Heat Treatment of Chrysotile Asbestos Fibres

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ABSTRACT

A commercial method has been developed for controlling the texture of chrysotile asbestos fibres so that they may possess properties comparable with natural semi-harsh fibres for use in wet processes.

The physical properties of the soft, silky and slimy fibres are partially altered by a flash-heating process which removes a portion of the molecular water.

The heat-treated fibres show an improvement in filterability, an increase in bulk, absorption, and surface area, and better electrical properties, such as volume resistivity.

* * *

Introduction

CHRYSOTILE ASBESTOS fibres are found in nature having varying degrees of texture, referred to as soft, semi-harsh, and harsh. Fibres of each type of texture have inherent characteristics which directly affect their usefulness to industry. Visual differences are apparent under a microscope where it is seen that the soft-textured fibres have a silky, serpentine or wavy appearance, whereas the harsh-textured fibres are coarser and spicular†. Semi-harsh fibres, of course, have properties intermediate between these extremes.

Fankuchen and Schneider (1) have shown by the use of low-angle X-ray scattering that the diameter of the harsh type of chrysotile fibre is somewhat greater than that of the soft variety. Surface area measurements on various chrysotiles of different textures tend to confirm their findings. By nitrogen adsorption methods, it was found that the surface areas of soft types of chrysotile asbestos are approximately $23M^2/g$ whereas for the harsh types they are as low as $11M^2/g$.

The reason for these differences in fibre texture has been a matter of conjecture for some time, and the literature (2) contains several suggested explanations, such as the MgO : SiO_2 ratio, lime content, presence of calcite, pressure of formation, weathering, transition between asbestos and talc, and molecular water content of the fibre. After examining fibres of widely differing textures, it was found that the best correlation seems to exist between the water of constitution and the degree of harshness. The paramount differences between harsh- and soft-textured fibres, however, are in their respective strengths and filtration characteristics. Furthermore, it is the wide difference in these properties which directly influences their industrial usages. For example, a soft, silky fibre usually has high tensile strength and is extremely flexible. However, it is also usually slimy and difficult to de-water when used commercially to produce products involving wet methods. On the other hand, harsh and semi-harsh fibres de-water rapidly, but are generally low in tensile strength, and, in many cases, brittle to the point that the flexing characteristics are vastly inferior to those of the soft chrysotiles.

Obviously, it would be desirable to produce a fibre incorporating the strength properties of the soft-textured fibres with the rapid filtering properties of the harsher types. The commercial or industrial importance of such a fibre would be an increase in the production rate of wet-machine products and possibly the utilization of lower grades of poorer filtering fibres were high product strength might not be of the utmost importance. Since the water content of chrysotile appears to be correlated with its texture, it was decided to examine heat-treatment as a means of modifying the texture of the soft fibres and improivng their physical properties.

Effect of Heat on Texture of Fibre

Samples of chrysotile crudes, carefully cleaned of wall-rock and fibreiaed, were prepared and classed as soft, silky, and slimy when wet by water. Careful heating of these samples in the laboratory under controlled conditions at various temperatures and for various durations of exposure definitely indicated that a soft fibre can be converted to one exhibiting the characteristics of a harsh or semi-harsh fibre.

Dehydration studies of chrysotile asbestos have been made by numerous investigators (3) and the effects of temperature are well known. However, the purpose in the present application was to dehydrate the chrysotile molecule only partially and to bring the water content in the range normally encountered in the harsh-textured fibres.

The "loss on ignition" shown in analyses of semi-harsh to harsh chrysotile fibres usually ranges from less than 12 per cent to 13 per cent, depending upon the degree of harshness. The theoretical percentage of molecular water or water of constitution in pure asbestos is approximately 13 per cent. This is represented by the hydroxyl radical in the molecular structure is expressed by the formula $Mg_6(OH)_8Si_4O_{10}$, where the heat first breaks down the components to $3Mg_2SiO_4$, SiO_2, and $4H_2O$. Therefore, any reduction in the number of hydroxy radicals present, as would be effected by heat, will decrease the total amount of water of constitution, and this affects the physical properties of the fibre.

For the applications under consideration, the water of constitution was to be reduced about 30 per cent, or, in other words, the fibre sample was to be heated until its loss in weight amounted to about 4 per cent. In most of the tests, however, this loss actually ranged from 0.3 per cent to 3 per cent. Excessive heating has a deleterious effect upon

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†Photomicrographs showing these differences were published in C.I.M. *Transactions*, Vol. LIV, 1951, p. 166.

(1) For references see end of paper.

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tons the severity required by the methods of the fibre as a reinforcing filler. Hence, a carefully controlled heat treatment process is required to attain the desired results.

Laboratory tests conducted also on Canadian [illegible] fibres from regular production in which they, too, were exposed to heat treatment at various temperatures for varying time intervals. Again, the fibres produced possessed texture characteristics similar to those of semi-harsh and harsh fibres. In the fibres from regular production, there are impurities such as brucite, carbonates, and others. Heating will result in ignition losses higher than the theoretical 13 per cent of water of constitution of pure asbestos.

Physical Properties of Heat-Treated 6D Fibre

Table I lists some of the physical properties of the 6D fibres before and after the heat treatment. The data show that as the heat-treatment temperatures and times are increased, filtration is improved, water of constitution is reduced, magnetite is decreased, and the strength of an asbestos-cement block containing the heat-treated fibre is decreased.

Figure 1, in which percentage increase in filterability is plotted against temperature, shows the effect of the heating at time intervals of fifteen minutes and three minutes.

Figure 2, showing the percentage increase in fibre filterability at different heating-time intervals at temperatures of 700°F. and 1,200°F., demonstrates that heating at a high temperature for a short period will yield a fibre having the same degree of filterability as that obtained by heating at a lower temperature for a longer period.

Temperature °F.	Time Min.	Increase in Filterability %	Residual H_2O in Sample %	Residual Magnetite %	Asbestos-Cement Panels	
					Modulus of Rupture, lbs. per sq. in.	Residual Strength %
—	—	—	100.0	100.0	3,340	100.0
600	15	7.0	98.4	90.2	—	—
600	30	25.0	98.7	86.9	—	—
900	7	25.0	97.1	90.2	3,280	98.2
900	15	79.0	95.3	82.0	2,490	74.5
1,200	1	25.0	99.4	—	—	—
1,200	2	67.0	94.9	85.3	—	—
1,200	3	71.0	95.3	78.7	2,760	82.6

Another interesting comparison is that of the percentage of residual water with the percentage of increase in filterability. As shown in Figure 3, there is a definite correlation, and the amount of water in the molecule governs the degree of filterability of the fibre.

The effect of heat upon the magnetite present in chrysotile from regular production is to convert, partially, the Fe_3O_4 to Fe_2O_3, which is non-magnetic. In Table I, the reduction in the amount of magnetite remaining in the fibre after heating at 600°, 900°, and 1,200°F. shows that the magnetic character of the chrysotile is considerably reduced by heat treatment.

Table I also shows the effect of heat treatment upon asbestos-cement panels made of a Canadian 6D fibre. In the Table, the strengths of these panels are expressed as modulus of rupture in pounds per square inch. Panels made with fibres heated at the temperature of 900°F. for 15 minutes still retained 74.5 per cent of their normal strength. Panels made with fibres heated at 1,200° F. for 3 minutes still retained 82.6 per cent of their normal strength.

Another advantage of heat-treatment of chrysotile is its effect upon the volume resistivity of the fibre. Table II illustrates the vast increase in the resistivity of a heat-treated Canadian 6D fibre which is used in the manufacture of asbestos paper.

These data show that, as the molecular water was reduced, the volume resistivity expressed as megohm inches was greatly increased. Figure 4 illustrates this graphically by a plot of the percentage of residual water against the logarithm of the volume resistivity. The area between these curves represents the decrease in electrical resistivity due to the adsorption of surface moisture upon the fibre surface. However, even when the fibres were tested at 74°F. and 44 per cent relative humidity, the improvement in electrical properties was highly significant. A log-log plot of residual water and resistivity has much the same contour as that in Figure 4. The combined effect of improved filterability and electrical

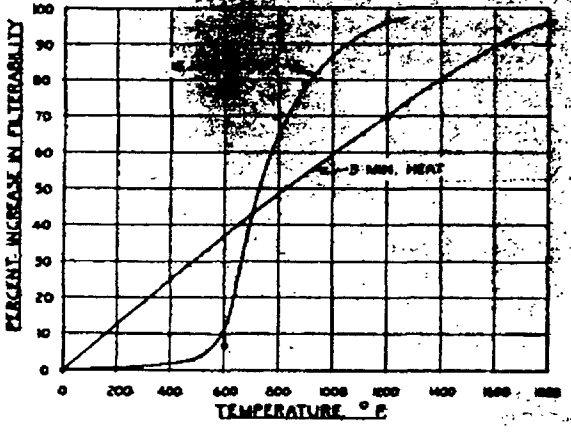


Figure 1.—Percent increase in filterability *vs.* temperature (°F.)

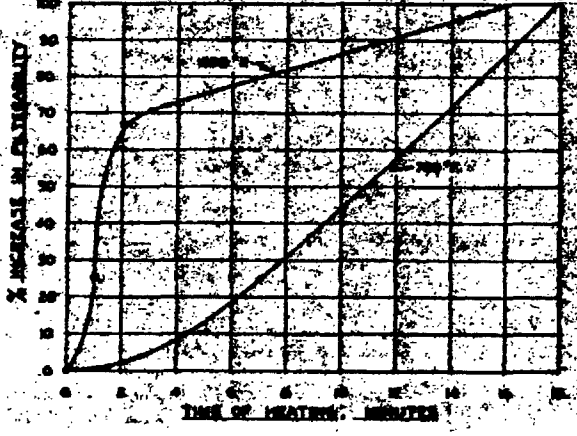


Figure 2.—Percent increase in filterability *vs.* time of heating (min.)

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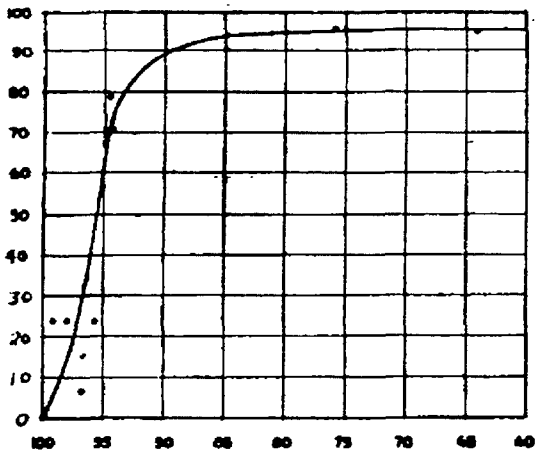


Figure 3.—Percent residual H_2O vs. percent increase in filterability.

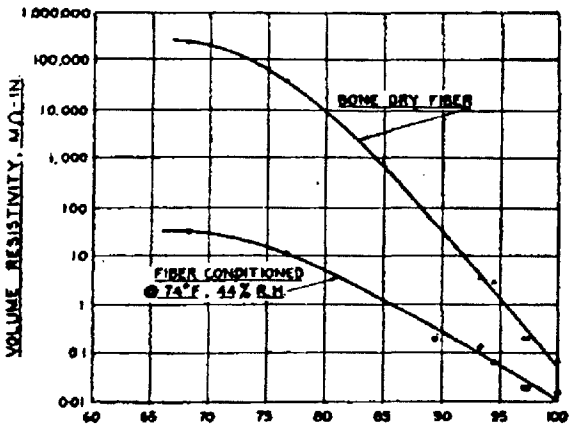


Figure 4.—Effect of heat treatment upon volume resistivity of 6D chrysotile asbestos.

properties is of direct interest and importance in the manufacture of electrical papers.

X-ray diffraction studies were made on a Canadian chrysotile fibre heated for one hour at temperatures of 400°, 500°, 600°, 700°, 800°, and 900°F. They showed that the structure remained typical of chrysotile. At 1,000°F. for one hour, the surface was amorphous, but, after carefully scraping off the surface, examination of the interior revealed the X-ray diffraction patterns were mostly those of chrysotile. At 1,400°F. for one hour, the entire mass had the structure of olivine. This study indicated that chrysotile, after losing small amounts of its molecular water, still retains much of its general structure. Anderson and Clark (5) heated chrysotile to constant weight at 900°C. and showed that the resulting fibre structure was not so definite as in natural fibre.

Application of Heat

Various types of heating units were investigated, such as muffle, infrared, dielectric, different types of commercial furnaces, and flash calcining. The main problem was to obtain a uniformly heated asbestos particle throughout any given mass, whether suspended in a gas atmosphere or as a thin or thick layer on a conveyor belt. Another problem was to devise a temperature control system that could be regulated manually or made automatic. A final problem was cooling of the treated fibre before it was bagged.

Several years were required to investigate all of the possible methods of applying heat to produce heat-treated fibre. Finally, the flash-calcining system was selected as the most appropriate.

Table II.—Effect of Heat Treatment on Resistivity of Fiber

Residual Water %	Residual Water, Log	Volume Resistivity 74°F., 44RH		Volume Resistivity Bone Dry	
		Megohm inches	Log resistivity	Megohm inches	Log resistivity
100	2.000	0.016	−1.796	0.08	−1.097
97.3	1.988	0.023	−1.638	0.29	−0.538
97.0	1.987	0.026	−1.585	0.29	−0.538
94.5	1.975	0.075	−1.1249	4.10	+0.613
93.3	1.970	0.110	−0.9586	4.80	0.681
76.7	1.885	13.30	+1.1239	52,000	4.716
89.4	1.951	0.25	−0.6021	41.0	1.613
68.2	1.834	45.30	1.656	300,000	5.477

Heat-Treatment Pilot Plant

A flash-calcining unit was purchased from the Nichols Engineering and Research Corporation, and a pilot plant with a processing capacity of two tons of fibre per hour was erected at Asbestos, Que.

A diagram of the unit is presented in Figure 5, which shows the path of asbestos particles and gases throughout the system. Thermocouples were installed at strategic points, and the temperatures were recorded on charts for a permanent record. After some experience, it was decided which thermocouple provided the most critical control, and from then on, the desired temperatures were regulated by this particular thermocouple reading.

The furnace, which was oil-fired, left no deposit of soot or other impurity in the fibre product since complete combustion took place in the chamber outside of the calcining tower. A gas-fired furnace would be ideal because the combustion chamber could be reduced in size or entirely eliminated.

The pilot plant building was a three-story structure located on a railway siding near the asbestos mill at Asbestos. In the basement was placed the mechanical driving mechanism for operating the air locks and a fan. The first floor contained the combustion chamber, pyrometer recorders, oil burner, and fibre-feeding conveyor. The second floor contained the bagging spouts where the fibre was sampled, bagged, sewed, and chuted to the boxcar for shipment.

The flash calciner unit was 26 ft. high by 8½ ft. in diameter, and was lined with fire brick. The bottom of the calciner was conical to enable the heated fibre to drop automatically into an air lock and be removed from the heating unit as rapidly as it collected.

The natural fibre was fed to a fan unit that gently willowed the fibre, freed it of lumps, and suspended it in an air stream so that it would fall by gravity down through the hot gas-heating zone. Peepholes

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into fibres possessing properties competitive with those of natural semi-harsh to harsh fibres. The process, a flash-heating system, was operated as a pilot plant at the rate of 2 tons per hour for several years.

(2) The process allows the mine and mill operator to control his product and to produce any desired texture for fibres grading from Group 3 to Group 7 and 'floats,' at nominal additional cost.

(3) By heat treatment, the physical properties of the fibres have been partially altered by the removal of small quantities of molecular water and a partial conversion of magnetic iron oxide (magnetite) to the non-magnetic oxide, Fe_2O_3.

(4) The improvements in filterability, increased bulk, increased absorption, increased surface area, and better electrical properties, such as volume resistivity, are all a direct function of the temperature and time of heating.

(5) The tensile strength of heat-treated fibres, as well as the strengths of asbestos-cement panels containing them, will decrease as the temperature and time of treatment is increased. However, this disadvantage is minor and the products are equal to those obtained by using natural semi-harsh to harsh fibres.

References

(1) FANKUCHEN, I., and SCHNEIDER, M., *Low-Angle X-ray Scattering from Chrysotiles;* Am. Chem. Soc., Jour., Vol. 66, 1944, p. 500.

(2) SOBOLEFF, N. D., and LATARINOFF, M. W., *The Cause of Brittleness in Chrysotile Asbestos;* Econ. Geol., Vol. 28, January—July, 1933, p. 171.

(3) NUTTING, P. G., *Some Standard Thermal Dehydration Curves of Minerals;* Professional Papers 196-198, P.T.B., 1941—1943.

GILL, A. F., *The Thermal Dehydration on Composition of Certain Minerals and Salts;* Can. Jour. Research, Vol. 10, 1934, pp. 703—712.
WOLOCHOW, D., and WHITE, W. H., *Thermal Studies on Asbestos;* Can. Jour. Research, Vol. 19, Feb., 1941, pp. 49—56.

(4) BADOLLET, M. S., *Asbestos; A Mineral of Unparalleled Properties;* C.I.M., Trans., Vol. LIV, 1951, pp. 151—160.

(5) ANDERSON, H. V., and CLARK, G. L., *Application of X-rays in the Classification of Fibrous Silicate Minerals Commonly Termed Asbestos;* Ind. and Eng. Chem., Vol. 21, No. 10, 1929, pp. 924—933.

(6) BADOLLET, M. S., and STREIB, W. C., U.S. Patent 2,616,801, *Partially Dehydrated Chrysotile Fibres and Method of Making;* also Canadian Patent 504,310.

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