mesh in a Pitchford Grinder, a high-intensity vibrating ball mill. It was known from the examination of numerous electron micrographs obtained during the course of other studies on chrysotile that these opening procedures did not cause longitudinal fractures or an unrolling of fibrils into laths. There may possibly have been some shortening of average fibril length. Chemical analyses showed that little (0.5% or less) of the magnesium of the chrysotile lattice was solubilized by the wet-opening procedures, hence effects due to any chemical modifications and/or leaching of fibril surfaces could be considered to be negligible.

Surface area data were obtained with a Perkin-Elmer-Shell Model 212B Sorptometer, a commercial version of the instrument described by Nelson and Eggertsen (1958). Specific surface areas were calculated using the conventional BET treatment (Brunauer, 1945).

Data for complete nitrogen adsorption isotherms were obtained at liquid nitrogen temperature by means of a silica spring balance with a sensitivity of 0.254 mg/mm. Spring extensions were determined to ± 0.01 mm using a Gaertner Model M342 micrometer slide and telescope. Buoyancy corrections were applied. Nitrogen vapor pressures were measured with a mercury manometer and a Gaertner Model M911 cathotometer. Nitrogen saturation pressures were determined by means of a nitrogen-filled, closed-tube manometer. Approximately 1-g chrysotile specimens were suspended from the spring in approximately 0.5-g aluminum buckets. Data were obtained for:

(a) handpicked pieces of New Idria chrysotile, (b) chrysotile from Cassiar, British Columbia, in the form of tangled, macroscopic filaments, and (c) strips of filter cake prepared from the Cassiar material by chemical dispersion.

Specimens were activated by heating in vacuum at 400° C. prior to the adsorption experiments.

Results and Discussion

Surface Area Measurements. Surface area results are summarized in Table I. The data for the four Canadian specimens agree with literature values for chrysotile with regard to magnitude, and also with regard to the manner in which apparent surface area varies with activation temperature (Young and Healey, 1954) and with mechanical and chemical opening treatments (Pundsack, 1955). The surface areas of all of the Canadian "as received" materials increased with increasing activation temperature.

Table I. Specific Surface Areas for Chrysotile Specimens

Material	Treatment	Activation Temperature 100° C.	200° C.	400° C.
Quebec Long Fiber	as received	15 m^2/g	18 m^2/g	22 m^2/g
Cassiar AC	as received	19	20	22
	mechanically opened, dry	34	36	38
	mechanically opened, wet	43	43	—
	dispersed chemically	51	50	49
Grade 7TF	as received	20	25	30
	dispersed chemically	45	45	44
Grade 7R	as received	31	30	44
	dispersed chemically	52	52	50
New Idria chrysotile	as received	79	80	76
	mechanically opened, wet	79	—	—
	dispersed chemically	78	—	—
Stragari chrysotile	as received	78	78	80
	dispersed chemically	88	—	—

These increases were not large, but were well within the ability of the chromatographic method to resolve differences. Surface area was also increased by either wet or dry opening treatments, and as area increased, the change in area with activation temperature became less pronounced. The fully opened, chemically dispersed samples showed no variation with activation temperature.

These results are consistent with the generally accepted view of the morphology of chrysotile, *i.e.*, a closely packed array of tubular asbestos fibrils with extra-fibril solid matter cementing the assemblage together. A solid made up this way would have a well-defined capillary pore structure and, because of the extra-fibril filling, would have something less than the

total surface of the individual fibrils as available surface. In terms of this close-packed structure, the Canadian materials had a relatively low surface area when activated at 100° C., because a large portion of the fibril surfaces are made unavailable by extra-fibril solid materials and by water condensed in capillary pores. Apparent surface area was larger at higher activation temperatures because of the removal of the capillary water. An additional variation with activation temperature occurs when accessory minerals that decompose to yield products of high surface area are present. As mentioned previously, both Grade 7R and 7TF contained brucite, which dehydrates to MgO at 350° to 400° C.

The increase in surface area with wet or dry mechanical opening may be attributed to liberation of individual fibrils. The effects of dry mechanical opening are shown directly by the samples of Cassiar AC, where grinding increased the surface area, and indirectly by the magnitudes of the areas of the four starting materials. The Quebec long-fiber samples, which had received the least mechanical work, had the smallest area; the commercial grades 7R and 7TF, whose powdery appearances were indicative of drastic mechanical treatments, had the largest. The products of the wet-opening treatments, especially those produced by the dispersion-centrifugation procedure, had the highest surface areas. This is to be expected, since liberated chrysotile fibrils were separated from gangue and from partially opened fibril agglomerates by centrifugation. Disaggregation was so complete that essentially all fibrils were separated from each other, and essentially all external fibril surfaces were available for adsorption.

The data obtained with fully defibrillated materials bear directly on the problem of whether the central pores of individual fibrils are empty or blocked, for with these data, complications due to pores between fibers, and pores developed in decomposable impurities such as brucite are avoided. No dependence of area on activation temperature was observed for any of the defibrillated samples, indicating that the pores associated with these materials in the undefibrillated state involved voids between, not within, fibrils.

Surface areas for the New Idria and Stragari specimens were considerably higher than have been reported for any natural chrysotile. The surface areas of untreated flakes of both materials were independent of activation temperature, and with New Idria chrysotile, area was not increased by either mechanical or chemical opening treatment. Chemical opening resulted in a 10 to 15% increase with the Stragari material, but this increase is small compared to those observed with the Canadian samples, where area was increased by a factor of two or more. These results suggest an open structure in the natural state, with essentially all

external fiber surfaces available for adsorption. The data also indicate the pores between fibrils were large enough to prevent capillary condensation of water. Again, there was no indication that the central pores of the fibrils were available for adsorption.

A series of electron micrographs of defibrillated Canadian Grade 7R and defibrillated New Idria flake were prepared, and the external diameters of a statistical sampling of the fibrils appearing on each photographic plate were measured using an optical microscope with filar eyepiece. Histograms of the distribution of fibril diameters determined in this way are given in Fig. 2. The Canadian specimen had a larger average

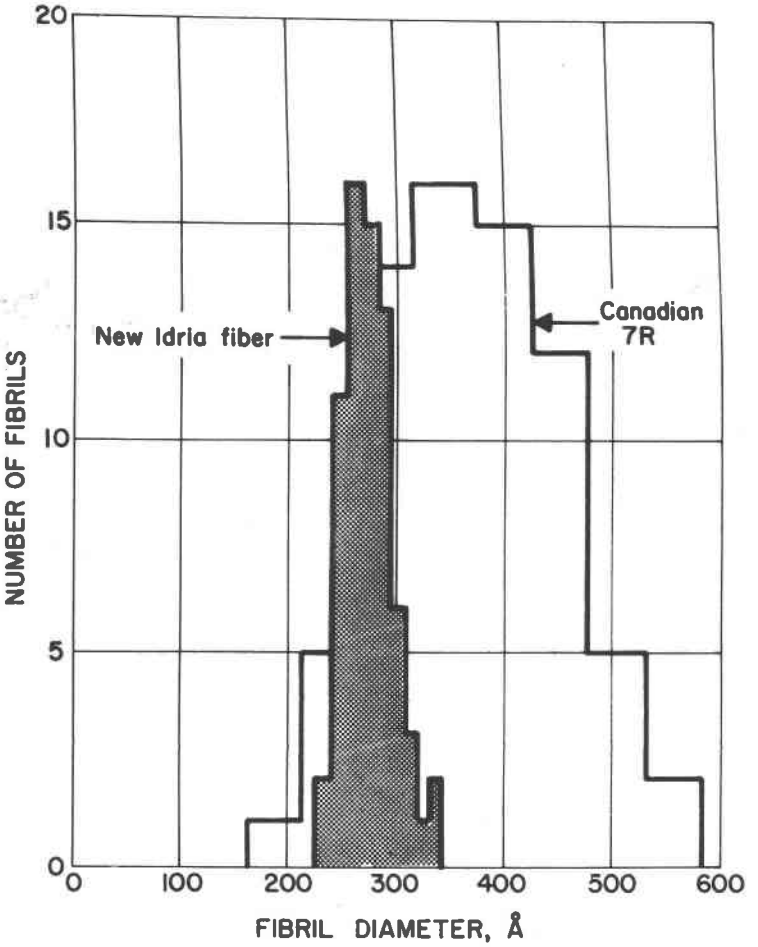

FIG. 2. Histogram of fibril diameter distribution.

diameter and a greater variation in diameter than the New Idria material. The average diameter for the Canadian sample was 375 Å with a standard deviation of 76 Å, as compared to 275 Å and 26 Å, respectively, for the New Idria specimen. Further statistical analysis of the data showed that diameters did not vary significantly along a given fiber of either material, but that the greater variation was with the Canadian sample. Surface areas calculated from the fibril dimensions were in satisfactory agreement with the nitrogen adsorption values.

	Observed	*Calculated*
Grade 7R	50 m^2/g	55 m^2/g
New Idria	78	76

A ratio of internal-to-external diameters of 0.5 and a density of 2.56 g/cm^2 for tube walls was assumed for the calculated values.

The fibrils of the New Idria sample were characteristically smooth and

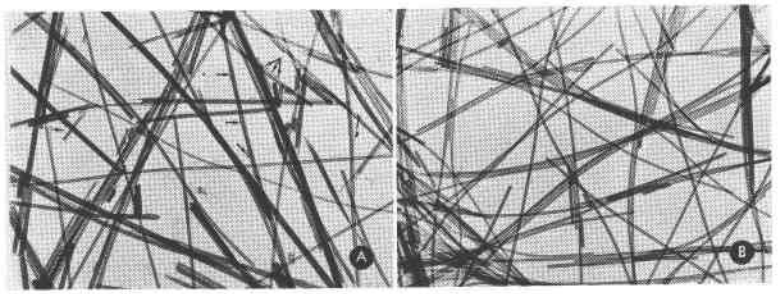

FIG. 3. Electron micrographs of chrysotile. a) Dispersed grade 7R chrysotile. b) Dispersed New Idria flake chrysotile.

regular along their entire length, as would be expected for a material that contained no extra-fibril solids. The fibrils of 7R appeared rough and lumpy along some segments and had bits of particulate matter adhering to them at others. The general appearance was consistent with the view that the fibrils had been broken from a solid matrix. Figure 3a is of dispersed grade 7R; Figure 3b of the New Idria sample. Both are prints of plates used for the fiber-dimension analysis, and both are at the same total magnification. Areas showing particulate matter adhering to the fibrils of 7R are indicated by arrows. Thus, the differences in surface area between the New Idria and Stragari materials on one hand, and the Canadian samples on the other, hinge on two factors: (a) the presence of extra-fibril solid matter in the Canadian chrysotile specimens, and its absence in the New Idria and Stragari specimens; and (b) a larger average fibril diameter for Canadian chrysotiles. This accounts for the approx-

imate 50 m^2/g area of defibrillated Canadian samples, compared to the approximate 80 m^2/g for the New Idria and Stragari samples.

A narrow range for the diameters of chrysotile is to be expected, since the lattice mismatch that causes curvature and tube formation gives rise to a strain-free configuration at a unique radius of curvature. There will be strain for larger or smaller radii that will increase with increasing departure from the ideal radius, thus limiting the number of layers that can be built up into a stable, cylindrical wall and controlling the average fibril dimensions and the distribution of sizes around that average. In view of these strain considerations, one might expect fibril diameters to be restricted to an even narrower range than is observed; and further, one might expect chrysotile from different localities to have the same average diameter. However, the elemental composition of specimens varies slightly for chrysotile from different sources; and, as discussed by Roy and Roy (1954), the kind and degree of isomorphous substitution influences the morphology of serpentine. Another source for variations in fibril diameters is strain relief through the formation of structures more complex than simple cylinders; for instance, the occasional "tube-within-tube" configuration observed by Maser *et al.* (1960).

Nitrogen Adsorption Isotherms. Adsorption and desorption occur reversibly with non-porous solids, but with most porous solids the desorption branch of the isotherm is displaced from the adsorption branch over a portion of the pressure range. As shown in Fig. 4, a hysteresis of this type occurs with undefibrillated Cassiar chrysotile. This is in agreement with other experimental observations for Canadian asbestos (Young and Healey, 1954) (Pundsack, 1961). Adsorption for defibrillated Cassiar, as shown in Fig. 5, was reversible, indicating that the pore network in the natural material was eliminated, and confirming the conclusions of the previous section that these pores were associated with voids between, rather than within, the fibrils. Adsorption was also reversible with New Idria flake chrysotile, as is shown in Fig. 6, indicating the absence of a capillary pore network even in the naturally occurring state. This is also in agreement with the conclusions of the chromatographic surface-area measurements.

Two procedures for calculating pore-size distributions from adsorption data were applied to the data for undefibrillated Cassiar chrysotile. The first was a method proposed by Barrett, *et al.* (1951) and later modified by Roberts (1963); the second, a method developed by Cranston and Inkley (1957). Both are based on the same model for adsorption and desorption, but different computational procedures are involved. The principal assumptions of the calculations are as follows:

1. The pressure at which a pore of a given radius empties follows the Kelvin equation:

$$\ln (P/P_0) = 2\gamma V/RTr$$

where

P = Pressure above an interface with radius of curvature, r
P_0 = normal pressure for temperature, T
γ = surface tension
V = molar volume
R = gas constant

2. As a pore empties, the wall of the pore retains an adsorbed layer whose thickness varies like that of a flat surface.
3. Pores larger than 300 Å in radius contribute little to the total surface area of the specimen.

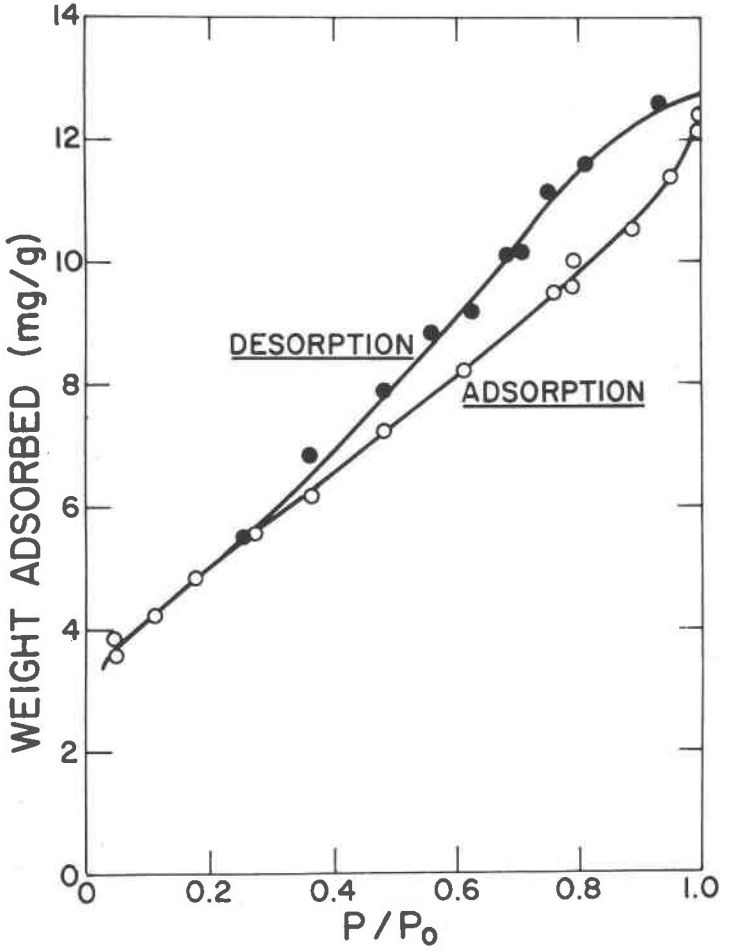

FIG. 4. Adsorption isotherm for undispersed Cassiar chrysotile.

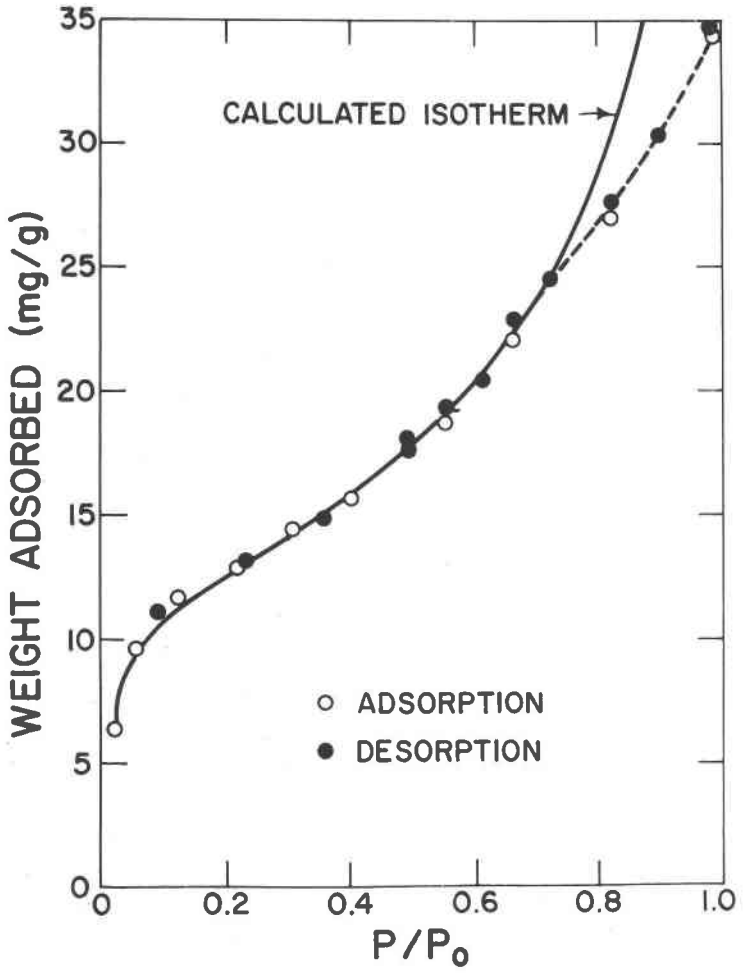

FIG. 5. Adsorption isotherm for dispersed Cassiar chrysotile.

The first two assumptions are of general applicability. In some cases, the last will not be valid, and possibly this is the case with asbestos. When adsorption isotherms level off at pressures below $P/P_0=1$, it is apparent that the specimen has become saturated with adsorbate and that all pores are filled. The adsorption isotherm for undefibrillated Cassiar did not behave in this way. Adsorption continued to increase in the neighborhood of $P/P_0=1$, indicating that large pores or, more likely, liberated fibrils or fibril bundles were contributing to the total surface. However, the low area of the Cassiar specimen, the slow rise in adsorption near $P/P_0=1$,

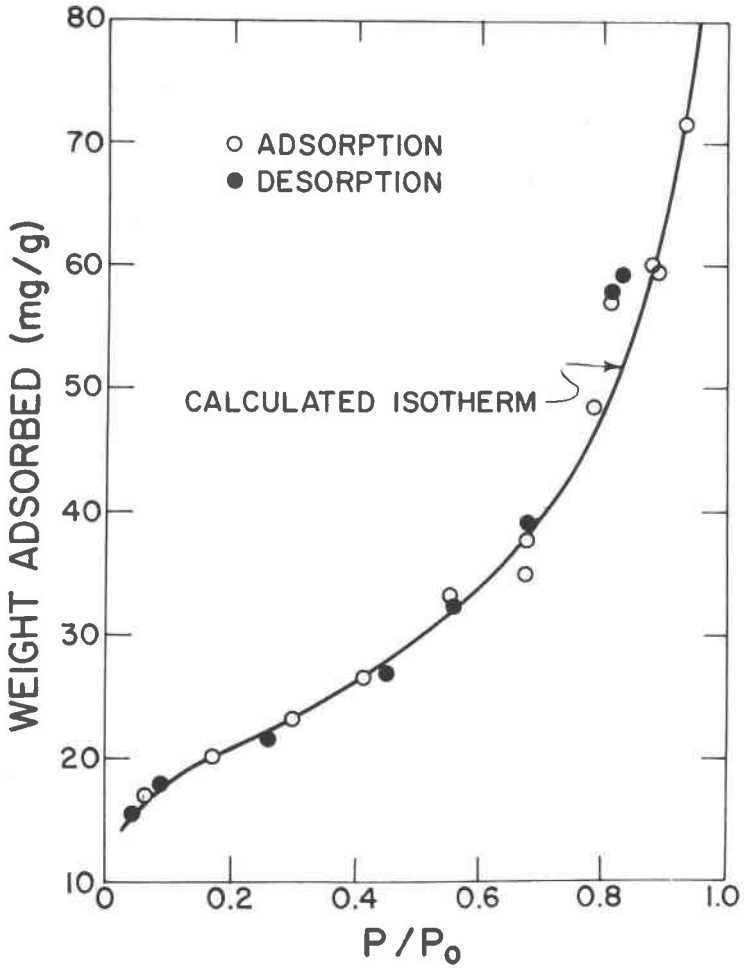

FIG. 6. Adsorption isotherm for New Idria chrysotile.

and the "flatness" of the desorption branch in this region all indicate that the free surface contribution was small.

The results of the two pore volume procedures were in surprisingly good agreement. Figure 7 shows that the calculated pore-size distributions show a maximum at about 25 Å, tailing off toward larger diameters. This is a reasonable value for a close-packed assemblage of solid, 300 Å cylinders. The work involved in displacing the liquid level a distance, dl, down a capillary channel may be expressed as follows:

$$\Delta P \times A \times dl = \gamma \times C \times dl$$

where ΔP is the pressure drop across the interface, A is the cross sectional

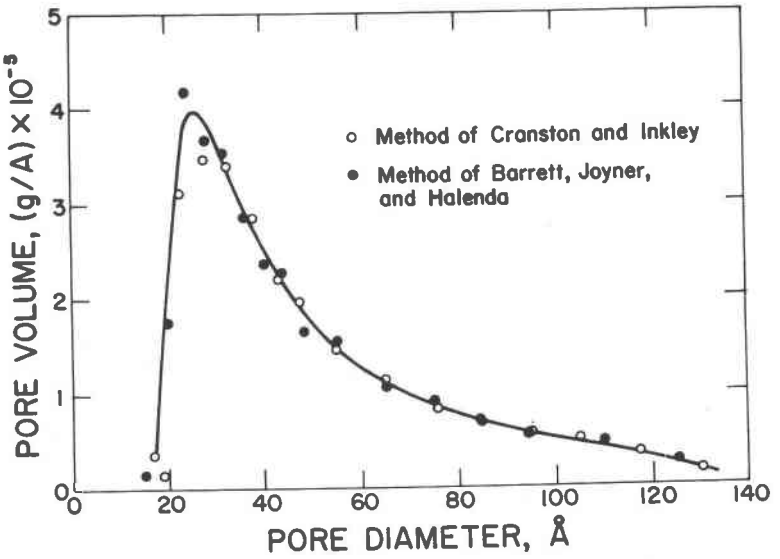

FIG. 7. Pore size distribution for undispersed Cassiar chrysotile.

area of the channel, γ is the surface tension, and C is the perimeter of the channel. For a cylindrical capillary of radius r, this reduces to the familiar expression: $\Delta P = 2\gamma/r$, but for the channel formed by three cylinders of radius R_0 in contact

$$A = 1/2 \times 2R_0 \times 2R_0 \sin 60° - 3 \times \pi R_0^2/6 = R_0^2(\sqrt{3} - \pi/2)$$

$$C = 3 \times 2\pi R_0/6 = \pi R_0$$

$$\Delta P = \frac{2\gamma}{R_0(2\sqrt{3}/\pi - 1)} \approx \frac{2\gamma}{0.1\ R_0}$$

Thus, for $R_0 = 150$ Å, the channel is equivalent to a cylindrical pore 30 Å in diameter, in good agreement with the observed value, 25 Å.

A pore volume corresponding to approximately 4% of the total volume was indicated. This is below the 9% calculated for close-packed solid cylinders, but is in line with other experimentally determined porosites (Pundsack, 1961). Surface areas calculated assuming a cylindrical geometry for the pores were in agreement with values calculated from the isotherm by the BET method:

BET method	15 m^2/g
Method of Barrett *et al.*	16 m^2/g
Method of Cranston and Inkley	15 m^2/g

Thus, while the assumption that external surfaces contributed little to the total surface area of undefibrillated Cassiar chrysotile was not established with certainty, the results of the pore-volume analyses are reason-

able and self-consistent. The surface areas listed above are smaller by 5 m^2/g than the values listed above for undefibrillated Cassiar chrysotile in Table I. This apparent discrepancy is due to the effect of mechanical opening on surface area. The sample used for the gravimetric determinations was coarser than that used for the chromatographic surface area measurements, where the design of the sample tubes dictated the use of filaments of the specimen.

It has been observed that for a given adsorption gas, the isotherm shapes for non-porous solids are remarkably similar. For example, data for such diverse materials as potassium chloride, titanium dioxide, egg albumin, graphite, and polyethylene have been shown to follow a common curve when adjusted for total surface area (Adamson, 1960). Conversely, from these data and total surface area it is possible to calculate the isotherm a sample would have if it were truly non-porous. This was done for the New Idria and defibrillated Cassiar specimens. The data for the New Idria chrysotile follows the calculated isotherm over the entire pressure range. The data for defibrillated Cassiar follows the calculated isotherm except at high pressures. Thus, a slight porosity is indicated. This may reflect less than complete opening during dispersion; or, since the data were obtained for strips of filter cake, that pores were formed during flocculation or filtration.

Acknowledgments

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