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DENSITY OF BULK CHRYSOTILE AND MASSIVE SERPENTINE

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ABSTRACT

Density measurements were made on twenty-three bulk specimens of chrysotile and seven massive serpentine samples, both by using mercury and by coating the samples with paraffin and immersing in water. Arizona chrysotile had densities of 2.19 to 2.25 gm/cc, whereas Canadian chrysotile gave slightly higher values that varied from 2.34 to 2.39 mg/cc. Arizona massive serpentine blocks had less porosity; the density ranged from 2.40 to 2.44 gm/cc. From published data obtained by electron microscopy, a single fiber of chrysotile has an average outside diameter of 340 Å and an inside diameter of 80 Å. The theoretical density of chrysotile, composed of parallel bundles of hollow cylinders of these dimensions, was calculated to be 2.19 gm/cc.

INTRODUCTION

Turkevich and Hillier (1949) first published electron micrographs indicating that chrysotile single fibers might be hollow tubes. Their work was verified by electron microscopic studies of chrysotile by Bates (1948) and Bates *et al.* (1950). The hollow tube theory gained support by the work of Noll *et al.* (1958) when he synthesized several substances that closely resembled chrysotile and showed that tubular structure was evident when the material was viewed with an electron microscope. Examination of Dr. Noll's cobalt chrysotile by Huggins (1962) also indicated tubular morphology Zussman, *et al.* (1957), Huggins (1959), and others have supported tubular morphology as electron micrographs of dispersed chrysotile appeared to show hollow cylinders for the ultimate structure. Maser *et al.* (1960) succeeded in cutting cross sections of chrysotile and showed several cross sections that were predominately doughnut shaped. Whittaker (1954, 1955a, b, c) contributed to the tubular morphology idea by comparing the x-ray diffraction effects expected from tubular or cylindrical lattices with those obtained experimentally.

Conversely Pundsack (1956) and Kalousek and Muttart (1957) concluded that the density of compact bundles of chrysotile fibers was incompatible with either tubular or solid cylindrical shapes. Kalousek and Muttart did not rule out tubular structure entirely since they did find a void volume in Globe, Arizona, chrysotile of 12.5 per cent. However, their measurements generally revealed a porosity far too low compared to that required for massive specimens consisting of tubular structure. Pundsack (1961) also presented experimental data which indicated that if any pores existed in chrysotile they were less than 60 Å in diameter. More recently, Whittaker (1963), and Bates (1958), have hypothesized that chrysotile fibers are filled with amorphous or partially oriented ma-

terial and that this accounts for the lack of voids in the fibers. Very surprising is the fact that nearly all of Pundsack's experimental bulk density determination gave values very close to the theoretical 2.56 gm/cc, the latter being derived from x-ray diffraction.

Several other literature sources have indicated a much lower value for the density. Bowles (1955) gave a specific gravity of 2.22 for pure chrysotile and said that higher values were always obtained because of the presence of impurities. Berger (1963) gave the density of cleaned chrysotile as 2.22, and Dana (1892) gave a specific gravity of 2.219.

The present investigation was initiated in an attempt to help resolve some of the conflicting data and also to see if the density determination would, or would not, support the tubular structure theory. It was reasoned that a valid bulk density value should be obtained if large blocks of choice specimens were used and corrections made for any contamination.

Materials

Many samples of chrysotile were obtained from Canada; the best of these were used for density measurements. Chrysotile from Africa and another thought to be from New York were received from the Smithsonian Institution. Arizona chrysotile blocks of the highest quality, obtained from D. W. Jacquays Company, Phoenix, Arizona, were nearly translucent and free of admixed minerals. All the chrysotile samples were nearly free of cracks and admixed mineral impurities, except for 0 to 20 per cent magnetite in the blocks of Canadian chrysotile. All of the fiber blocks except one exceeded $\frac{3}{4}$ of an inch in cross-section and one inch in length. The massive serpentine blocks were from Arizona and were the highest purity we could obtain.

Density Measurements

The blocks of chrysotile were dried at 130° C. for 36 hours to remove the sorbed water and then weighed. Most were then immersed in mercury (Figs. 1, 2) and the density determined. The crank on the apparatus, (Fig. 1) was used to raise the tank until the block of chrysotile was completely immersed in the mercury and the tip of the pointer just touched the top of the mercury (Fig. 2, center). The following equation was then used to calculate the density of the block from the experimental data:

$$d_g = \frac{(W)(d)}{W + F}$$

where

W = weight of sample in grams
d = density of mercury at its temperature during measurement

F = force to immerse, which equals weight without sample, minus weight with sample.

After determination of density in mercury, the blocks were dipped in molten paraffin until a smooth, impervious coating resulted. The density of the paraffin-coated blocks was determined in water, and a correction was made for the paraffin. The measured density of the paraffin was 0.904 gm/cc.

Theoretical. Figure 3 is a drawing of a cross-section of a bundle of fibers predicted on perfect cylinders; the white areas are the void spaces. The absolute density of the solid portion may be calculated if one knows the diameter (inner and outer) of the fibers:

$$D_s = \frac{2\sqrt{3}}{\pi}\left(\frac{r_1^2}{r_1^2 - r_2^2}\right) D_g$$

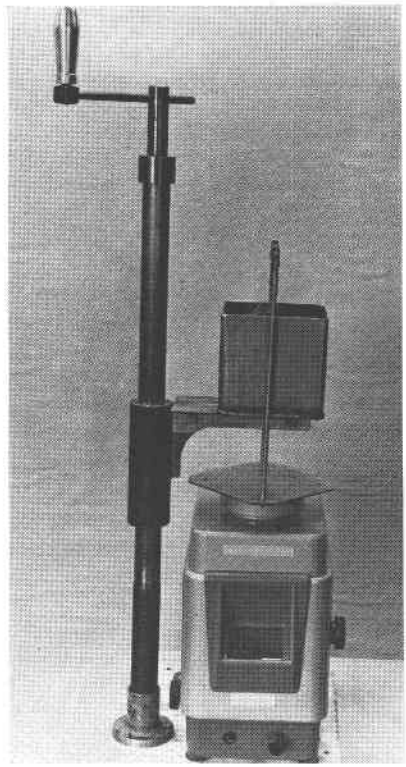

FIG. 1. Apparatus for the determination of density by immersion in mercury. Scale: 1 inch in photograph = 4 inches on actual apparatus.

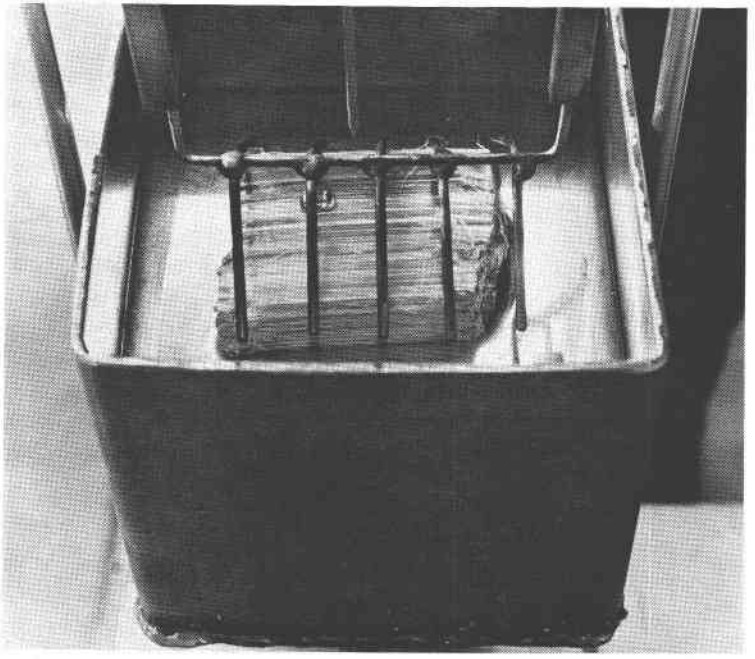

FIG. 2. Close up of mercury container (Fig. 1) showing relationship of pointer, sample holder, and mercury. Dimensions of mercury container are $4\frac{1}{2}'' \times 5'' \times 4\frac{3}{4}''$.

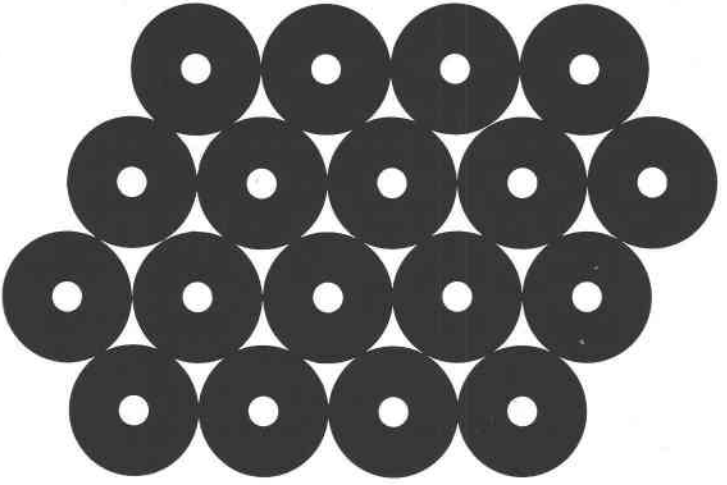

FIG. 3. Cross sectional view of chrysotile fiber bundle in hexagonal close packing.

where:

D_s = absolute density of solid
D_g = observed density of fiber block
r_1 = outer radius
r_2 = inner radius

The model in Fig. 3 is idealized and in nature irregularities would be expected in the diameters and packing arrangement. The electron micrographs have shown the fibers to vary in outside diameter from 150–400 Å.

The percentage of volume taken up by the voids between rigid solid cylinders of equal diameter is a constant independent of the number and size of the cylinders. If the ratio between outer and inner diameters of the tubes were constant, the bulk density would be constant. Nonuniform outside diameters would increase the bulk density, if the "hole" diameter remained constant or decreased.

If the average diameters (inner and outer) and the theoretical density of the fibers is known, these values can be substituted into the previous equation and the bulk density can be calculated very closely. By *x*-ray diffraction, the unit cell dimensions of chrysotile have been accurately determined; the theoretical density (*i.e.* of space occupied by solid) based on these measurements is 2.56 gm/cc. Kalousek and Muttart (1957) and Maser *et al.* (1960) gave, as an average, the outside diameter of chrysotile as 340 Å and the inside diameter as 80 Å. Using these two values (340 Å and 80 Å) in the above equation, the bulk density value obtained is 2.19 gm/cc. The average taken for the inside diameter may be a little high, Pundsack (1961), and might possibly be as low as 50 Å. Using as the outside diameter 340 Å and the inside value of 50 Å in solving the equation, a bulk density of 2.27 gm/cc was obtained. Therefore, one would expect the density of the bulk fiber block to be between 2.19 and 2.27 provided that no impurities filled the void areas. Also the use of an average outside diameter does not cause too large a deviation from the theoretical model because the fibers measured were at or near 340 Å.

Chemical Composition

The bulk specimens were checked for impurities by chemical analysis, optical methods, and *x*-ray diffraction. Except for magnetite in the Canadian chrysotile, all of the fiber blocks were nearly free of foreign minerals. The only other appreciable mineral detected was calcite, but this was present in the Arizona massive serpentine only. Table 1 gives the analysis of three samples. The first is typical high-purity Arizona chrysotile (note the low iron content). The second is Arizona massive serpentine blocks, with the Ca^{2+} and CO_2 being largely or completely present as

TABLE 1. CHEMICAL ANALYSES

Constituent	Arizona chrysotile[1] wt. per cent	Massive serpentine[2] wt. per cent	Canadian chrysotile[3] (Thetford) wt. per cent
SiO_2	43.29	40.23	41.41
Al_2O_3	.23	.37	.55
Fe_2O_3	.40	.44	1.03
FeO	.06	—	.72
CaO	.25	3.00	0
MgO	41.54	39.09	41.52
K_2O	0	0	0
Na_2O	.04	.02	—
TiO_2	0	0	0
CO_2	.24	2.36	.34
H_2O^-	1.07	1.19	1.47
H_2O^+	12.91	13.33	12.90
MnO	.02	0	.02
NiO	.02	0	.03
Cr_2O_3	.02	0	0
Total	100.09	100.03	99.99

[1] Chrysotile from D. W. Jacquays Company, Phoenix, Arizona.

[2] Massive serpentine from D. W. Jacquays Company, Phoenix, Arizona.

[3] Chrysotile from Johns-Manville Company, Ltd., Box 1500, Asbestos, Quebec.

Analysis of chrysotiles by R. L. Craig, and of massive serpentine by E. E. Sutton, both of Norris Metallurgy Research Laboratory, Bureau of Mines, Norris, Tenn.

TABLE 2. DENSITY OF REFERENCE MATERIALS

Reference material	Density using Mercury gm/cc	Density in water gm/cc	Probable true density gm/cc
Aluminum, pure[1]	2.696	2.708	2.702
Quartz, clear	2.644	2.653	2.648
Large test ball	7.665	—	7.666[2]
Small test ball	7.657	—	7.666[2]
Steel block, machined	7.841	7.831	7.830

[1] Alcoa spectrographic standard.

[2] Based on values for volume of test balls furnished with air pyrconometer, by Beckman Instruments, Pasadena, California.

calcite. The third is hand-picked Canadian chrysotile and, at 100 magnification, was free of magnetite.

Results and Discussion

Several reference materials were selected to check the newly designed and built apparatus for density measurements in mercury. The densities of three of these were also determined in water. The results are given in Table 2. Aluminum and quartz were chosen because they have a density

Table 3. Density of Sealed and Unsealed blocks of Chrysotile

Sample No.	Sample wt. gms.	Sorbed water wt. per cent	Density, using mercury, as measured,[1] gm/cc	Density, using paraffin coating as measured[2]	Bulk density, after all corrections (magnetite structural Fe, air buoyancy, gm/cc)
1[3]	148.2870	1.18	2.20	2.19	2.19
2	78.3715	1.09	2.22	2.22	2.22
3	40.6490	1.08	—	2.25	2.24
4	166.5995	1.05	2.24	2.25	2.24
5	162.8144	1.08	2.22	2.23	2.22
6	64.3568	1.09	2.24	2.25	2.25
7	77.3860	1.10	2.25	2.25	2.25
8	185.6378	1.04	2.23	2.23	2.22
9	32.1743	1.08	—	2.23	2.22
10[4]	13.7456	.93	—	2.39	—
11[5]	41.6885	1.10	—	2.25	—
12[6]	205.6065	.84	2.40	2.39	2.36
13	167.6960	.89	2.41	2.40	2.37
14	111.2180	.80	2.51	2.51	2.34
15	94.1775	.89	2.40	2.41	2.38
16	41.9352	.89	—	2.38	—
17	33.0130	.80	—	2.53	—
18[7]	84.5540	.89	2.40	2.41	2.38
19	104.0106	.83	2.49	2.50	2.38
20	60.8961	.88	2.43	2.43	2.38
21	39.2374	.76	—	2.54	—
22	70.1196	.91	2.42	2.44	2.36
23	67.5001	.69	2.66	2.67	2.39

[1] Density of sample excluding sorbed water.

[2] Density of sample excluding sorbed water and paraffin.

[3] Samples 1 through 9 from D. W. Jacquays Co., Phoenix, Arizona.

[4] Sample No. 10, Aboutville (?), New York, Smithsonian Cat. No. 91261.

[5] Sample No. 11 from Kaapsche Hoop near Barberton E. Transval, Africa, Smithsonian No. 91197.

[6] Sample No. 12–17, Johns-Manville Co., Ltd., Box 1500, Asbestos, Quebec.

[7] Samples No. 18–23, Bell Asbestos Mines, Ltd., Thetford Mines, Quebec.

TABLE 4. DENSITY OF ARIZONA MASSIVE SERPENTINE WITH CONCOIDAL FRACTURES

Sample No.	Sample[1] wt., gms.	Density after soaking in water[2] gm/cc	Density by mercury[3] immersion gm/cc	Density by paraffin coating gm/cc
1	117.4810	2.56	2.43	2.42
2	63.4768	2.56	2.41	2.41
3	78.1780	2.57	2.43	2.43
4	59.4592	2.55	2.40	2.40
5	55.5614	2.56	2.41	2.40
6	80.5733	2.56	2.44	2.42
7	101.0990	2.56	2.44	2.44

[1] Samples dried 125° C. for 36 hours.

[2] Samples soaked in warm water for 48 hours, and density was determined.

[3] Samples again dried and density determined in Hg, and then by coating with paraffin and immersing in water.

near the theoretical value for chrysotile. The apparatus for determining density by weighing in mercury was very easy to manipulate, and based on the values found for reference materials listed in Table 2, had an accuracy of $\pm .01$ gm/cc.

The results of the density measurements on the block samples are given in Table 3. Considerable magnetite was present in many of the blocks of Canadian chrysotile. The magnetite was separated magnetically after heating to destroy the chrysotile structure and determined chemically. The density values obtained were corrected both for the magnetite and for the Fe^{2+} and Fe^{3+} in the structure. The corrected density for the fiber blocks is given in the right hand column of Table 3.

The densities of Arizona and African blocks of chrysotile show that void areas exist, and the density measurements agree very closely with theoretical data calculated from previously published electron microscopic measurements of the single fibers (Kalousek and Muttart, 1957; Maser *et al.*, 1960). Canadian chrysotile is a little too high in density to be completely tubular, but the data in Table 3 certainly indicate that over half of the chrysotile must exist as hollow tubes.

The authors have examined massive serpentine in the past and have noted tubular structure. However, the present specimens of Arizona massive (rock-like) serpentine were largely filled with unknown material (Fig. 4).

Also, the determined density (Table 4) confirms considerable filling of the tubes. Immersion in water gave density values approximately equal to the theoretical as determined by *x*-ray diffraction. This means that the void spaces were filled with water during the 48 hour immersion. Chryso-

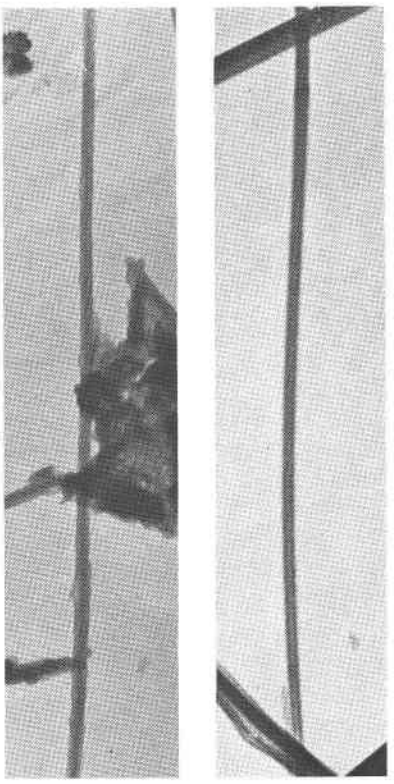

FIG. 4. Examples of filled and unfilled single fibers: serpentine on left, chrysotile on right. Both are from Arizona. Dark line up the middle of the serpentine fiber indicates filling; the light line up the middle of the chrysotile fiber indicates a hollow tube. Magnification 54,000×.

tile from some localities might exist with the void areas being all or partially filled. At least one-third of the possible void volume of Canadian chrysotile, that we examined, must be filled with solid material; or alternately, most or even all of the possible void volume could be filled with a material or materials with a density considerably less than 2.56 gm/cc.

CONCLUSIONS

1. The density of bulk chrysotile is lower than that postulated from x-ray diffraction data—in some chrysotiles by an amount approximately equal to the calculated void volume based on hollow tubes. The actual values are in the range 2.2 to 2.4 gm/cc.

2. The density values presented in this report essentially agree with those given by early investigators (Berger, 1963; Bowles, 1955; Dana, 1892), but disagree and are irreconcilable with some more recently pub-

lished data (Pundsack, 1956). The latter allowed only a solid structure without holes or spaces between fibers, and has been the subject of considerable controversy.

3. The density of both bulk chrysotile and massive serpentine indicates a hollow-tube or partially filled hollow-tube structure.

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