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The Surface Energetics of Asbestos Minerals

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Nitrogen and argon isotherms were determined on amosite and on chrysotile asbestos at −183° and −195°C, and in three states of subdivision. BET surface area determinations showed that milling increased the amosite surface area from 1.3 to 11.0 m^2/g, and the chrysotile from 15.3 to 48.4 m^2/g. Changes in hysteresis of the adsorption isotherms indicated that the increased surface area after milling was mostly external for amosite and the increase for chrysotile was primarily caused by the greater availability of micropores. Measurements of pore size showed averages of 58.5Å for amosite and 80.5Å for chrysotile. Heat of adsorption determinations, calculated from the Clausius-Clapeyron equation, showed only minor differences between the two minerals.

Introduction

ASBESTOS IS a generic term applied to certain fibrous, inorganic minerals. Chrysotile is a serpentine mineral with an idealized empirical formula of $3MgO \cdot 2SiO_2 \cdot 2H_2O$. It is estimated that 96% of all commercial asbestos material mined is chrysotile.[1]

Amosite is a member of the amphibole group of minerals and is monoclinic in shape. Chemically it is a magnesium iron silicate $(Fe^{2+}{}_{5.5}Mg_{1.5}Si_3O_{22}(OH)_2$. Amosite fibers are made of laths which appear to be made of layer upon layer of thin, sheetlike material.[2]

The purpose of this study is to determine whether any correlation exists between the surface properties of samples of amosite and chrysotile and their toxicities. Both samples were studied by electron microscopy. Adsorption isotherms were made at −183° and −195°C using argon and nitrogen as adsorbates. From these isotherms isosteric heats of adsorption were calculated using the Clausius-Clapeyron equation. The amosite used was from the H. K. Porter Company operation in South Africa. It was designated 202-901. The chrysotile used consisted of loose fibers obtained from the Bell mines in Canada and designated as Grade 3T.

Since 1935, when Lynch and Smith[3] suggested the association between asbestos exposure and lung cancer in man, this possible factor in environmental carcinogenesis has attracted considerable attention. In the succeeding years evidence has accumulated to show that certain types of asbestos, in addition to their fibrogenic property, apparently also possess carcinogenic potential.[4]

In a recent study, Reeves *et al.*[5] exposed laboratory rodents to asbestos dusts in inhalation chambers. Additional rodents were injected intratracheally, intrapleurally, or intraperitoneally with these dusts. Following local implantation into the pleura or peritoneum, it was concluded that amosite was less carcinogenic than chrysotile. However, amosite was more fibrogenic than chrysotile in this study causing much higher early mortality, especially in guinea pigs. Current thinking favors the hypothesis that organic

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[*] Mention of commercial names or concerns does not constitute endorsement by the Department of Health, Education, and Welfare.

compounds which may become adsorbed on the fibers could be one of the factors in the carcinogenic potential of asbestos.

Electron Microscopy

Both asbestos samples were examined by electron microscopy to determine the difference in shape. The samples were prepared for electron miscroscopy by suspending them in water and adding a drop of the suspension to a Formvar-coated grid or by use of the viscous shear method. Electron micrographs were made of the individual fibers of amosite and chrysotile at magnifications of approximately 65,000×. These are shown in Figures 1 and 2. Figures 3 and 4 show micrographs of the asbestos fibers at 10,200×.

The electron micrograph of chrysotile at 65,000× shows that the fibers are, apparently, tubular, which confirms the work of previous investigators.[2,6] The amosite fibers are considerably greater in diameter than the chrysotile and are solid.

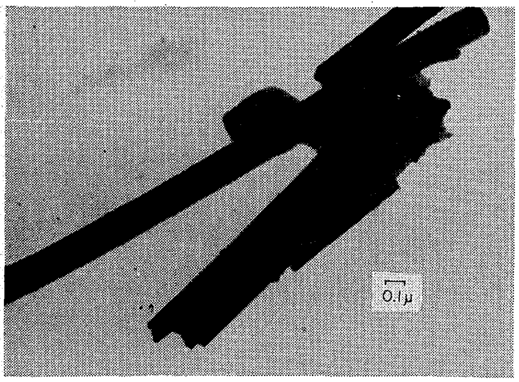

Figure 1. Amosite fibers at 65,800 ×.

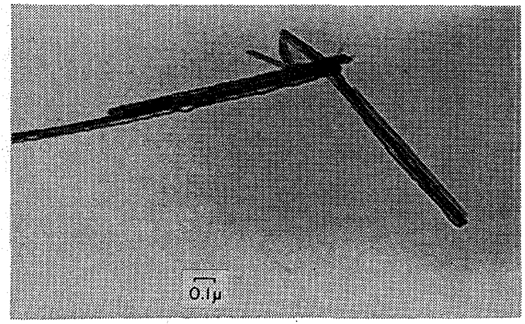

Figure 2. Chrysotile fibers at 65,100 ×.

The structure of chrysotile fibers is still a matter of dispute. Currently, they are considered to be tubular with material of lower electron density filling the tubes.[7] The material filling the tubes has not yet been positively identified

Experimental Work

Adsorption-desorption isotherms were made using the surface properties equipment described by Scheel *et al.*[8] In brief, this system consists of a Cahn RH electrobalance for measuring weight change of the sample during adsorption, a Wallace and Tiernan Model FA145 Bourdon gauge for measuring pressure from 1 to 800 torr, and a Bendix

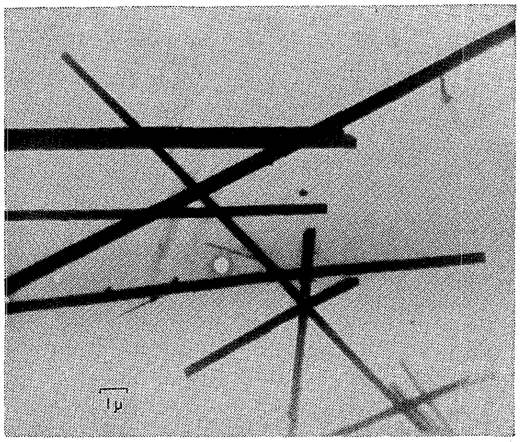

Figure 3. Amosite fibers at 10,200 ×.

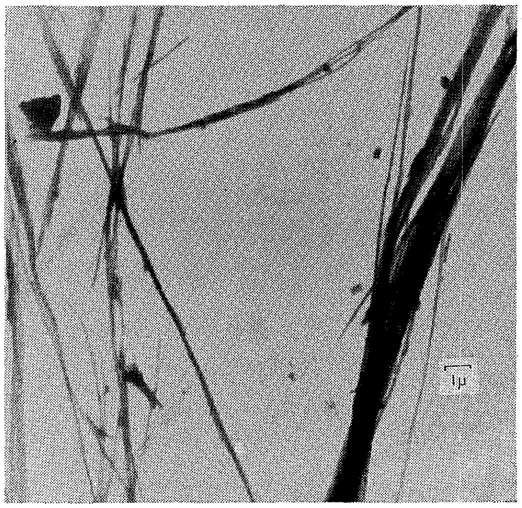

Figure 4. Chrysotile fibers at 10,200 ×.

GT-340 thermistor gauge for measuring pressure from 0 to 1 torr.

Experiments were made with both asbestos samples in three states of subdivision, namely, as received, mechanically dispersed, and impact milled at the temperature of liquid nitrogen. The mechanically dispersed asbestos was prepared by mixing 5 grams of the sample and 1,000 grams of distilled water in a Ver-Tis mixer for 20 minutes at 20,000 RPM using a tantalum impeller. This method has been used in the National Institute for Occupational Safety and Health laboratory for preparing asbestos samples for animal exposure tests. The impact milled material was prepared by grinding in a Spex mill cooled with a liquid nitrogen bath. This effectively broke up the fibers so their geometric mean sizes were 0.8 μ in length and 0.3 μ in diameter for amosite, and 0.6 μ in length and 0.15 μ in diameter for chrysotile.

The gases used were obtained from Air Reduction Company. The argon contained 1 ppm oxygen with no impurities detectable by mass spectrometry. The nitrogen contained 5.3 ppm argon, 0.5 ppm hydrocarbons and had a dewpoint of -105°C.

Before making adsorption isotherms, the samples were preconditioned by pumping at 25, 150, 250 and 400°C. After the first set of experiments, it was apparent that no significant difference was found in the samples conditioned at 25° and 150°C, so preconditioning at 150°C was eliminated. All the samples were pumped to a final pressure of $0.4\text{-}1.5\text{x}10^{-7}$ torr with a preconditioning time of at least 16 hours. A series of experiments was performed by adding a sample of asbestos to the balance, calibrating the balance, evacuating the system at room temperature for 16 hours or longer, and obtaining an adsorption isotherm at -195°C with nitrogen. After reaching essentially saturation conditions, the gas was desorbed in small increments to measure the amount of hysteresis. After all the nitrogen was desorbed, the sample was evacuated again at room temperature and an argon adsorption isotherm was obtained at -195°C. This procedure was repeated at -183°C for both gases. Then the asbestos sample was heated to 250°C and 400°C. Argon and nitrogen isotherms were obtained at -183°C, and -195°C at both preconditioning temperatures.

Surface Area Determinations

Surfaces areas were calculated from the adsorption isotherms obtained at -195°C with both argon and nitrogen using the Brunauer-Emmett-Teller[9] method of calculation. The data are summarized in Table I.

As expected, mechanically dispersing and impact milling both asbestos samples increased their surface areas. Part of this increase in surface area was due to breaking up of fiber bundles, and part was caused by making the micropores more available to the adsorbates as a consequence of grinding.

Preconditioning at 250° and 400°C also increased surface area, with the increase obtained from raising the temperature from 25° to 250°C generally being greater than that obtained by increasing the temperature from 250° to 400°C. This surface area increase was caused principally by removing the water of hydration from the asbestos. Most of this hydration water is removed at 150° to 250°C, as evidenced by surface area determinations. At 400°C the structure of the asbestos is unchanged except for a slight darkening in color. As can be seen, when both samples are mechanically dispersed, increasing the preconditioning temperature from 250° to 400°C has only a minor effect on surface area as compared to the "as received" sample. Evidently, mechanical dispersion breaks up the fiber bundles so that the hydration water becomes more readily available. If the "as received" samples were preconditioned at 250°C for a longer time, their surface areas might be increased. Electron micrographs of both samples preconditioned at 400°C are essentially the same as the original material. Heating at temperatures above 600°C destroys the

TABLE I
Surface Areas of Asbestos Samples at −195°

Sample	Preconditioning Temperature, °C	N_2 Surface Area m^2/g	Ar Surface Area* m^2/g
Amosite, as received	25	1.3	1.2
	250	2.2	2.0
	400	2.8	2.5
Amosite, mech. dispersed	25	5.9	5.4
	250	6.9	6.3
	400	7.0	6.3
Amosite, impact milled	250	11.9	11.2
Chrysotile, as received	25	15.3	13.1
	250	19.3	20.8
	400	22.1	21.0
Chrysotile, mech. dispersed	25	30.6	24.6
	250	36.1	31.0
	400	36.3	30.9
Chrysotile, impact milled	250	48.4	48.2

*Assuming an area of $14.4A^2$ for the argon molecule as calculated from the liquid density of argon.

crystalline structure of both asbestos minerals by removing the water of constitution.

In 13 of 14 cases, the surface area determined by argon adsorption is less than that obtained by nitrogen adsorption. In most cases the discrepancy between the two adsorbates is minor and is most probably caused by the uncertainty in the values of the areas of the individual molecules.

Adsorption-Desorption Isotherms

A total of 56 adsorption-desorption isotherms were determined. The data are summarized in Tables II and III. They show more hysteresis with the chrysotile than with amosite. Increasing the preconditioning temperature increases the amount of hysteresis in most cases. This is undoubtedly the result of removing adsorbed water, particularly from micropores, with increasing temperature.

Less hysteresis was found with nitrogen at −183° than at −195°C. Most of the hysteresis occurred at relative pressures higher than 0.4. At −183°C, the highest relative pressures obtained were 0.25-0.30.

Typical adsorption isotherms are shown in Figures 5 and 6. All of the isotherms are Type 2, as expected.

Porosity

The pore volumes of the unground amosite and chrysotile samples were determined by the mercury penetration method.[10] From the total pore volume and the surface area, as determined by low temperature nitrogen adsorption, the average pore diameter has been calculated from the formula $d = 4V_t/S$ where V_t is expressed in cm^3/g and S in m^2/g. The average pore diameter for amosite was 18.36 μ and for chrysotile 0.50 μ. The smallest pore diameter found was 0.02526 μ for both samples.

In recent years, Sing[11] has suggested an empirical method for analysis of adsorption isotherms. He uses a nonporous reference adsorbent similar in composition to the test materials and prepares a nitrogen isotherm at −195°C. Values of $(W/W_x)_s$, termed α_s, are calculated. W is the weight of gas adsorbed at a particular relative pressure and W_x is the weight of gas adsorbed at a relative pressure of 0.4. The value of W_x was selected arbitrarily, because with nitrogen,

TABLE II
Adsorption-Desorption Isotherms With Amosite

Sample	Preconditioning Temperature °C	Adsorbate	Adsorption Temperature °C	Maximum Hysteresis. μg/g sample
Unground Amosite	25	Nitrogen	−183	<10
			−195	<10
		Argon	−183	27
			−195	<10
	250	Nitrogen	−183	34
			−195	59
		Argon	−183	38
			−195	34
	400	Nitrogen	−183	51
			−195	102
		Argon	−183	119
			−195	102
Mechanically Dispersed Amosite	25	Nitrogen	−183	<10
			−195	<10
		Argon	−183	<10
			−195	102
	250	Nitrogen	−183	17
			−195	102
		Argon	−183	67
			−195	67
	400	Nitrogen	−183	<10
			−195	102
		Argon	−183	<10
			−195	<10
Impact Milled Amosite	250	Nitrogen	−183	63
			−195	254
		Argon	−183	84
			−195	190

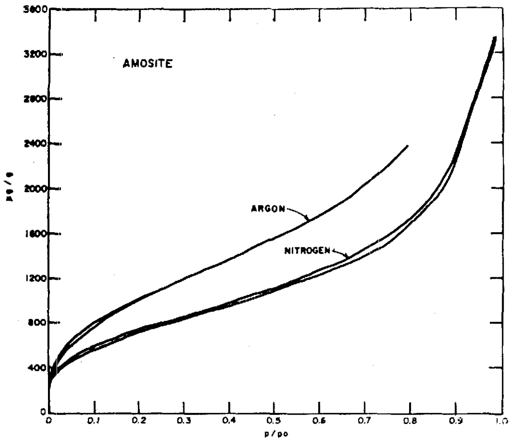

Figure 5. Adsorption isotherms of argon and of nitrogen on amosite.

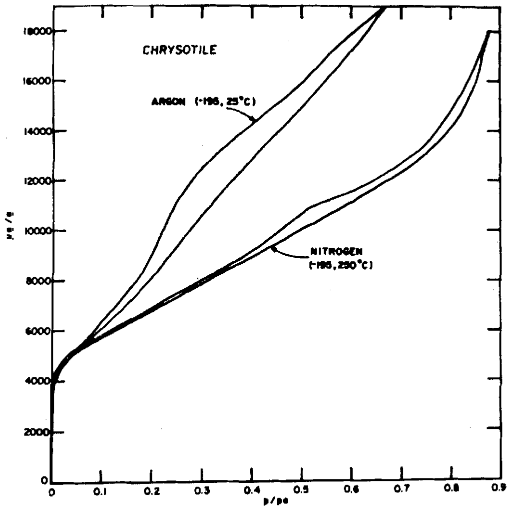

Figure 6. Adsorption isotherms of argon and of nitrogen on chrysotile.

TABLE III

Summary of Adsorption-Desorption Isotherms With Chrysotile

Sample	Preconditioning Temperature °C	Absorbate	Adsorption Temperature °C	Maximum Hysteresis μg/g sample
Unground Chrysotile	25	Nitrogen	−183	100
			−195	720
		Argon	−183	572
			−195	1923
	250	Nitrogen	−183	250
			−195	750
		Argon	−183	1304
			−195	2671
	400	Nitrogen	−183	<10
			−195	1100
		Argon	−183	1720
			−195	2764
Mechanically Dispersed Chrysotile	25	Nitrogen	−183	<10
			−195	325
		Argon	−183	853
			−195	650
	250	Nitrogen	−183	<10
			−195	771
		Argon	−183	974
			−195	1340
	400	Nitrogen	−183	<10
			−195	974
		Argon	−183	1218
			−195	1624
Impact Milled Chrysotile	250	Nitrogen	−183	<10
			−195	3717
		Argon	−183	2424
			−195	4040

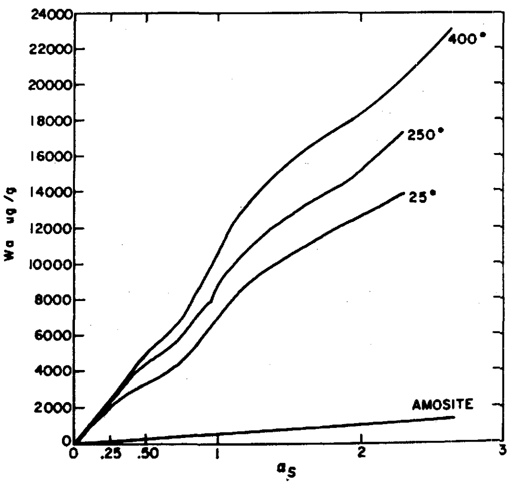

Figure 7. Curves of α_s for unground chrysotile preconditioned at 25°C, 250°C and 400°C and amosite preconditioned at 25°C.

monolayer and micropore filling occur at $p/p_o<0.4$ and any hysteresis loop present is generally located at $p/p_o>0.4$. A sample of glass sand with a geometric mean particle size of 0.25 μ was used as a standard material, and a nitrogen isotherm was made on it at −195°C. From this isotherm, values of α_s were calculated and plotted vs relative pressure. Figure 7 is a plot of a sample of unground chrysotile preconditioned at 25°, 250°, and 400°C, and unground amosite preconditioned at 25°C.

The data show that amosite gives a linear plot while the chrysotile plots show divergence from linearity at α_s values between 0.4 and 0.5 equivalent to relative pressures of 0.005 to 0.015. This indicates that the chrysotile contains some micropores while the amosite contains only minor amounts of micropores.

Cranston and Inkley[12] have developed a method of deriving pore size distributions from adsorption isotherms by refinement of the Barrett, Joyner, and Hallenda[13] method, which is based on the Kelvin equation. The critical pore diameter was taken as twice the sum of the calculated Kelvin radius and the experimentally determined thickness of the multilayer existing on a flat surface at the same relative pressure. This thickness was determined from published isotherms on 15 nonporous materials by dividing the volume of nitrogen absorbed by the BET surface area.

Figure 8 shows the pore size distributions of impact milled chrysotile and unground amosite both on a volume and surface area basis. Table IV is a summary of the pertinent data of both asbestos samples.

The data show the amosite to be considerably less porous than the chrysotile although the pore size distributions show the amosite to contain a larger percentage of pores less than 50A in diameter.

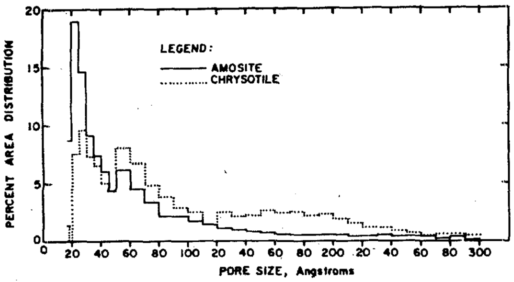

Figure 8. Pore size distribution of chrysotile and amosite on a surface area basis.

The difference in average pore size noted between the mercury penetration method and the Cranston-Inkley method is readily explained. The mercury penetration method measures the voids between particles, as well as all of the pores, while the Cranston-Inkley method measures only the pores less than 300A in diameter. Because of physical restrictions the mercury penetration method is unsuitable for making microporosity determinations.

Isosteric Heats of Adsorption

For a long time surface scientists have realized that the heat evolved during the physical adsorption of gases upon solids might give considerable information concerning the nature of the solid surface.

The isosteric heat of adsorption may be readily determined by use of the Clausius-Clapeyron equation in the form

$$\Delta H = 2.303R\,\frac{(T_1T_2)}{T_2 - T_1}\log\left(\frac{P_2}{P_1}\right)_\theta$$

where R is the gas constant, T_1 and T_2 are temperatures in °K at which the adsorptions were performed, and P_1 and P_2 are the corresponding pressures, at constant surface coverage, θ.

Adsorption isotherms were determined at $-183°$ and $-195°C$ using liquid oxygen

TABLE IV

Porosity Data of Asbestos Samples

	Chrysotile	Amosite
1) BET specific surface area m²/g (S)	48.4	1.3
2) Cumulative surface area (pores 300 Å diam.)	42.8	1.6
3) Total pore volume (pores 300 Å diam.)	0.0975 ml/g	0.0019 ml/g
4) Average pore diameter: $d = \frac{4V}{S} \times 10^4$ (Å)	80.5	58.5

and liquid nitrogen as coolants. Surface coverage was determined by dividing the weight of gas adsorbed by the weight of a monolayer of gas as calculated from a BET surface area plot. Surface coverage is plotted against relative pressure and from these curves pressures are determined at constant surface coverage and substituted into the Clausius-Clapeyron equation to calculate heats of adsorption. Heats of adsorption were then plotted versus surface coverage.

Plots of the heats of adsorption of nitrogen on mechanically dispersed amosite and mechanically dispersed chrysotile, both of which had been preconditioned at 250°C, show that there is little difference in the heats of adsorption of both materials. The amosite gives lower heats at surface coverage below 0.9 and slightly higher heats above 0.9. Similar plots made with argon showed only minor differences in heats of adsorption also. Thus, it may be concluded that heats of adsorption of argon and nitrogen on the asbestos minerals studied were not satisfactory parameters for determining differences in their surface properties. This may be due to the similarity of the composition of the two minerals.

The heats of adsorption obtained are in the same range as those obtained by other investigators for physical adsorption, thus confirming the absence of chemisorption. The shape of the heat of adsorption curves show that the surfaces studied are heterogeneous.

Conclusions

A study of the surface properties of two asbestos minerals, amosite and chrysotile, in three states of subdivision, shows the amosite to have lower surface areas when determined with argon and nitrogen. Argon and nitrogen isotherms show more hysteresis with chrysotile than with amosite, thus indicating more porosity for the chrysotile. Cranston-Inkley calculations confirm these results although the mean pore size for the amosite is less than for the chrysotile. Heat of adsorption determinations show only minor differences between the two minerals.

If the hypothesis that adsorption of certain organic vapors on asbestos fibers is a factor in carcinogenesis is accepted, it is readily apparent that chrysotile, with its higher surface area and porosity, could be more carcinogenic than amosite. If freshly ground chrysotile would immediately come in contact with an organic vapor, adsorption would occur. As noted, previously adsorbed vapors in micropores are removed with difficulty and thus, if lodged in the human lung, might be released over a long period of time. However, this is only one hypothesis concerning the carcinogenicity of asbestos minerals. Dixon *et al.*,[14] have shown considerable evidence that trace metals play an active role in the induction of asbestos cancer.

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1975 American Industrial Hygiene Conference Invitation for Papers

The Program Committee for the 1975 meeting at the Leamington Hotel, Minneapolis, Minnesota, June 1-6, 1975, invites submission of papers for the program of this meeting. The title and an informative abstract of your proposed paper should be forwarded to the Program Chairman or to the appropriate Session Arranger as soon as possible. The Committee will meet in mid-October to establish the preliminary program.

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