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CHEMICALS AND PLASTICS

RESEARCH AND DEVELOPMENT DEPARTMENT

P. O. BOX 579 • NIAGARA FALLS, N. Y.

PLAINTIFF'S EXHIBIT

Union Carbide 127

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Project No. 458-N11

Niagara Falls, New York
December 19, 1968

PROPERTIES OF COLLOIDAL CHRYSOTILE ASBESTOS FROM THE COALINGA REGION OF CALIFORNIA

INTRODUCTION

An asbestos group was formed under the auspices of the Nuclear Company to exploit colloidal chrysotile asbestos from a huge deposit located in the Coalinga region of California. The ore was in a high-grade, friable, massive deposit found on the surface and could be mined very cheaply. The fiber in the ore was very short, comparable in size to the Grade 7 sold by the traditional asbestos producers. This is the poorest grade and consists of fine rejects from the production of long-fiber grades of asbestos. The Grade 7 product is very impure, containing much rock dust and abrasive particles in addition to the fine asbestos fiber. It was recognized early in the investigation that the Coalinga ore could be processed in an aqueous circuit to make a very pure colloidal fiber product which would be unique in the asbestos industry. A mandate was given to a research and development group to study the properties of this chrysotile and develop new uses for colloidal products made from Coalinga asbestos.

The group was located at the Research Center, Tuxedo Park, New York. F. A. Mumpton and C. S. Thompson established the mineralogy of the deposit. The other research aspects of the project were done by W. H. Dresher and A. W. Naumann. They measured such properties of the asbestos as the dimensions of the fibers and their surface area, textural and thermal characteristics. In addition, they began investigation of the surface and colloidal properties of chrysotile. I joined this group in 1963 and concentrated on further study of the surface chemistry of chrysotile asbestos.

The asbestos group was transferred to the Mining and Metals Division in 1965 and relocated at their facilities in Niagara Falls, New York. At this time the emphasis of the research was changed to finding ways of chemically modifying the surface properties for applications in systems where the intrinsic surface properties of chrysotile were unsuitable. This was considered to be practical since our processing was done in an aqueous circuit. K. Park joined the group in 1966 to study the rheological properties of chrysotile suspensions. The asbestos group formally became part of Chemicals & Plastics in 1967, but it continued to be located at the Niagara Falls plant site.

The object of this report is to record my contributions to the study of chrysotile properties. My data are presented in detail with specific comments about them, and an over-all description of the asbestos system is given under the section on Discussion. Where I have not personally studied areas critically important to an understanding of the system, I have liberally quoted results and conclusions from the works of Mumpton, Dresher, Naumann, and Park, and from the literature. It should be cautioned that some of the data reported have been submitted to us on a personal basis, and those data from publications are the property of the publishers, so permission must be obtained from these people before public use can be made of them.

ACKNOWLEDGMENTS

Even the most simple understanding of a system such as this one comes about after discussions with many people and often it is difficult to attribute ideas specifically to any one person. The whole staff of the asbestos group has contributed by discussion to the ideas proposed in this report. Fred Mumpton has been particularly helpful about the structure and mineralogy of silicate minerals. Wayne Naumann and Bill Dresher, whose data have been so extensively quoted, started me effectively in this project. Kisoon Park has helped in my understanding of thickening mechanisms and his data are also quoted. Professor R. S. Hansen contributed to the analysis of adsorption data. Bob Byrne assisted in the development of modified products and was the driving force in their utilization.

Facts are still the prime justification for any research group and so I am most grateful for the services of two excellent technicians, Dave Wilson at Tuxedo Park, N. Y., and Al Gonas of Niagara Falls, N. Y. They collected the data patiently and precisely and so made it possible to present this work with confidence.

STRUCTURE

Much work has been done on determining the structure of chrysotile asbestos and it is adequately discussed in a recent standard reference work (1). The main feature of the mineral is that it is composed of two-layer sheets, each of which consists of a layer of silica bonded to a layer of brucite. A unit of composition $Mg_6(OH)_8Si_4O_{10}$ has average dimensions in the plane of the sheet of 5.3 x 9.2 A.U. and a height perpendicular to the sheet of 7.3 A. The brucite portion, containing 6 magnesium hydroxyl groups, actually is slightly larger than the silica part, which has only 4 silicon dioxide groups, so each sheet curves around with brucite groups on the outer part of the curvature. This results in the formation of a hollow, cylindrical structure, and a typical fibril will have 10 to 20 individual sheets. There is no chemical bonding between the sheets, which are held together strictly by Van der Waal's forces. It is most important for an understanding of the surface properties of the chrysotile to note that the outer surface of the fibril is always composed of brucite groups. For example, lizardite is a serpentine mineral with the same composition as chrysotile but has a platy structure; it has radically different surface properties. A schematic drawing of the chrysotile structure is shown in Figure 1. The 6 lines radiating from the magnesium atom to surrounding atoms indicate that it is in 6-fold co-ordination (octahedral), while the silicon atoms are shown to be in 4-fold co-ordination (tetrahedral).

There has been a controversy in the past about whether the hole in the middle of the fibril really existed and whether it was filled with material or existed as an empty space (2). Electron microscope observations distinctly indicated the trace of a hole, but density measurements on the crystals were too high to permit an empty hole to exist (3). Surface area measurements and pore distribution measurements also were too low to allow for the presence of a significant cavity (4). This contradiction was resolved when it was found that an amorphous material of the same composition as chrysotile would have sufficient difference in diffractive index to be distinguished by an electron microscope (5), and it is now generally accepted that the hole is, to a large extent, filled by amorphous material (4).

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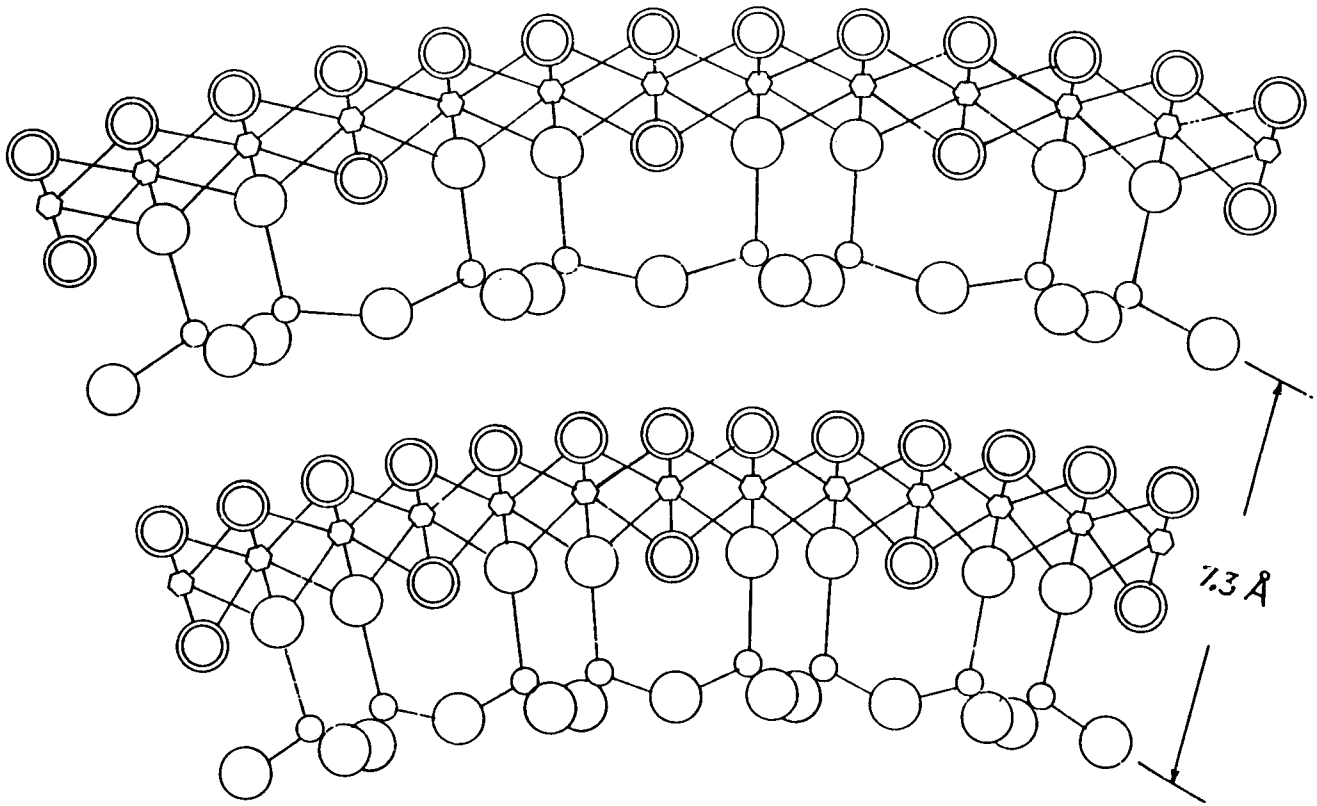


FIGURE 1 - CRYSTAL STRUCTURE OF CHRYSOTILE ASBESTOS

$Mg_6(OH)_8Si_4O_{10}$

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Similar amorphous material is said to fill the spaces between fibrils in asbestos from Quebec (6), but such inter-fibril material is lacking in ore from the Coalinga deposit (4). This has important bearing on our practical ability to reduce the ore particles to separate fibrils. Quebec ore is difficult to comminute to a colloidal size, while Coalinga asbestos is relatively easy to break down to its fundamental colloidal particles. This difference between cross-fiber asbestos and Coalinga asbestos is so vital that it will be discussed again under the topic heading of Texture.

Yada has achieved sufficient resolution with an electron microscope to show the individual layers (7). Groups of sheets are seen to spiral around the central core of the individual fibrils. A micrograph illustrating this pattern is shown in Figure 2. In Figure 3, a bundle of fibrils is seen to have filler material between the individual fibrils. The asbestos used by Dr. Yada is from the Jeffrey mine in Canada. A sample of Coalinga asbestos was submitted by Dr. F. A. Mumpton to Dr. Yada for observation and the pictures in Figure 4 were obtained (8). The asbestos shown there has no filler material between the fibrils.

Similar conclusions on the differences between Coalinga asbestos and Quebec asbestos were reached by Naumann and Dresher earlier, based on morphological studies (4). They also comment that Canadian asbestos fibrils often have particulate matter adhering to them, consistent with the view that the fibrils had been broken from a solid matrix.

The recognition that the structure is composed of groups of sheets curling around a core in a spiral arrangement makes plausible the idea that the fiber can be unrolled under the proper conditions. Kenney, et al. have described a reaction of chrysotile with hydrochloric acid and chlorotrimethylsilane which yields a stable, organosilicon polymer (9). The brucite portion of the unit cell is leached out in the presence of the silane which replaces it and maintains the integrity of the silica layer. Exposure of the altered fibers to organic solvents causes them to swell or uncoil into ribbons. The entire suspension becomes gelatinous, forming a colorless, fluid jelly. On exposure to water, the jelly collapses, and as the solvent is removed, the ribbons curl back up into fibers with the original dimensions of the chrysotile.

PHYSICAL PROPERTIES

Ore

Chrysotile occurs in the Coalinga deposit as a friable flake and as a green bladed aggregate (10). However, the processing in the mill at King City removes most of the latter so most of the mill product comes from flake ore material. An electron micrograph of the surface of a flake is shown in Figure 5. There are some veins of aligned fibers, but many of the fibrils occur in disordered regions which are very porous.

In addition to some serpentinite rock fragments (lizardite and antigorite) the principal mineral impurities are magnetite, brucite, a trace of calcite, and some Coalingite. The latter is a new mineral first identified by F. A. Mumpton in this deposit. While it is normally white in color, its presence is significant since under oxidation and weathering conditions, the mineral breaks down, causing a rusty discoloration. This affects the brightness of our asbestos products.

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FIGURE 2 - CROSS-SECTION OF CHRYSOTILE FIBRILS FROM QUEBEC SHOWING SPIRAL ARRANGEMENT IN THE STRUCTURE (7)

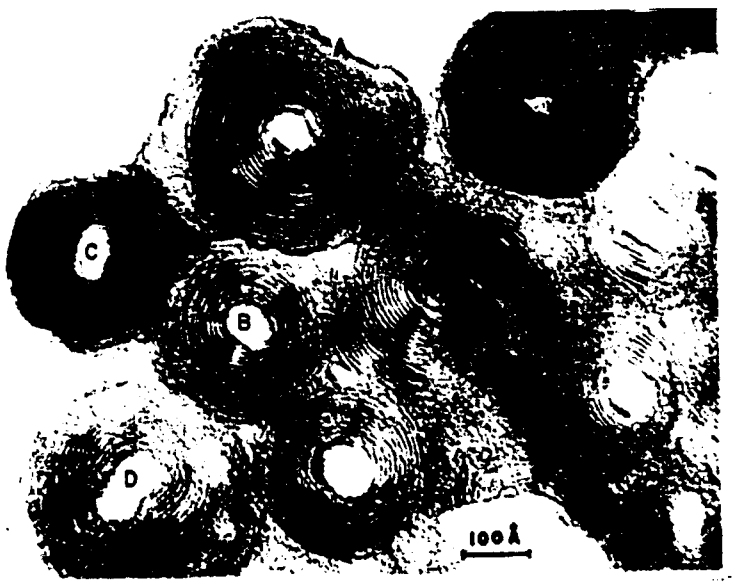


FIGURE 3 - CROSS-SECTION OF CHRYSOTILE FIBER BUNDLE FROM QUEBEC SHOWING FILLER MATERIAL BETWEEN FIBRILS (7)

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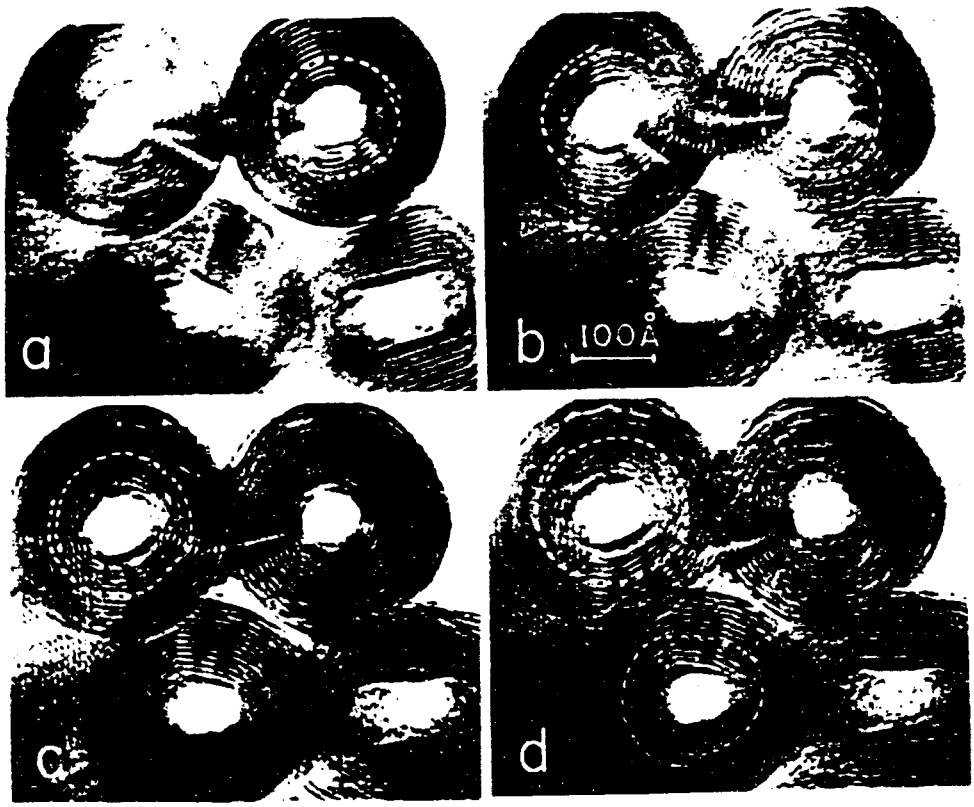


FIGURE 4 - CROSS-SECTIONS OF COALINGA FIBER BUNDLES SHOWING NO FILLER MATTER BETWEEN FIBRILS (8)

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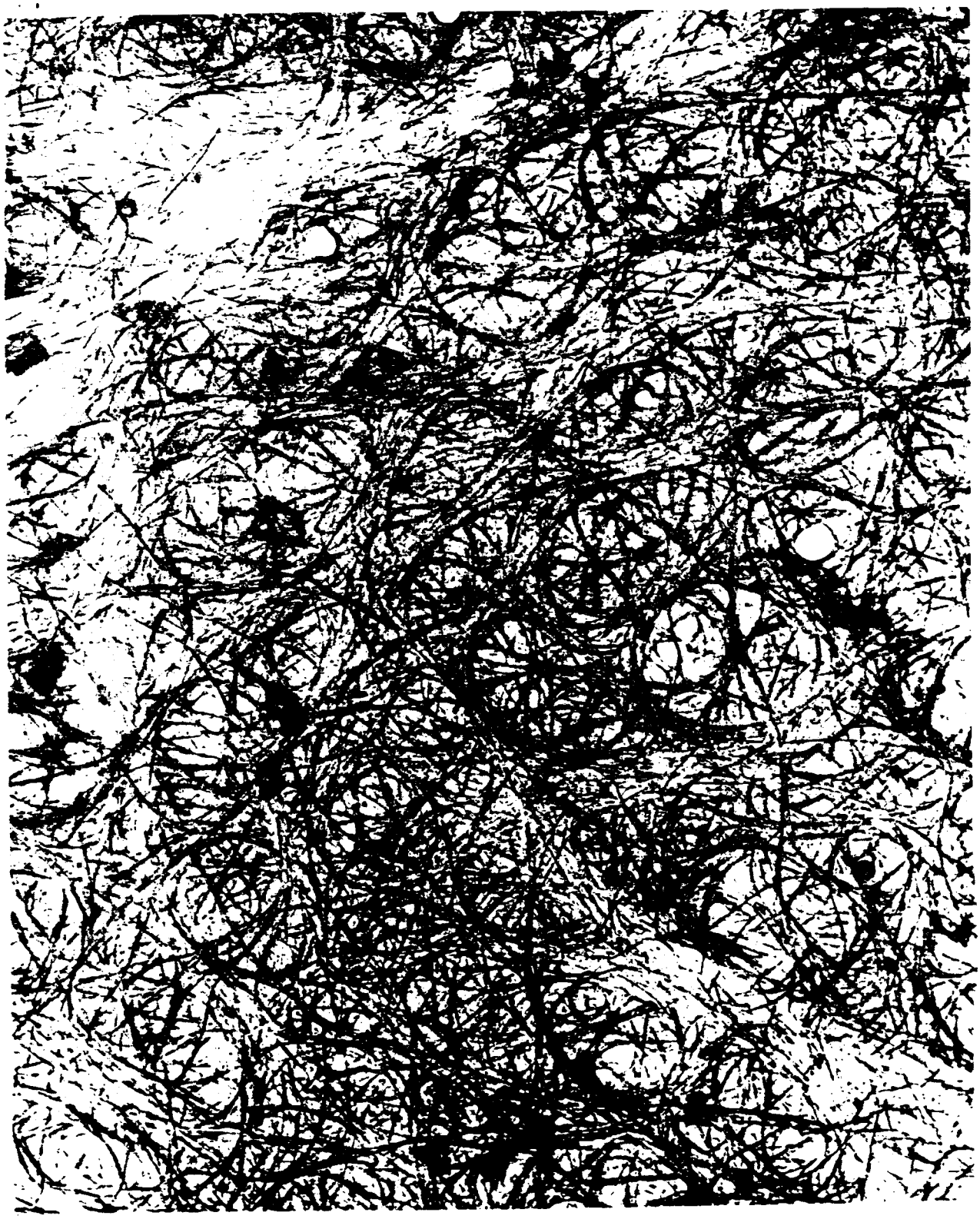


FIGURE 5 - REPLICA OF ASBESTOS FLAKE FROM THE COALINGA DEPOSIT

Magnification 9000X, Photo No. 2549

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The ore is gray with a greenish tinge, but as the gange minerals, mainly magnetite, are removed, the whiteness increases. A normal, refined asbestos product will have a brightness* of 72 to 76 per cent, but this can be increased by further refining and washing to nearly 80 per cent (11).

Much work has been done on the optical properties of high-purity asbestos product in paper by Mr. Blair Ingalls. Typically, high-purity grade of asbestos will have a scattering coefficient ranging between 350 to 700 cm^2/g and an absorption coefficient of 50 to 150 cm^2/g in paper (12).

Texture

Some comments have already been made during discussion of structure about the textural differences between asbestos samples. Naumann and Dresher studied in detail the morphology of chrysotile asbestos samples from the Coalinga deposit, from the Stratigari deposit of Yugoslavia, from the Cassiar mine in British Columbia, and from Quebec deposits (4). The latter two are typical cross-fiber asbestos materails. The Stratigari asbestos sample appears to be very similar to the Coalinga asbestos. They set out to find whether the hollow asbestos fibrils comprising these samples are filled or empty, and whether there is solid matter filling the voids between the fibrils in massive specimens of the samples.

A hexagonal close-packed assembly of tubes with a 300 Å outer diameter, a 150 Å inner diameter, and a wall density of 2.56 g/cc should have an external surface area of 69 m^2/g and an internal surface area of 35 m^2/g. The porosity of massive specimens should consist of about 9 per cent occurring as voids between the fibrils and 23 per cent occurring in the central pores of the fibrils. The previous literature about chrysotile samples reports surface areas ranging from 10 to 20 m^2/g and porosities from 1 to 10 per cent. Density measurements favor the interpretation that all voids of massive specimens are filled with matter of the same density as chrysotile itself (3).

Naumann and Dresher got some increases in surface area of cross-fiber asbestos as they increased the activation temperature from 100 to 400°C, but they got larger increases yet by chemically dispersing the asbestos. A well-opened asbestos, regardless of source, showed little effect of activation temperature. Coalinga and Stratigari asbestos samples both had a consistently high surface area regardless of the degree of opening or the activation temperature. This is interpreted to mean that the pores of the cross-fiber asbestos are filled with water and that better water removal is obtained at higher temperatures. Any brucite occurring between the fibrils of these samples should also dehydrate at a temperature of 350-400°C, leading to an opening of the structure. The increase in surface area with wet or dry mechanical opening is attributed to the liberation of fibrils. The lack of influence of activation temperature on surface area of well-liberated asbestos samples indicates that the pores associated with the bulk state of these materials involve voids between the fibrils and not the pores within the fibrils.

* Relative to a brightness of 98 per cent for pure MgO

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These results show that there is an open texture in the natural state of Coalinga and Stratigari asbestos samples, with essentially all of the external fiber surfaces available for sorption. The pores between fibrils were also large enough to prevent capillary condensation of water. Particulate matter was seen on fibrils of Quebec asbestos, but none on Coalinga asbestos. The adsorption of nitrogen gas on Coalinga asbestos, the Stratigari asbestos, and on the fibrillated samples of Cassiar asbestos was always reversible. However, for undefibrillated Cassiar asbestos, the desorption branch of the isotherm is displaced from the sorption branch. Analysis of these data leads to a pore diameter distribution peaking at about 20-25 A.

Fripiat and Faille also compare the textures of asbestos materials from various ore deposits (13). They conclude that only Coalinga asbestos is free from any amorphous material blocking the pore systems. All other chrysotile samples had an appreciable degree of pore filling, greater than 50 per cent, and their sorbed hydration water could only be driven off at 300 to 400°C. They came to the conclusion that both the external pores between fibrils and the internal pores within the fibrils are available for filling by water. Their data conflict with that of Naumann and Dresher, and it seems more convincing to this author that the internal pores within the fibers are not generally available for sorption or filling by liquids.

Size of Fibrils

The diameters of the fibrils have been measured by Naumann and Dresher, and the data are given in Figure 6 (4). The diameter ranges between 220 and 350 Å, with the average at 275 Å. At the same time, for comparison, a sample of Canadian asbestos was found to average 375 Å, with a greater variation in diameter. There have been some data published which claim that the diameter of Coalinga asbestos averages 220 Å and that Quebec asbestos is less, about 160 Å in diameter (13). However, data furnished by Yada to F. A. Mumpton on Coalinga asbestos agree with the data of Naumann and Dresher (8). Yada's data are given in Figure 7.

The average length of fibrils is much harder to determine. A guess, based on observations of electron micrographs of asbestos products, is that the majority of the particles (by weight) have length to diameter ratios ranging between 100 and 1,000, with a conservative average taken as about 200. Thus, an average fibril length would be about 5 microns.

Microscopic lengths of slip-fiber asbestos are composed of many aligned fibrils apparently held together by an amorphous phase between the fibrils. Under the right conditions, these fibers can be subdivided into their component fibrils. A measure of fiber lengths is the fluffiness or "dry bulk volume" of well liberated fibrils. The highest dry bulk volume achieved with Coalinga asbestos has been about 80 cc/g, but the dry bulk volume of fibrils prepared from Johns-Manville Crude No. 2 asbestos (3/8" to 3/4" lengths of macroscopic slip-veins) was about 800 cc/g. If the influence of a fiber in producing a structure in the dry state is proportional to the cube of its length, the Crude No. 2 fibril must be at least twice as long in average length as the Coalinga fibrils; i.e., they must be longer than 10 microns.

Summarizing the dimensions of the fibrils, Coalinga fibrils must have an average diameter of 275 Å and a length of about 5 microns. The average fibrils made from Quebec long-fiber asbestos are about 50 per cent larger in diameter and at least twice as long as the Coalinga average dimensions.

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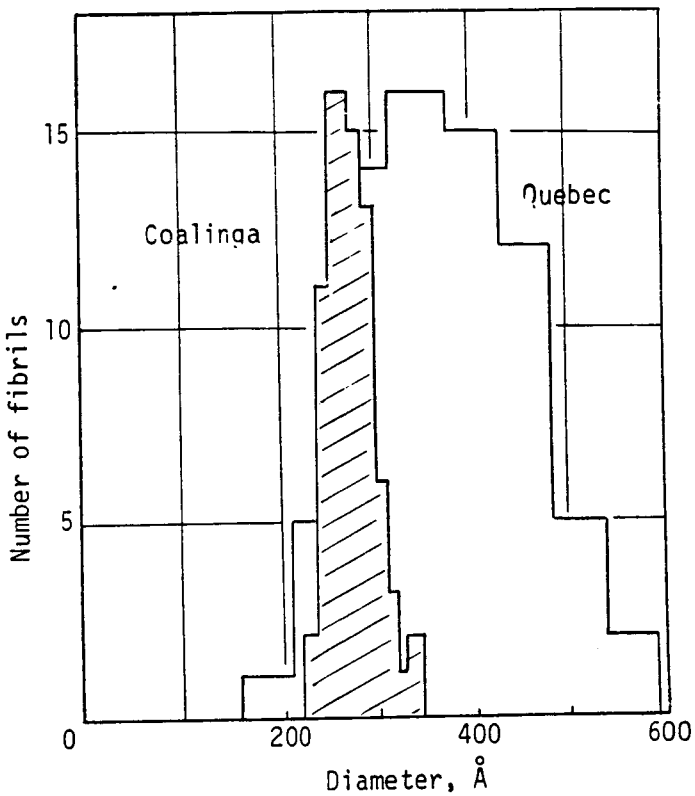


FIGURE 6 - HISTOGRAM OF FIBRIL DIAMETER DISTRIBUTIONS OF COALINGA AND QUEBEC CHRYSOTILE (4)

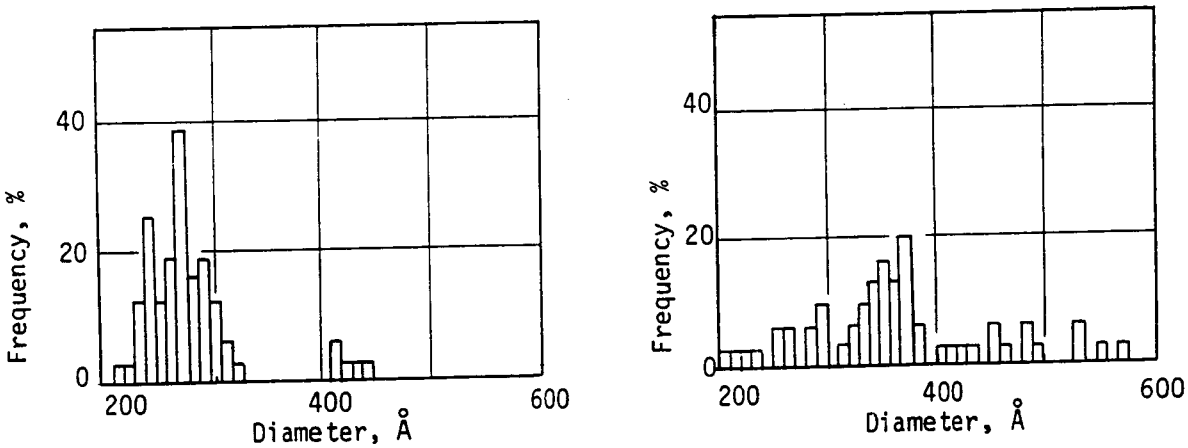


FIGURE 7 - HISTOGRAM OF FIBRIL DIAMETER DISTRIBUTIONS OF COALINGA AND CANADIAN ASBESTOS AFTER YADA (8)

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Surface Area

The specific surface area of a solid cylinder depends strictly on its diameter and its density if the small contributions to areas at the ends of the cylinder are ignored. The equation relating these variables is:

$$\text{Specific Surface Area} = \frac{4}{\rho d}$$

For a density, ρ, of 2.5 g/cc and for a diameter of 275 Å (2.75×10^{-6} cm), the specific surface area is 58 m^2/g.

Measured surface areas of refined Coalinga asbestos average between 60 and 68 m^2/g, with the most common value of about 64 m^2/g.* This is consistent with a cylinder diameter of about 250 Å. The implication is very strong that the holes in the fibrils are filled with matter of the same density as the chrysotile crystal itself and that the surface area of the hole is not available for adsorption of nitrogen gas.

The surface areas reported here are lower than those reported by Naumann and Dresher for Coalinga chrysotile (76 to 80 m^2/g) (4), but there have been indications that their measurements were somewhat high. Fripiat and Faille report values of 52 to 54 m^2/g (13), which are even lower than those obtained in our laboratory for Coalinga asbestos.

Liberation and Sizing

Based on the average dimensions of the Coalinga fibrils reported earlier, there must be about 10^{14} fibrils in a gram of fully liberated asbestos. Any practical product will have many less particles, of course, since numerous strongly bonded units of fibrils will still be present. One of the main functions of our mill at King City is to break down the flakes into sufficiently small particulates so that the asbestos product can be used effectively by our customers.

The asbestos fibrils occur in the compacted form of flakes, as described earlier, which are held together by secondary forces which are relatively weak compared to the primary bonding forces holding a continuous solid phase together. Thus, the energy that we must expend in making colloidal material is small compared, for example, to those processes making fine silica by grinding. Actually, there are industries that put enough energy into their process so that, for their purposes, flakes of asbestos from Coalinga can be considered to be well enough liberated, e.g., the tile industry. The same process, however, might not be able to utilize coarse aggregates of asbestos from deposits in Quebec since the amorphous binder between fibrils holds the fibrils together with forces approaching those present in solid materials.

For applications in paper and in paint, a chief requirement would be that the aggregates must be too small to affect the texture and visual appearance of the product. Thus, for paper, a first criterion of liberation is that there be an insignificant amount of +65 mesh particles. The paper-making process does not use enough shear or mixing energy to break down these particulates.

* Perkins and Elmer Absorptometer, Model 212B, used to measure N_2 adsorption and the data were analyzed by the B.E.T. method

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The feed material used in making treated asbestos for thickening applications of resins must be fine enough so that 95 per cent of its weight will pass through a 10-micron screen. It is vital that this high degree of liberation be achieved so that as much fibril area as possible is exposed to the treatment process.

It is apparent that no single criterion of liberation will suffice for all asbestos applications. In general, as more energy used in comminution, the absolute lengths of the fiber bundles become less, but their number per unit weight increases and their aspect ratio, length to diameter, also increases.

A picture of an intermediate stage of liberation is given in Figure 8 and an idealized, completely liberated field of fibrils is shown in Figure 9. Depending on the criterion for liberation, the bundles shown in Figure 8 might be considered as liberated.

The problem of distinguishing between various forms of particulates has been discussed by various authors. Medalia has discussed the computer simulation of floc formation by spheres colliding randomly and then being permanently attached to each other (14). This is the situation that occurs when carbon or pyrogenic silica particles, e.g. Cab-O-Sil, are formed at high temperatures and sintering takes place between colliding, primary particles. Sutherland has also discussed this type of floc simulation but for the purpose of understanding floc formation in solution (15). For our purpose, there have been more appropriate discussions of aggregation appearing in the literature of a qualitative type. Lapple (16) has classified the various states possible in a particulate system. Buttignol and Gerhart (17) describe the physical form of particulates from a pigment dispersion and coating point of view. Based on the classifications of the latter two authors, I propose the use of the nomenclature given in Table I for an asbestos system.

The mechanism of breakdown of flakes into the fibrils has been studied extensively by Dresher (18). His conclusions were that the liberation in an apparatus with a spinning blade, such as a Waring Blendor, is accomplished by cavitation. The fiber yield, defined by the dimensionless group $\frac{f}{1-f}$, was found to be proportional to the square of the linear velocity at the edge of the spinning blade. The dimensionless quantity, the cavitation number, is also proportional to the square of the velocity, so the following relationship is likely:

$$\frac{f}{1-f} = K\left(\frac{\rho}{P - Pv} \cdot \frac{V^2}{2g}\right)$$

where f = maximum amount (fraction) of fiber liberation achievable under the given conditions
ρ = density of slurry
P = ambient pressure, usually 1 atmosphere
Pv = the vapor pressure of the media
g = gravitational constant
V = linear velocity of the eddy shear zone

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FIGURE 8 - INTERMEDIATE STAGE OF LIBERATION SHOWING BUNDLES OF FIBRILS

Magnification 8,500X, Photo No. 1996-11

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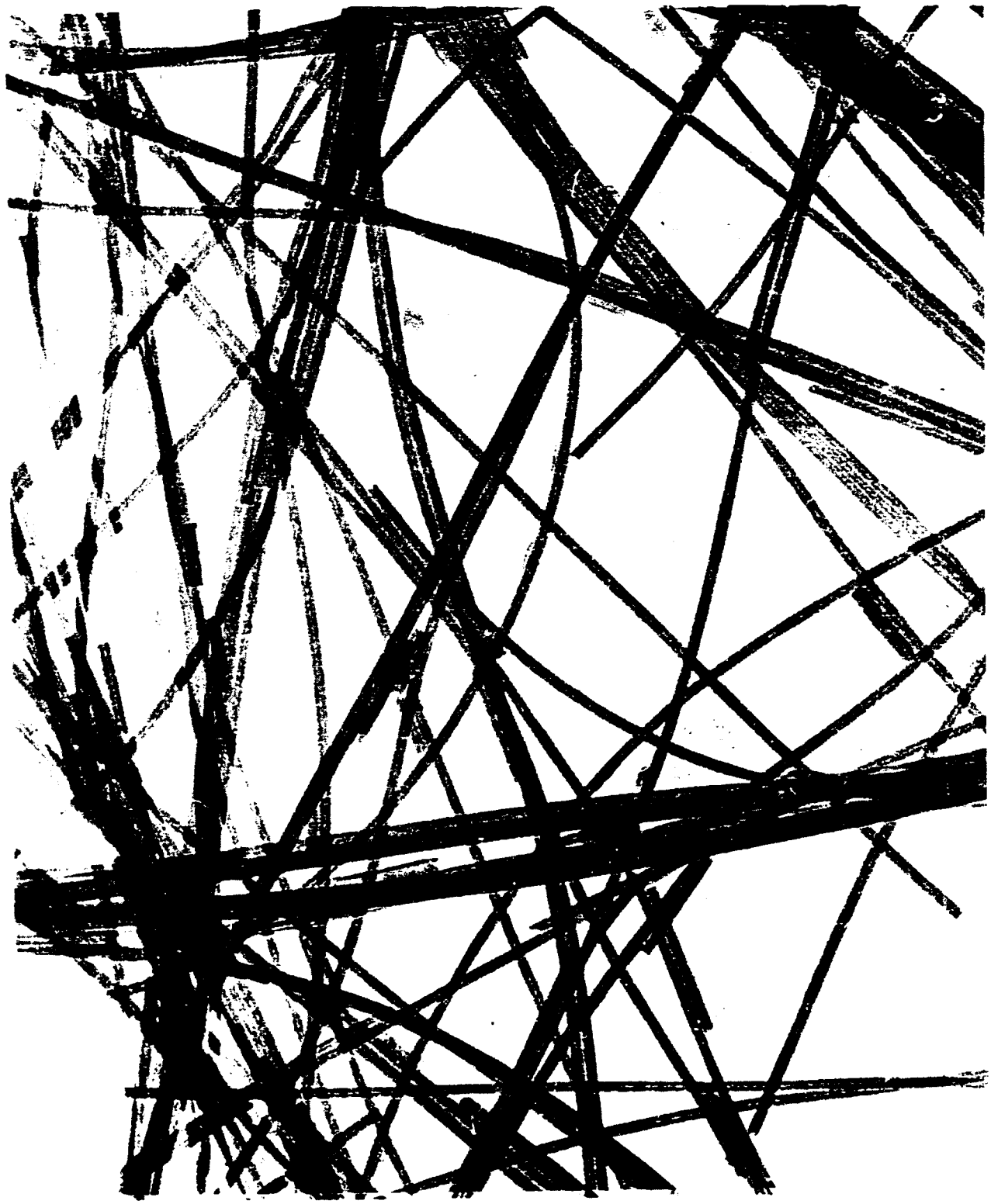


FIGURE 9 - LIBERATED FIBRILS OF CHRYSOTILE

Magnification 75,000X, Photo No. 2340

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TABLE I

PHYSICAL FORMS OF "OPENED" ASBESTOS

Unit	Description	Example	Remarks
(1) fibril	discrete particle held together by crystalline forces	present in well liberated and dispersed suspensions	can only be sub-divided further with high energy
(2) fiber or fiber bundles	(a) aligned fibrils, in maximum contact possible for cylinders, held by Van der Waal's forces	veins from Coalinga asbestos flakes	medium amount of energy to separate into fibrils
	(b) aligned fibrils with solid phase present between them, held together strongly by chemical forces	macroscopic fibers from slip-vein deposits, e.g., Quebec asbestos	large amount of energy needed to separate into fibrils
(3) aggregate	randomly oriented masses of fibrils and fiber bundles held together strongly at points of contact by chemical forces	silica treated asbestos, EMA treated asbestos	medium energy required to break down into fibrils and bundles
(4) agglomerate	highly compacted masses of fibrils, bundles and aggregates held together weakly by Van der Waal's forces	asbestos flakes, asbestos pellets, filter cakes, high density slurries	takes low amount of energy to break down
(5) flocs	loose masses of fibrils, bundles and aggregates held together weakly by Van der Waal's forces	dilute floccu-lated suspensions	only chemical dispersion forces needed to break down into particles
(6) powder	dry state, a mix-ture of large bundles, large aggregates and agglomerates	"opened" asbestos	no fibrils, small bundles or small aggregates present since these are flocculated before filtering and then agglomerated during compaction

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The tests for liberation used in these experiments have been described in detail elsewhere (10,19). It consists essentially of chemically dispersing the product, allowing the large particles to settle by gravity or by centrifuging, and pouring off the non-settled, dispersed portion of the suspension. The fractional amount of asbestos in the supernatant is considered to represent the amount of liberated fiber.

The test has been useful in the past, but the dispersed phase is poorly defined in size. Quite large aggregates may not settle under the conditions of the tests and so may be counted as liberated. The settling data for presumably well liberated asbestos suspensions (HPP opened for three minutes at high speed in a Waring Blendor at 1 per cent solids) are shown in Figure 10. The experiments were done in an Andreasen Pipette which was thermostated in a constant temperature bath at 30.0±0.1°C. In spite of this precaution, the majority of the particles did not settle. The impression was that, even under the best dispersing conditions, it was not possible to keep the suspension from gelling slightly over long periods of time. A calculated curve in Figure 10, based on stokesian settling, indicated that even apparently liberated fibers were not settling at predictable rates. It must be concluded that settling is not a reliable way of making an accurate sizing split.

A better way of making a sizing determination is with sieves. This still can only be an empirical test since fibrous particles might be finer than the screen opening in one dimension but much larger than the screen opening in the other dimension. Therefore, there must be a statistical distribution of fibers of a given size between the products that pass through the screen and those that are retained on the screen.

The first objective of sizing is to determine the relative amounts of fibrils (liberated asbestos), bundles, and aggregates. The presence of agglomerates and flocs obscures the results of screening because their existence is tenuous, depending very much on the amount of low-level shear applied to the system during preparation or measurement of the sample. Accordingly, they must be eliminated by low-energy mixing under chemical dispersing conditions. In preparation for screening, the suspensions are preferably dispersed in a solution containing 1 or 2 weight per cent of an anionic surfactant, such as Triton X-200 or Tergitol Anionic 7. In addition to dispersing, the surfactant performs the function of reducing the surface tension of the suspension which makes it possible to pass the suspension through openings so fine that even pure water will not pass through them. Any screening tests done on 200 mesh or finer sieves are definitely aided by dispersion with a surfactant.

The results of screening some asbestos suspensions subjected to different degrees and amounts of mechanical energy are given in Table II. It is apparent that well-liberated products show differences in screen sizes only in the very fine range. It is interesting to note that there is a great improvement in the effectiveness of liberation when a Waring Blendor is used as the opening device with a chemically dispersed suspension compared to the use of a Waring Blendor with a flocculated suspension.

An attempt was made to correlate differences in the amounts retained on a 10-micron screen with differences in viscosity of the flocculated suspensions of asbestos. At low shear rates (170 sec^{-1}) there was a correlation, but little difference was seen at high shear rates (1,022 sec-1). These data are shown in Figure 11.

Typical sizing data are given in Table III for various open asbestos products.

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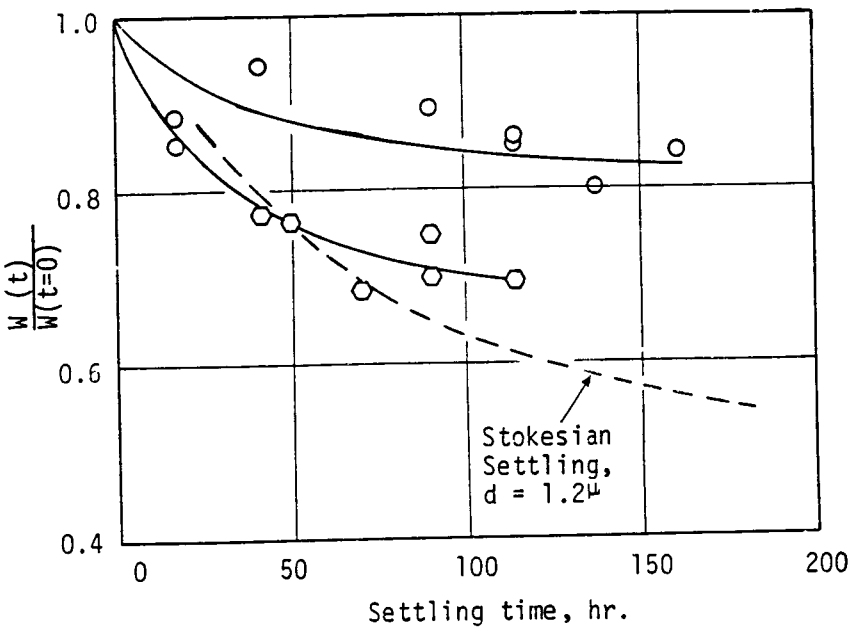


FIGURE 10 - SETTLING OF OPENED ASBESTOS IN ANDREASEN PIPETTE
Dispersed with: acetic acid and aluminum acetate....OOO
Triton X-200....OOO

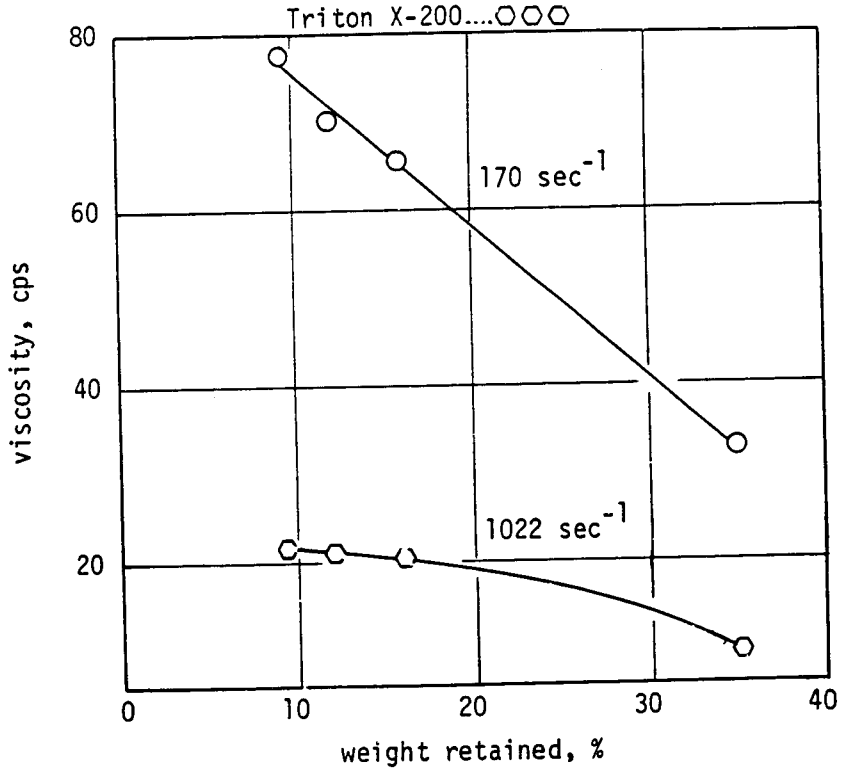


FIGURE 11 - CORRELATION OF VISCOSITY OF FLOCCULATED ASBESTOS SUSPENSION WITH 10-MICRON SCREEN SIZE OF ASBESTOS

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TABLE II

SCREEN ANALYSES OF ASBESTOS PRODUCTS
OPENED UNDER VARIOUS CONDITIONS

Material	Opening Time, minutes		Retention on Screen,* %					
	Herman	Waring Blendor	65 mesh 208μ flocc'd.	65 mesh 208μ disp'd.	200 mesh 74μ	325 mesh 44μ	25μ	10μ
HPP, 2% susp. in water	1	0	41	0.1	34	47 49	52	58
	2	0	15	0.3	12	27 30	30	45
	4	0	3	0.5	3	22 20	16	25
	8	0	1.5	0.3	3	15 6	10	13
SG P, 2% susp. in water	8	0	8.3	-	25	33	32	35
	8	1	0.5	-	6.3	13	13	16
	8	2	0.1	-	4.0	7.8	8.3	12
	8	3	0.01	-	1.5	5.5	5.8	9.3
SG P, 2% susp. in water	8	3 at pH 4.0	-	-	-	2.0	2.6	4.6

* 1 gram asbestos in 300 ml distilled water dispersed with 7 ml of Triton X-200 (Rohm and Haas)

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TABLE III

SCREEN ANALYSES OF ASBESTOS PRODUCTS

Product	Sieve Size	Wt. % Oversize
(1) King City mill slurry	10μ	8.9
	400 mesh	2.8
(2) HPP opened at 4% solids in a Rietz mill	10μ	5.2
	400 mesh	1.5
(3) HPP opened at 4% solids in a Rietz mill:		
(a) 1 pass	10μ	5.4
(b) 2 passes	10μ	5.8
(4) HPP, 1.0 g/300 ml water in a small Waring Blendor at high speed for 3 minutes:		
(a) at natural pH	10μ	7.5
repeat	10μ	8.5
(b) at pH <5	10μ	2.0

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CHEMICAL PROPERTIES

Composition

The unit cell of chrysotile theoretically contains 43.6 weight per cent MgO, 43.5 weight per cent SiO_2, and 13.0 weight per cent H_2O. In naturally occurring chrysotile, substitution occurs for the magnesium and silicon cations, primarily by iron and aluminum cations. It is common for up to 2 weight per cent of water to be adsorbed on Coalinga asbestos fibers, and some of this water may not be driven off even at temperatures slightly in excess of 100°C. "Dry" asbestos picks up water rapidly on exposure to air, so even "dried" asbestos often is found to assay 14 weight per cent of water or more.

Analyses have been made in the past of many random Coalinga asbestos products. These data have been gathered and evaluated, and the results are summarized in Table IV for two classes of products--high purity production pellets and asbestos carefully refined and purified in the laboratory. An analysis of a leathery sheet, copied directly from a mineralogical report (10), and analyses for a Coalinga sample taken from a published paper (20) have also been included in Table IV for comparison. The results of a spectrographic analysis follow in Table V.

TABLE IV

CHEMICAL ANALYSES OF COALINGA CHRYSOTILE SAMPLES

Sample Description	% MgO	SiO_2	Al_2O_3	Fe	Refl.
Theoretical $Mg_6(OH)_8Si_4O_{10}$	43.6	43.5	-	-	-
Leathery Sheet (10)	43.04	41.75	0.05	1.19	-
Production Pellets Lot No. 2625-9	41.4	40.9	0.5	1.6	75
Purified and Refined Asb.	41.8	41.7	0.5	1.3	-
Faust and Fahey (20)	40.42	41.54	2.48	1.37*	-

* FeO

TABLE V

SPECTROGRAPHIC ANALYSES OF REFINED COALINGA CHRYSOTILE

	Estimate of Percentage Present								
Ag	.0002-.002	Co	.02-.2	La	-	Pd	-	Th	-
Al	.2-2	Cr	.06-.6	Li	-	Pt	-	TL	-
As	-	Cu	.004-.04	Mg	M	Rh	-	Ti	.003-.03
Au	-	Fe	1-10	Mn	.04-.4	Sb	-	U	-
B	.002-.02	Ga	-	Mo	.003-.03	Sc	.001-.01	V	.008-.08
Ba	-	Ge	-	Na	.005-.05	Si	M	W	-
Be	-	Hf	-	Ni	.05-.5	Sn	-	Y	-
Bi	-	Hg	-	Os	-	Sr	-	Yb	-
Ca	I.P.* <.002	In	-	P	-	Ta	-	Zn	-
Cb	-	Ir	-	Pb	.01-.1	Te	-	Zr	-
Cd	-								

* I.P. = if present

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The leathery sheets seem to contain too much magnesium, so either brucite or some other material high in magnesium must be present. However, this sample is very low in alumina. The MgO and SiO_2 analyses for the other three samples are quite close, although Faust and Fahey's sample seems to contain too much aluminum (20). It is certain that some of the iron reported is present in the samples as discrete particles of iron oxide. The exact amount cannot be determined readily, nor can the particles be removed easily. For the purposes of calculation, all of the iron will be considered as in the lattice.

The structural formula for chrysotile is $4M^{IV}6M^{VI}O_{10}(OH)_8$. Faust and Fahey analyzed hundreds of serpentine samples and concluded that the "average" number of the cations in the tetrahedral layer (silica layer) is from 4.00 to 4.10, while that for the cation in the octahedral layer (brucite layer) ranges from 5.80 to 6.05 (20). Based on their analyses of Coalinga asbestos, they have calculated the quantities of foreign cations occurring in each layer. Their results are in Table VI. Following their procedure but with our analyses, similar calculations were made which are reported in Table VI also. In addition, the results reported by Fripiat and Faille are given there (13). The latter sample must have been excessively high in alumina, but they do not report their analyses.

TABLE VI

SUBSTITUTION OF FOREIGN CATIONS IN COALINGA CHRYSOTILE LATTICE

	Tetrahedral Layer			Octahedral Layer				
Reference	Si^{4+}	Al^{3+}	MIV(total)	Mg^{2+}	Fe^{2+}	Fe^{3+}	Al^{3+}	MVI(total)
Faust and Fahey (20)	3.91	0.09	4.00	5.66	0.11	-	0.19	5.96
Fripiat and Faille (13)	3.82	0.18	4.00	5.62	-	0.15	0.41	6.18
This work*	3.95	0.05	4.00	5.85		0.12**	nil	5.97

* based on purified and refined asbestos
** assumed to be a mixture of Fe^{3+} and Fe^{2+}

It seems to be standard to assume that the tetrahedral silica layer will be satisfied first and then to assign the remainder of the cations to the octahedral layer. According to the best estimates for the composition of pure Coalinga fiber, only a small amount of aluminum substitutes in the silica layer and some iron occurs in the brucite layer. Our values are significantly less than those reported by the other two investigators.

Synthesis

According to reports in the literature, chrysotile can be synthesized in relatively short intervals under hydrothermal conditions. Suitable conditions for rapid reaction of the chemical components are a temperature of 300 to 500°C and a pressure of 1000 to 40,000 psi (21). Yang gives some of the references to previous work in her paper describing reactions in the ternary system $MgO-SiO_2-H_2O$ over the temperature range 100 to 300°C. In a later paper, she describes a procedure for the growth of synthetic chrysotile fiber (22). Previously, only mattes of fibers could be obtained, but with the proper mineralizers, she obtained fiber bundles averaging 100 microns or more in length, although individual fibrils were only 15 to 20 microns long.

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Her conditions were:

-magnesium oxide (C.P.) and special bulkly silicic acid at an MgO/SiO_2 molar ratio of 1.5
-water to solid ratio of 10
-temperature.....300 to 500°C
-pressure.....1230 to 1800 psi
-time.....5 to 10 days
-pH (Na_2CO_3-$NaHCO_3$ buffer).....10.3 to 10.7
-mineralizer.....an amount of F^- equivalent to 1 to 2 by weight per cent of starting material, added as a 0.01 N solution of NH_3F

It is interesting that she did not find any foreign ions in the synthetic chrysotile, although Russian investigators claim to make a chrysotile phase with substantial replacement of hydroxyl groups by fluoride ion in the lattice.

A preliminary batch of synthetic chrysotile was made by F. A. Mumpton using a procedure similar to that described above. Electron microscope observations were made and two fields of view are shown in Figure 12. The concentric, cylindrical structure is very apparent in these pictures. The surface areas of the synthetic fiber are quite variable between samples, but they range between 80 and 90 m^2/g. This is significantly higher than natural Coalinga asbestos which has one of the highest surface areas found for natural asbestos materials.

The purpose of this program was to study the effect of substitution of foreign ions into the lattice, but it was not continued.

Thermal Stability

The most definitive work on this subject seems to be that of Naumann and Dresher (23). Their conclusions are that open-textured materials, characterized by high surface area as measured with nitrogen gas adsorption, dehydrate endothermically with increasing temperature to form an X-ray amorphous phase which is stable for another 150°C. A transformation of the amorphous phase then takes place to forsterite and, at still higher temperatures, some enstatite may form. Earlier investigations reported in the literature were on cross-fiber (long fiber) chrysotile where the thermal effects on the structure were obscured by the texture of the samples (24).

The temperatures of the endothermic dehydroxylation and the exothermic transformation as determined by DTA* are at about 700 and about 800°C, respectively, depending on the programmed rate of temperature increase. A typical DTA trace is shown in Figure 13. Under static heating conditions in air, however, the dehydroxylation takes place between 500 and 550°C, and the first forsterite phase forms in the temperature interval between 650 to 700°C. The surface area is not changed until the forsterite phase starts to appear. At increasingly higher temperatures, the surface area decreases drastically so that, at 850°C, it is only 2 m^2/g. It seems that there is no great change in the shape of the fibers during dehydroxylation from the chrysotile to the amorphous state, nor are there any pores opened up which are large enough to admit nitrogen gas molecules. However, recrystallization must be accompanied by consolidation of the individual amorphous fibrils into larger particles to account for the large decrease in surface area at very high temperatures (23).

* DTA - differential thermal analysis

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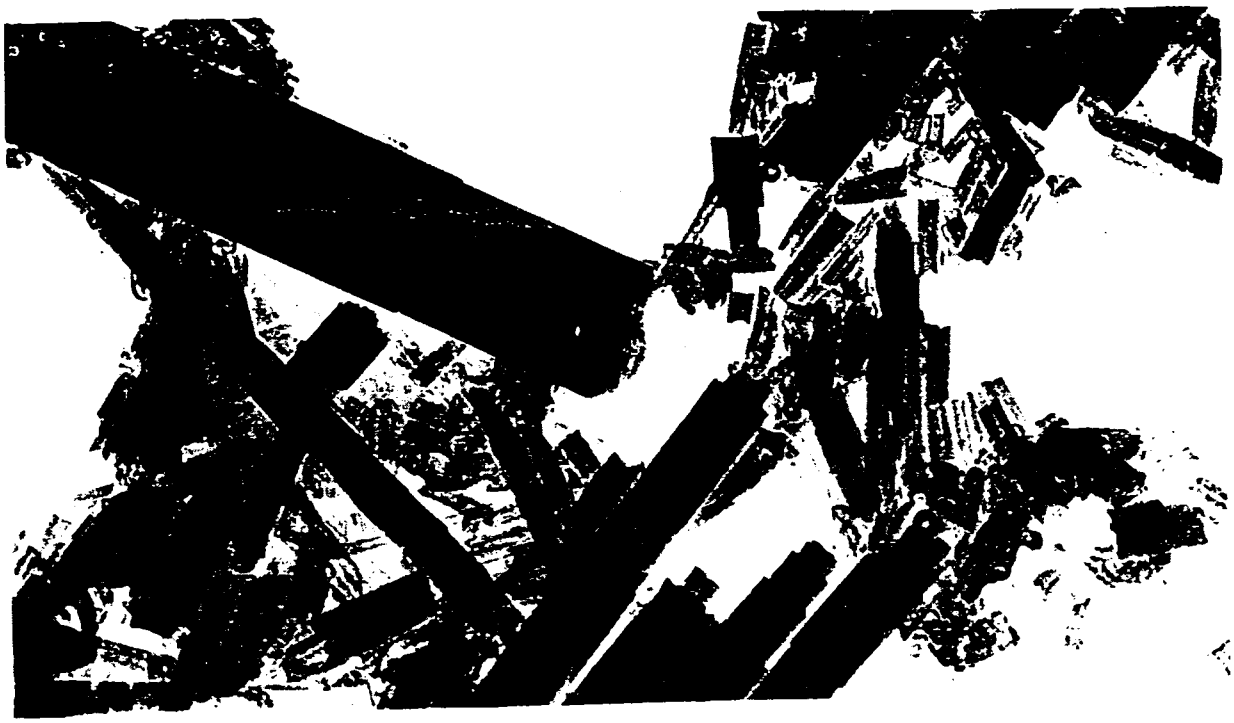


Photo No. 3711



Photo No. 3713

FIGURE 12 - SYNTHETIC CHRYSOTILE

Magnification 135,000X

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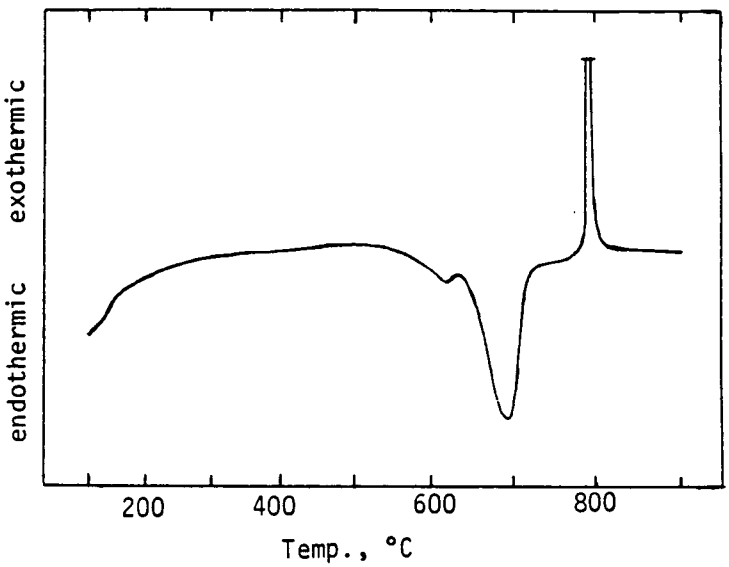


FIGURE 13 - TYPICAL DTA TRACE FOR COALINGA CHRYSOTILE

The rate limiting step for the endothermic thermal reaction seems to be the ease with which water can be removed from the fibrils. More compact samples of asbestos fibrils, which are characterized by low surface areas, do not show the three distinct regions of behavior on heating, but forsterite starts to appear even when a small amount of chrysotile is still present. A completely amorphous phase never occurs. The endothermic dehydroxylation peak on a DTA trace is broader for compact asbestos samples and the exothermic transformation peak becomes much smaller or is not found at all (23).

An interesting feature that Naumann and Dresher observed on their DTA traces for all high surface area samples of chrysotile is that a small endotherm at approximately 600°C precedes the major one at about 700°C. They attribute the small endotherm to removal of surface hydroxyl groups. They found that it can be eliminated by a mild acid leach or by a stearic acid treatment at monolayer coverages. This raises the possibility that the surface composition of the fibrils can be changed by a careful heat treatment without destroying the main body of the fiber (23).

It was proposed by one of our potential customers that heat-treated asbestos might be applicable as a reinforcing filler for polypropylene. He suggested that a weight loss of about 1 per cent would be appropriate for the treatment. Polypropylene containing chrysotile asbestos degrades rapidly at 150°F and this is attributed by some to the basic character of chrysotile surface. They cite the fact that anthophyllite asbestos, with its more acidic surface properties, does not cause as rapid degradation of polypropylene.

A program was initiated to determine the best conditions for removing the surface hydroxyl groups on chrysotile. If it is assumed that the outer layer occupies 14 per cent of the total asbestos fiber weight, and that 13 per cent is the amount of water in the bulk crystal, dehydroxylation of the outer layer would lead

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to a 1.8 weight per cent loss. Asbestos samples were heated at various temperatures and for various lengths of time, and then their TGA* traces were compared with those of regular asbestos to determine the quantitative amount of water driven off in the heating process. It was found that a weight loss of about 2 weight per cent occurred by heating for 4 hours at 500°C under an atmosphere of flowing air. A 1/2 ton lot of asbestos was then heated at a temperature between 500 and 550°C in a production kiln. The heated asbestos was studied in a TGA apparatus and its trace is compared to normal asbestos in Figure 14. It is seen that about 1 weight per cent loss can be attributed to the heat treatment. This was considered to be satisfactory in terms of the original objectives of the program so the material was submitted for incorporation into polypropylene. It did not prove to be any better than untreated asbestos but the idea of a controlled heat treatment to alter surface properties remains valid.

A lag occurs between the temperature recorded on the TGA apparatus and the actual temperature of reaction due to the fact that there is a constantly increasing temperature in the TGA furnace. This reaction temperature uncertainty was eliminated by doing steady-state determinations in the TGA apparatus. The sample was held at a temperature until no more weight loss took place with time, and then the temperature was increased to another higher level. The data are given in Figure 15 along with the data obtained at a nominal heating rate of 10° per minute (observed heating rate of about 8°C per minute). It is seen that, at a temperature of 500°C, about 2-1/2 weight per cent loss should be obtained at steady state, although the regular TGA shows less than 1 weight per cent loss at this temperature. The major weight loss at steady state occurs at 520 to 550°C although the TGA data indicate a higher temperature for this major weight loss (about 650 to 700°C). Asbestos heated at 500°C and then exposed to water vapor subsequently has similar TGA characteristics to normal asbestos. However, after a heat treatment at 550°C, the asbestos sorbed the same amount of water as it held originally, but this water is more loosely bound than is the water of normal asbestos This is illustrated in Figure 16.

Asbestos which has been calcined at 720°C to its amorphous state also soaks up slightly more water than it held previously, and its binding of this water is very different than it was before. The desorption characteristics of amorphous asbestos soaked in water are compared in Figure 17 to the desorption characteristics of two natural zeolites which had been soaked in water just prior to analysis. The amorphous asbestos not only binds some of the water just as strongly as the zeolites but also has a greater absolute capacity than do the zeolites

Asbestos transformed to the amorphous state at 720°C contains a water-soluble species which is not present in asbestos heated at 900°C. It is assumed that the soluble matter is a species of magnesium which becomes fixed after recrystallization.

The surface charges of heated asbestos products were measured and also the surface areas were determined by the adsorption of nitrogen gas. The data are presented in Table VII.

* Thermogravimetric analysis, samples preheated at 100°C in apparatus until no more weight loss occurred before starting with the analysis.

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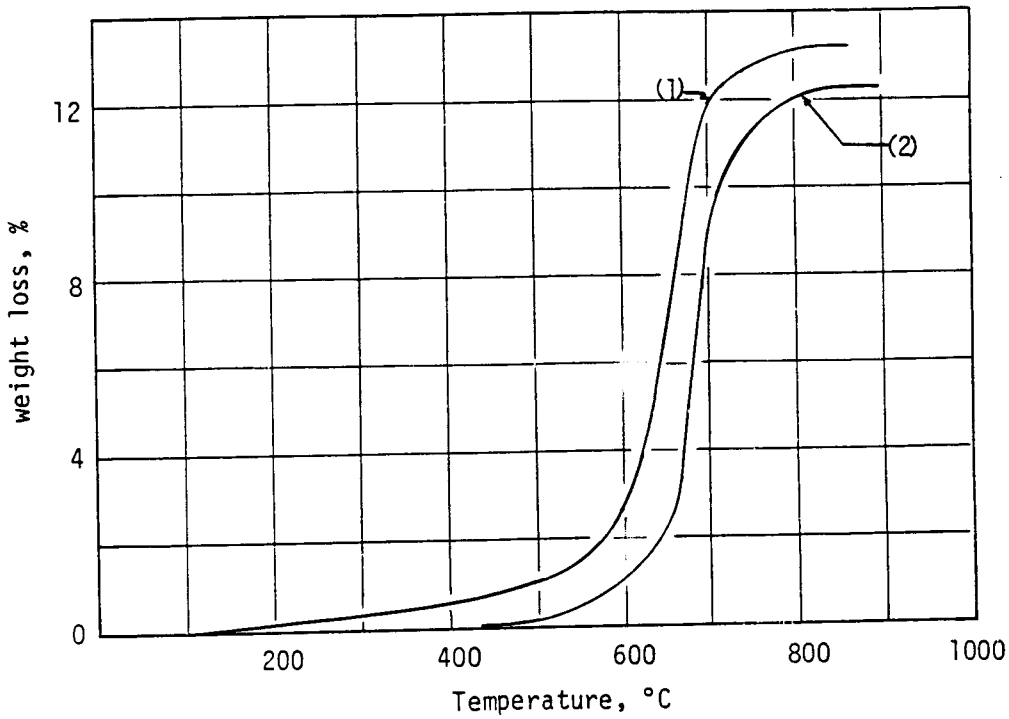


FIGURE 14 - COMPARISON OF TGA TRACES FOR ASBESTOS AND FOR ONE-HALF TON LOT OF ASBESTOS PREHEATED AT 500 TO 550°C (1) Asbestos (2) Preheated asbestos

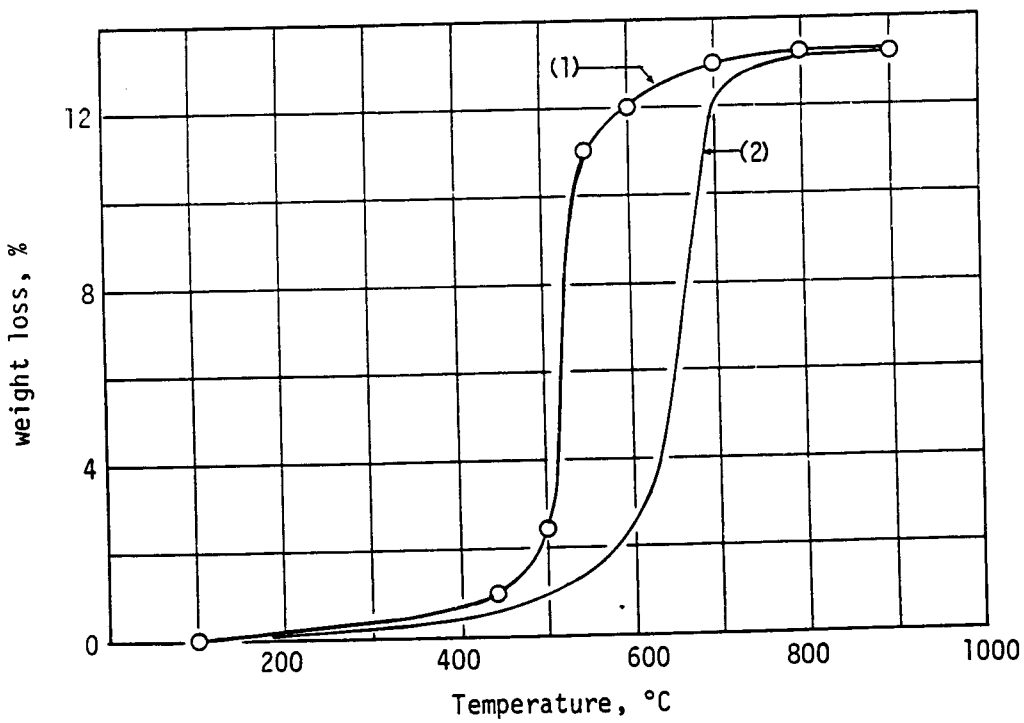


FIGURE 15 - COMPARISON OF STEADY STATE THERMAL WEIGHT LOSSES WITH TGA TRACE FOR NORMAL ASBESTOS
(1) Steady State (2) TGA at 10°/min

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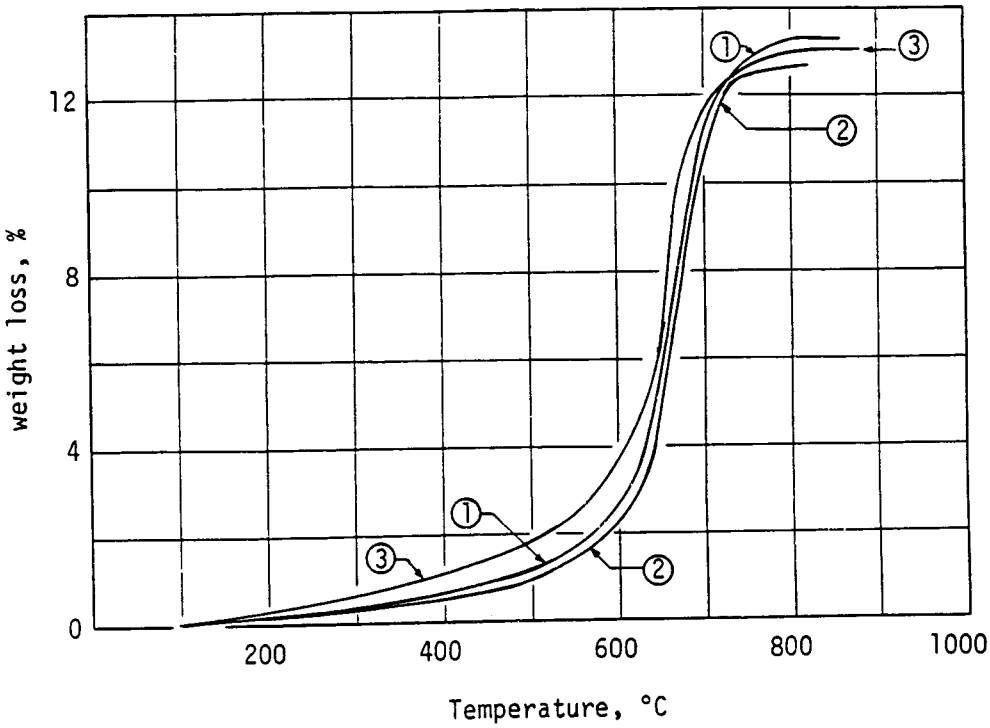


FIGURE 16 - TGA TRACES OF CALCINED AND WATER EQUILIBRATED ASBESTOS PRODUCTS

Calcining: ① none, ② 500°C, ③ 550°C.

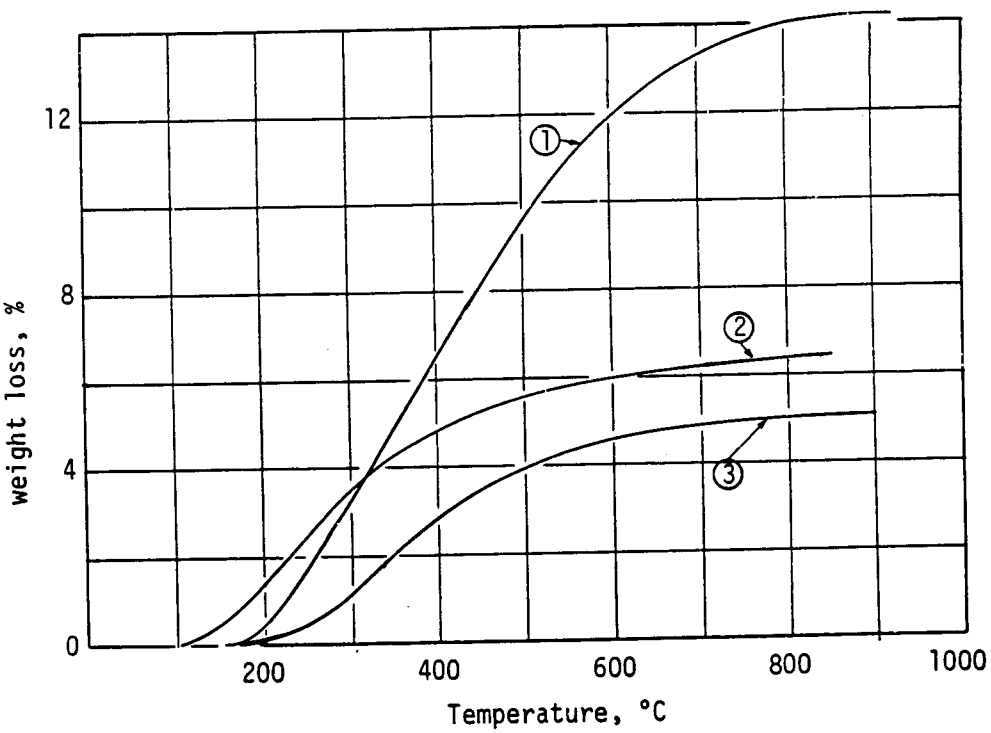


FIGURE 17 - COMPARISON OF TGA TRACES FOR AMORPHOUS ASBESTOS WITH TWO NATURAL ZEOLITES

① Amorphous asbestos
② Neofil #3000
③ Neofil #1000

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TABLE VII

PROPERTIES OF HEATED ASBESTOS

Heat Treatment			Surface Charge in Water(2)		Surface Area(3)
Temp., °C	Time Hr	Weight(1) Loss, %	pH	Sign	m^2/g
R.T.	-	~13.2	~9	pos.	66
550	4	9 to 3	8.8	pos.	-
720	2	none	8.7	neg.	36
900	2	none	7.3	neg.	4
600(4)	-	~1	-	-	56

(1) in subsequent TGA determination
(2) by electrophoresis
(3) activated at 200°C in vacuum, 10^{-3} mm Hg
(4) held at 600°C in TGA apparatus until no more weight loss

These results bear out Naumann and Dresher's observation that the surface area of the asbestos decreases drastically only after recrystallization starts to take place (23). Even the partly amorphous asbestos still retains a positive surface charge in water, but the completely amorphous asbestos becomes negatively charged. The much coarser forsterite phase is also negatively charged in water.

Solubility

The outer surface of chrysotile asbestos can be expected to be quite susceptible to attack by acid solutions and indeed it is. This outer layer comprises about 14 per cent of the mass of the crystalline portion of the fiber or about 11 to 12 per cent of the total mass of the fiber. This is based on assuming a hollow fibril whose basic dimensions for the crystalline portion are 256 Å outer diameter and 110 Å inner diameter. The hole is considered to contain amorphous material with the same composition as the crystalline phase.

If the inner amorphous region is as susceptible to the acid attack as the outer layer, the total mass of readily leachable material in an asbestos fibril would be about 36 per cent. Acid leaching studies carried out by J. D. Koetting did indicate that faster leaching occurred after the asbestos had been heated to sufficient temperatures to break down the crystalline portion of the fibril (25), so the amorphous matter could be quite susceptible to acid attack. Evidence that at least the outer layer is more susceptible to breakdown has already been described: a small dip occurring in the DTA trace of chrysotile at 600°C before the large one centering at 700°C. The first dip is attributed to breakdown of brucite in the outer layer, while the latter shows the breakdown of the brucite in the bulk crystal. Under static heating conditions, the breakdown of the outer layer occurs at about 500°C.

It is generally accepted that chrysotile asbestos has poor acid resistance, while the other forms of asbestos which are reported to have outer layers composed

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predominantly, or at least in part, of silica are acid resistant. Chrysotile should have the best resistance to attack by alkalies. Sinclair's data bear this out (26). All two-layer minerals should be very susceptible to attack by alternating conditions of acidity and alkalinity.

An attempt was made to measure equilibrium solubility of Coalinga asbestos which was washed and purified as described in the previous section. The results of the first test in 0.1 molar potassium chloride solution are shown in Figure 18. It was seen that irreversible effects started taking place after the pH had been reduced to the range below pH 4.5 and the apparent solubility was increased by a factor of 2 to 3 as judged by magnesium analysis in solution. The concentration of magnesium did decrease substantially as the pH was increased to about pH 11. This is attributed to association of the brucite groups at the asbestos surface according to the reversible reaction:

$$Mg(OH)_2 = Mg^{2+} + 2(OH^-), \qquad K_{SP} = (Mg^{2+})(OH^-)^2$$

Values of pK for the solubility product of magnesium hydroxide found in the literature range between 10 and 11, and these relationships are included later on Figure 20. The high salt content of the solution could be expected to increase the solubility somewhat. However, the high salt content was necessary, for experimental purposes, to flocculate the suspension at low pH values, enabling samples of clear solution to be obtained by filtration.

Another experiment was conducted in pure water where the only extraneous ions present were from the base, potassium hydroxide, used to increase the solution pH. To fully determine the solubility, the samples of solution taken were assayed for both magnesium and silica. These data are in Figure 19. The magnesium assays are significantly lower than in the first test, about 10 micromoles per liter in the pH region 8.5 to 10.5, but the pattern of behavior is the same; as pH 11 is approached, the concentration of magnesium decreases substantially. The silica analyses actually show a minimum solubility of 0.6 micromoles per liter of silica to occur at pH 11. This is an interesting observation because Parks and de Bruyn report that the pH of minimum solubility and the pH of zero point of charge of a mineral coincide (27). Experiments to be described in the next section indicate that the zpc* of Coalinga asbestos is actually at pH 10.8 so the two conditions do seem to coincide in this case. The over-all solubility properties of Coalinga chrysotile asbestos are summarized in Figure 20.

It is well known that many layer-silicate minerals can be selectively leached by acid to remove their basic components and leave skeletons of silica which are vaguely or even strongly pseudomorphic after the original structure. Such total leaching of Coalinga asbestos had been carried out by Koetting with the object of making a fine silica product and obtaining a solution from which magnesia could be recovered (25). Leaching in strong sulfuric acid solutions, especially at elevated temperature (90°C), did result in silica skeletons which were seen to be somewhat fibrous in character by electron microscope examination, but the fibers were brittle and weak and the over-all economics of the process did not seem favorable. The analysis of a product made under that program is given in Table VIII. It was noted that no significant alumina was found by spectrographic analysis in the leached product.

* zpc - zero-point-of-charge

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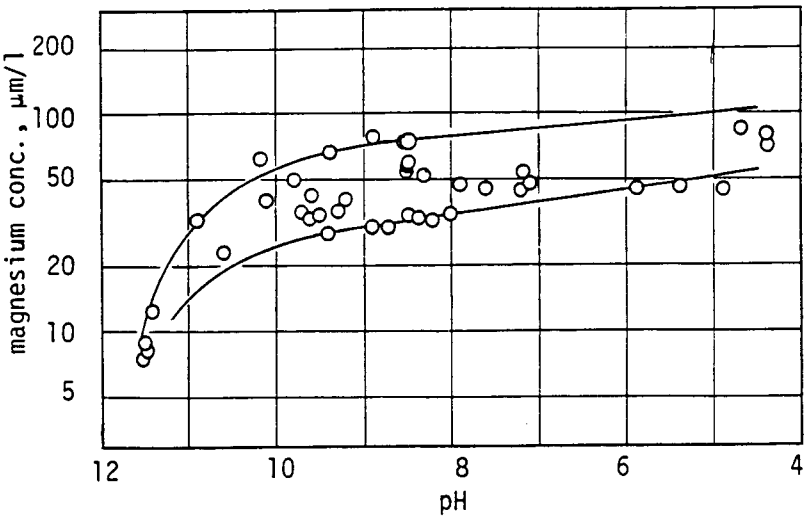


FIGURE 18 - SOLUBILITY OF COALINGA CHRYSOTILE IN 0.1 MOLAR POTASSIUM CHLORIDE SOLUTION AS A FUNCTION OF PH

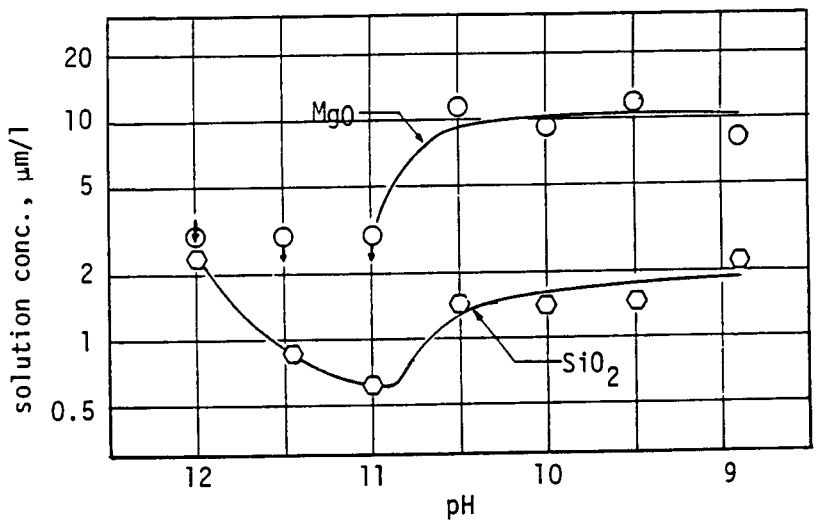


FIGURE 19 - SOLUBILITY OF COALINGA CHRYSOTILE IN WATER AS A FUNCTION OF PH

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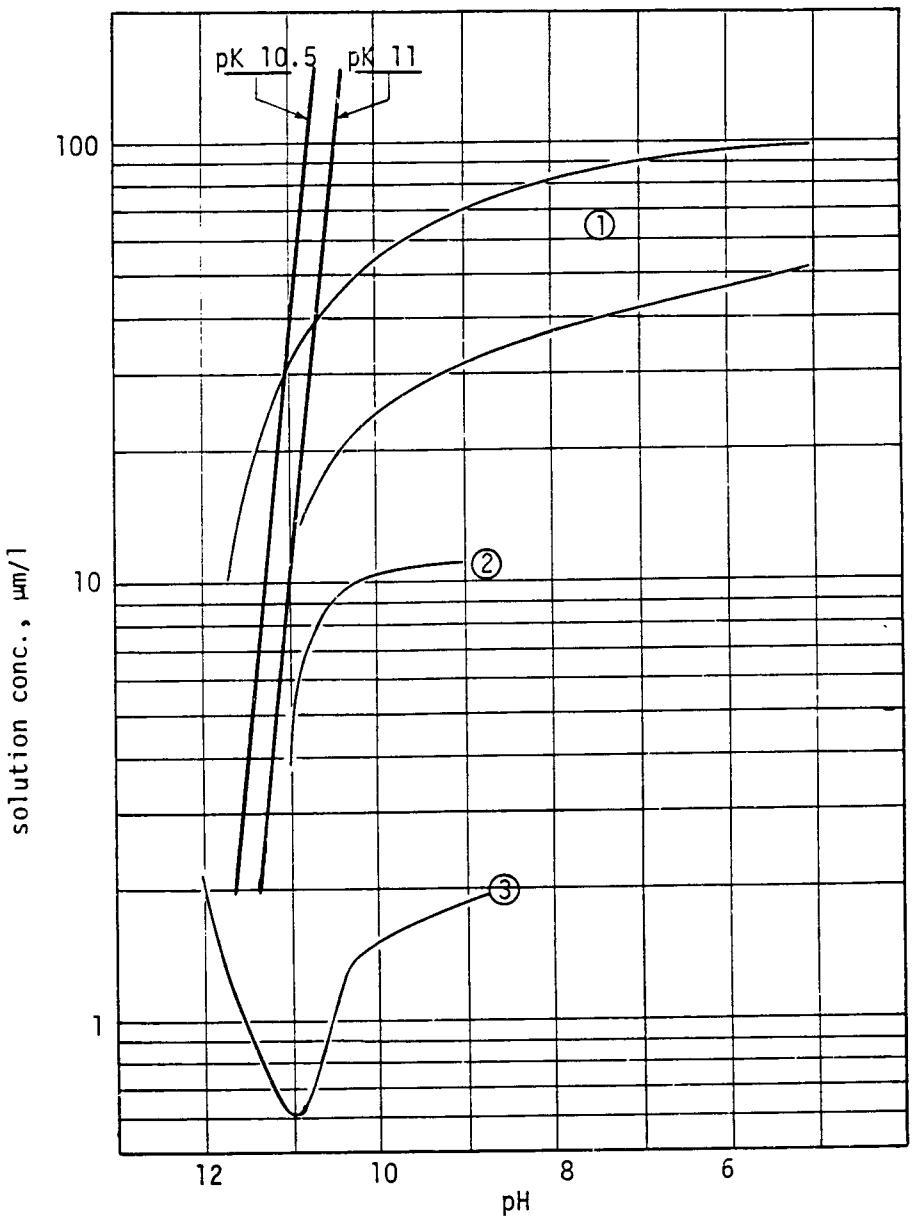


FIGURE 20 - SUMMARY OF SOLUBILITY DATA FOR COALINGA CHRYSOTILE IN AQUEOUS MEDIUM

① magnesium conc. in 0.1 M KCl
② magnesium conc. in water
③ silica conc. in water

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TABLE VIII

ANALYSIS OF AMORPHOUS SILICA, LOT 603-5,
MADE BY LEACHING COALINGA CHRYSOTILE ASBESTOS (25)

Moisture at 105°C	17.83%
Magnesium	0.077%*
Iron	0.5%*
Silica, SiO_2	91.22%*
Sulfate	0.18%
LOI at 1000°C	23.79%
Refl.	87%
Oil absorption	125 lb/100 lb

* dry basis

Another possibility is that by leaching out the brucite in the outer layer a silica surface would be left on the fibril which would then have different properties than normal chrysotile asbestos. In a preliminary test, asbestos was leached in a dilute aqueous slurry by reducing the pH to 1 with hydrochloric acid. After setting overnight, the pH had arisen to 1.3 and, from solution analysis, it was calculated that 18 per cent of the magnesium in the bulk fiber had been removed. After washing to neutral pH, the leached fiber was found to be negatively charged in water, which is indirect evidence that a silica-like surface was formed.

In a second test at pH 1, the analysis of the asbestos was only reduced from 24.8 to 24.4 per cent in one hour so no significant leaching had taken place in this length of time at this acidity. The progress of the leaching was followed in more detail in another test. The data are given in Table IX.

TABLE IX

LEACHING ASBESTOS IN MODERATE-STRENGTH HYDROCHLORIC ACID SOLUTION

Elapsed Time, Hr	HCl(1) Added, ml	pH	Surface Charge	Assay Mg, %
0	42	1.2	pos.	25
0.5	-	1.2	pos.	25.2
1.5	-	1.2	pos.	25.3
18	-	1.4	pos.	23.5
25	-	1.4	pos.	23.2
40	-	1.6	pos.	21.8
-	42	0.9	-	-
43	-	0.9	pos.	20.9
58	-	1.05	neg.	17.8

(1) concentrated HCl added to 4 liters of suspension containing 50 g of asbestos

The leaching was much slower than had been expected. Acid had to be added to reduce the pH below 1 before leaching took place at an appreciable rate. The sample taken after 43 hours should have been negatively charged as predicted from its magnesium assay; i.e., the outer layer of the asbestos should be stripped

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of all of its magnesium hydroxide. However, this did not occur until later, based on a direct determination of its charge. It seems that there was somewhat more magnesium dissolved than is associated with the outer layer alone. Possibly some of the inner layers were significantly attacked before all of the outer layers had been dissolved.

R. W. Luce, under the direction of G. A. Parks at Stanford University, has started a program to investigate the mechanism of dissolution of serpentine minerals (28). In later work, he expects to relate the surface charge with the chemical nature of the surface as dissolution proceeds. In the report available at present, he gives the analyses of solutions which have been in contact with the chrysotile asbestos for long periods of time, e.g., 9 months and 12 months. He correlates his data with an assumed solubility reaction of the type:

$$Mg_3(OH)_4Si_2O_5 + 5\ H_2O = 3\ Mg^{2+} + 2\ H_4SiO_4 + 6(OH)^-,$$

$$\text{where } K_{sp} = (Mg^{2+})^3(H_4SiO_4)^2(OH^-)^6.$$

The amount of magnesium present as $MgOH^+$ was subtracted from the total magnesium analysis of the solution, and similarly the amount of $H_3SiO_4^-$ was subtracted from the reactive silica content in solution by using the appropriate stability contents listed by Sillen (29). The corrected data are given in Table X.

TABLE X

LONG TERM SOLUBILITY OF CHRYSOTILE
IN DILUTE AQUEOUS SUSPENSIONS (28)

Conditions		Solution Conc., μ moles/l			
		After 9 mo.		After 12 mo.	
Susp.	pH	Mg^{2+}	H_4SiO_4	Mg^{2+}	H_4SiO_4
0.1 g asbestos stirred in 500 g water under N_2 atmosphere	9.00±0.02	74	62	82	70
	7.6 ±0.1	180	100	200	100

The pK values calculated from these data range from 50 to 58. These solubilities are significantly higher than those shown in Figure 20. Pundsack reports that magnesium concentrations in equilibrium with chrysotile samples from various sources range from 90 to 290 micromoles per liter (30). He has found that the concentration of soluble silica in solution is about 70 micromoles per liter. While there only seems to be one source of hydroxyl ions in the system - the chrysotile, the magnesium ions come from both the chrysotile and from a soluble electrolyte component in the ore. This may be associated with the amorphous phase present in most cross-fiber asbestos samples.

A similar component may be biasing the samples of chrysotile used by Luce since they are probably cross-fiber asbestos also (28). As noted earlier, Coalinga asbestos should be free of this impurity so its solubility should reflect most closely the intrinsic solubility of the chrysotile structure.

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Pundsack made the further observation during acid titration of asbestos suspensions that the total dissolution takes place in three distinct stages (30):

1) Reaction of surface hydroxyl groups,

2) reaction of the remaining, structural hydroxyl groups,

3) reaction to form a hydrated silica residue.

Mechanical Properties

Chrysotile-type minerals have been estimated to have a theoretical tensile strength of 1.5×10^6 psi (31), and this figure is now quoted in the asbestos literature (32). However, these strengths have not ever been approached experimentally. Based on their size, purity, and well-ordered crystal structures, it might be expected that the asbestos fibrils would come closer to their ultimate tensile strength than would most synthetic whiskers. The problem is that single fibrils are too small to test experimentally - only bundles of fibrils which make up a fiber can be measured. The probability of finding a defect in a bundle is proportional to the volume of the bundle, so small bundles tend to be stronger than large ones. This same reasoning holds true for large, individual whiskers. It has been found that measured tensile strengths of whiskers go up significantly for smaller cross-sectional areas, especially when the diameters are less than a micron (33). However, a scatter in measured tensile and modulus values of ±80 per cent is found to be due to the large experimental errors involved and due to undetectable flaws in the fine whiskers measured. A unique way of determining the properties of submicroscopic whiskers was devised by Sears (34). He measured the largest radius of curvature that he could find for a forsterite whisker (0.2 micron in diameter) and calculated that there must have been a minimum of 11 per cent strain in the whisker. The tensile strength then can be calculated from knowledge of the modulus of forsterite since the whisker is obviously bending elastically.

The tensile strengths of various asbestos fibers were measured by Zukowski and Gaze (35). They worked with various lengths of asbestos fibers whose diameters were less than 6 microns. They obtained highest tensile strengths for their shortest specimens, 0.2 centimeter in length. The maximum tensile strengths for chrysotile fibers were approximately 800,000 psi, with average values of 400,000 psi, but both values were still increasing with diminishing length of tensile specimens. The measured Young's modulus was 23×10^6 psi.

It must be concluded that individual chrysotile fibers must have tensile strengths in excess of a million psi. However, in any practical system, there will be at least some bundles of fibrils present and their over-all tensile strength would be expected to be significantly less. A scatter in the strength of individual fibrils has an effect on both the strength of the fiber bundles and on the stress strain behavior of fiber composites. If all the fiber components of a bundle are equal in strength, the stress-strain curve will be linear to the point of fracture. If there is a 25 per cent coefficient of variation in the strengths of the fibrils, the stress-strain curve will bend toward the strain axis and the over-all bundle strength will only be 80 per cent of its theoretical value (33). With a 50 per cent coefficient of variation in the strengths of fibrils, a great apparent yielding or ductility of the fiber bundle is found and the strength of the bundle is only 60 per cent of its maximum calculated from the strengths of its individual fibrils.

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SURFACE PROPERTIES

Electrokinetic Behavior

The classical investigation carried out to determine the surface properties of chrysotile asbestos was by Martinez and Zucker (36). They measured the streaming potential produced by flowing an aqueous solution (10^{-5} M KCl) through a porous plug of fiberized chrysotile asbestos from the Thetford region of Quebec. The sample was considered to be of the semi-harsh type, and the fiberizing of the coarse asbestos in a Mikro Sample mill did not reduce the fibers to a fine size. Consequently, the data shown in Figure 21 are specifically for coarse asbestos which is similar in its fibrous characteristics to that of commercially produced Quebec long-fiber product.

It is seen that at pH 11.8 there is no net charge present. At higher pH values, the charge becomes increasingly negative. As the pH is reduced from 11.8, the surface charge becomes quite positive as is represented by a zeta potential of nearly +100 mv in the pH range 10 to 6. At pH values from 5 to 3, the zeta potential becomes extremely positive, reaching a peak value of nearly +400 mv at pH 3. This is one of the highest zeta potential values for a mineral ever reported. As the pH is decreased from 3 to 2, the zeta potential drops dramatically to about +50 mv. The authors speculate that this is due to the completion of the leaching of the magnesium hydroxide in the outer layer, leaving a hydrated silica surface. Based on our experience (see the section on Solubility), this is not likely, but it is possible that enough surface attack has taken place to reduce the density of positively charged sites. In addition, the concentration of ionic species from the hydrochloric acid solution used to obtain a pH of 2 must have increased drastically, and it is known that the zeta potential decreases in the presence of high salt concentrations.

The viscosity behavior of Coalinga asbestos suspensions in water indicates that similar charge properties exist on this asbestos. In the pH region above pH 8, the suspensions are seen to be flocculated and are quite viscous even at low concentrations (1 weight per cent asbestos). This indicates that attractive forces between the particles dominate over the repulsive forces which are due to the presence of like-charges on the particles. However, the suspensions become dispersed at pH values below 5 where Martinez and Zucker indicate that the charge increases very rapidly. The viscosity approaches that of water and the characteristic shimmering patterns of streaming birefringence are seen. The electrical forces of repulsion are now dominant over the attractive Van der Waal's forces. Since the latter are independent of pH, it is apparent that the electrical forces have increased greatly to cause the deflocculation. It must be stressed that fibrous-shaped particles show a strong desire to flocculate and only very powerful electrical forces can counteract this tendency.

It was considered desirable to obtain similar measurements on Coalinga asbestos. The very fine, friable ore particles of Coalinga asbestos, which have a tendency to swell and to smear out under shear forces, would not make a satisfactory plug for streaming potential measurements. Instead, a microelectrophoretic apparatus* was used to make zeta potential determinations on particles of asbestos in a very dilute aqueous suspension. The technique consists of measuring the velocity of a particle moving under the influence of an electrical field of known gradient. The

* Zetameter

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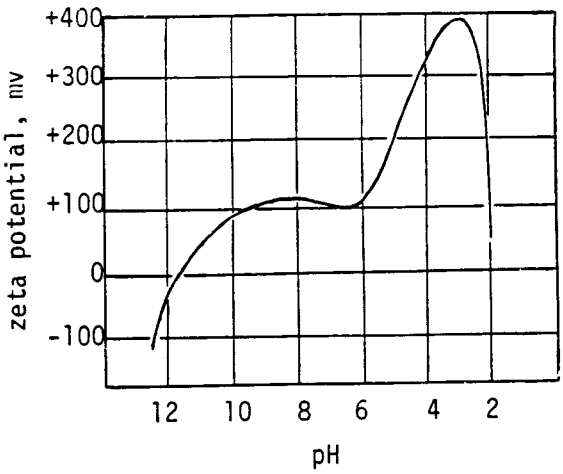


FIGURE 21 - ZETA POTENTIALS OF QUEBEC CHRYSOTILE AS A FUNCTION OF PH IN 10^{-5} MOLAR POTASSIUM CHLORIDE SOLUTIONS (36)

measurement by streaming potential apparatus

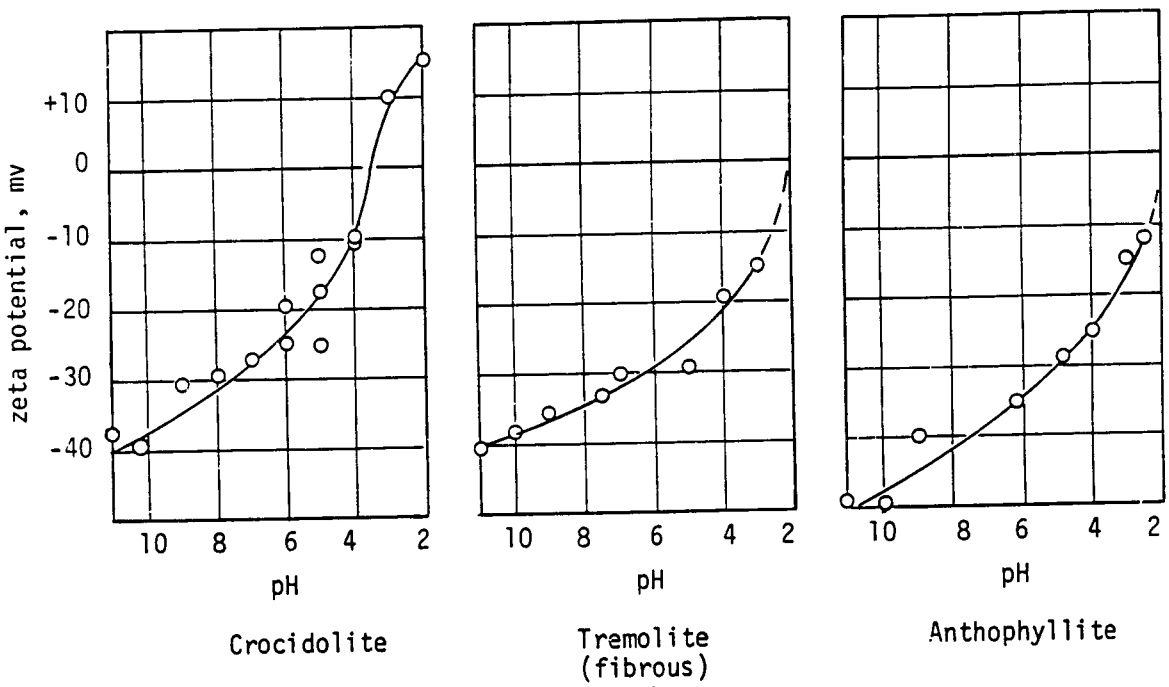


FIGURE 22 - ZETA POTENTIALS OF THREE ASBESTOS MINERALS

measurement by microelectrophoresis apparatus

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von Smoluchowski formula was used to calculate the zeta potential. At room temperature in water, the variables are related by the equation:

$$\zeta = 12.85\mu_o = 12.85 \frac{v}{x} \text{ mv.}$$

The velocity, v, is measured in microns per second and the field gradient, x, is in volts per centimeter. The electrophoretic mobility, μ_o, is often reported instead of the zeta potential since the von Smoluchowski relation only applies for the case where the particle is large with respect to the size of the diffuse layer of ions around it (37). The diffuse layer can extend up to several hundred angstroms from the surface, so in one dimension, an asbestos fibril does not meet this criterion. Therefore, retardation and relaxation corrections must be applied to the von Smoluchowski equation (37). Unfortunately, for cylinders of this size it is difficult to do this precisely (38). A second consideration is that asbestos fibrils are too small to be seen optically so an ultra-microscope technique must be used in which spots of light scattered by the particles are observed instead of looking directly at the particles. There is some doubt as to whether individual fibrils are being seen in the microscope (maximum magnification, 80X) of our apparatus. It is most likely that only the velocities of aggregates are being measured since these are seen more readily. When the particles in the suspension are dispersed, the mobility data obtained by observing coherent bundles of chrysotile fibers can be converted to zeta potential values with the use of von Smoluchowski equation. However, when flocculated particles are being observed two complications arise. The first is that the flocs can be so large that they distort the normal flow patterns in the capillary of the electrophoretic cell. The second difficulty is that the formation of the diffuse layer around the porous aggregate is quite different than for the idealized formation of the diffuse layer around a sphere where the von Smoluchowski equation applies strictly. Corrections could not be made even if it were theoretically possible because the structure of each individual aggregate must vary (39).

All the electrophoretic measurements presented in this report were obtained by multiplying the electrophoretic mobility values by the factor 12.85. However, all the limitations discussed above must be considered before accepting any of the values of zeta potential as being correct in an absolute sense. The zeta potential values are useful primarily in a relative sense to compare different asbestos products or modifications.

Electrophoretic measurements on pure chrysotile suspensions produced totally unsatisfactory results. Typical zeta potentials are in the order of +40 mv at pH 5. The most that can be said is that asbestos particles are quite strongly positively charged although the absolute magnitudes of the calculated zeta potentials are much lower than those reported by Martinez and Zucker (36).

Perversely, much more plausible and reproducible data are obtained on most other minerals. As an example, in Figure 22 the electrophoretic data are given for three other asbestos minerals. These are all seen to be anionic in character.

Electrophoresis data reported further in this report on modified forms of asbestos were also obtained with relative ease. It is now felt that the difficulty in obtaining measurements on pure asbestos was due to the use of very fine fractions of asbestos. It would have been easier to get measurements on coarser fractions of asbestos. Most modified products had many aggregates present whose movements could be readily followed under a microscope.

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Indifferent Electrolytes and Anion Effects

The concept of an indifferent electrolyte is very critical in the study of aqueous surface chemistry. The ionic species of a "perfect" indifferent electrolyte will have no specific affinity for the surface. However, these indifferent species must be present to allow the full development of surface charge since they become the counter ions in the diffuse layer adjacent to the charge surface. A lack of enough ions in the diffuse layer will inhibit full surface charge development since the energy required to form the diffuse layer becomes very high. It is generally observed in surface studies that the surface charge density increases as the indifferent electrolyte concentration increases. This is opposite to the effect that electrolyte has on the magnitude of the zeta potential. The zeta potential becomes lower as the electrolyte concentration increases due to the compaction of the diffuse layer around the particle. The rapid compaction of the diffuse layer has more effect on the zeta potential than does the modest increase in charge as the electrolyte concentration is increased, so there is a corresponding tendency for dispersed particles to flocculate.

Accurate determinations of surface charge density can only be made in the presence of an indifferent electrolyte. Since stable dispersions of asbestos in distilled water can be obtained with acetic acid at pH values below 5, acetate ion has the characteristics of an indifferent anion. It is possible to alternatively disperse asbestos suspensions with acetic acid (to pH <5), and flocculate with a base such as potassium hydroxide. It is shown in Table XI that at least 3 cycles can be made, and indications were that the process could go on many more times. Each cycle, of course, increased the acetate ion concentration, but dispersions have been achieved even in the presence of 1 molar potassium acetate salt. A practical difficulty is that acetic acid dissociates only weakly, so that the suspension eventually buffers and a pH <5 becomes difficult to achieve with acetic acid.

TABLE XI

DISPERSION-FLOCCULATION CYCLES OF ASBESTOS SUSPENSIONS*
IN THE PRESENCE OF INDIFFERENT ANIONS

Cycle No.	Starting pH	Dispersion Cycle: Acid, m moles Add'n	Dispersion Cycle: Acid, m moles Cum	Dispersion Cycle: Final pH	Flocculation Cycle: KOH, m moles Add'n	Flocculation Cycle: KOH, m moles Cum	Flocculation Cycle: Final pH
Acetic Acid							
(1)	9.4	1.91	1.91	4.5	1.59	1.59	9.4
(2)	9.4	4.14	6.05	4.5	4.06	5.65	10.0
(3)	10.0	4.15	10.20	5.0	3.18	8.83	9.5
Methane Sulfonic Acid							
(1)	9.4	0.82	0.82	4.5	0.31	0.31	9.3
(2)	9.3	0.48	1.30	4.5	0.27	0.58	9.6
(3)	9.6	0.30	1.60	4.5	0.23	0.81	9.4
(4)	9.4	0.28	1.88	4.5	0.23	1.04	9.5
Acrylic Acid							
(1)	9.4	1.51	1.51	4.5	1.00	1.00	9.5
(2)	9.5	1.81	3.32	4.5	1.37	2.37	9.4
(3)	9.4	2.54	5.85	4.5	2.00	4.37	9.4

* 6 g HPP in 300 ml distilled water, opened 3 minutes at high speed in small Waring Blendor

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It has been found that both acrylic acid, a medium strength acid, and methane sulfonic acid, a stronger acid yet, also disperse asbestos even in the presence of high concentrations of their salts. Some data are included in Table XI about dispersion-flocculation cycles with these acids. It is seen that the least amount is required of the strongest acid - methane sulfonic acid, and that the least amount of base is required subsequently to flocculate the dispersed suspension.

The criterion for an apparently indifferent species for asbestos surfaces is that it should be bulky, i.e., large volume in solution, and that it should have no groups with specific attraction for asbestos surfaces. For example, aromatics absorb readily on asbestos from the gas phase, and it has been found that benzene sulfonate salt is not indifferent to asbestos surfaces in water also.

Naumann has tried to determine the class or type of organic acids that are effective for dispersing asbestos suspensions (40). The following series of hydrocarbon acids were found to be effective, although he noted that foaming increased with increasing carbon chain length: formic, acetic, propionic, butanoic, pentanoic. Other effective acids were: chloroacetic, lactic, acrylic, and crotonic. However, dicarboxylic acids and citric acid were not effective. He concluded that monobasic carboxylic acids having a carbon chain length of less than 6 carbon atoms would disperse asbestos suspensions. It should be cautioned, however, that there is no satisfactory quantitative criterion for dispersion. This is a subjective evaluation based primarily on the appearance, viscosity, and stability of a suspension, and by our standards, formic acid does not produce a satisfactory dispersion.

Using the principle that asbestos suspensions can be dispersed by acetic acid, Naumann and Dresher established an order of specific attraction of anions for the asbestos surface by determining the critical coagulation concentration of anion which will just flocculate an asbestos dispersion in an arbitrary time (41). They used a time of 5 minutes. If a different flocculation time were used, the magnitudes of the critical concentrations would vary, but the order of the specific attractions of the anions should remain the same. Data are given in Table XII. Least harmful of the anions listed (highest coagulation concentration) is chloride ion, and the most specific monovalent anion is permanganate ion. The authors correlate harmful effects with size, indicating the smallest ions are the least detrimental to dispersion stability. This is contrary to this author's observation about the nature of indifferent anions, and in his opinion, a more pertinent correlation would have been with the size of the hydrated anion.

The data in Table XII refer only to monovalent anions, but multivalent anions are attracted much more strongly to asbestos surfaces. For example, divalent sulfate ion at concentrations less than 10^{-5} m/l is enough to irreversibly flocculate asbestos suspensions. Since the ground water in the region where Coalinga asbestos is mined contains large quantities of sulfate salts, the processed asbestos has significant amounts of adsorbed sulfate anions and dispersions made from unwashed asbestos tend not to be stable over a long period of time.

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TABLE XII

CRITICAL COAGULATION CONCENTRATIONS OF ANIONS ADDED TO ASBESTOS DISPERSIONS* (41)

Anion	Added As	Critical Coagulation Conc, m moles/l
MnO_4^-	$KMnO_4$	0.4
CNS^-	NaCNS	0.6
I^-	KI	0.9
NO_3^-	$NaNO_3$	1.2
Br^-	KBr	2.0
IO_3^-	KIO_3	2.0
ClO_4^-	$KClO_4$	2.1
NO_2^-	$NaNO_2$	4.0
Cl^-	NaCl	4.0
	KCl	4.3
	NH_4Cl	4.7
	$CaCl_2$	4.7
	$MgCl_2$	4.0

* 0.5 weight per cent asbestos in deionized water, opened for 3 minutes at pH 4.2 (with acetic acid) in a Waring Blendor

The mechanism of specific adsorption is not well understood for most mineral systems, although it has been studied comprehensively at the aqueous solution-mercury interface (42). Surfaces of minerals in water are hydrated and charged sites on the surfaces are well surrounded by water molecules. Ions in solution are also well protected by a sheath of water. Therefore, when an anion approaches a positively charged surface site, there are one or more layers of water molecules between it and the physical source of the charge. If the attraction between the ion and the charged site is small, less than a couple of kilocalories per mole, random thermal forces are eventually sufficient at room temperature to move the anion from its position. The physical separation, relatively large on an atomic scale, between the charged site and the ion in the counter layer adjacent to the surface leads to a "space charge" effect, and the surface has a "zeta potential" extending some distance into the solution. If there is a chemical affinity between the ion and a specific species making up the site, this attraction can bring the ion very close to that site, expelling the water of hydration that would normally separate them. This would be called specific adsorption and could have an interaction energy as large as 10 kilocalories per mole. Thermal forces would no longer be capable of separating them, and desorption could be caused only by some application of energy to break the bond or by a change in chemical conditions in solution. Since the physical distance between the site and its adsorbed ion is small, their effect would not extend very far from the surface into solution. Thus, a particle with significant numbers of its surface sites neutralized by specifically adsorbed species could not be readily dispersed.

A washing procedure is given in the following section which is designed to remove contaminating adsorbed species on the asbestos particles.

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Purifying and Washing Chrysotile Asbestos

The two requirements of a material to be used for studying the intrinsic properties of chrysotile are that it be free of other solid phases and that the surface be uncontaminated. A preparation must be devised to meet these two requirements.

The most likely solid contaminants are magnetite, serpentine rock fragments, brucite, and Coalingite. Surface samples may also have some organic contamination from plant life, but deeper samples should be relatively free of this matter. The magnetite rock fragments and coarse particles of brucite and Coalingite can be removed by breaking down the asbestos into fine fibrils, dispersing them chemically with acetic acid, centrifuging to settle the contaminants, and pouring off the supernatant which contains the pure chrysotile. Fine particulates of brucite, and maybe of Coalingite, will need to be dissolved for removal. Fortunately, both can be expected to dissolve readily in moderately acidic solutions (pH approximately 4).

Thus, a suspension at approximately pH 4 containing pure chrysotile fibers is obtained. The surfaces of the fibers are contaminated by sulfate ions and traces of organics, while the suspension solution contains at least dissolved magnesium ions and ferrous ions. Large additions of potassium chloride should aid in desorbing both organic materials and sulfate ions and, at the same time, will flocculate the suspension without any danger of precipitating iron or magnesium hydroxides. The solution can be washed out of the suspension by centrifuging to settle the solids and decanting the clear supernatant to remove the solution containing the contaminants. After a few cycles, it is safe to increase the pH to the alkaline region with potassium or sodium hydroxide (pH >12). The high pH desorbs both the remaining adsorbed sulfate ions and any weakly adsorbed chloride ions. Any adsorbed cationic impurities will tend to desorb. The suspension remains flocculated so the potassium hydroxide can be washed out by centrifuging and decanting the clear supernatant. The washing should be continued until a nearly neutral pH is obtained and the clear supernatant liquid has a specific resistivity of 200,000 ohm-cm. Double distilled water with a specific resistivity of about 10^6 ohm-cm was used for the early stages of washing, and tripled distilled water with a specific resistivity greater than 2×10^6 ohm-cm was used for final washes. The washed suspension was stored in a cleaned, tightly capped polyethylene bottle at a concentration of about 4 per cent solids.

Asbestos prepared in this manner will be referred to as refined and washed asbestos. It was used for all the critical adsorption experiments where quantitative data were collected.

Suspension Potentials

Since the electrophoretic technique was not suitable for measurements on the flocculated asbestos suspensions that occur near the zero point of charge of asbestos, the suspension potential technique was tried to at least find the pH of the zpc of Coalinga asbestos. Suspension potential measurements were expected to work well on flocculated suspensions.

The basis of this experimental procedure is that there is an apparent change in the potential of a calomel electrode due to the presence of charged particles around the flowing junction at its tip (43). The change in the potential across this flowing junction due to the proximity of the charged particles is called the suspension potential. In practice the procedure calls for measuring

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the potential of a calomel electrode when it is placed in the settled portion of a suspension and then measuring its potential again when it is placed in the supernatant liquid above the settled sediment. The reference electrode can be another calomel electrode placed in the supernatant or a glass electrode if the pH of the suspension is very stable.

When a sediment that has no charge settles around the tip of the calomel electrode, it generally does not affect the potential of the electrode. However, when the sediment is positively charged, the apparent potential of the electrode is decreased, and when the sediment is negatively charged, the apparent potential of the electrode is increased. This is not a quantitative measurement since the magnitude of the suspension potential cannot be related to the magnitude of the surface potential. At a given pH of the solution, the suspension potential is higher with firmer packing of the sediment around the calomel, and it becomes lower as the salt content of the solution phase increases. However, in a series of measurements on the same sample with a controlled amount of salt in solution, the magnitude of the suspension potential is approximately proportional to the potential at the surface. This technique can only be used for the determination of the sign of the surface and to locate the pH of the zero charge condition.

The results of measurements made with coarse asbestos particles being allowed to settle by gravity are given in Figure 23. The suspension potential rapidly decreases as the pH is increased from 10 to 11, but then the data scatter at low values of the suspension potential and no reproducible pH can be found where a change occurs in the sign of suspension potential.

It was felt that the coarse particles of asbestos might have enough brucite yet to be affecting these data, so the particles were washed in a Soxlet extractor at approximately 100°C with a 5 per cent acetic acid solution. Many rust-colored particles appeared among the asbestos particles, probably indicating that Coalingite was being broken down and leaving behind iron oxides which are insoluble in this weak acid.

Suspension potential measurements made with this acid-washed sample showed the anomalous behavior that the surface charge seemed to change from negative to positive as the pH of the suspension was increased. These data are given in Figure 24(a). The sample was removed and washed with distilled water to remove the base added during pH adjustments. Washed asbestos was again used for a second series of suspension potential measurements. The data in Figure 24(b) show a more normal behavior with a well-defined zpc at pH 10.4 However, when the sample was again washed and used in a third series of suspension potential measurements, the behavior, depicted in Figure 24(c), was the same as in the test before acid washing. The magnitude of the potential decreased rapidly at pH values above 9, but reproducible measurements could not be obtained to show the presence of a negative surface charge even at a pH value of 11.9.

None of these data is felt to represent the intrinsic properties of pure asbestos. The sample of asbestos appears to have been affected by contaminants originally. The most likely explanation for the results after the moderate acid washing is that the acid dissolved or neutralized positive sites on the surface, creating a metastable surface which only slowly came to equilibrium when it was contacted with alkaline solutions. This was the first indication that negatively charged surfaces could be made by acid treatments.

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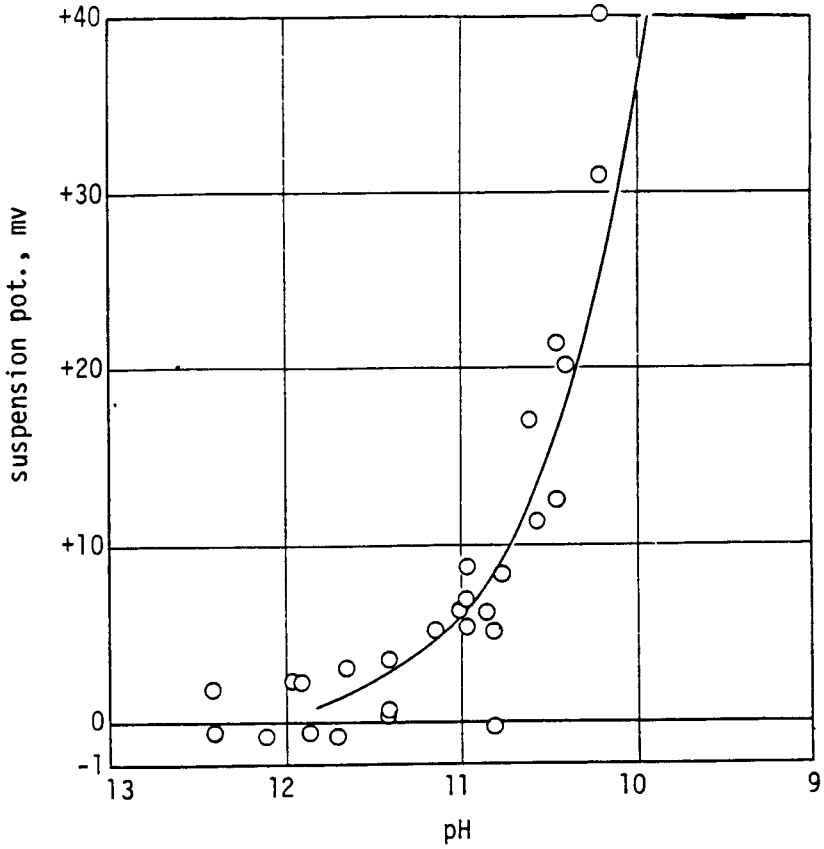


FIGURE 23 - SUSPENSION POTENTIALS OF COARSE COALINGA ASBESTOS VERSUS PH

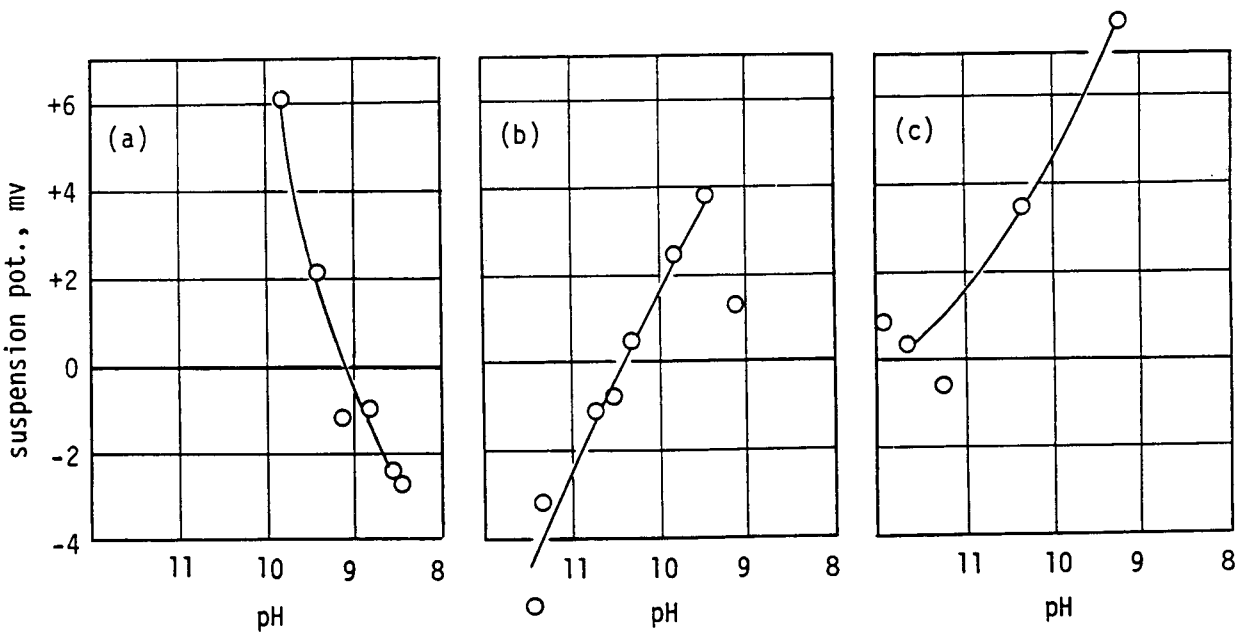


FIGURE 24 - EFFECT OF ACID-WASHING COARSE ASBESTOS ON ITS SUSPENSION POTENTIAL
(a) after acid treatment,
(b) after water wash,
(c) repeat

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Suspension potential measurements on washed asbestos were difficult to perform since uniform packing could not be achieved around the calomel tip. An alternative apparatus was constructed which made possible measurements analogous to suspension potential measurements. Two reservoirs were connected by a capillary tube; a Teflon stopcock at the middle of the capillary tube aided in operation of the apparatus. An asbestos suspension adjusted to a desired pH value was centrifuged. The supernatant liquid was placed in one reservoir and it was also allowed to fill the capillary tube completely. The sediment was then placed in the other reservoir. The potential was measured between electrodes in the two reservoirs. The potential between the electrodes in the supernatant solution alone was then measured and the differences in the two values of the potential reflected the surface charge on the asbestos in a situation similar to that in suspension potential measurements. These determinations will be called membrane potentials in this report to distinguish them from the suspension potential technique. The data shown in Figure 25, however, follow the same pattern as the suspension potential data - the membrane potential decreased as the pH increased, but their values did not definitely reverse their sign at high pH values. The indication is again that the asbestos never does become permanently negatively charged at high pH values.

Potentiometric Titrations

A successful experiment of this type measures the surface electrical properties of a solid in water completely. From the relationships between the surface charged density, the concentration of potential determining ions, and the concentration of indifferent electrolyte, all of the equilibrium charge properties can be established. For oxide minerals, hydrogen ions and hydroxyl ions are potential determining (27). The experimental procedure, in essence, consists of a very careful acid-base titration of an asbestos suspension in water in the presence of various concentrations of sodium or potassium acetate in solution.

In the earliest tests, potassium chloride was used as the indifferent electrolyte and the indications were that the apparent zpc was at a pH value of about 9. The same result was indicated when potassium chloride contamination was suspected from the calomel electrodes or from residual amounts left after washing and purifying the asbestos.

In the two last tests, the asbestos was carefully washed to exclude traces of chloride ion, and a lithium acetate salt bridge was used between the calomel electrode and the experimental asbestos suspension to exclude any further chloride contamination.

The results of the two experiments are shown in Figure 26. The two sets of adsorption density data do not agree within 50 per cent in magnitude and the reliability of the zpc determination is very low by these experiments. At least part of the difficulty is that in the region of the zpc, about pH 11, the charge densities approach zero, but a large error appears in the calculated value for the surface charge density. Its magnitude is calculated as the difference of two large numbers - the net amount of base added to the suspension and the amount of hydroxyl ion left in solution after adsorption at the surface. The latter value is arrived at from pH measurements and the error in concentration in solution is given by the relation:

$$\frac{\Delta C}{C} \simeq \frac{\Delta E}{26} \qquad (1)$$

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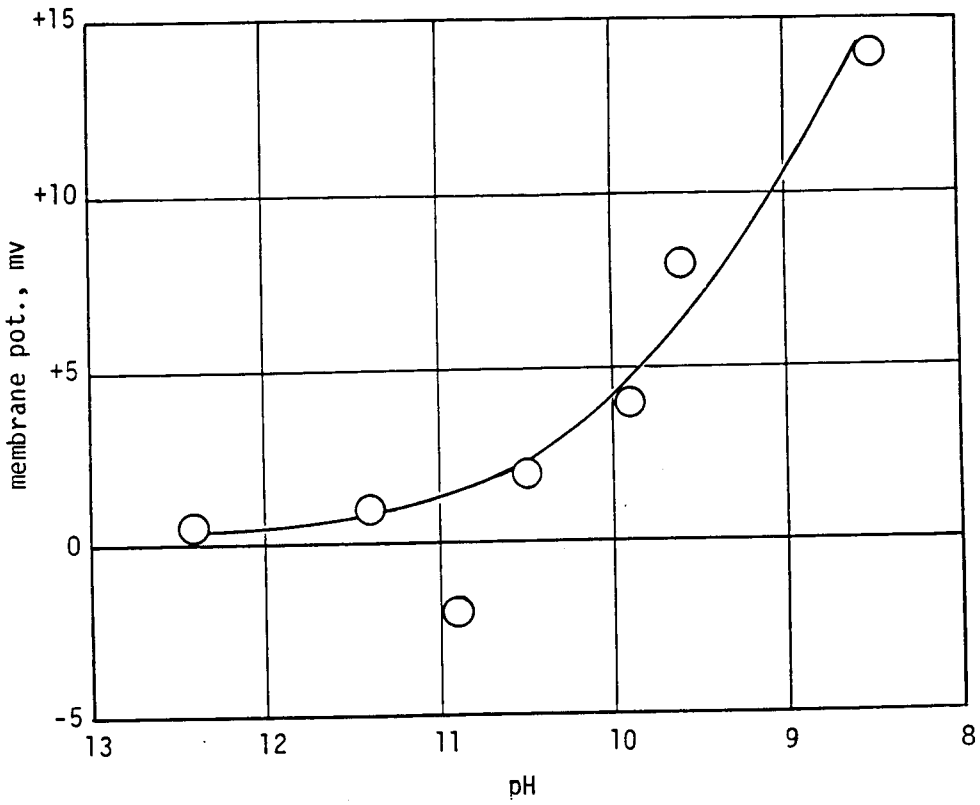


FIGURE 25 - MEMBRANE POTENTIAL MEASUREMENTS WITH WASHED AND REFINED COALINGA CHRYSOTILE

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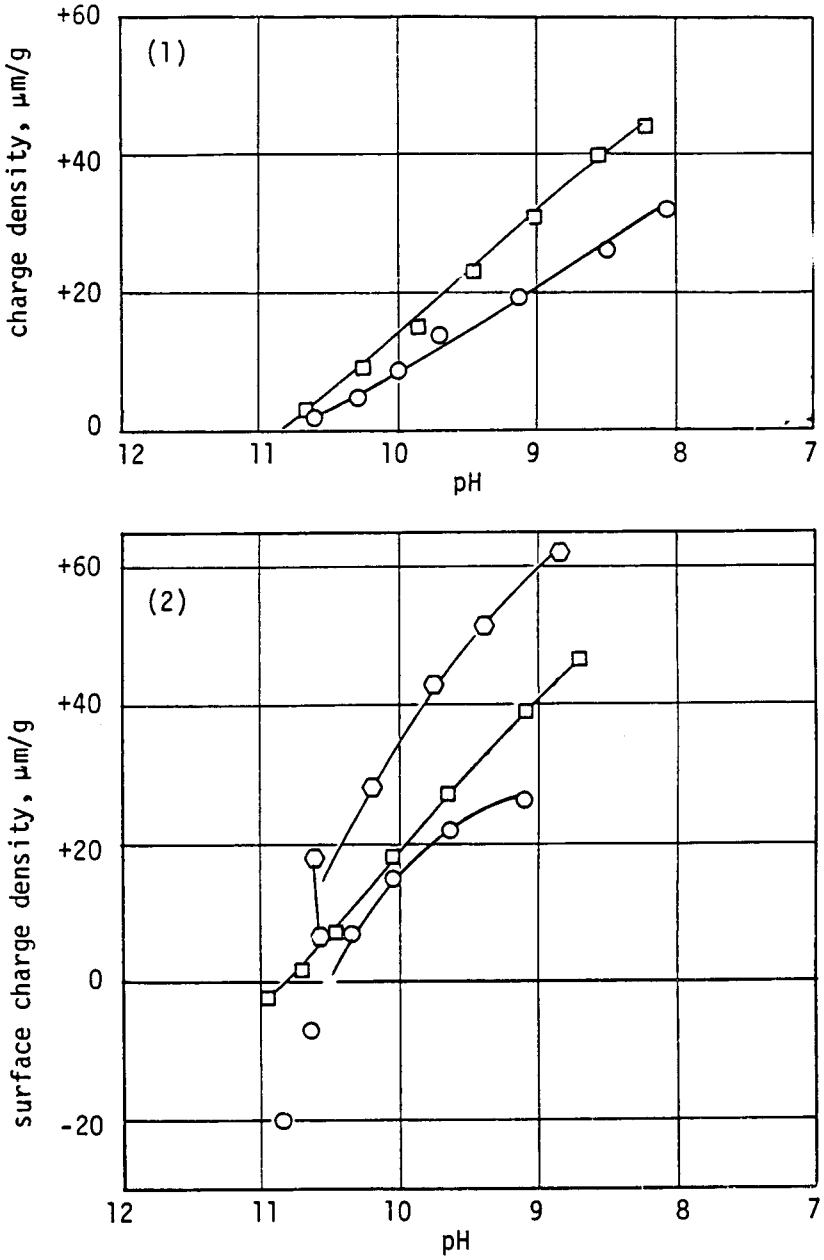


FIGURE 26 - POTENTIOMETRIC TITRATIONS OF COALINGA CHRYSOTILE SUSPENSIONS IN POTASSIUM ACETATE SOLUTIONS AT 30°C

Ionic strength: ○○○ 10^{-3} M
□□□ 10^{-2} M
⬡⬡⬡ 10^{-1} M

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where ΔC is the error in the magnitude of the concentration, C, and ΔE is the error in the potential reading between the glass and the calomel electrodes. For an error of ± 1.0 mv which is the best obtained in our system, the error in concentration is approximately ± 4 per cent. This is too large to be able to get significant data in the pH region above 10 where the hydroxyl concentration in solution is large. At lower pH values, however, there was significant consumption of the acid added to the suspension in dissolving asbestos, apparently irreversibly, so that the amount of acid used in developing the positive surface charge sites on the asbestos again became indeterminate.

It was concluded that a potentiometric titration is not a satisfactory way of determining the surface properties of chrysotile asbestos in water.

Acetate Ion Adsorption

Up to this point in the investigation it had not been possible to determine the charge properties of the asbestos surface. Direct measurements of surface charge density did not work nor did the less direct indications from electrophoresis and from suspension potential measurements. A new approach was needed. H. C. Li faced similar problems in determining surface properties of silica in water, and a technique that he used consisted of measuring the adsorption of a counter ion, iodide ion, at low pH values where he suspected that the silica surface was positively charged (44). Unfortunately, he failed in his purpose because the iodide ion was not known to be indifferent and may have had some tendency to adsorb specifically.

The principle of this technique is that oppositely charged ions are attracted to the vicinity of a charged surface by electrostatic forces. The number of ions in this diffuse layer is exactly equal to the number of positively charged sites present on the surface. It was known that acetate ions do not specifically adsorb on asbestos so their attraction to the positively charged asbestos surfaces was only due to the intrinsic surface charge.

Solutions of sodium acetate were obtained with C^{14} tagging from the New England Nuclear Company. These were added in small quantities to concentrated solutions of untagged reagent-grade sodium acetate. The adsorption of the acetate ions on washed and refined asbestos was measured by making additions of known quantities to an asbestos suspension at constant pH and then measuring the residual concentration in the solution phase with a scintillation counter. The separation between asbestos and solution was accomplished by centrifuging, so the measurements were limited to pH values above pH 9. Below pH 9, very small but significant amounts of asbestos remained dispersed in solution, preventing accurate solution analyses.

The acetate adsorption isotherms are given in Figure 27. The qualitative interpretations of the data are that little acetate adsorption takes place above pH 10.5, so the zpc must lie at a value just about that pH.

Quantitative interpretation depends on use of equations from double layer theory. The number of adsorbed counter ions, η_d, is related to the potential, ψ_d, at the distance of closest approach of ions to the surface (45):

$$\eta_d = -\left(\frac{Z\epsilon kT}{\pi}\right)^{1/2} C^{1/2} \mathrm{Sinh}\left(\frac{Ze\psi_d}{2kT}\right) \qquad (1)$$

$$= -11.8 \; C^{1/2} \mathrm{Sinh}\; 19.1\psi_d \text{ at } 30°C$$

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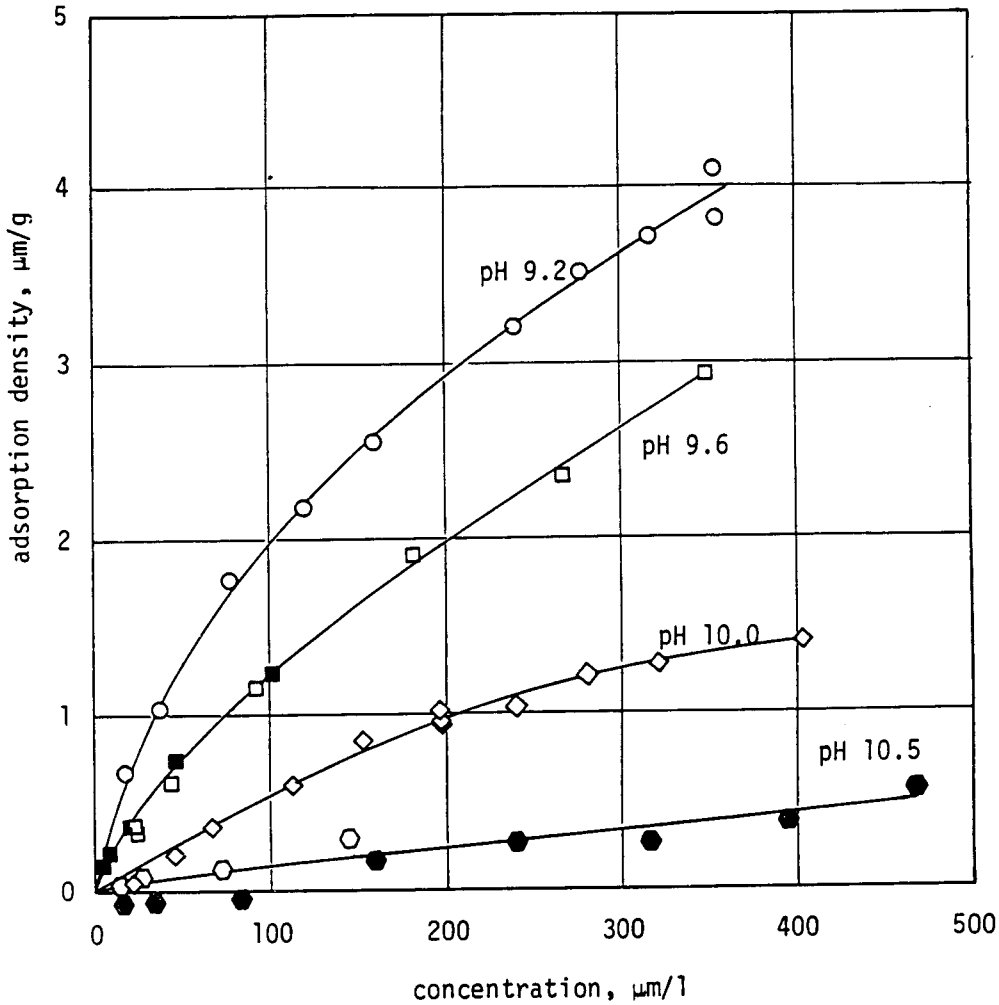


FIGURE 27 - ADSORPTION ISOTHERMS AT 30°C FOR ACETATE IONS ON CHRYSOTILE AT VARIOUS PH VALUES

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where "C" is the concentration of anions in bulk solution.

The concentration, "C," is ideally the concentration of indifferent electrolyte, but in this case the concentration of hydroxyl ions is also significant at the higher pH values with respect to that of acetate ion, so the sum of the concentrations of the two species is taken for "C." The concentration of hydroxyl ions was calculated from standardization curves of pH versus potassium hydroxide addition for pure aqueous solutions of potassium acetate.

The composition of the double layer is:

$$\eta_d = \eta(A_c^-) + \eta(OH^-) - \eta(K^+) \qquad (2)$$

which shows that the double layer is made up of the sum of the number of acetate ions and hydroxyl ions present and the deficiency of potassium ions in that layer.

Then, by combining Equations (1) and (2) and differentiating, the following equation is obtained:

$$\left[\frac{d\eta\,(A_c^-)}{d\,\eta\,([KA_c] + [KOH])^{1/2}}\right]_{KOH} = -11.8 \text{ Sinh } 19.1\psi_d \qquad (3)$$

The justification for this approximation is that the resulting plot of adsorption density of acetate ions versus the square root of the concentration "C" is a straight line as shown in Figure 28. The surface potential values, ψ_d, were then calculated from the data of Figure 28 by using Equation (4) and are plotted in Figure 29. The surface potential values are extrapolated to zero at pH 10.8 which then is the pH of the zero point of charge of the asbestos surface.

After the adsorption data were gathered at pH 9.2, the pH of the experimental suspensions was increased in stages and the desorption of acetate ions from the surface was followed by analysis of the solution. The data from this test are given in Figure 30. Similar data were obtained at the end of the test at pH 9.5. It is apparent that no more adsorption of acetate ion occurred above pH 10.6, although the data above pH 10 are becoming increasingly inaccurate. However, at least these data are not inconsistent with a zpc value of pH 10.8. The pH adjustments in the tests were made rapidly, followed by immediate sampling of the solution after centrifuging (less than 5 minutes required per data point). The adsorption value of 1.65 micromoles per gram of asbestos at pH 10, from Figure 30, falls on the pH 10 curve of Figure 27 within experimental accuracy. It is apparent that the acetate ion adsorption-desorption process takes place quickly and reversibly as would be expected for an ion in the diffuse layer. Furthermore, the charging process at the chrysotile surface is fast and reversible.

It is concluded that the experimental measurement of acetate adsorption on chrysotile asbestos from aqueous solutions is a useful and valid way to determine the charge properties of the asbestos.

Sulfate Ion Adsorption

Sulfate ion not only occurs naturally in the ground waters saturating the ore deposit but is also the most common, detrimental, divalent anion present in the water used to make up the suspensions of asbestos in commerical applications.

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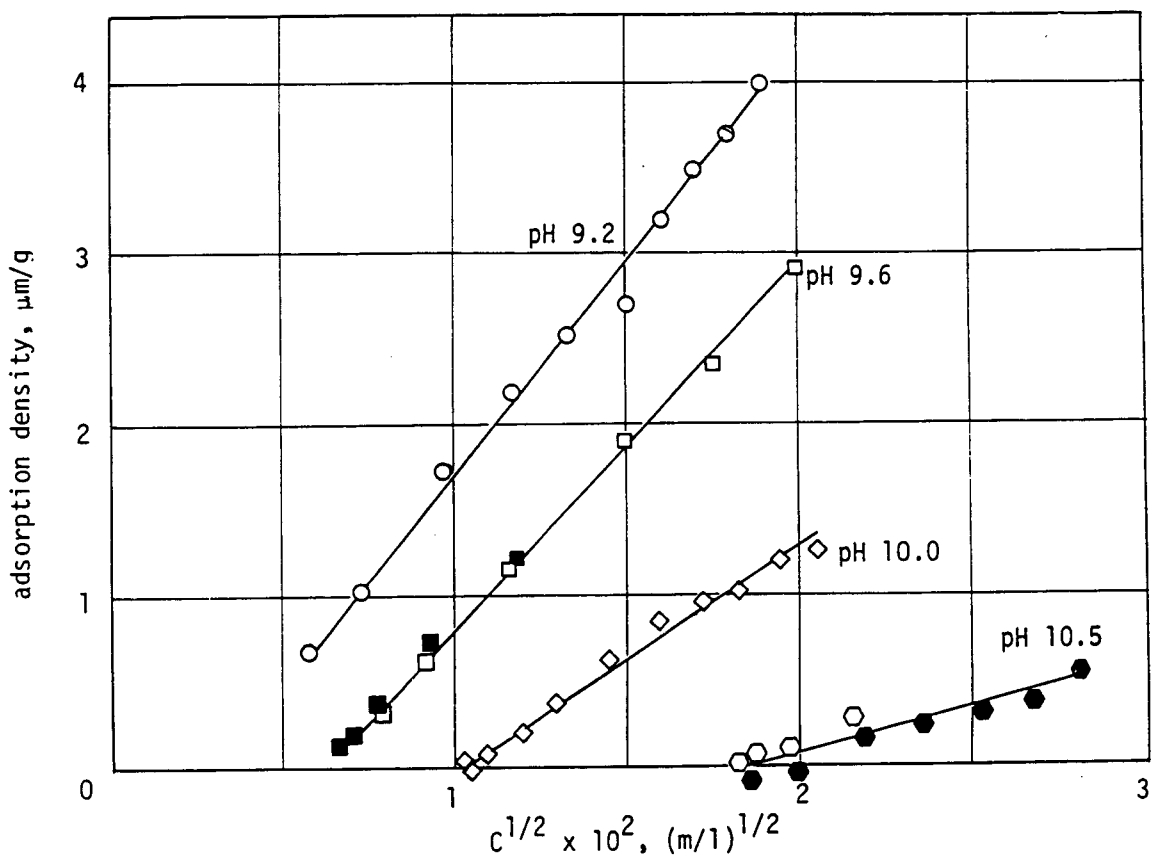


FIGURE 28 - ADSORPTION OF ACETATE AT 30°C VERSUS THE SQUARE ROOT OF SALT CONCENTRATION IN SOLUTION AT VARIOUS PH VALUES

"C" is salt concentration, sum of potassium acetate and potassium hydroxide concentrations

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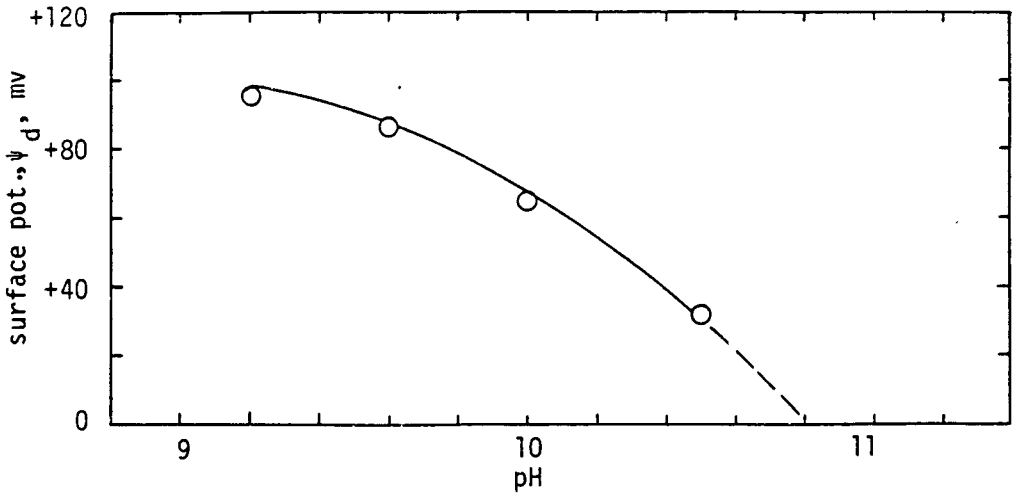


FIGURE 29 - SURFACE POTENTIAL, ψ_d, AT THE CHRYSOTILE SURFACE AS A FUNCTION OF PH

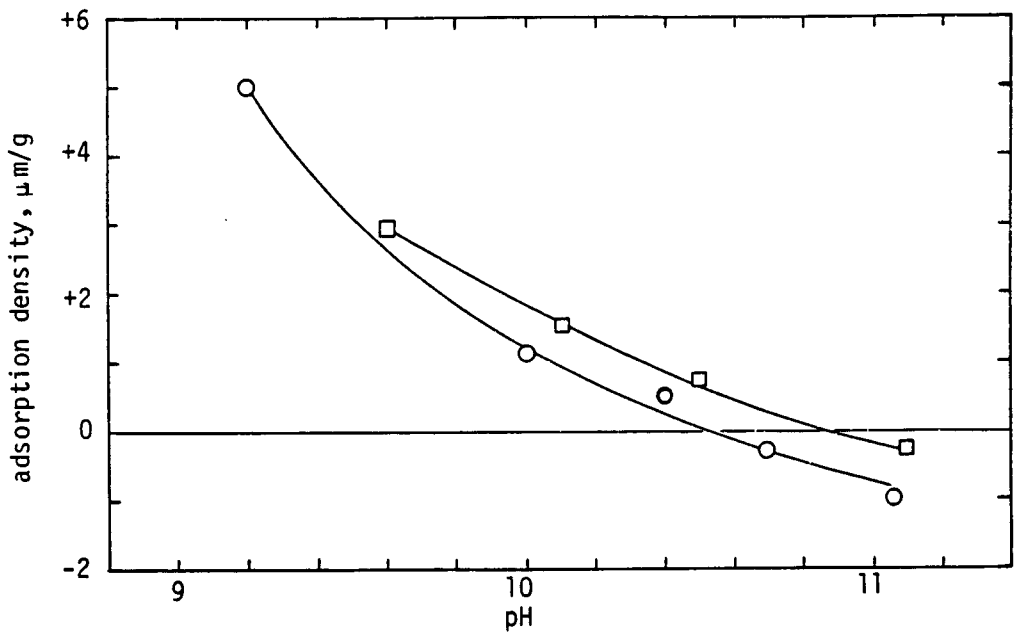


FIGURE 30 - DESORPTION OF ACETATE ION BY INCREASING THE PH OF THE SOLUTION

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Since even a small amount of sulfate ion in an asbestos suspension can have a very great effect on its flow properties, a program was carried out to determine its adsorption characteristics on asbestos.

The same radioactive tracer procedure was used as for acetate adsorption. The Nuclear Division of Union Carbide provided a sodium sulfate solution tagged with S^{35} isotope which was made at the Tuxedo Research Center reactor. The starting material for S^{35} isotope was a chloride salt, so the amount of detrimental contamination by chloride was felt to be negligible, especially considering the differences in the adsorbability of chloride ion and sulfate ion. In addition, only very small quantities of the radioactive solution were used to spike concentrated solutions of potassium sulfate.

The sulfate adsorption density was calculated as the difference between the amount of sulfate added to an asbestos suspension and the amount remaining in pure solution as determined by radioactive analysis.* The independent parameters in this study were generally pH and salt concentration in solution (potassium chloride and potassium acetate salts).

The asbestos in all sulfate adsorption experiments was carefully refined and washed. This was especially necessary since it was known that sulfate ion contamination occurs in the source material of this asbestos - Coalinga ore.

The adsorption isotherms for sulfate ions on asbestos from aqueous solutions containing 10^{-3} molar potassium chloride are shown at pH values of 4.3, 6.0, 8.0, 9.5, and 11.0 in Figure 31. The only components present besides potassium sulfate and potassium chloride were the potassium hydroxide and acetic acid used for pH adjustment. The adsorption density is very pH dependent at low solution concentrations of sulfate ion, but it is startling that all of the isotherms approach the same adsorption density, 46 micromoles per gram of asbestos, at high sulfate additions. It seems that there are a maximum number of positively charged sites present, regardless of pH. These sites are activated by lowering the pH of the suspension or in the presence of high concentrations of sulfate ion.

Similar results are found for adsorption of sulfate on asbestos from solutions containing no added potassium chloride. However, no precautions were taken to exclude contamination by chloride from the calomel electrode used in measuring the pH of the suspensions, so some chloride must be present. The results are shown in Figure 32.

The effect of potassium chloride concentration on the sulfate adsorption isotherms at a constant pH of 9.5 is shown in Figure 33. There is very little difference in the adsorption density between no potassium chloride added and 10^{-3} molar potassium chloride added, so it is apparent that at low concentrations of potassium chloride in solution, the chloride ion does not compete strongly with sulfate ion for positively charged surface sites. At very high concentrations of potassium chloride, 10^{-2} molar or 10^{-1} molar, there is effective competition between chloride ions and sulfate ions for surface sites.

A sulfate adsorption isotherm at pH 9.5 is also shown in Figure 33 which was measured in the presence of 10^{-2} molar potassium acetate solution. This amount of acetate ion in solution does decrease the adsorption of sulfate ion somewhat, but

* Scintillation counter

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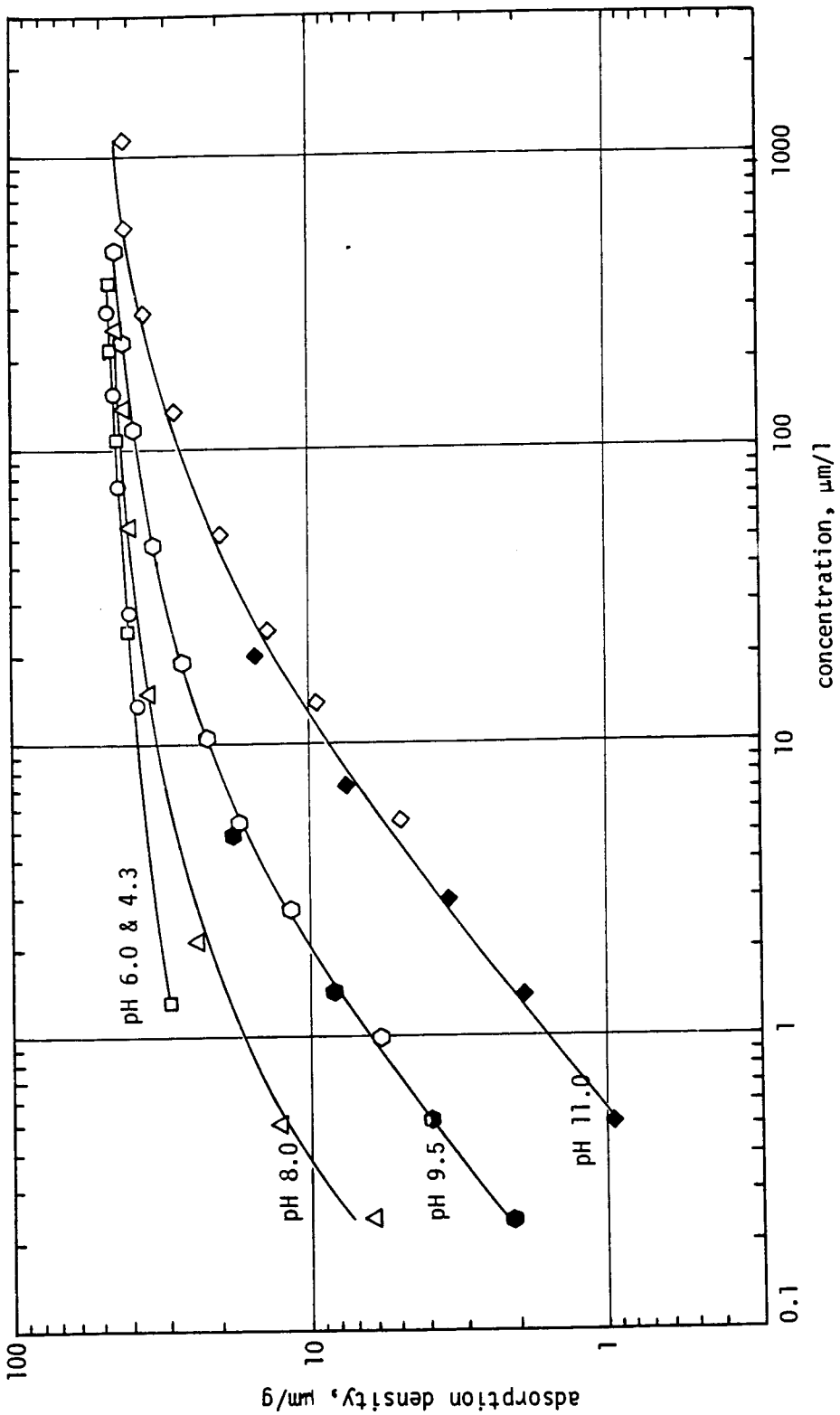


FIGURE 31 - ADSORPTION ISOTHERMS AT 30°C FOR SULFATE ION ON CHRYSOTILE IN 10^{-3} MOLAR POTASSIUM ACETATE SOLUTIONS AT VARIOUS PH VALUES

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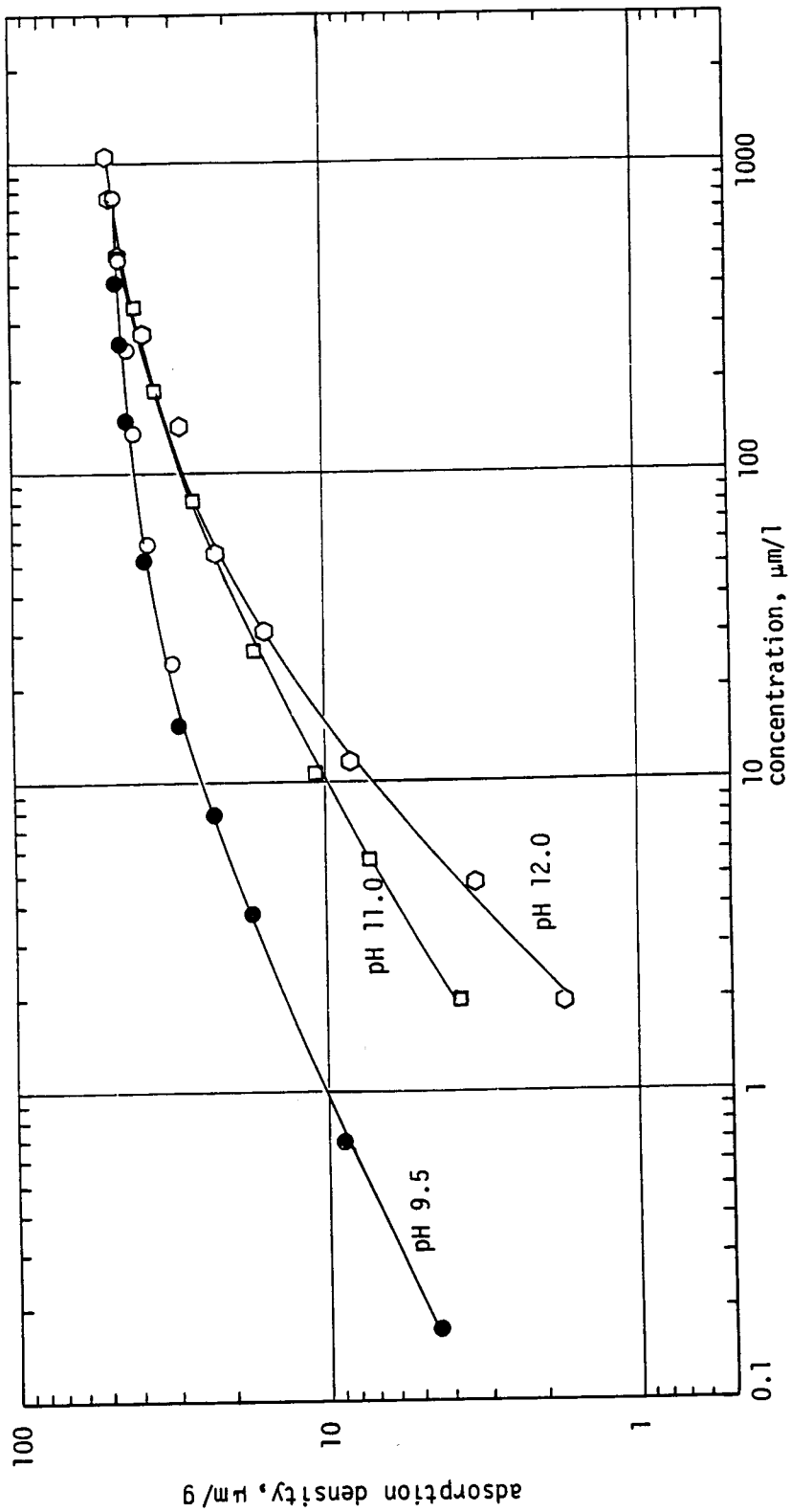


FIGURE 32 - ADSORPTION ISOTHERMS AT 30°C FOR SULFATE ION ON CHRYSOTILE IN WATER AT VARIOUS PH VALUES

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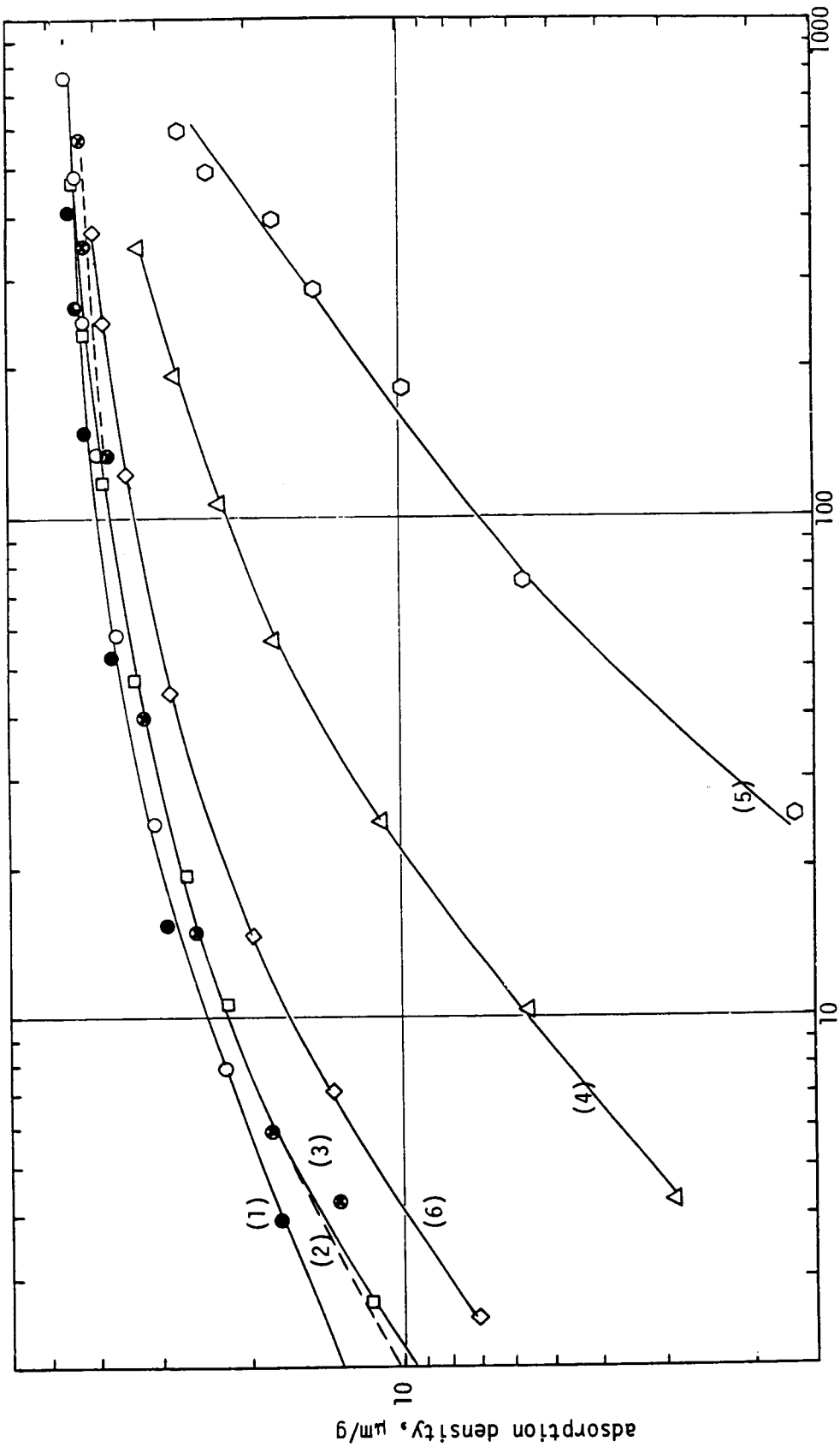


FIGURE 33 - THE EFFECT OF ADDED ELECTROLYTE AT PH 9.5 ON THE SULFATE ADSORPTION

(1) no electrolyte, 30°C
(2) no electrolyte, 50°C
(3) 10^{-3} M KCl, 30°C
(4) 10^{-2} M KCl, 30°C
(5) 10^{-1} M KCl, 30°C
(6) 10^{-2} M sodium acetate, 30°C

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not as much as does the equivalent amount of chloride ion in solution. It is apparent that chloride ion actively competes with sulfate ion for specific surface sites, while acetate ion only displaces some of the sulfate ion in the diffuse layer since earlier data indicate that acetate ion is not specifically adsorbed.

The data were all plotted in a Langmuirian form on log-log paper, but only the adsorption isotherm in 10^{-1} molar potassium chloride solution approached a slope of 1, indicating Langmuir-type adsorption characteristics. The others all had slopes less than 1. One interpretation of these data is that sulfate ions adsorb both specifically on the surface and also adsorb physically to make up a significant part of the ions in the diffuse layer. Only when the potassium chloride concentration is 0.1 molar does the chloride ion completely displace the sulfate ion from the diffuse layer portion of the interface, so all of the adsorbed sulfate is then specifically adsorbed.

An adsorption isotherm at 50°C is also shown in Figure 33. The adsorption is slightly less than at 30°C, as would be expected. The isosteric heat of adsorption for sulfate ion adsorbing on the asbestos from water at pH 9.5 has been calculated from these two isotherms to be 4.2 kilocalories per mole using the equation given in the following section entitled Hydrophobic Modification. The magnitude of the heat of adsorption is in the mid-range for specific adsorption. It included the thermal effects for all of the side reactions accompanying the sulfate ion adsorption, such as simultaneous desorption of hydrogen ions.

It is known from the work of Matijevic that multivalent cations can reverse the charge on sols from negative to positive (46). The question arose whether sulfate ions adsorb in sufficient quantities on asbestos surfaces to change the surface charge from positive to net negative. This determination is complicated by the fact that hydroxyl ions are desorbed, or hydrogen ions are adsorbed, as sulfate ions are adsorbed. Mechanistically, one might interpret this to mean that the sulfate ion will tend to displace a neighboring hydroxyl ion when it adsorbs on a site with a single charge. Alternatively, the strong affinity of sulfate ions for the surface may cause charged sites to form which did not exist previously, i.e., a sulfate ion displaces a hydroxyl ion which is only weakly bonded to its site.

A relationship has been found where the number of additional hydrogen ions adsorbed is proportional directly to the number of sulfate ions adsorbed:

$$\Gamma_s = k \cdot \Delta\Gamma_H \qquad (1)$$

The magnitude of this change in hydrogen ion adsorption diminishes drastically at high potassium chloride electrolyte concentration in the suspension. It appears that chloride ion has some of the same ability to alter the surface as does sulfate ion. Thus, when sulfate ion adsorbs on some sites, it must displace chloride ions previously adsorbed there, so no net effect is seen on the pH value of the suspension.

The over-all effect occurring at the asbestos surface when sulfate ions are adsorbed from a pure water phase is then described by the following relation:

$$\sigma' = \sigma^\circ - 2\Gamma_s + \Delta\Gamma_H \qquad (2)$$

where σ' is the apparent charge, σ° is the initial surface charge, Γ_s is the sulfate adsorption density and $\Delta\Gamma_H$ is the change in hydrogen ion adsorption.

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However, the value of σ° is not known with any confidence.

Furthermore, in the presence of potassium chloride in solution, terms for the effect of chloride ion at the surface are needed:

$$\sigma' = \sigma^\circ - 2\Gamma_s + \Delta\Gamma_H - \Gamma^\circ_{Cl} + \Delta\Gamma_{Cl} \qquad (3)$$

where Γ°_{Cl} is the initial adsorption density of chloride ions, and $\Delta\Gamma_{Cl}$ is the amount of chloride ions displaced from the surface by adsorption of sulfate ions.

A number of experiments were done to measure these effects quantitatively. These data were collected in experiments separate from those where sulfate adsorption data were gathered since the atmosphere above the suspensions was not closely enough controlled in the latter experiments to exclude some possible pH changes due to carbon dioxide adsorption from the surrounding air. Known sulfate additions were made to a suspension of asbestos and the amount of acid required to maintain a constant pH value was measured. The adsorption of sulfate ion after each addition was calculated from the sulfate adsorption isotherms measured earlier. The data for 5 different runs are given in Figure 34.

It does appear that, initially, one hydrogen ion would be adsorbed (or one hydroxyl ion desorbed) for every sulfate ion adsorbed if the suspension were sufficiently free of contaminating ions. At high concentrations of sulfate, this process probably would deviate from this stoichiometry. When the solution contained significant amounts of chloride ions, there was much less than a stoichiometric correlation between the number of sulfate ions adsorbed and the number of hydrogen ions adsorbed. This does indicate that the Γ°_{Cl} and $\Delta\Gamma_{Cl}$ terms in Equation (3) are significant. However, there is still not enough data to apply Equation (3) for calculating the apparent surface charge after adsorbing sulfate ions.

A direct observation of the sign of the apparent surface charge was attempted by measurement of membrane potentials as described earlier. The potentials were measured at a constant pH as a function of increasing sulfate concentration. The data are in Figure 35. The potentials decrease to zero but do not definitely reverse in sign. The method is not very sensitive, so a small negative surface charge might not be detected.

Another experiment was done to determine the possibility of charge reversal by following the desorption of C^{14} tagged acetate ion from asbestos surfaces as sulfate ion was added to the system. The data are shown in Table XIII. The sulfate was added as sulfuric acid so the pH decreased as the sulfate concentration was increased. The adsorption density of sulfate ion was calculated from the adsorption isotherms reported earlier. Again, it cannot be shown conclusively that the sulfate ion does not reverse the sign of the surface, but it is apparent that little net charge exists when the sulfate ion concentration in solution exceeds about 20 micromoles per liter.

Two adsorption experiments were carried out on two different samples of asbestos ore. The magnetite and rock fragments were removed by dispersing and centrifuging, and the dispersed portions were used directly without any washing. The adsorption densities were significantly less for both samples than those obtained with washed and refined chrysotile (in 10^{-3} molar potassium chloride solution). It is apparent that sulfate contamination in the ore is causing the differences. This illustrates the need for washing chrysotile obtained from the ore before using it to make quantitative measurements. The data are shown in Figure 36.

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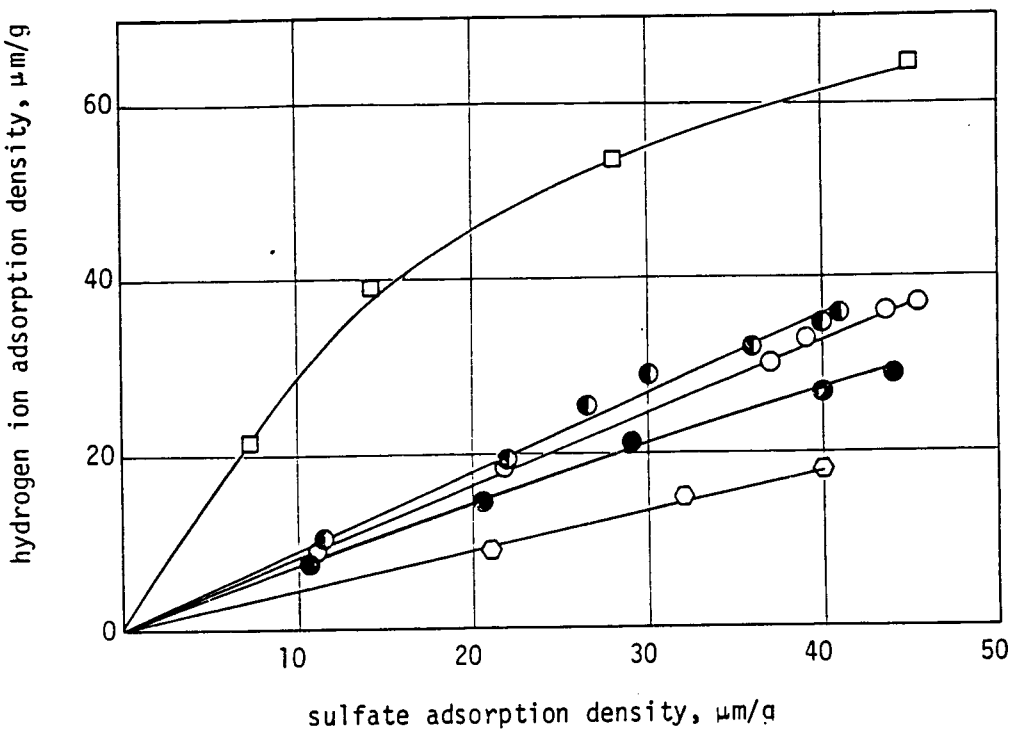


FIGURE 34 - HYDROGEN ION ADSORPTION AS A FUNCTION OF SULFATE ION ADSORPTION ON CHRYSOTILE

□□□ pH 6, no salt added
○◐● pH 9.5, no salt added
○○○ pH 9.5, 10^{-2} M potassium acetate

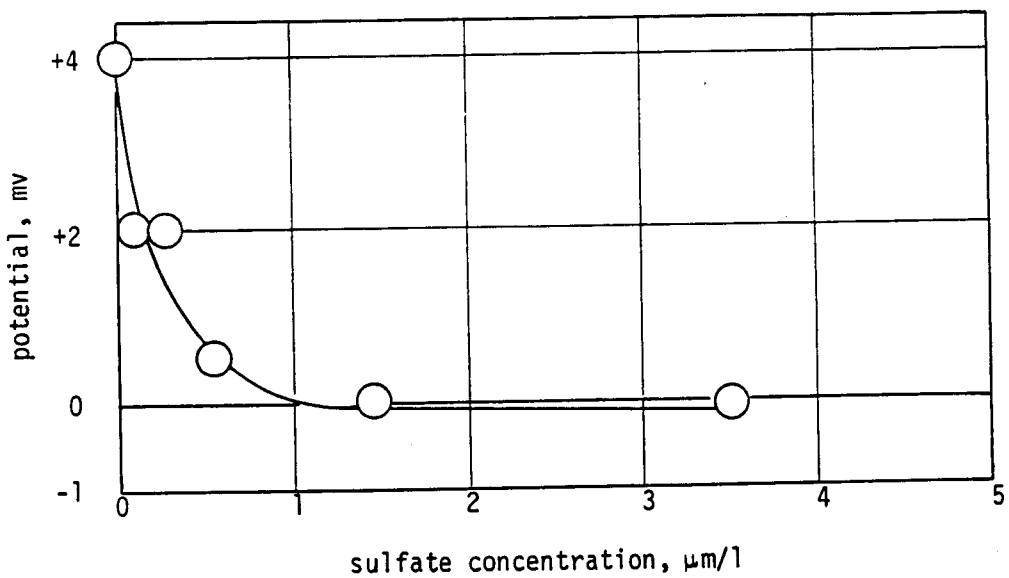


FIGURE 35.- MEMBRANE POTENTIALS OF CHRYSOTILE SUSPENSIONS AT PH 9.5 AS A FUNCTION OF SULFATE ADDITION

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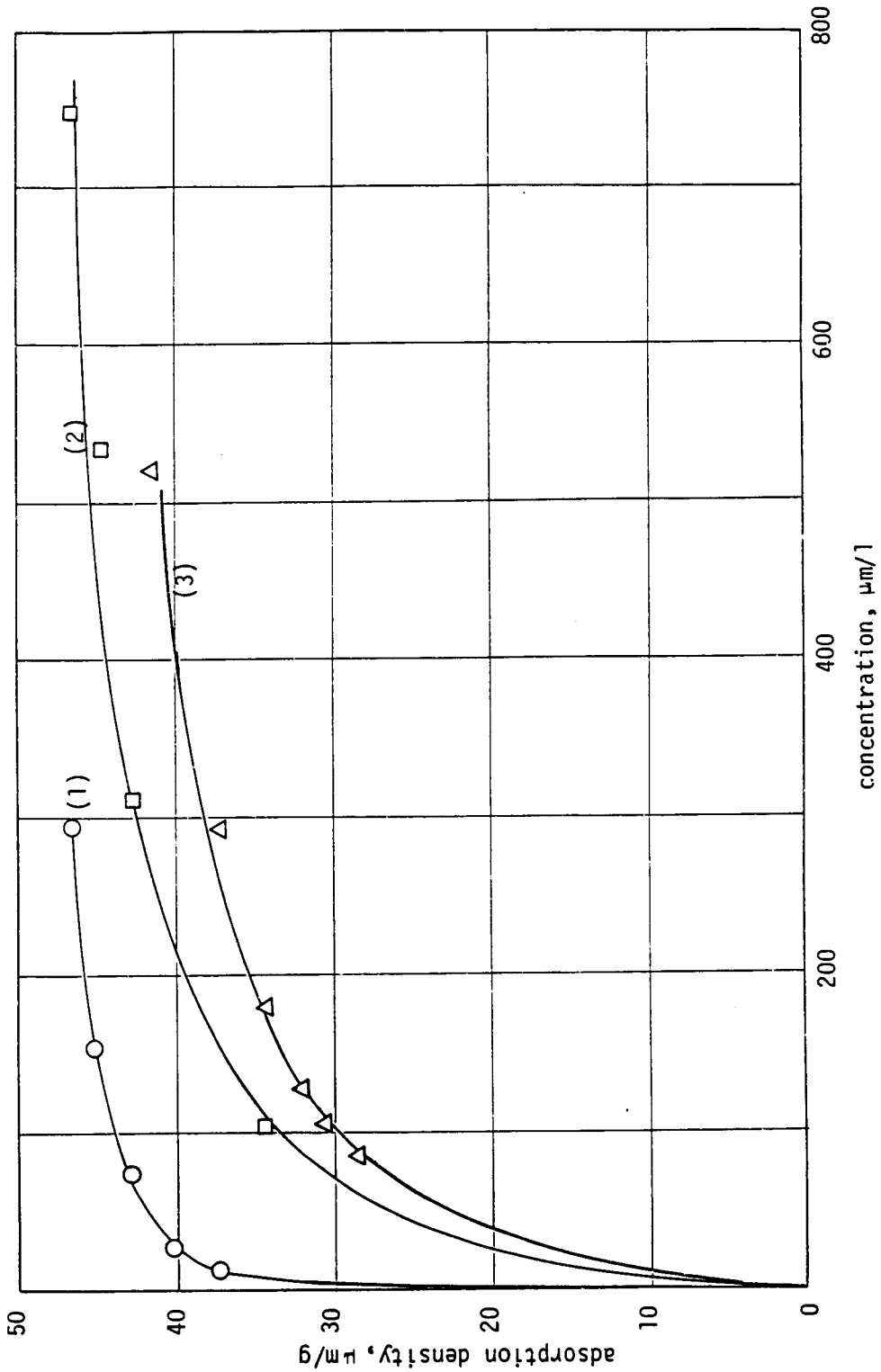


FIGURE 36 - COMPARISON OF ADSORPTION OF SULFATE ON UNWASHED CHRYSOTILE ASBESTOS WITH ADSORPTION ON WASHED AND REFINED CHRYSOTILE

(1) Washed and refined, pH 4.3, 10^{-3} M KCl
(2) Opened asbestos ore, pH 4.5
(3) Opened asbestos ore, pH 4.5

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TABLE XIII

DESORPTION OF ACETATE IONS AS SULFATE
IS ADDED TO AN ASBESTOS SUSPENSION

	Acetate Adsorption (Measured)			Sulfate Adsorption (Calculated)		
pH	Added, μ moles/g	Sol'n Conc μ moles/l	Adsorption μ moles/g	Added, μ moles/g	Sol'n Conc μ moles/l	Adsorption μ moles/g
9.3	0.316	3.48	0.095	0	0	0
8.9	0.314	3.50	0.091	2.4	0.14	2.4
8.6	0.312	3.36	0.100	4.7	0.23	4.7
8.1	0.310	3.12	0.115	9.4	0.41	9.4
7.7	0.309	2.92	0.126	14	0.61	14
7.3	0.308	2.74	0.136	19	0.95	19
7.0	0.308	2.85	0.128	24	1.2	24
6.8	0.306	2.96	0.120	28	2.5	28
7.2(1)	0.304	3.54	0.083	28	~3	28
7.9(1)	0.302	4.01	0.053	28	~4	28
8.1(2)	0.301	4.06	0.051	28	~4	28
7.1	0.300	4.01	0.050	38	~15	37
6.5	0.296	4.51	0.014	47	~60	~42
6.7(3)	0.294	4.50	0.015	47	~60	~42
6.9(4)	0.291	4.51	0.009	57	~200	~44
7.9(1)	0.288	4.51	0.008	57	~200	~44
9.0(1)	0.285	4.51	0.007	57	~200	~44
9.6(1)	0.283	4.51	0.006	57	~250	~42
10.0(1)	0.282	4.51	0.006	57	~300	~40

(1) KOH added
(2) pH drift over night
(3) Check on previous point
(4) K_2SO_4 added

Dodecyl Sulfonate Adsorption

The experimental procedure was the same as described for the other adsorption studies. Known amounts of surfactant were added to a suspension and allowed to equilibrate. The suspensions were centrifuged to obtain a sample of clear solution and the residual sulfonate in solution was analyzed.

Sodium dodecyl sulfonate was prepared by reacting dodecyl bromide with sodium sulfite solution at about 200°C and 150 psi gauge pressure in a pressure reactor (47). The salt was recrystallized from distilled absolute alcohol and washed with petroleum ether. Surface tension measurements indicated that it was of satisfactory purity. Determination of surfactant concentration in solution was by a spectrographic analytical procedure, measuring the optical density of sulfonate-methylene blue complexes which were extracted from aqueous samples into a chloroform phase (48).

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The adsorption isotherms at different pH values are given in Figure 37. With one exception, the adsorption densities tend to level off at a saturation value in the order of 90 micromoles per gram of asbestos, which is consistent with the view that the species adsorb primarily due to electrostatic forces between the negatively charged sulfonate group and discrete, positively charged sites. This value agrees with the conclusion from the sulfate adsorption experiments that a maximum number of about 93 micromoles of positively charged sites is present per gram of asbestos.

At the lowest pH value studied, 4.5, the adsorption density exceeds 90 micromoles per gram. There may be enough undissociated species of dodecyl sulfonic acid present in solution (pK of the acid is approximately 1) so that significant adsorption of it may be taking place at this pH value. Since it is not charged, the number of positively charged sites on the asbestos would not limit its adsorption density.

An important implication of these data is that the dodecyl chain is not long enough so that, energetically, the surfactant species would adsorb, but that the additional energy from the electrostatic interactions is also needed. Later, the adsorption of stearic acid, 18 carbon chain-length, will be discussed where the energy from the tendency of the hydrocarbon chain to go to the interfacial region is enough alone to cause the stearate ion to adsorb.

Dye Adsorption

A. W. Naumann reports that a saturation amount of one weight per cent of methylene blue chloride adsorbs on asbestos (49). This is equivalent to 31 micromoles per gram of asbestos. Data gathered at this laboratory show a somewhat lower saturation value, about 23 micromoles per gram of asbestos. The data are given in Figure 38.

Dresher has reported data where even more methylene blue chloride is adsorbed (50). He claims that this amount of adsorbed dye was not influenced by previous treatments nor by the pH of the suspension during equilibration with the dye. He also found that the adsorption density of metanil yellow, an anionic dye, did not level off to a saturation density up to adsorption values of 6 weight per cent, i.e., ~300 micromoles per gram, so he concluded that multi-layer adsorption was taking place. Both methylene bue and metanil yellow have dimensions of about 18 Å x 9 Å (51), so a maximum of 70 micromoles on a gram of asbestos should form a physically close-packed monolayer. The adsorption data for metanil yellow were collected at a pH value of 5.2 to 6.0, which is low enough so that the adsorbing species may have been in the non-ionic form.

The advantage of dye adsorption experiments is that solution analysis, even in the ppm range, is done readily with a colorimeter. The disadvantages are that dye of high purity is hard to obtain, and the state of dye - monomer, dimer (52), aggregate (53) or some chemically altered form of the dye, is difficult to define.

The most that can be said from the dye adsorption experiments is that there is some affinity for cationic dye species which is probably due to attraction for negatively charged surface sites on the asbestos fiber surface. The quantity of these sites is probably between 20 and 30 micromoles per gram of asbestos.

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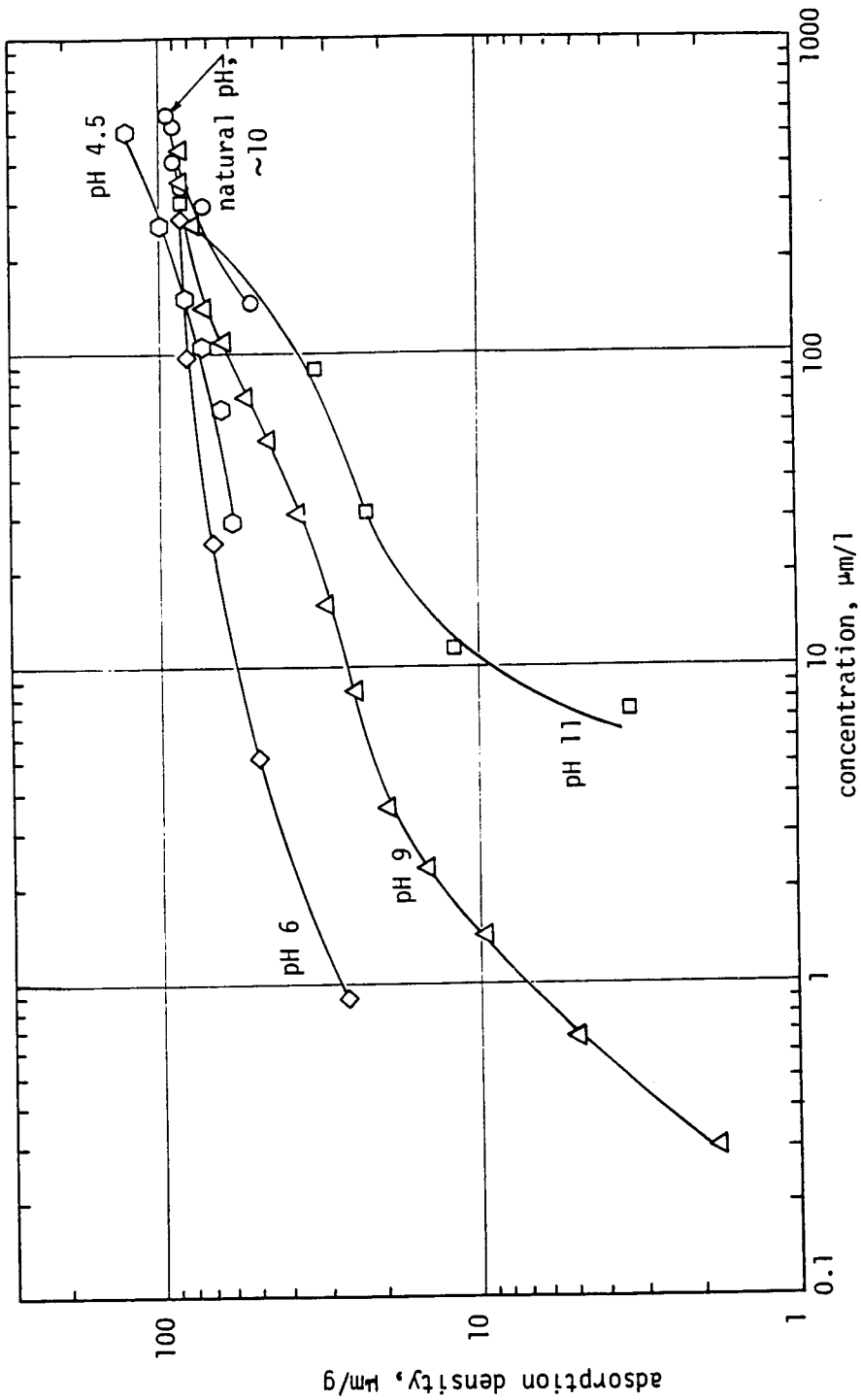


FIGURE 37 - ADSORPTION ISOTHERMS AT 30°C FOR SODIUM DODECYL SULFONATE ON CHRYSOTILE AT VARIOUS PH VALUES

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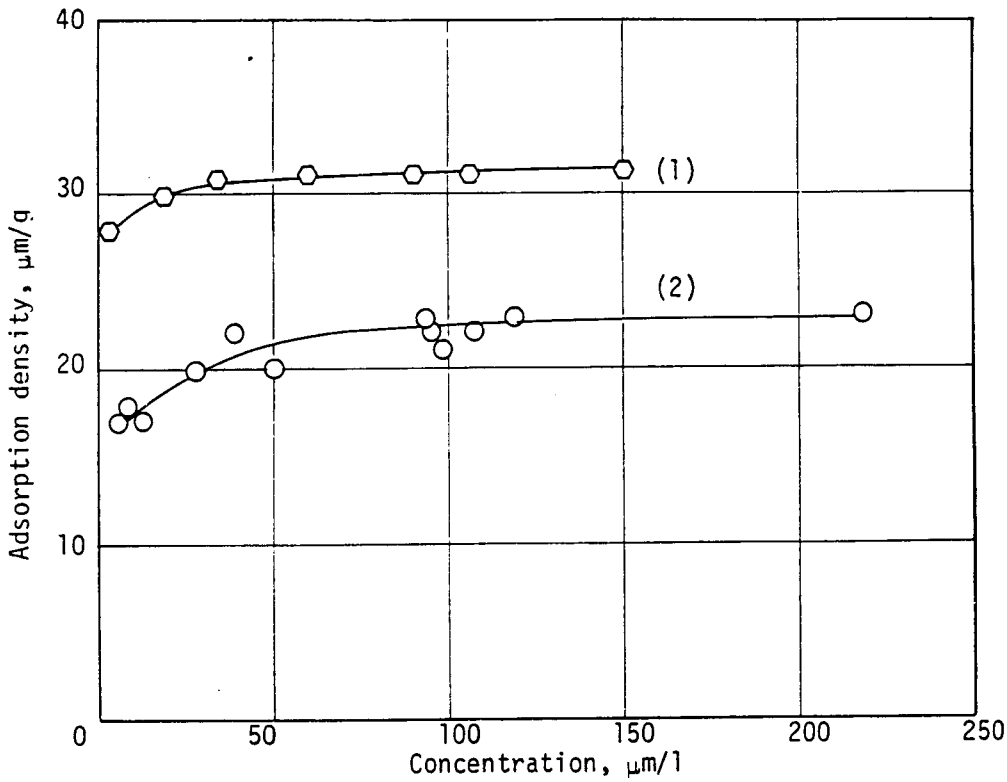


FIGURE 38 - ADSORPTION ISOTHERMS AT ROOM TEMPERATURE FOR METHYLENE BLUE CHLORIDE ON CHRYSOTILE

(1) After Naumann (49)
(2) This work

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Iodide Ion Adsorption

An iodide electrode was used to measure iodide concentrations in solution with a calomel as a reference electrode. Washed and refined asbestos was the source of material for these experiments. A lithium acetate salt bridge was used to connect the calomel with the suspension during measurements to prevent chloride ion contamination of the suspension by the calomel.

The adsorption isotherms were determined at pH 6 and at pH 4.5. Acetic acid was used to obtain the desired pH value and then also to keep a constant pH, since after each addition of potassium iodide solution, the pH of the suspension increased somewhat. During the experiment at pH 6, the amount of acid was recorded but at pH 4.5, the pH increase was too small to measure accurately amounts of acid needed to maintain a constant pH. This is due to the strong buffering action of acetic acid at that pH value.

The iodide adsorption data are given in Figure 39. The iodide adsorption increases more rapidly at pH 4.5 than at pH 6, as would be expected from the charge characteristics of asbestos. At pH 4.5, the suspension remained in the dispersed state until a concentration of about 400 micromoles per liter of iodide in solution had been exceeded. It then flocculated, implying that enough charge reduction had taken place so that the attractive forces between asbestos fibrils were then greater than the electrical repulsive forces. Naumann and Dresher report a value of 900 micromoles per liter (0.9 millimole per liter) as the critical coagulation concentration (41), but their criterion is that the viscosity remains low, one to three centipoise, for only one minute after addition of the salt. This is not inconsistent since it is conceivable that, in our experiments, the suspension took significantly longer than one minute to coagulate.

The data showing the consumption of acid as the iodide ion was adsorbed at pH 6.0 are in Figure 40. The amounts are stoichiometric up to a value of 20 micromoles per gram of asbestos, and then there is somewhat less than stoichiometric consumption of acid as further iodide ion adsorption takes place.

It does appear as if the saturation amount of adsorbed iodide will be much less than the maximum number of possible cationic sites of about 90 micromoles per gram. This might have been expected since iodide ion does not have a great affinity for the asbestos surface, so it may only replace the most weakly held hydroxyl ions.

An undesirable characteristic of iodide adsorption for characterizing the asbestos surface is Dresher's discovery that iodide is catalytically converted to iodine by an oxidation-reduction process during strong agitation of aqueous asbestos suspensions (54). No explanation is available to account for this phenomenon.

Fluoride Ion Adsorption

Magnesium fluoride is the most insoluble of the magnesium halide salts. Its solubility at room temperature is about 0.1 millimole per liter, while that of the other three halides is in the order of 5 molal. It was felt that this difference in solubility should be reflected in the tendency of fluoride ion to adsorb very strongly and specifically on asbestos surfaces. Fluoride ion electrodes are available which would make the adsorption measurements easy to do,

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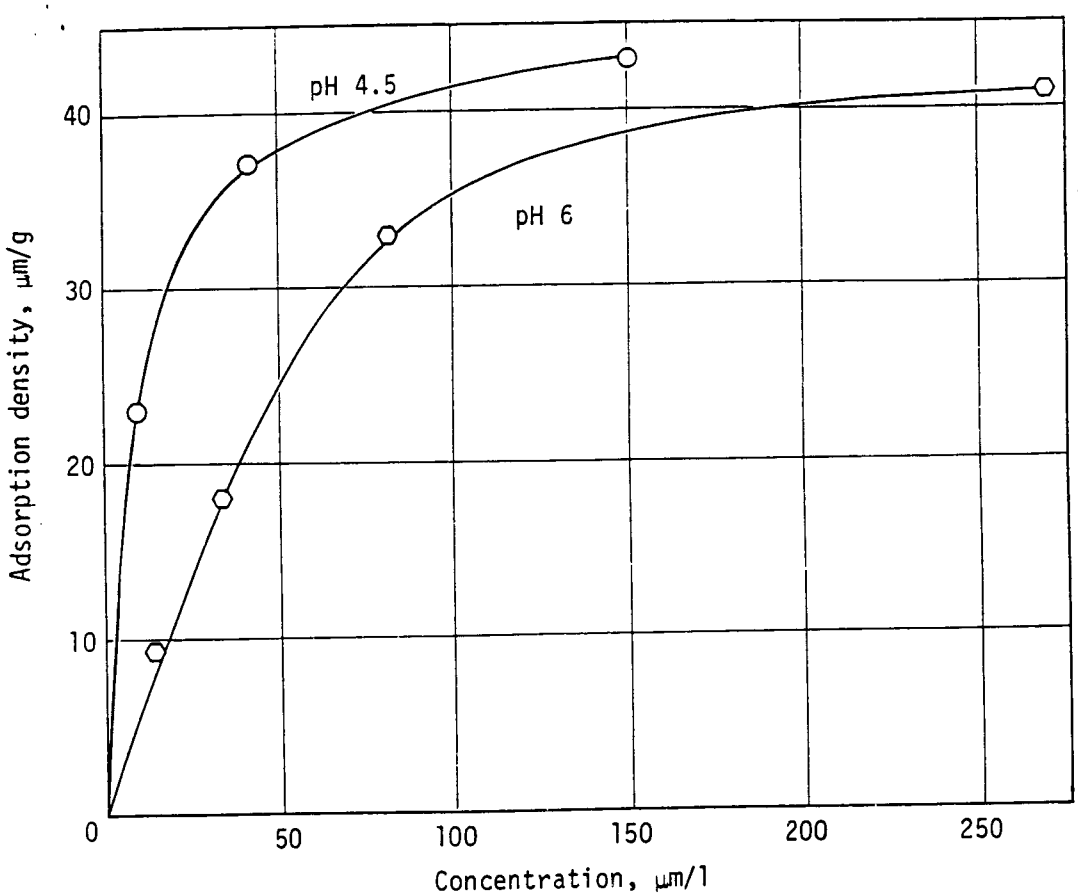


FIGURE 39 - ADSORPTION ISOTHERMS AT 30°C FOR IODIDE ION ON CHRYSOTILE AT PH 6 AND PH 4.5

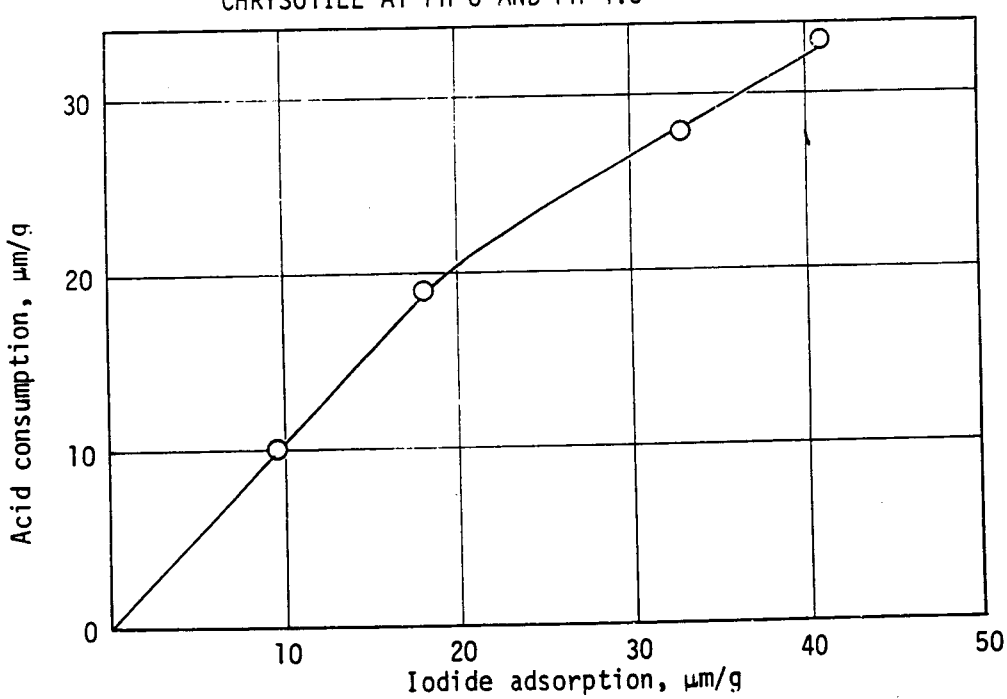


FIGURE 40 - CONSUMPTION OF ACID CONCURRENT WITH IODIDE ION ADSORPTION ON CHRYSOTILE AT PH 6

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but as a preliminary test, only the change in hydrogen ion adsorption was measured as potassium fluoride solution was added to an asbestos suspension at pH 8. There is enough experience now with this type of measurement to have some confidence that the results can be reasonably interpreted.

Two duplicate experiments were conducted and the data are shown in Figure 41, along with the data for potassium sulfate and potassium iodide as comparison. It is very evident that fluoride ion has surprisingly little specific affinity for the asbestos surface, so no more work was done on this system.

Comparison of Cassiar, Quebec and Coalinga Chrysotile Asbestos

It has been speculated that the maximum number of adsorption sites on chrysotile asbestos may be related to the presence of the impurities in the lattice. The only foreign element present in sufficient quantity to account for a significant number of sites is iron. Accordingly, washed and purified samples of asbestos from three different locations were studied to see if any relation could be found between their iron content and their maximum sulfate adsorption density. The results of such experiments are in Table XIV.

TABLE XIV

SULFATE SATURATION ADSORPTION DENSITY AND IRON CONTENT OF CASSIAR, QUEBEC AND COALINGA CHRYSOTILE

Origin	Surface Area m^2/g	Iron %	Sulfate Sat'n Density	
			μ moles/g	μ moles/m^2
Cassiar	46	1.29	37	0.80
Quebec	50	1.06	40	0.80
Coalinga	69	1.24	47	0.68

No correlation between the iron content and the sulfate adsorption density is apparent in the data of Table XIV.

MODIFICATION OF SURFACE PROPERTIES

Surface Charge Enhancement

Although asbestos is naturally positively charged, it has been found that the apparent surface charge can be increased. This topic has been the subject of a paper by Naumann and Dresher (55). Presumably, the same mechanism occurs as in the phenomena of charge reversal of negative sols to positive sols by the addition of salts of multivalent cations. The latter has been extensively studied by Matijevic (46). Naumann and Dresher feel that charge enhancement is the result of the attachment of highly positively charged hydrolysis products on the surface of the asbestos.

There seems to be some merit in that hypothesis since asbestos soaked in strong solutions of aluminum salts does pick up more aluminum than would be expected from adsorption of individual dissolved species. For example, 50 grams of asbestos in 4 liters of water were treated with 2.04 grams of aluminum acetate containing 0.68 gram alumina. After filtering and washing, the asbestos was found to contain 78 per cent of the alumina as shown in Table XV.

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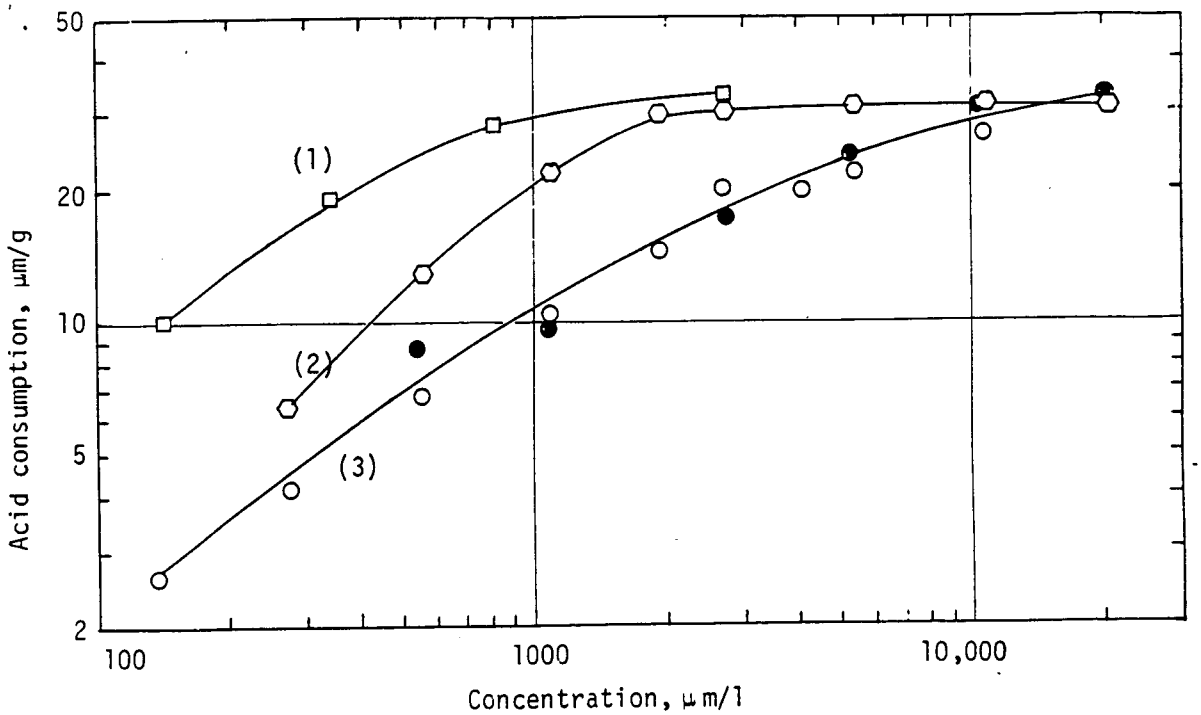


FIGURE 41 - EFFECT OF FLUORIDE, IODIDE AND SULFATE SOLUTIONS ON ACETIC ACID CONSUMPTION BY CHRYSOTILE IN AQUEOUS SOLUTIONS

(1) potassium iodide added at pH 6
(2) potassium sulfate added at pH 8
(3) potassium fluoride added at pH 8

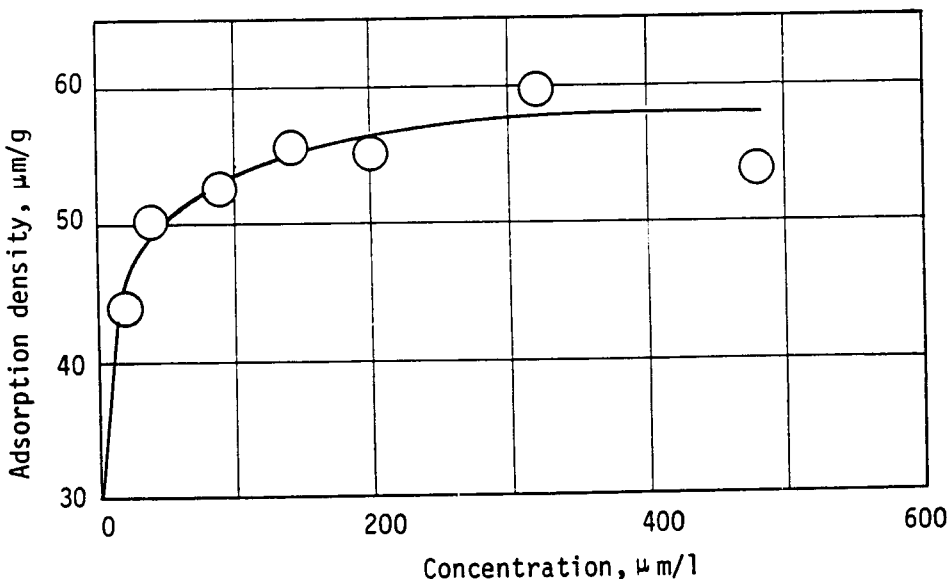


FIGURE 42 - SULFATE ION ADSORPTION AT PH 5 ON ASBESTOS TREATED WITH ALUMINUM ACETATE

Addition: 1.2 µm of alumina per gram of asbestos

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TABLE XV

ABSTRACTION OF ALUMINA FROM SOLUTION BY ASBESTOS

Test No.	Assay, % Mg	Assay, % Al_2O_3	Remarks
681-51	25.35	0.47	Control sample
681-52	27.77	1.57	Treated with 1300 μ moles alumina per gram of asbestos

Even stronger treatments were tried. Asbestos suspensions were made up containing 1 weight per cent in 0.01 molar aluminum acetate solution. This represents 500 micromoles of alumina available per gram of asbestos. The suspensions were allowed to react for various lengths of time before they were flocculated with additions of potassium sulfate and filtered. The products were assayed and the reflectances were also measured. The data are shown in Table XVI.

TABLE XVI

TREATING ASBESTOS IN 0.01 MOLAR ALUMINUM ACETATE SOLUTIONS

Test No.	Treatment Time, Hours	pH	(%) Asbestos Assay, Al_2O_3	Rec. on Asbestos %	Refl. of Asbestos %
	none	-	0.47	-	~ 76
681-93-1	1	5.3	1.53	30	77
681-91-3	1	5.3	1.34	26	79
681-91-2	5	5.3	1.95	38	80
681-91-1	25	5.3	2.00	39	80

It is readily apparent from the rheological behavior of asbestos suspensions which have been treated with aluminum salts that charge enhancement has taken place, but the amount of enhancement is hard to quantify. Even zeta potential measurements are not always satisfactory. Therefore, sulfate adsorption determinations were made to see if the sulfate saturation adsorption density was increased by such a procedure.

One hundred micromoles of aluminum acetate were added to 140 ml of an asbestos suspension containing 0.8 gram of asbestos. This is a rate of 120 micromoles per gram, or 60 micromoles of alumina per gram of asbestos. The pH was adjusted to pH 5 and the adsorption of sulfate was measured. The results are in Figure 42. The saturation adsorption density is seen to be 20 per cent higher than any achieved previously, showing that there has been a real increase in the number of positively charged sites on the surface of the asbestos particles.

As reported by Dresher and Naumann, other multivalent cations can be used for charge enhancement (55). Thorium chloride solutions seem to be nearly as effective as aluminum salts based on our experience.

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Matijevic has reported that certain metallic organic complexes are very effective in positive charge enhancement (56). Nickel o-phenanthroline was tried with one weight per cent asbestos suspensions and good dispersions were obtained with washed asbestos at alkalinities as high as pH 8.5, which is over 3 pH units higher than normal for dispersion even after treatments with multivalent cations. The suspensions could be flocculated at pH values greater than 8.5 so such a system is of potential interest for processing asbestos ores. However, the costs of these particular chemical complexes are too high to be practical.

Silica Treatment

This procedure is fully described in a U.C.C. report by Byrne and Chwastiak, so the work on this product will only be summarized here (57). For certain thickening applications, specifically for thickening polyester resins, it has been found desirable to have an acidic surface rather than the brucite (basic) surface of regular asbestos. The rheological properties of suspensions of asbestos and of silica-treated asbestos in styrene solutions of polyester will be described in a U.C.C. report by Dr. Kisoon Park. It seems that polyester molecules are commonly terminated by a carboxylic acid group and any long-chain species containing carboxyl groups adsorb on a normal asbestos surface in such a way as to cause a drastic decrease in thickening. The silica surface has a different reaction with polyester molecules which permits some flocculation and consequent thickening of polyester resins.

It has been reported by Martinez and Zucker that asbestos becomes negatively charged in solutions of sodium silicate whose concentrations are greater than about 10^{-2} moles per liter (36). However, if such suspensions are filtered and dried, very little silica is found to be adsorbed on the asbestos and samples reslurried in water are no longer negatively charged (57). A way is necessary to achieve a permanent silica coating on the asbestos. As reported in the section on solubility of asbestos, the asbestos can be leached to remove selectively the surface brucite groups and leave exposed a silica layer. Such a leaching treatment was felt to be difficult to control and expensive in acid cost, so an alternative chemical procedure was developed.

The silica treatment procedure consists of adding sodium silicate solution (water glass) to an asbestos suspension at a level of 8 to 10 parts silica per 100 parts of asbestos and then neutralizing the resulting basic suspension with acetic acid to pH 8. This generally results in 5 to 7 weight per cent of silica, based on the weight of asbestos, adsorbing on the asbestos surface. The silica layer should be about 10 to 15 Å thick, depending on its density, and thus should be too thin to be seen with most electron microscopes. An electron micrograph of some silica-treated asbestos fibers is given in Figure 43. Some rough areas on the fibrils are seen which could be due to deposited silica, but generally no silica layer can be seen at this magnification.

A circuit has been incorporated into the King City mill to perform the chemical treatment, and the commercial product, called R-G244 asbestos, is presently being sold as a thickener for polyester resins. For comparison, the data in Figure 44 show the thickening abilities of R-G244, R-G144 (normal, commercial asbestos), and Cab-O-Sil, the most commonly used pyrogenic silica for thickening polyester resins. The R-G244 asbestos is seen to be far superior to normal asbestos and also to Cab-O-Sil.

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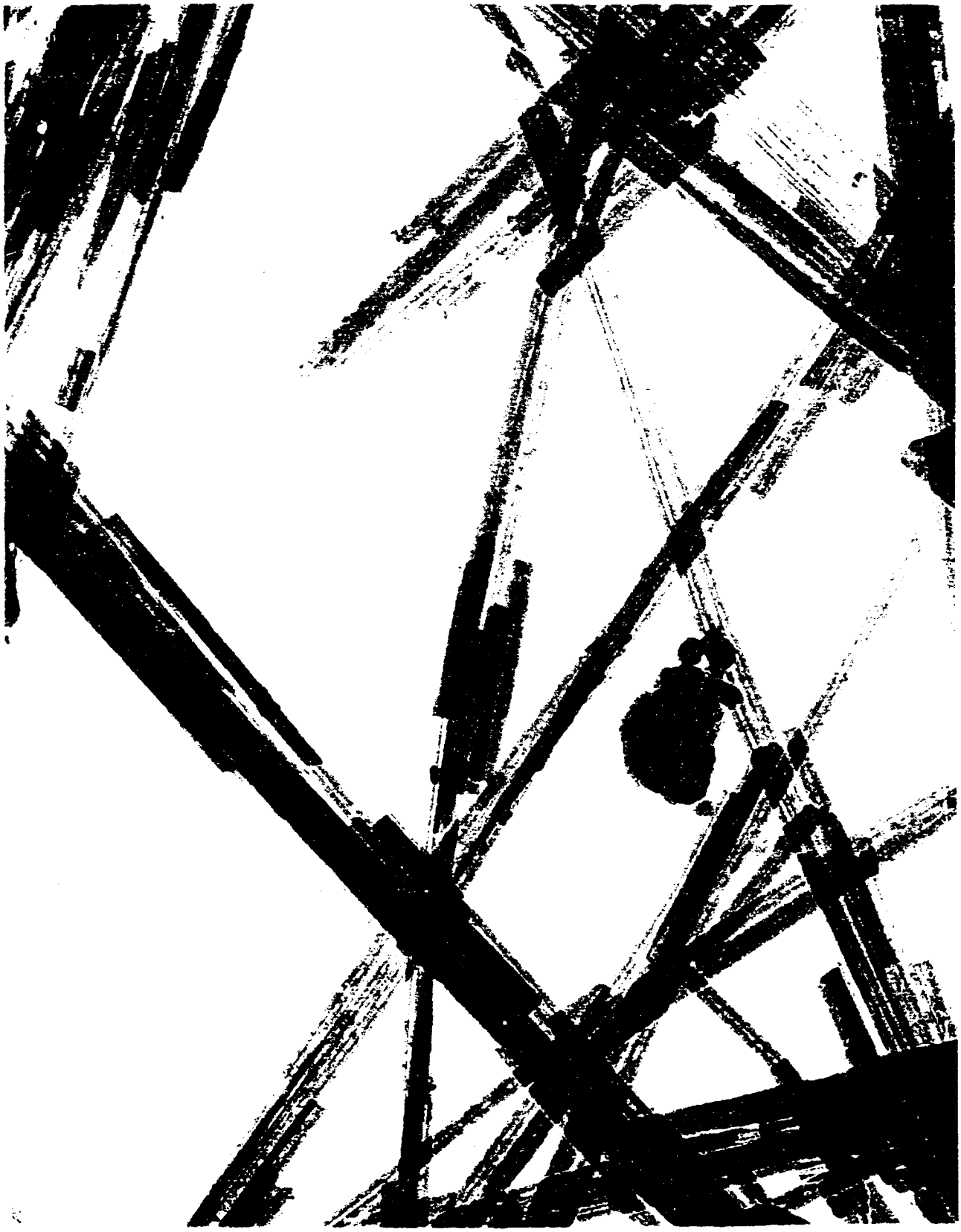


FIGURE 43 - SILICA-TREATED ASBESTOS

Test No. 1644-71-1 - Photo No. 4605 - Magnification 125,000X

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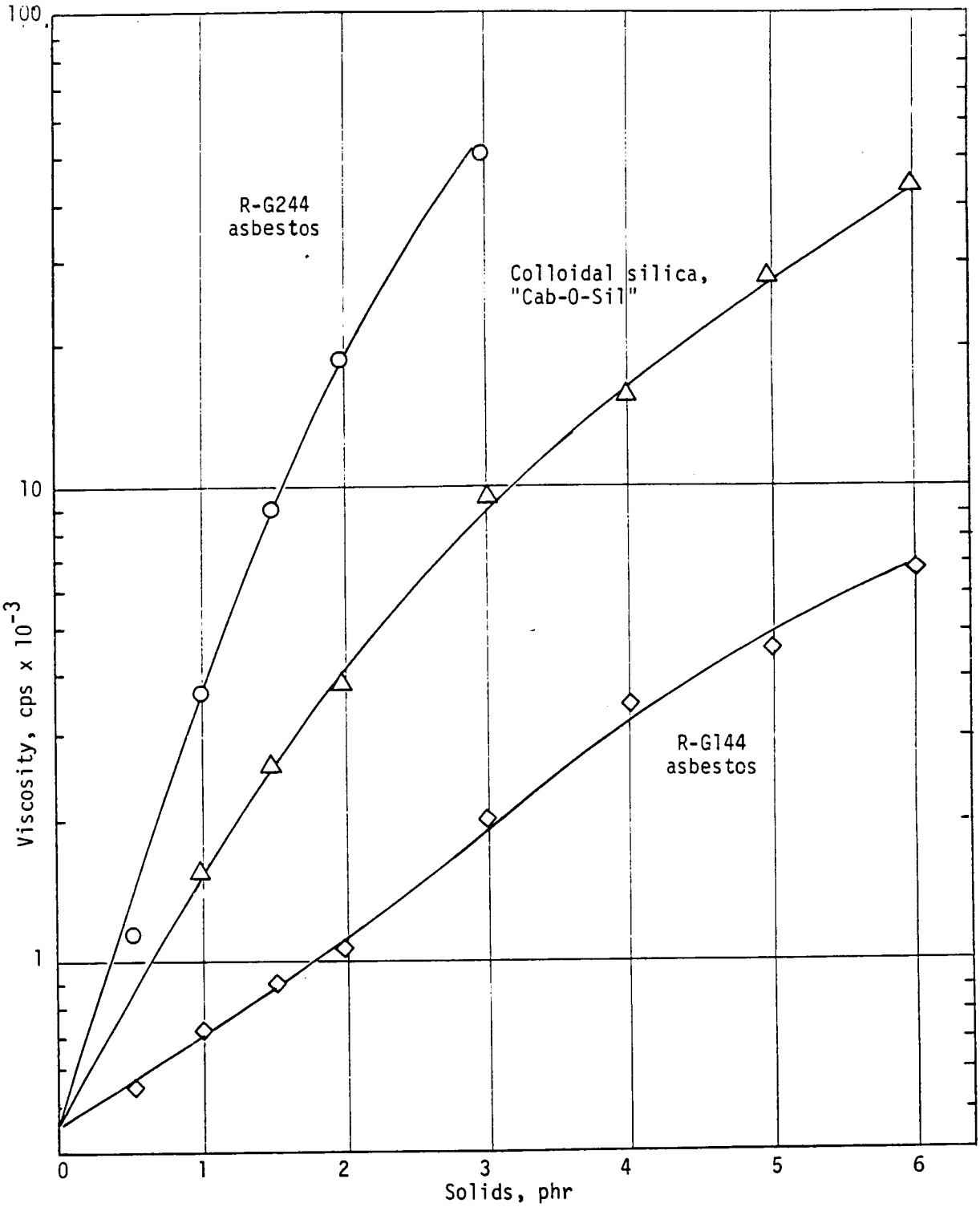


FIGURE 44 - THICKENING OF POLYESTER RESINS BY R-G144, R-G244, AND CAB-O-SIL (57)

Viscosity measurement, Brookfield Viscometer, spindle 4 at 12 rpm

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Typical physical properties of silica-treated asbestos prepared in the laboratory are compared with asbestos in Table XVII and their chemical analyses are compared in Table XVIII.

TABLE XVII

PHYSICAL PROPERTIES OF SILICA-TREATED ASBESTOS, ASBESTOS AND CAB-O-SIL

Property	Asbestos	Silica-Treated Asbestos	Cab-O-Sil
Brightness, %	76	80-82	93
Dry bulk, cc/g	30	50	30
Wet bulk, cc/g	40-50	160	20

TABLE XVIII

TYPICAL ANALYSIS OF SILICA-TREATED ASBESTOS

Component	Silica-Treated Asbestos	Asbestos
MgO, %	39-38	41.5
SiO_2, %	44-45	41.4
"Free" SiO_2,* %	5-7	0

* amount of silica deposited on asbestos surface as calculated from chemical analysis of silica-treated asbestos

The recoveries of silica on asbestos by treatment at pH 8 with different amounts of silica are given in Figure 45, and the thickening power of the resulting product is shown in Figure 46. In spite of the fact that more silica is put on the asbestos at treatment levels above 10 phr of silica (parts per 100 parts of asbestos), the thickening power of the product decreases. This is probably due to a significant amount of binding of asbestos by excess silica into large, hard particulates which are not effective as thickeners, but which reduce the number of fibrils available for thickening. The process of thickening by asbestos products depends both on the strength of interaction between particles and on the number of particles (flow units) per unit weight present to interact. Silica treatment at successively higher levels probably continued to improve the interaction force between particulates, but beyond an optimum level, it has a greater effect on the viscosity by decreasing the number of particulates present.

At a treatment level above 10 pha of silica, the particles have enough silica to become negatively charged right after treatment. However, after filtering and drying the treated asbestos, it no longer has a negative charge in water (57). The mechanism of this charge reversal from negative to positive by drying is not understood. It can be prevented by additions of small amounts of aluminum salts, and this will be discussed in the following section.

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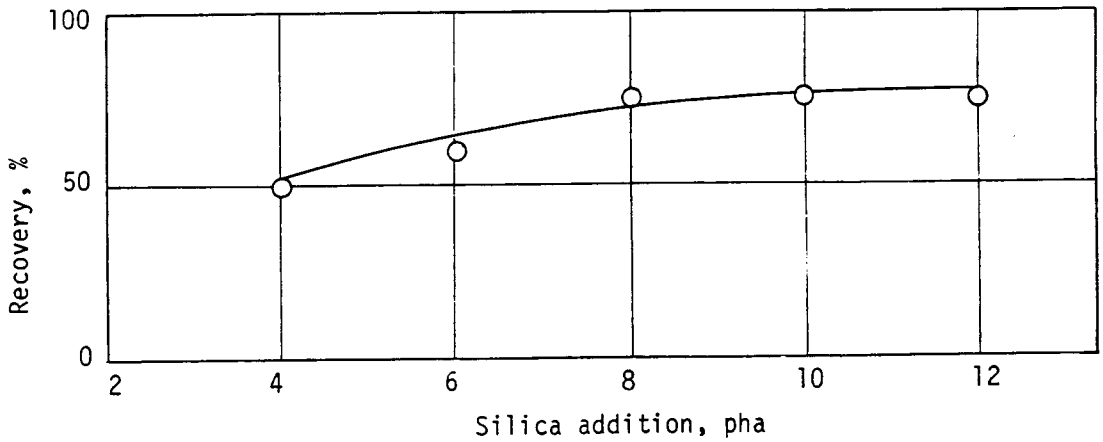


FIGURE 45 - RECOVERY OF SILICA ON ASBESTOS DURING TREATMENT AT PH 8 WITH DIFFERENT AMOUNTS OF SILICA (57)

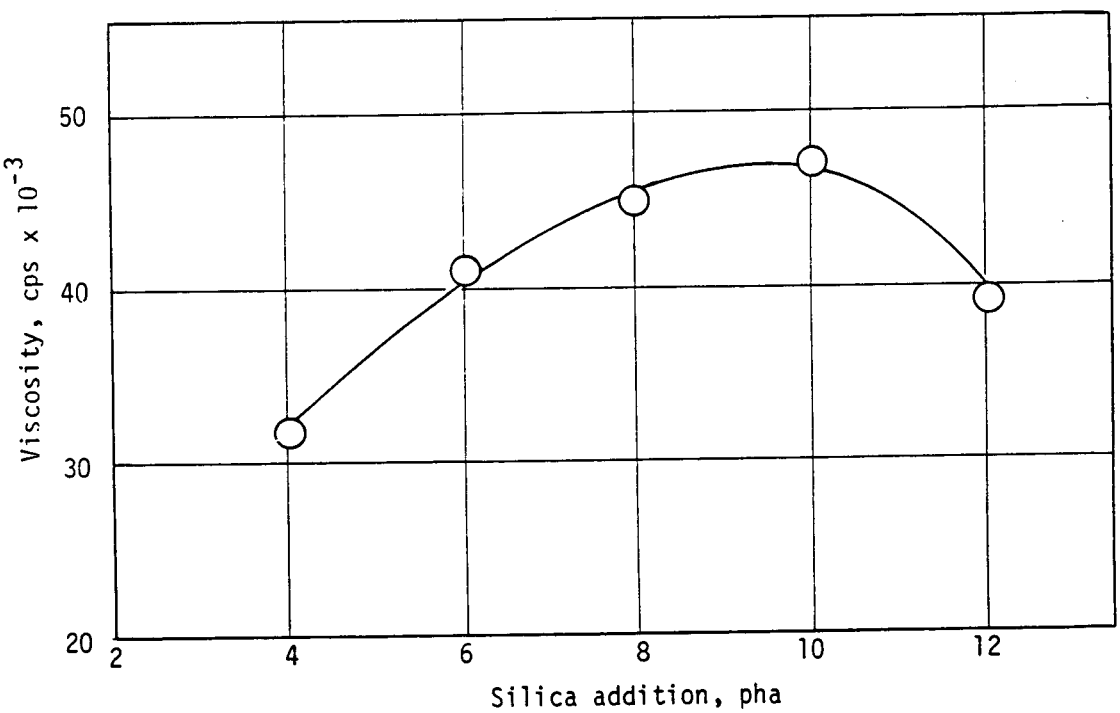


FIGURE 46 - THICKENING OF POLYESTER RESIN BY ASBESTOS TREATED AT PH 8 WITH DIFFERENT AMOUNTS OF SILICA (57)

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Typical zeta potential data are shown in Figure 47 to illustrate the charge reversal after drying an R-G244 slurry.

In a previous section, the adsorption of methylene blue chloride on normal asbestos was interpreted to mean that some negative sites exist there. Similar data were obtained for R-G244 asbestos before and after drying. The data in Figure 48 show that there is a decrease in the number of negative surface sites after drying R-G244.

The precise mechanism of silica treatment is only vaguely understood. The highest treatment level recommended in this report, 12 pha of silica, is achieved by mixing 50 ml of 1 molar sodium silicate solution into 2.5 liters of suspension containing 25 grams of asbestos. The resulting pH of the suspension is about 12. The solution in the suspension contains 2×10^{-2} moles per liter of sodium silicate at a pH of 12. From the data reported by Lagerström (58), it is evident that this solution is stable. When the pH is reduced to 8, however, the solution becomes supersaturated by a factor of 10 with respect to the formation of amorphous silica; i.e., solubility of silica is about 2×10^{-3} moles per liter at pH 8.

One mechanism proposed for silica treatment was that silica precipitates from solution, coating the asbestos in the suspension. A pure solution of sodium silicate under these conditions (2×10^{-2} moles per liter, pH 8) remains clear for a long period of time, exceeding the normal treatment time of about 10 to 30 minutes. This observation does not totally rule out the possibility of precipitation in an asbestos suspension since the asbestos particles might act as nuclei for silica precipitation.

A second possible mechanism is that silica polymers, which can be strongly negatively charged, adsorb on the silica surface. This mechanism was tested by treating asbestos with solutions containing polymerized silica species. Four solutions were prepared by diluting 50 ml of 1 mole per liter sodium silicate solution to 400 ml with distilled water, adjusting the pH to 8, and allowing the solutions to age for 1 min, 5 min, 20 min, and 3 hours. The aged solutions were used to treat 2.5 liters of suspension (1 per cent asbestos by weight) and the resulting solids were tested as thickeners for polyester resin. The results in Table XIX show that a minimum of silica polymerization is desirable in the treatment solution.

TABLE XIX

THICKENING POLYESTER RESIN BY ASBESTOS TREATED WITH AGED SILICA SOLUTIONS (POLYMERIZED)

Test No. NB 1708	Aging Time, min	Silica Solution	Visc in Polyester cps x 10^{-3}
93-1	~1	clear solution	42
54-1	5	clear solution	22
53-1	20	turbid solution	12
56-1	180	gelled solution	7

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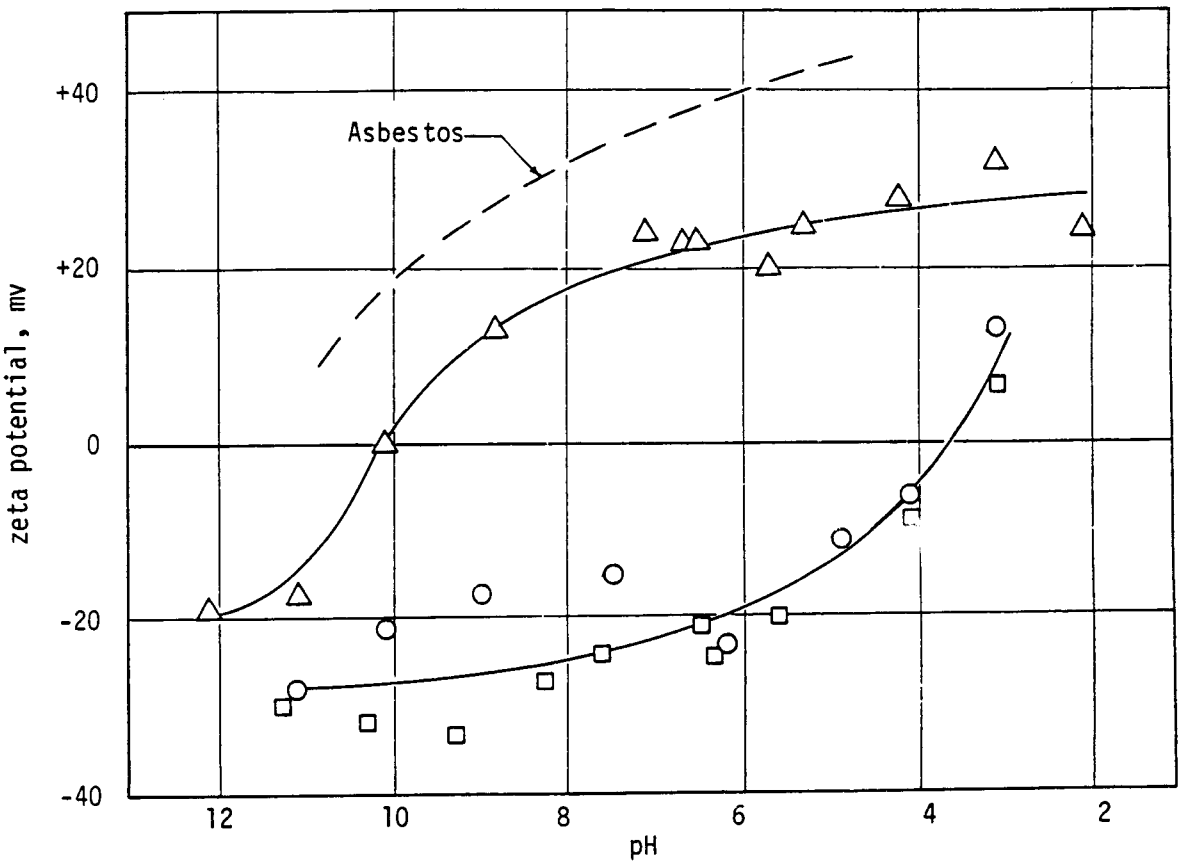


FIGURE 47 - ZETA POTENTIALS OF TREATED ASBESTOS SLURRY AND OF TREATED ASBESTOS AFTER DRYING

Symbol	Preparation	Condition	Measurement	Analysis, % MgO	Analysis, % SiO_2	"Free" SiO_2, %
○○○	Run 25	slurry	1685-67	37.0	46.1	9.2
△△△	Run 59A	dried	1708-89	41.2	44.5	3.4
□□□	1708-99-1	slurry	1730-3	(~39)	(~45)	(~6)

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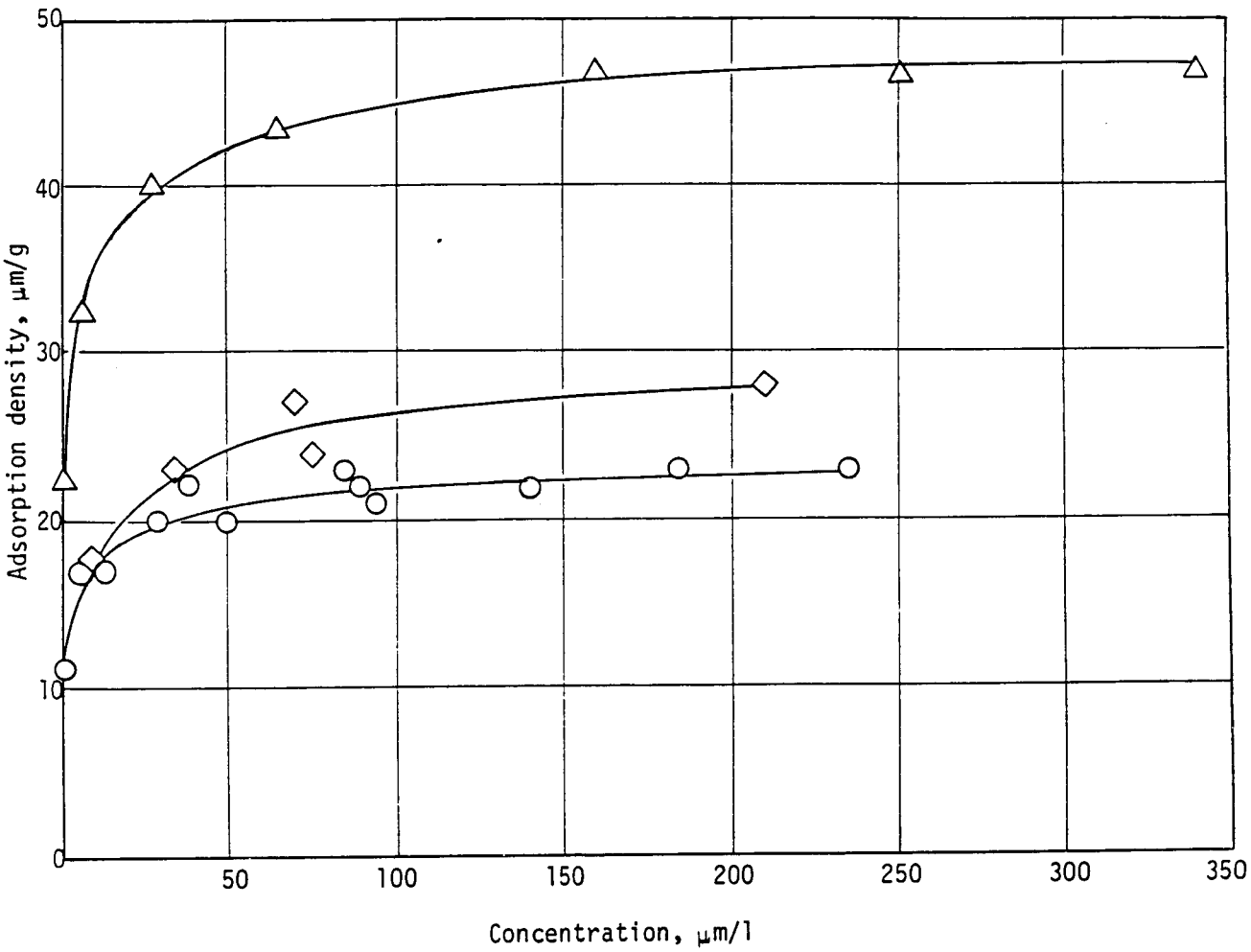


FIGURE 48 - ADSORPTION OF METHYLENE BLUE ON ASBESTOS PRODUCTS

Symbol	Product	Surface Charge
△△△	silica-treated asbestos slurry	negative
◇◇◇	silica-treated asbestos	positive
○○○	high-purity asbestos	positive

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Thus, the mechanism of silica treatment is most likely by adsorption of very short silica polymers or by adsorption of monomeric silica species followed by polymerization in place on the asbestos surface. The thickness of the adsorbed layer of silica, estimated earlier in this report as 10-15 Å, is such that a number of silica layers must form.

There have been no observable effects of aging R-G244 suspensions in their solutions after preparation as long as the levels of treatment were 8 pha of silica or lower, but at the 16 pha level of silica treatment, very distinct effects of aging are apparent. For example, a highly treated suspension is flocculated at its final pH (pH 8) and it remains flocculated after shearing in a Waring Blendor. However, if it is aged for 1-2 days and then sheared, the flocculated suspension changes into a very fluid dispersion. An extensive investigation was made to determine the reasons for this effect, but it was not successful. It is felt, however, that the observed change due to aging is a chemical effect and not a morphological effect.

Anionic Surface Modification

Small amounts of aluminum salt added at the end of the silica treatment procedure result in a product which has a permanent negative charge. For example, asbestos has been treated with 11 pha*of silica followed by an addition of 1 pha of alumina added as aluminum acetate solution. The resulting product was anionic before and after drying as shown in Figure 49. The optimum addition level of aluminum salt for this treatment was sought in a series of tests with increasing aluminum salt solution additions to a suspension containing asbestos treated with 12 pha of silica. The zeta potentials of the products were measured to determine the most anionic product. The data, plotted in Figure 50, show that a 1 pha of alumina, added as an aluminum salt is a good compromise treatment level. Two pilot plant batches have been made according to these conditions and the procedure seems both simple and reproducible.

The effects of the order of addition of sodium silicate solution and aluminum salt solution were studied. It was found that the aluminum salt solution could be added equally effectively either after the sodium silicate solution or after the sodium silicate addition had been neutralized.

The mechanism probably involves the formation of a defect structure where an occasional trivalent aluminum ion replaces a tetravalent silicon ion in the silica layer on the asbestos. Thus, a negatively charged site is built into the lattice of the silica layer. This would be analogous to the formation of alumina-silica catalysts which are found to be much more acidic or anionic in nature than are pure silica materials.

Asbestos could also be treated with vanadyl sulfate ($VOSO_4$) or ammonium vanadate (NH_4VO_3) solution to make it anionic, but the product tended to be colored. Anionic asbestos has been found to be very effective in thickening UCAR latexes (59).

Alumina-Silica Treatment

Small additions of aluminum salt make silica-treated asbestos more anionic, but increasingly larger amounts of aluminum salts result in a product with progressively more cationic surface characteristics. This is illustrated in Figure 51 which gives the zeta potential data for silica-treated asbestos products with various amounts of alumina incorporated into the silica layer. It was found

* pha - parts per 100 parts asbestos

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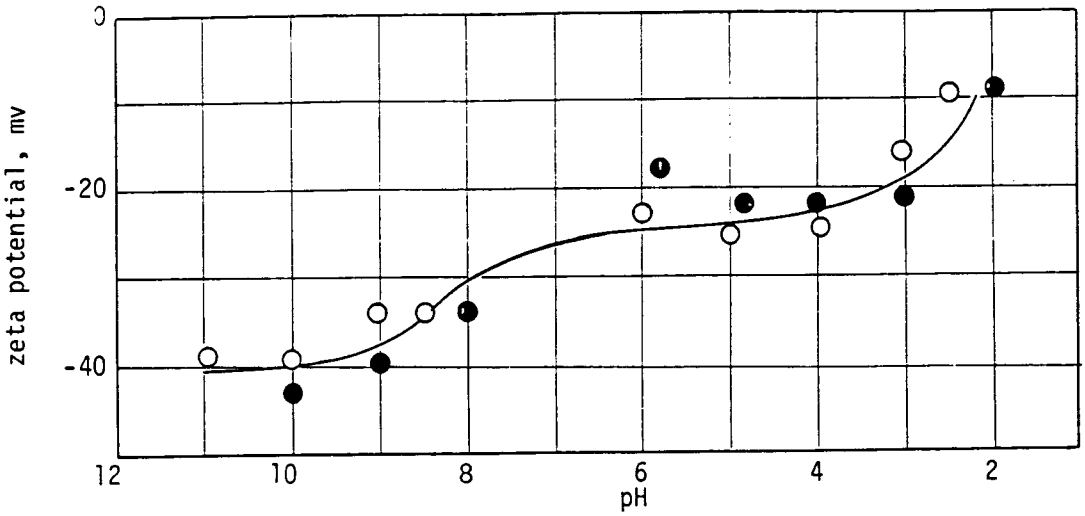


FIGURE 49 - ZETA POTENTIALS OF ANIONIC ASBESTOS BEFORE AND AFTER DRYING

Before drying ●●●
After drying ○○○

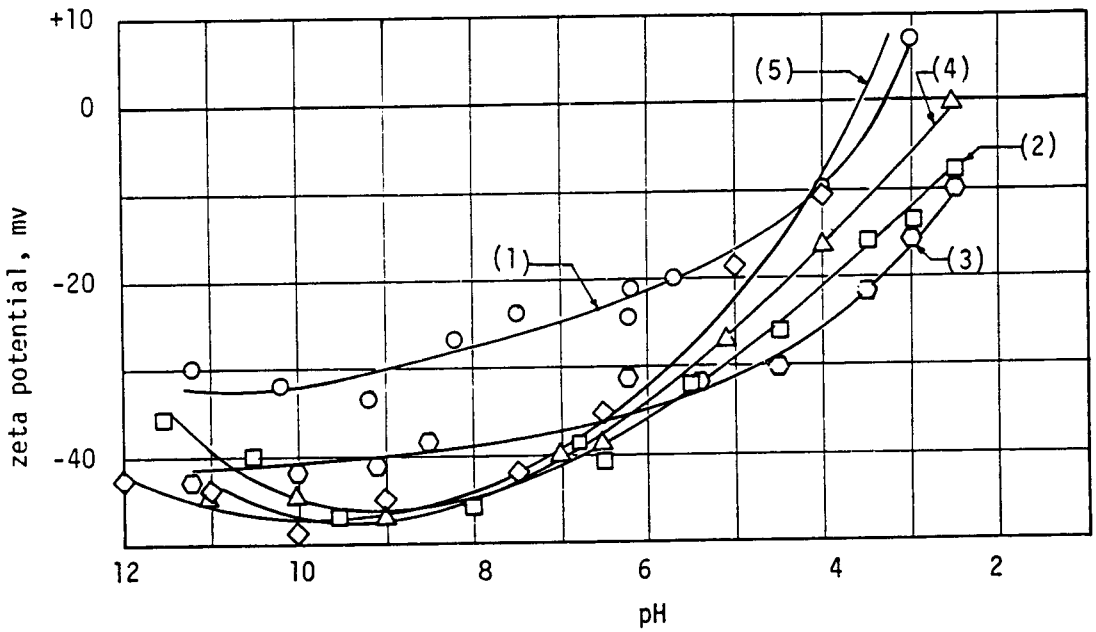


FIGURE 50 - ZETA POTENTIALS OF ANIONIC ASBESTOS PREPARED WITH DIFFERENT ADDITIONS OF ALUMINA

Alumina additions:
(1) ○○○ - none
(2) □□□ - 0.2 pha
(3) ⬡⬡⬡ - 0.6 pha
(4) △△△ - 2.0 pha
(5) ◇◇◇ - 4.0 pha

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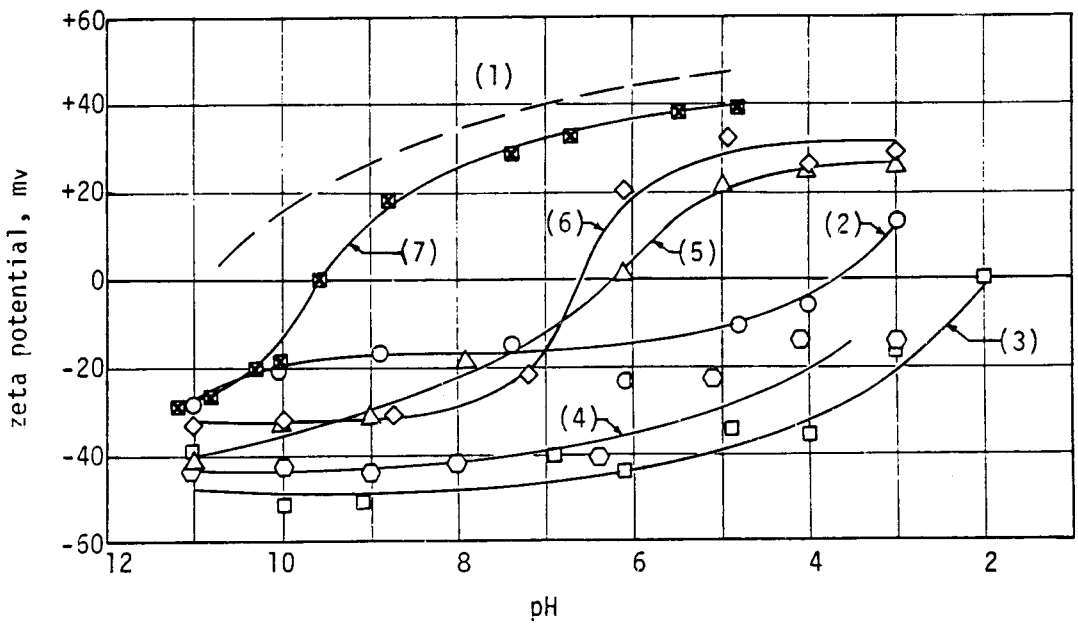


FIGURE 51 - ZETA POTENTIALS OF ALUMINA-SILICA ASBESTOS PRODUCTS

Symbol	Product	Assay, Al_2O_3, %
(1) — — —	untreated asbestos	~0.5
(2) ○○○	silica treated asbestos	0.38
(3) □□□	alumina-silica treated asbestos	1.30
(4) ⬡⬡⬡	alumina-silica treated asbestos	2.72
(5) △△△	alumina-silica treated asbestos	5.25
(6) ◇◇◇	alumina-silica treated asbestos	7.35
(7) ⊠⊠⊠	alumina-silica treated asbestos	8.1

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by analysis that essentially all of the alumina added to the suspension was recovered with the solid asbestos product, indicating that the silica-asbestos has a very high affinity for alumina. Electron microscope photographs reveal that the alumina-silica layer is thick enough to be visible at 150,000 magnifications. It is not uniform but is, instead, a rough and jagged layer, as seen in Figure 52. The details of this treatment have been reported elsewhere (60).

Such products have been studied by G. L. Dickson for applications in paper. One of them (7.35 per cent Al_2O_3), was found to have the best ink show-through properties of all materials tested, including Zeolex, which is a synthetic sodium-aluminum silicate used commercially to improve ink show-through properties in paper (60). Its properties should be compared to those of other paper-making additives, shown in Figure 53. Only the alumina-silica asbestos and normal asbestos are cationic at pH 5, the usual value for a paper-making circuit. Accordingly, Zeolex can be expected to be retained poorly by cellulose, which is anionic also. This does seem to happen, and Zeolex probably loses some of its effectiveness for this reason.

A competitive asbestos product has been developed by Vanderbilt. It involves a complex starch-calcium salt-aluminum salt-silica treatment. Its properties have not been quite as good as those of the alumina-silica asbestos. Its zpc is just below pH 3, so it is also anionic at pH 5.

HYDROPHOBIC MODIFICATIONS OF SURFACE PROPERTIES

Asbestos is naturally hydrophilic so treatment with an organic surfactant is necessary to make the asbestos compatible with organic liquids. Stearic acid is a low-cost surfactant which is commonly used for such purposes, so its adsorption characteristics were studied.

Stearic acid from Matheson, Coleman, and Bell (melting point, 69-70°C) has been used directly in the experiments. A 10^{-2} molar stock solution was made by heating stearic acid in water containing a slight stoichiometric excess of potassium hydroxide. The solids dissolved completely at about 60°C and colloidal potassium stearate crystallized when the solution cooled to room temperature. For the purpose of easy analyses, this stock material was spiked with a small amount of C^{14} tagged potassium stearate purchased from New England Nuclear Corporation. Representative aliquots of this suspension could be taken after gentle manual agitation. Solutions containing 10^{-4} molar or more of potassium stearate were seen to contain appreciable amounts of suspended solids.

The surface tensions of solutions of potassium stearate were determined by using a DuNouy ring tensiometer. The ring method of measuring surface tension was modified to take into consideration the aging of the interface by finding the force which would pull the ring through the interface after being applied for 10 minutes. The surface tension curve for the potassium stearate solution is given in Figure 54. A sharp discontinuity in this property is characteristic of pure surfactant solutions. The break at the concentration of about 5×10^{-5} moles per liter can be due to reaching the limit of solubility of the potassium stearate or to the beginning of the formation of micelles. The former possibility is more likely for this system.

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FIGURE 52 - PICTURE OF SILICA-ALUMINA ASBESTOS

Photo No. 4501 - Magnification 150,000X

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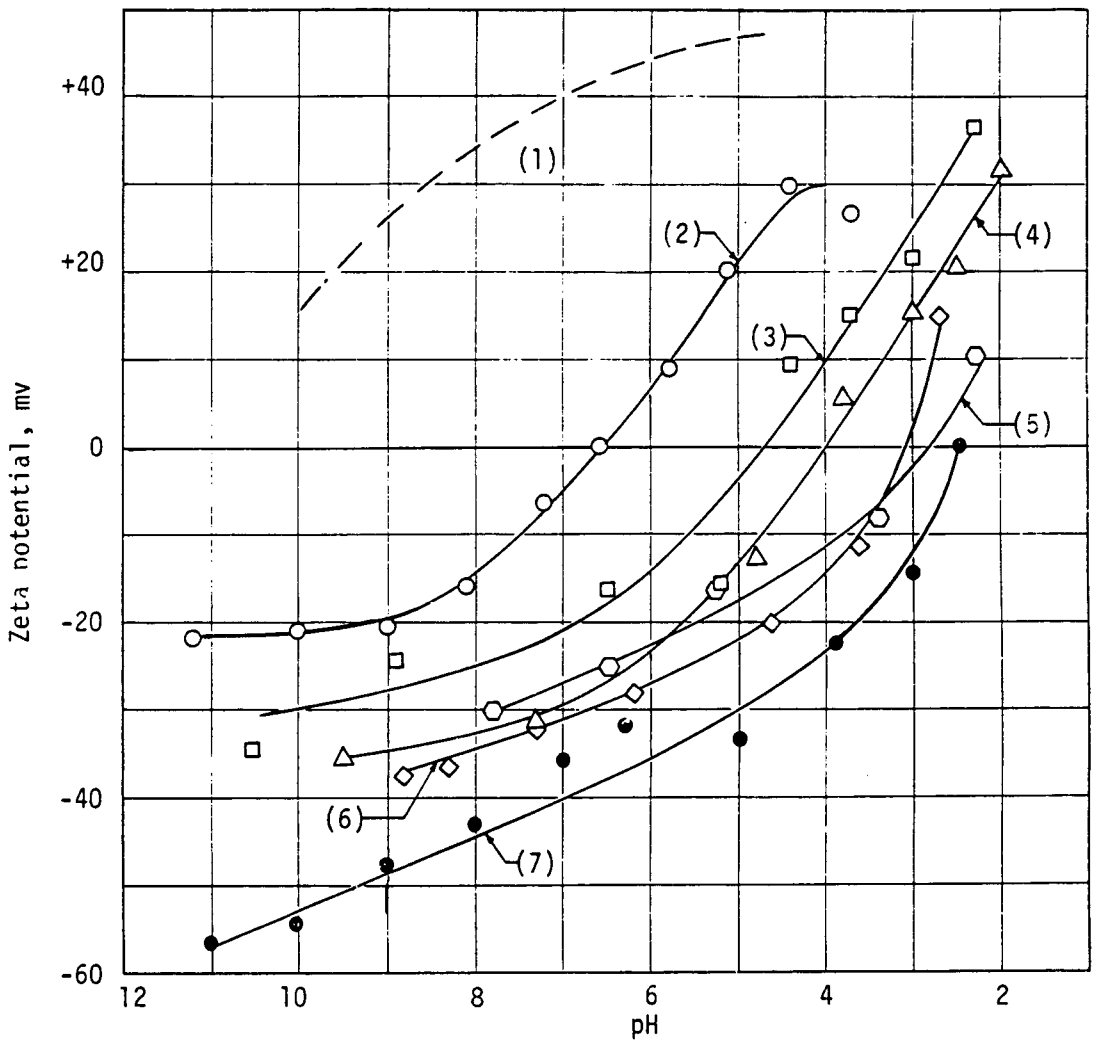


FIGURE 53 - ZETA POTENTIALS OF SOME PAPER-MAKING ADDITIVES

Symbol	Product	Remarks
(1) — — —	chrysotile	high-purity asbestos
(2) ○○○	rutile (TiO_2)	synthetic
(3) □□□	titanium dioxide	Titanox AWD
(4) △△△	titanium dioxide	Suntiox, used in making Asbestos-T
(5) ⬡⬡⬡	kaolinite	Georgia Kaolin
(6) ◇◇◇	sodium-aluminum silicate	Zeolex 23P
(7) ●●●	talc	St. Lawrence County

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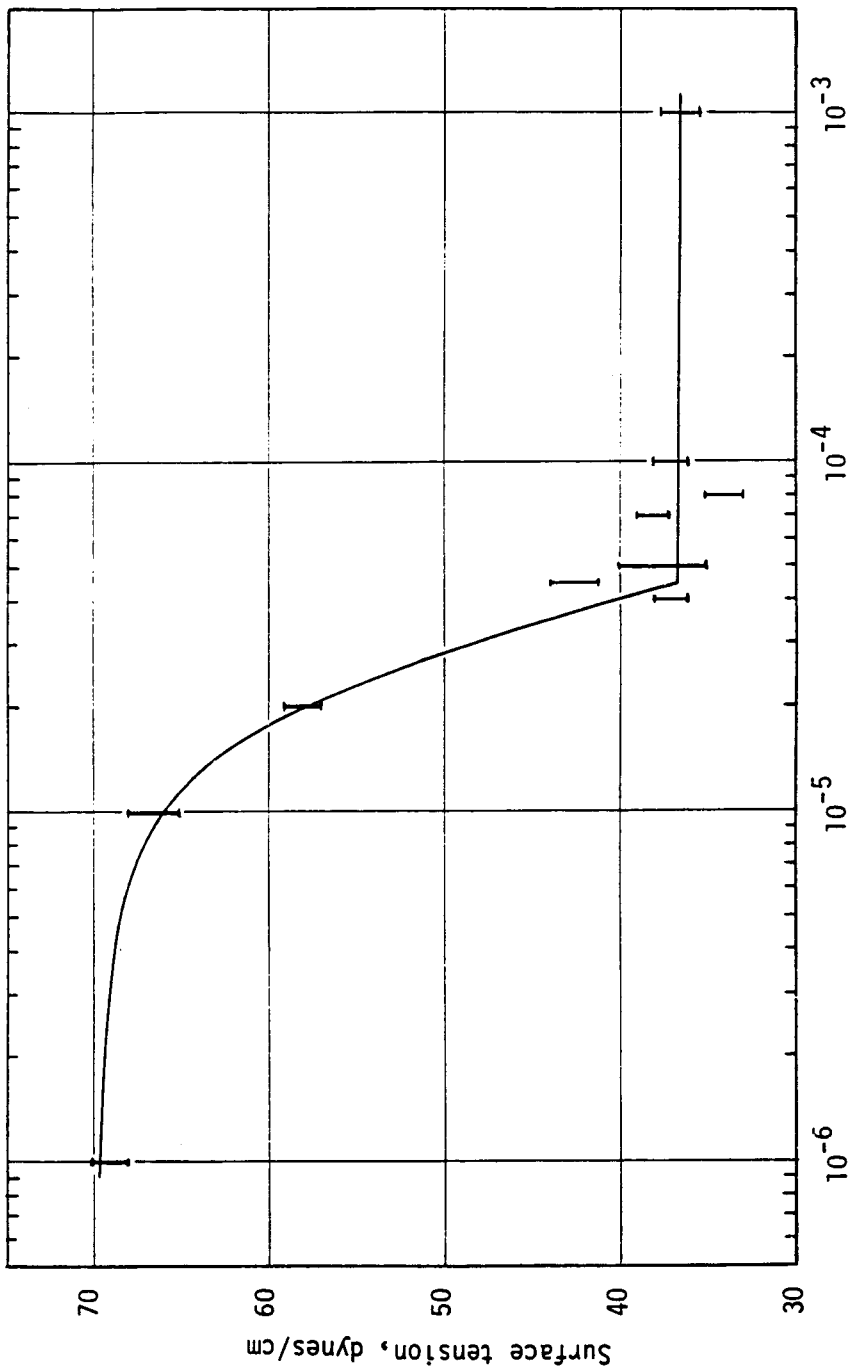


FIGURE 54 - SURFACE TENSIONS OF ALKALINE POTASSIUM STEARATE SOLUTIONS

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Adsorption isotherms of stearate on asbestos have been measured at four different pH values. These data are shown in Figure 55. Either the undissociated stearic acid molecule or the stearate ion may be the species of surfactant being adsorbed. The magnitude of the acid dissociation constant for stearic acid is about 10^{-5} so, in a solution whose pH is less than 5, the most abundant species will be undissociated stearic acid, while at higher pH values, the stearate ion will predominate. In the pH range studied, between 6 and 12, the negatively charged stearate ion is expected to be the adsorbing species. As the pH of an asbestos suspension is increased the positive surface charge of the asbestos decreases, so there should be less adsorption of stearate ion. The data in Figure 55 bear out this prediction.

Based on a surface area of 70 square meters per gram of asbestos, a close-packed monolayer of stearate would occur at an adsorption density of 650 to 550 micromoles per gram of asbestos, depending on whether a cross-sectional area of 18 $Å^2$ or of 22 $Å^2$ is assumed for an ion of stearate at the surface. An inflection occurs in the adsorption isotherm at pH 8 at the adsorption density calculated for a monolayer, and such an inflection has often been interpreted as indicating that another layer of adsorption is beginning. The asbestos suspensions dispersed at relatively low adsorption densities at pH 12. In another suspension similarly dispersed, the asbestos particles were observed to have a zeta potential of -47 millivolts, calculated from electrophoretic mobilities. It is apparent that the adsorption mechanism for the stearate onto the asbestos surface occurs even at pH values above the zero point of charge of the surface (pH 10.8), and that the absorbing species must be the anionic stearate ion since its adsorption causes the particle to assume a negative charge.

Adsorption isotherms for stearate on asbestos at 50°C are shown in Figure 56 for pH 8 and for pH 12. The adsorption was slightly less at 50°C than at 30°C as was expected, but the rate of equilibration was faster. Previous data, obtained at 30°C, are also shown in Figure 56 for comparison.

The isosteric heats of adsorption were calculated at pH 8 and at pH 12 from the adsorption data at 30°C and 50°C. The formula used was:

$$\Delta H^\circ = -R \frac{\partial \ln(\Gamma/C)}{\partial (1/T)} \quad \text{at const } \Gamma$$

$$= \frac{2.303\ R\ T_1 T_2}{T_1 - T_2} \log \left[\frac{C_2}{C_1}\right] \quad "$$

$$= -22{,}500 \log \left[\frac{C_2}{C_1}\right] \quad "$$

The results of these calculations are shown in Figure 57. Below monolayer coverages the heats of adsorption at pH 8 range from 2 to 5 kilocalories per mole. This is surprisingly low for the specific adsorption of a surfactant; the results must be applied with some caution since these calculations are based on very few experimental data. The heat of adsorption above monolayer coverages was larger, but this, presumably, was due to the interaction of hydrocarbon chains with each other rather than due to the reaction between the stearate and the surface.

An attempt has been made to evaluate the bonding strength of stearate to asbestos by trying to remove it with water and with alcohol in a soxhlet extractor. Asbestos loaded with about 4 per cent stearic acid was tested. No stearate was removed by 6 hours of refluxing at 100°C with water. The treatment with ethyl

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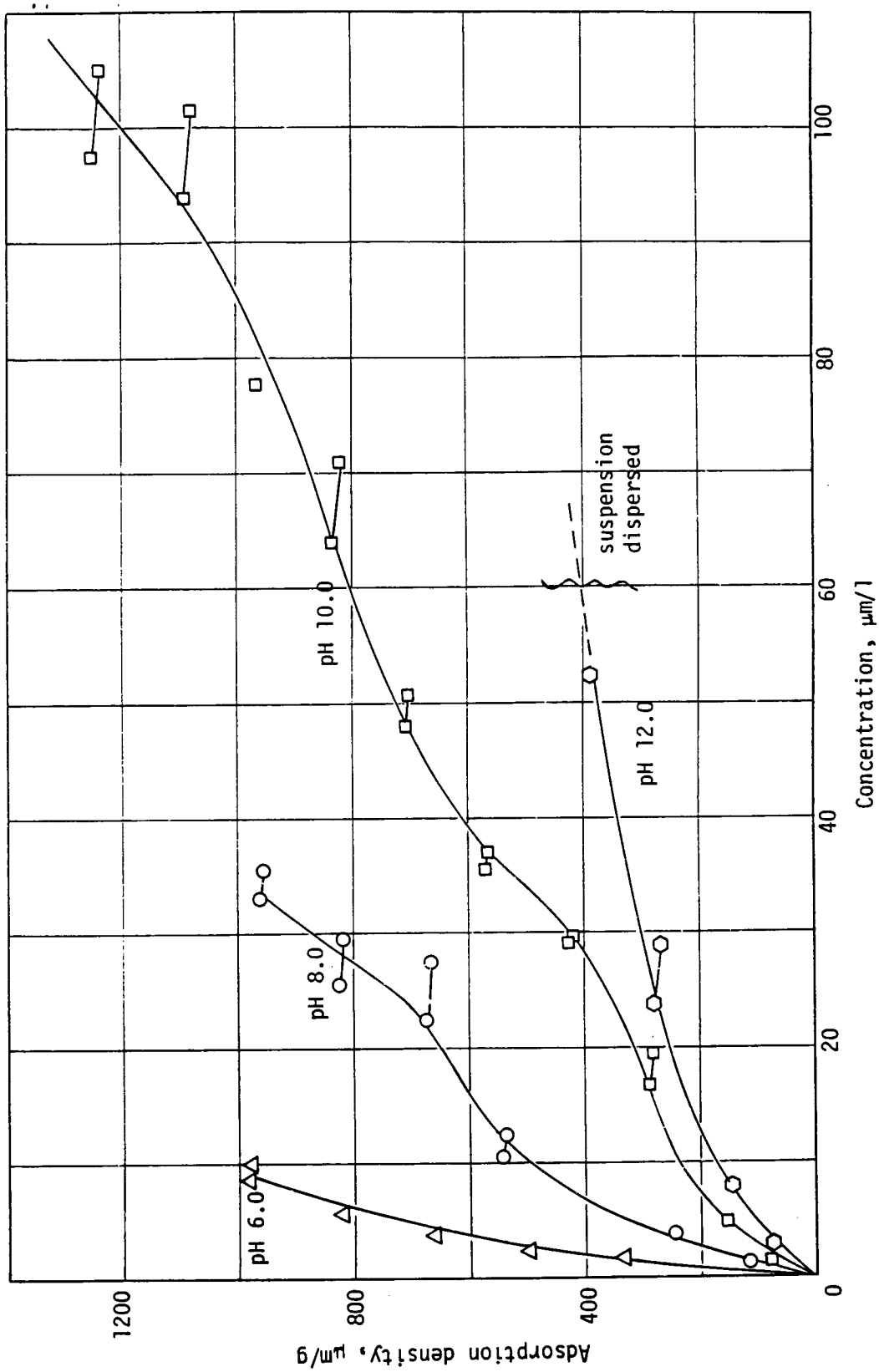


FIGURE 55 - ADSORPTION ISOTHERMS AT 30°C FOR POTASSIUM STEARATE ON CHRYSOTILE AT VARIOUS PH VALUES

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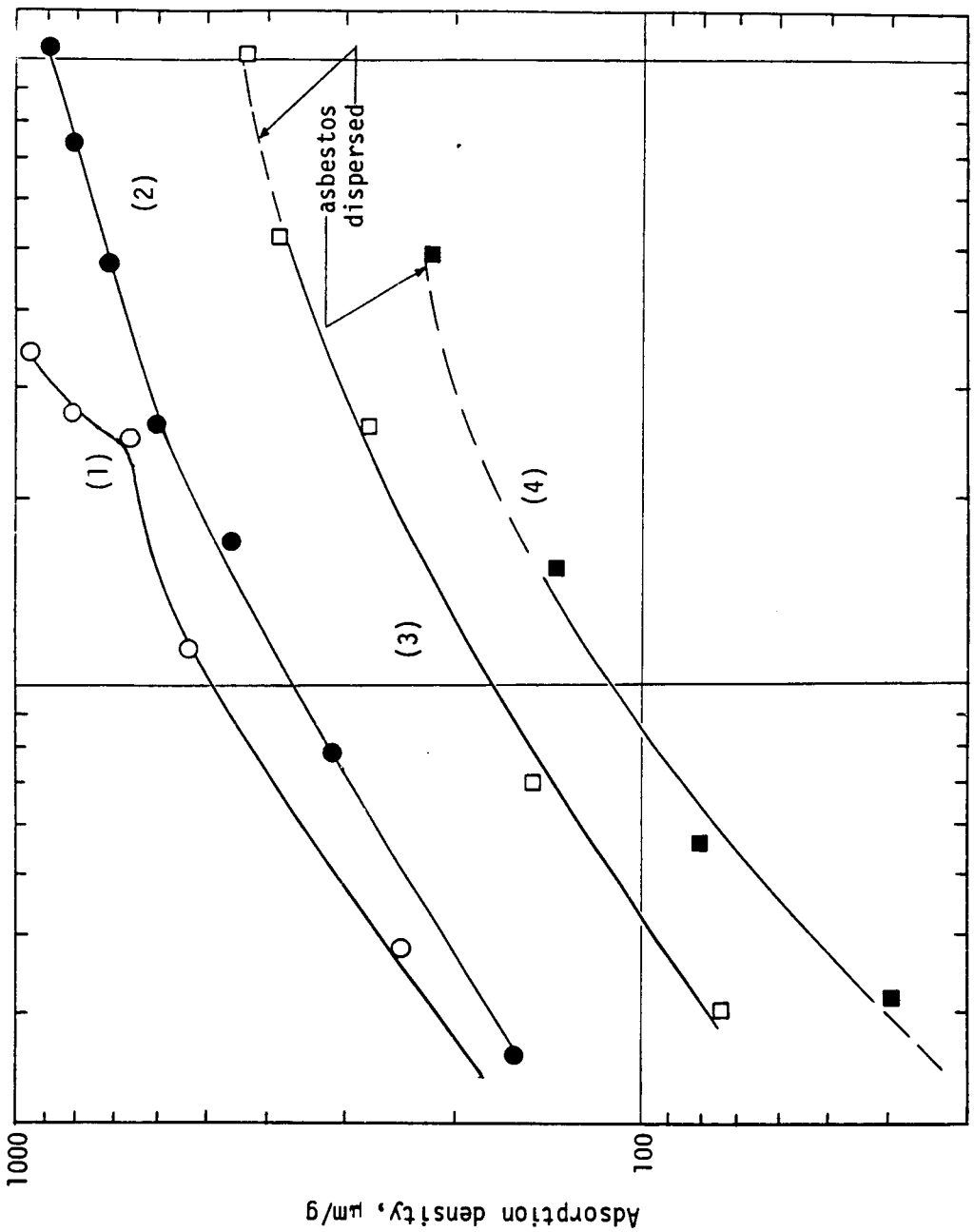


FIGURE 56 - ADSORPTION ISOTHERMS AT 50°C AND AT 30°C FOR POTASSIUM STEARATE ON ASBESTOS

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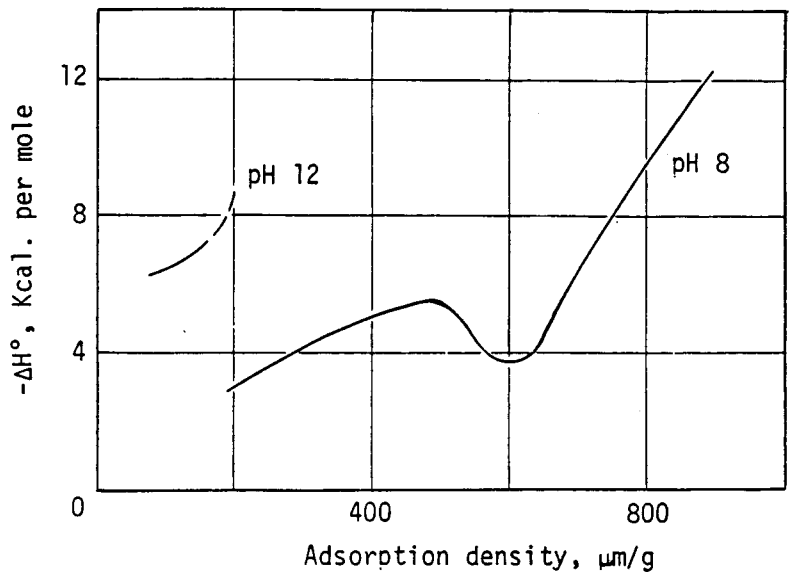


FIGURE 57 - ISOSTERIC HEATS OF ADSORPTION FOR POTASSIUM STEARATE ON CHRYSOTILE

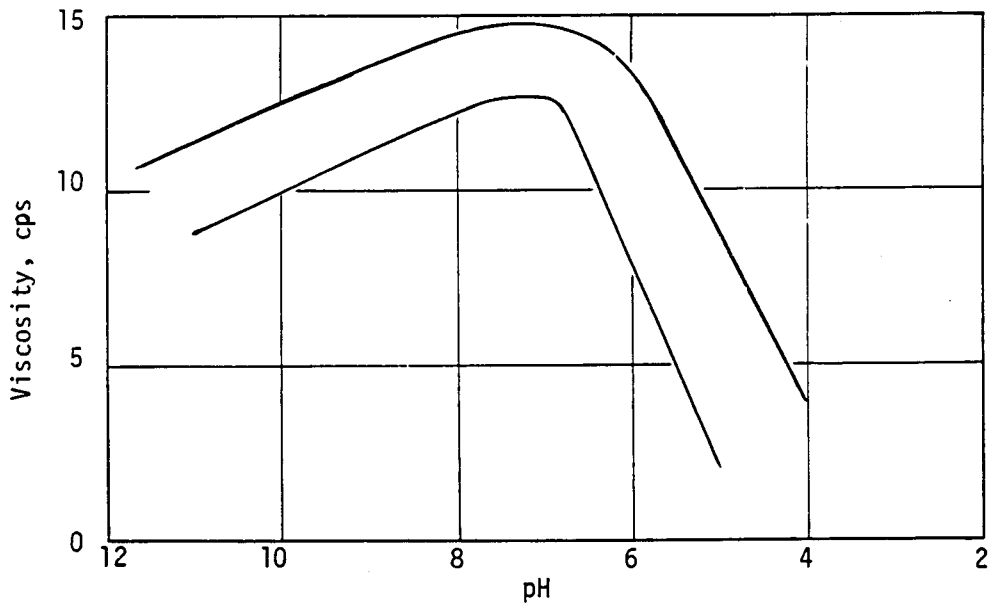


FIGURE 58 - APPARENT VISCOSITY OF ONE WEIGHT PER CENT SUSPENSION OF ASBESTOS IN WATER AS A FUNCTION OF PH

Shear rate, 1000 sec^{-1}; Temp. 23-25°C

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alcohol at its boiling point left about 1.8 per cent stearate on the asbestos after 6 hours. This stearic acid must be very strongly adsorbed to resist these conditions (solubility at room temperatures is about 9 grams of stearic acid per 100 grams of absolute alcohol).

A number of filter cakes of asbestos were prepared from aqueous solutions at pH 8 containing known amounts of stearate. The filter cakes were dried at 60°C and then pressed to form smooth surfaces. Portions of the filter cakes were immersed in decane; then a drop of pure water was placed on the cake in the decane. The magnitude of the contact angle, measured through the decane phase, was estimated visually, with an accuracy estimated at no greater than about 10°.

The results are given in Table XX. The coverages reported are based on an adsorption density of 600 micromoles per gram required for a monolayer. A large contact angle indicates affinity for water. Zero contact angle represents complete wetting of the asbestos by decane. A 90° contact angle means that the asbestos is equally compatible with water and decane.

TABLE XX

CONTACT ANGLES BETWEEN WATER AND DECANE
ON STEARATE-COATED ASBESTOS

Coverage		
No. of Monolayers	g/g Asbestos	Contact Angle*
0	0	150°
1/4	0.04	90°
1/2	0.08	45°
3/4	0.13	small
1	0.17	no contact
1.5	0.25	"
2.5	0.42	"

* measured through the decane phase

The data show that a 90° angle is obtained at a coverage approaching 1/4 of a monolayer while 3/4 of a monolayer is needed to get nearly complete hydrophobicity. It is somewhat surprising that such large coverages are needed for the asbestos to become completely hydrophobic. Based on previous work only about 90 micromoles of positively charged sites are present on asbestos. It would be expected that these would be the principal points of interaction with water, so when they are tied up with stearate ions, at about 1/6 of a monolayer, the surface might be expected to have much less affinity for water. Since this is not true, even the uncharged portion of the asbestos surface must hydrate strongly.

The data for adsorption of dodecyl sulfonate have already been presented in a previous section. Since it is adsorbed at values much less than a monolayer, its wetting behavior was also of interest. Some contact angle measurements were made with asbestos loaded with sodium dodecyl sulfate whose characteristics should be similar to those of the dodecyl sulfonate. The data are given in Table XXI. A minimum level of wetting by decane can be achieved corresponding to an angle of about 60°. Thus, complete wetting by a non-polar organic liquid cannot be achieved by treatments of asbestos with this chain length of surfactant.

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TABLE XXI

CONTACT ANGLES BETWEEN WATER AND DECANE
ON VARIOUS SURFACTANT-COATED ASBESTOS PRODUCTS

Surfactant	Addition[1] Level, pha	Contact[2] Angle	Surface[3] Charge
(1) None	0	150	pos.
(2) Sodium dodecyl sulfate	2	90	pos.
	5	60	pos.
	10	60	neg.
	20	60	neg.
(3) Sodium dodecyl benzene sulfonate	2	80	-
	5	80	-
	10	70	-
	20	45	-
(4) Sodium dodecyl benzene sulfate	2	80	-
	5	70	-
	10	60	-
	20	45	-
(5) Lignin sulfonate- "Marosperse C"	2	130	-
	5	100	-
	10	95	-
	20	70	-
(6) Polymer H[4] "UCC"	7	90	pos.
	15	50	nil
	25	20	neg.

(1) 1 g asbestos in 300 ml distilled water at pH 6
(2) measured through the decane phase
(3) measured by electroosmosis on filter cakes
(4) pH of treatment varies, pH 6.7, pH 7.6, and pH 8.8, consecutively

Other contact angle data have been obtained with various other surfactants. These are also summarized in Table XXI as a matter of record.

RHEOLOGY OF ASBESTOS SUSPENSIONS

Three characteristic types of dilute asbestos suspensions in water are readily distinguishable in Figure 58:

(1) At less than pH 5, the asbestos suspensions are dispersed. Visually, they are homogeneous and when stirred, they show a characteristic shimmering birefringence which is characteristic of aligned particles flowing in a unit mass. The flow properties are nearly Newtonian at low concentrations. It is apparent that the electrical repulsion forces predominate over the van der Waal's attractive forces so the particles remain separated and free of each other's influence.

(2) At pH 6 to pH 8, the asbestos suspensions are gelled. They are also homogeneous, but they tend to have a high viscosity, a yield point, and plastic flow characteristics. No streaming birefringence is seen. It appears

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that there must be a balance between the electrical repulsive forces and the Van der Waal's attractive forces so that a continuous network, made up of particles in close proximity to each other or actually touching each other, occurs throughout the solution.

(3) At pH values greater than 8, the asbestos suspensions are flocculated. Visually, particulates can be seen. These are obviously masses or clumps of asbestos fibrils since individual fibrils are too small to be seen by eye. The flow properties of this system are pseudoplastic and no well-defined yield point can be found. The values of apparent viscosity are somewhat lower than they are for the suspensions in the gelled state. It seems that, under this condition, the van der Waal's attractive forces predominate greatly over the electrical repulsive forces, causing the asbestos fibrils to gather together into flocs. This reduces drastically the number of flow units present in the suspension, so, in spite of the fact that the attraction forces between the fibrils are the greatest under these conditions, the net effect on the viscosity is to lower it.

The general characteristics of the last two types of suspensions are that they exhibit an apparently high viscosity at low shear rates and a low viscosity at high shear rates. This seems to be due to the fact that under high shear rates the elongated fibers tend to line up parallel to each other and interact less, resulting in less flow resistance in the suspension. This is a very desirable property for applications in many industrial problems. Typical flow characteristics, measured by Park (61), are shown for flocculated suspensions and for defloccualted suspensions in Figures 59 and 60. The deflocculated suspensions show some tendency to gel. However, in the presence of high concentrations of detrimental anions, it is not possible to obtain a dispersed condition or even, in many cases, a gelled condition. Some sort of treatment to make asbestos suspensions insensitive to the salt content and to the acidity of the solution would be highly desirable. Consequently, the interaction of chrysotile asbestos with a series of water-soluble polymers has been investigated by Dr. K. Park. The data have been reported and only a summary of his findings will be given here (62). Most of the water-soluble polymers studied interacted with chrysotile and altered the stability of its suspensions.

Anionic polyelectrolytes exhibited the strongest interaction with chrysotile asbestos. An asbestos suspension could be either dispersed or flocculated by the polyanions. Adsorption of large amounts of anionic polyelectrolytes on the asbestos resulted in reversal of the surface polarity of the latter from positive to negative and, in some cases, the negative charge developed was enough to cause dispersion of the suspension. The adsorption was usually irreversible. The rheological properties of suspensions made from asbestos treated with anionic polyelectrolytes became much less susceptible to the effect of salts, acids, or bases.

Non-ionic polymers also interacted with chrysotile to some extent. Some polymers either dispersed asbestos suspensions or displayed a protective action in the presence of anions which normally flocculate the suspensions. However, the interaction capacity of the non-ionic polymers was much less pronounced than that of the anionic polymers.

Cationic polyelectrolytes generally contributed only to an increase in the viscosity of the suspension containing the chrysotile and the polymer. It appeared as if there was little or no interaction between chrysotile and these polymers.

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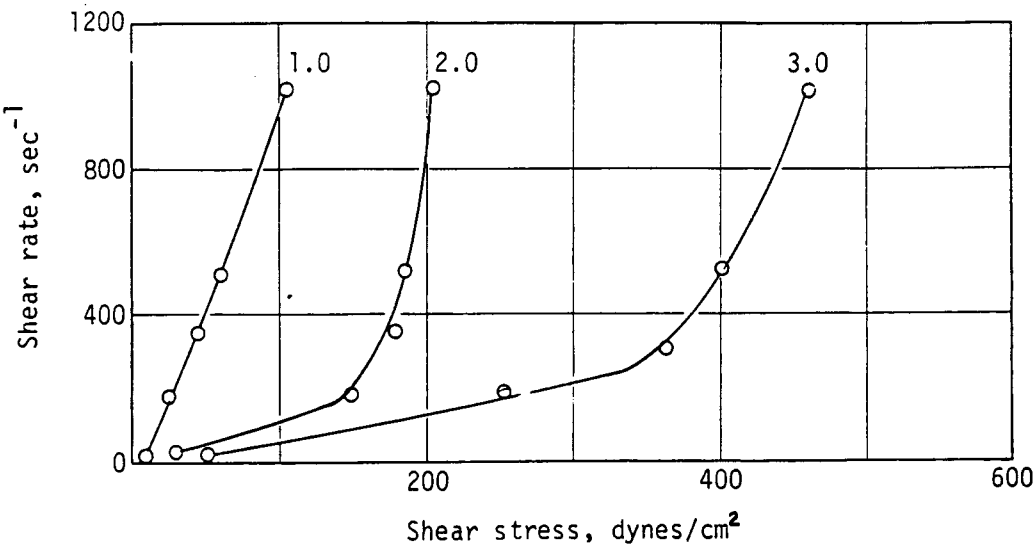


FIGURE 59 - FLOW CURVES FOR FLOCCULATED ASBESTOS SUSPENSIONS IN WATER (61)

Weight per cent asbestos given on figure

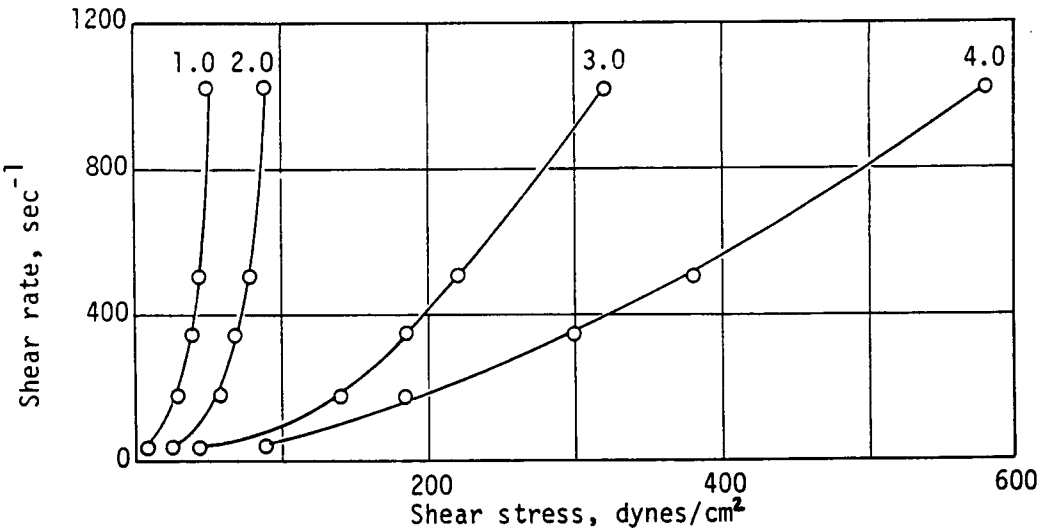


FIGURE 60 - FLOW CURVES OF DEFLOCCULATED ASBESTOS SUSPENSIONS IN WATER (61)

Weight per cent asbestos given on figure

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The rheological properties of asbestos in non-aqueous liquids have also been studied by Dr. Park. It seems that examples of dispersed, gelled, and flocculated states of asbestos in these liquids can also be found. Since the asbestos surface is naturally hydrophilic, it would be expected that the asbestos fibrils would strongly flocculate in any non-polar liquids. Consequently, a dispersing species must be present in the solvent before the asbestos suspension will become fluid since the mechanism of electrostatic repulsion due to surface electrical charges is not available in non-polar liquids. A system which has been extensively studied is the thickening of polyester resins by asbestos products. The basic solvent is styrene monomer and the dispersing species appears to be the polyester polymer. The polyester species does adsorb on normal asbestos, causing it to disperse and making it ineffective as a thickener for polyester resins. However, R-G244 asbestos, which has a different type of surface, is not dispersed by the polyester species in styrene and so becomes an effective thickener for polyester resins. The subject is covered in a report by Dr. Park (63).

A dispersion of asbestos in a non-polar liquid is very different in stability than one in water. In the latter case, a repulsive force occurs between particles due to similar electrical charges on them, so settling is retarded. Asbestos is dispersed in a non-polar liquid by the adsorption of species which solvate and form a protective layer around each particle. The particles cannot approach each other to a sufficiently close distance for van der Waal's forces to cause them to flocculate. However, no repulsive forces act between the particles so they settle out of solution readily. In fact, they compact with rather low sediment volumes and can be appreciably more difficult to stir up again than are flocculated sediments.

INTERACTION WITH PARTICULATE SOLIDS

Chrysotile is one of the most positively charged of all natural minerals in water. Its zpc is in the pH range 11 to 12 and so it becomes increasingly positively charged as its aqueous suspensions are made progressively more acidic. Brucite (magnesium hydroxide) is also positively charged, but it is too soluble to exist in dilute suspensions below about pH 10.5 (64). Precipitated alumina and ferric oxide have zpc values at about pH 9, although their natural counterparts have a zpc at neutral pH. To this writer's knowledge, all natural silicates other than chrysotile are electronegative in water. In fact, it may be generalized that most materials in nature tend to be electronegative.

It is apparent that chrysotile will be attracted to or will attract most other particulate materials in slightly alkaline water due to their dissimilar charges. Zeta potentials of many materials, natural minerals or synthetic products, have been measured in the past and the pH of their zpc is listed in Table XXII. These materials are all positively charged at pH values below their zpc and they are negatively charged at pH values above their zpc. It must be cautioned that the charge properties are very dependent on trace impurities, especially adsorbed ones. For example, various titanium dioxide products made for special applications are given surface treatments which change their surface properties, as shown in Table XXII. A good summary of the surface properties of natural minerals has been compiled by Parks (65).

The attraction between asbestos and titanium dioxide is used to make a commercial product, Asbestos-"T," which is made by mixing titanium dioxide slurry with an asbestos slurry. The object of this procedure is to distribute titanium dioxide particles evenly along the length of each asbestos fiber. The

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TABLE XXII

PH OF ZERO-POINT-OF-CHARGE FOR
VARIOUS PARTICULATE MATERIALS IN WATER

Material	pH of zpc	Notebook Reference	Remarks
antimony trioxide	3	1708-3	Fisher Scientific, 0.2% As
chrysotile	10.8	this report	Coalinga, California
chrysotile	11.8	(36)	Quebec, Canada
crocidolite	3.5	1708-7	
anthophyllite	<2.5	1708-9	Portugese E. Africa
sepiolite	3.5	1708-10	Vallacas, Spain
polygorskite	4.5	1708-11	
tremolite, fibrous	2-2.5	1708-13	
tremolite, black	3-3.5	1708-15	Balmat, N. Y.
serpentinite	10.5-11	514-68	Warren County serpentine
antigorite	4.5	1708-14	F.A.M., 1619-50-16
talc	~2.5	1708-16	St. Lawrence County
wollastonite	~2	1708-12	Willsboro, N. Y.
blue BG, organic pigment	5.5	1730-95(a)	Am. Hoechst Co.
yellow H10G, organic pigment	~2	1730-95(a)	DuPont Co.
magadiite	~2	2271-9	F.A.M. 1619-91-1-1
sodium aluminosilicate	3	(b)	Zeolex 23P, J. M. Huber Co.
potassium titanate	4.5	(b)	fibrous filler for paper, DuPont Co.
kaolinite	3	(b)	Georgia kaolin
rutile, TiO_2	6.3	575-78	synthetic, made by hydrolysis of $TiCl_4$
Commercial TiO_2			
Unitane 450A	7	(b)	Am. Cyanamid Co.
Suntiox	4	(b)	Japanese
Titanox AWD	4.5	(b)	Titanium Pigment Corp.
Zopaque R.G.	5.5	(b)	Glidden Co.
Zopaque S.D.	6	(b)	Glidden Co.
Titanox ACG	8	(b)	Titanium Pigment Corp.

(a) Other organic pigments in water were negatively charged in water, reference: S. Chwastiak, "Zeta Potentials of Some Organic Pigments in Water," Interim Report dated Sept. 19, 1967 to Union Carbide Chemicals and Plastics, Niagara Falls, N. Y.

(b) G. L. Dickson, "The Zeta Potential Measurement of Several Paper-Making Materials," Report dated Sept. 7, 1967, to R. G. Woolery, Union Carbide Chemicals and Plastics, Niagara Falls, N. Y.

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idealized elements of an asbestos-titanium dioxide manufacturing process are:

1) Separate the titanium dioxide particles into fundamental particles, i.e., disperse in aqueous solution.

2) Separate asbestos into fundamental fibrils, i.e., disperse in aqueous solution.

3) Mix suspensions, preferably maintaining a dispersion in the mixture.

4) Change the chemical conditions in the mixture to cause particles of titanium dioxide and asbestos to coflocculate.

5) Filter and dry.

This process is possible with Titanox-A CG brand of titanium dioxide which has a zpc at a pH value of approximately 8. Thus, it can be dispersed at pH 4.5 with acetic acid and mixed with a dispersed suspension of asbestos. On raising the pH to 9.0, the titanium dioxide becomes negatively charged and coflocculates with the asbestos, which is still positively charged. The effectiveness of a product made in this way remains to be evaluated. A product of this sort would be highly desirable in pigment dispersion processes (17).

The normal Asbestos-"T" manufacturing procedure as practiced in our mill consists of mixing a titanium dioxide slurry in water with a flocculated suspension of asbestos at its natural pH, approximately 9. Attempts to pre-disperse the titanium dioxide more effectively by additions of a polyphosphate dispersing agent have not been successful, possibly due to the detrimental effect that any polyphosphates in solution would have after mixing on the state of aggregation of the asbestos. The best titanium dioxide for this process has been Suntiox which is seen to be the most anionic of the ones tested. It should remain coflocculated with asbestos even at the normal pH of a paper circuit, 5 to 5.5.

A system which has been more extensively studied is the coflocculation of asbestos and silica particles. As little as one part of silica will flocculate 10 parts of asbestos prepared as a 1 per cent dispersion. However, when an excess of silica is added, an amount equal in weight to that of the asbestos, the flocculated asbestos becomes extremely well dispersed. Zeta potential measurements proved that the particles are now negatively charged. Electron micrographs of the asbestos flocculated with silica and of the asbestos redispersed with the excess silica are shown in Figure 61. The silica appears only at the intersections of the asbestos fibers in the first case, but in the second case, the surfaces of the fibers are thoroughly covered with a layer or more of silica particles. So much has adsorbed that the fibers look like pretzel sticks. The high specific affinity of the silica for the asbestos is shown by the fact that particles of silica continued to adsorb even after the over-all charge of the fiber and its adsorbed silica particles was negative.

It is significant that the amount of silica required to redisperse asbestos did depend on the charge density on the asbestos. It took less silica to redisperse asbestos in the presence of sulfate ions. In other tests, the asbestos was partly leached to remove some positively charged sites on the surface and much less silica was needed to redisperse this sample also.

This leads to the interesting conclusion that there is probably an optimum ratio of asbestos and any given material for interaction. This ratio depends on the surface charge density of the two particulates.

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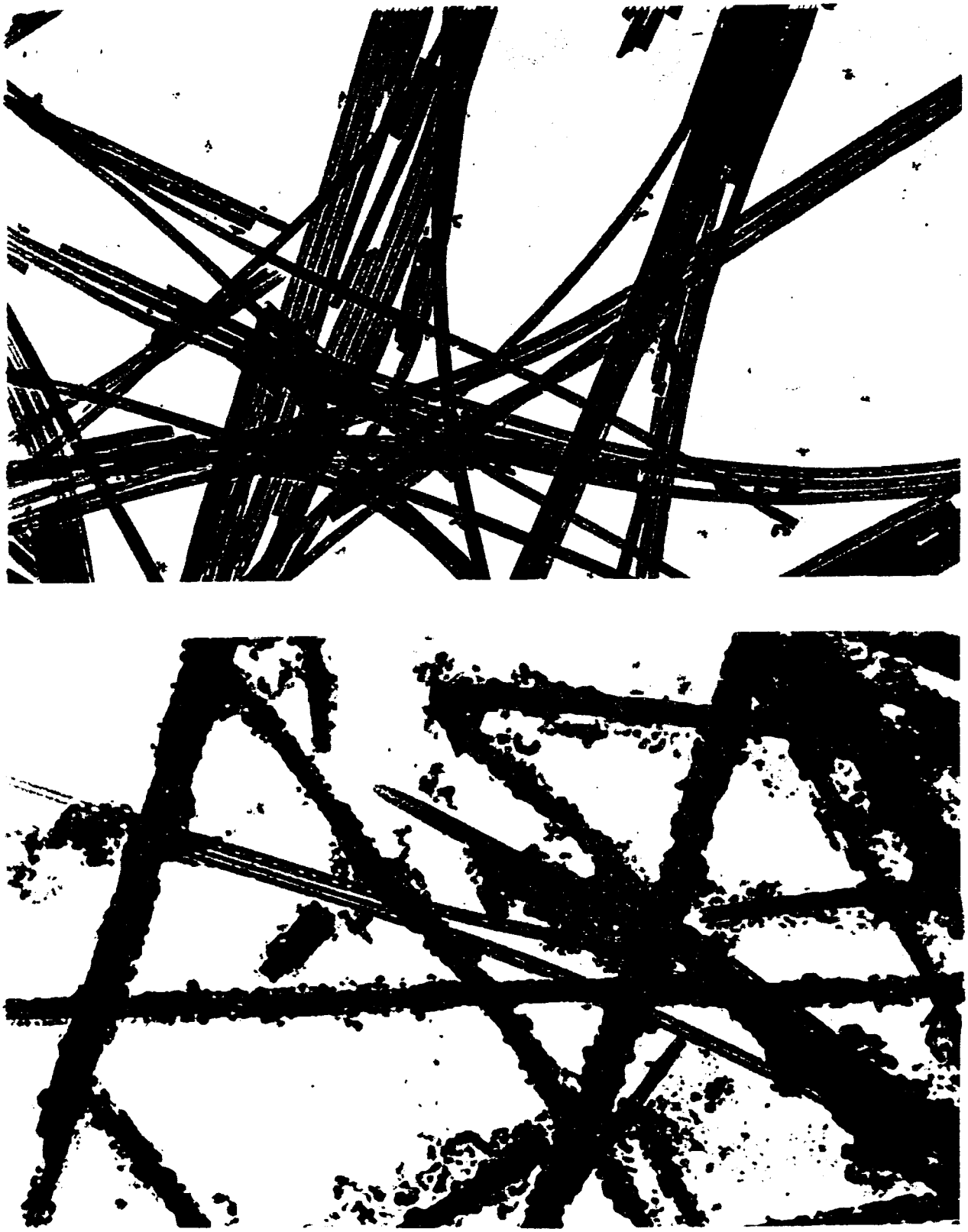


FIGURE 61 - INTERACTION OF ASBESTOS FIBRILS WITH SILICA PARTICLES (LUDOX)

Top: Asbestos/silica ratio, 10:1
Bottom: Asbestos/silica ratio, 1:1

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REINFORCING PLASTICS

Chrysotile asbestos should be valuable for reinforcing plastics, based on the strength and purity of its fibers. In actual practice, little reinforcement has been achieved. Generally there is some increase in modulus, accompanied by a decrease in tensile strength, when conventional incorporation techniques are used. This topic has been covered in a U.C.C. report by R. E. Bryne (66). His generalization is that polymers with polar functional groups react best with the ionic surface of asbestos and thus make the strongest composites. On a practical scale, the best performance to date has been achieved in reinforcing nylon; its tensile strength has been doubled. However, there has been no success in reinforcing polyolefin materials.

The problem seems to be that there are too many particles, 10^{14} particles per gram of asbestos. The first requirement for a composite is that good wetting must be present inherently for the fibers by the polymer matrix, and the second is that the proper mechanical action must be used to replace the air at all the interfaces with the polymer and then to remove the entrained air from the composite. The proper mechanical conditions are hard to achieve since most polymers are already viscous in their liquid state and the addition of asbestos makes them even more viscous. In the laboratory, this problem has been avoided by dispersing the asbestos in a liquid monomer.

Styrene has been the most commonly used monomer, but methyl methacrylate, ethyl acrylate, and vinyl acetate were all tried successfully for use in this procedure also. A typical experiment is as follows:

1. Ten grams of asbestos dispersed in a solution of 100 grams of Rohm and Haas P-43 polyester resin in 500 grams of styrene, i.e., 13 phr polyester in styrene.
2. Open at high speed in Waring Blendor for 2 minutes.
3. Mix in 5 grams of benzoyl peroxide.
4. Deaerate in a vacuum flask at about 29 inches of mercury.
5. Filter on a 2" x 10" filter under about 3" of vacuum.
6. Press cake in filter to get desired liquid to solids ratio.
7. Place cake between two metal plates and wrap in aluminum foil.
8. Heat for about two hours at 100°C.
9. Place in press and heat under slight pressure for two hours at 150°C.

The mechanical properties of the plaques were measured by the Bound Brook Testing Laboratories. The data in Figure 62 show the tensile strength and tensile modulus of polystyrene-asbestos composites. For comparison, the same asbestos samples have been incorporated into polystyrene (SMD 3500) at 320°F on a 2-roll differential-speed mill.

The laboratory samples show true reinforcing with a tripling of the tensile strength by the addition of about 50 weight per cent of asbestos. Asbestos treated with 15 pha stearic acid is slightly better for making composites. The elongation at break for these samples averaged about 1 per cent. Other data, not shown, seem to indicate that a treatment level of 5 pha stearic acid or slightly less would have resulted in nearly 50 per cent stronger plaques.

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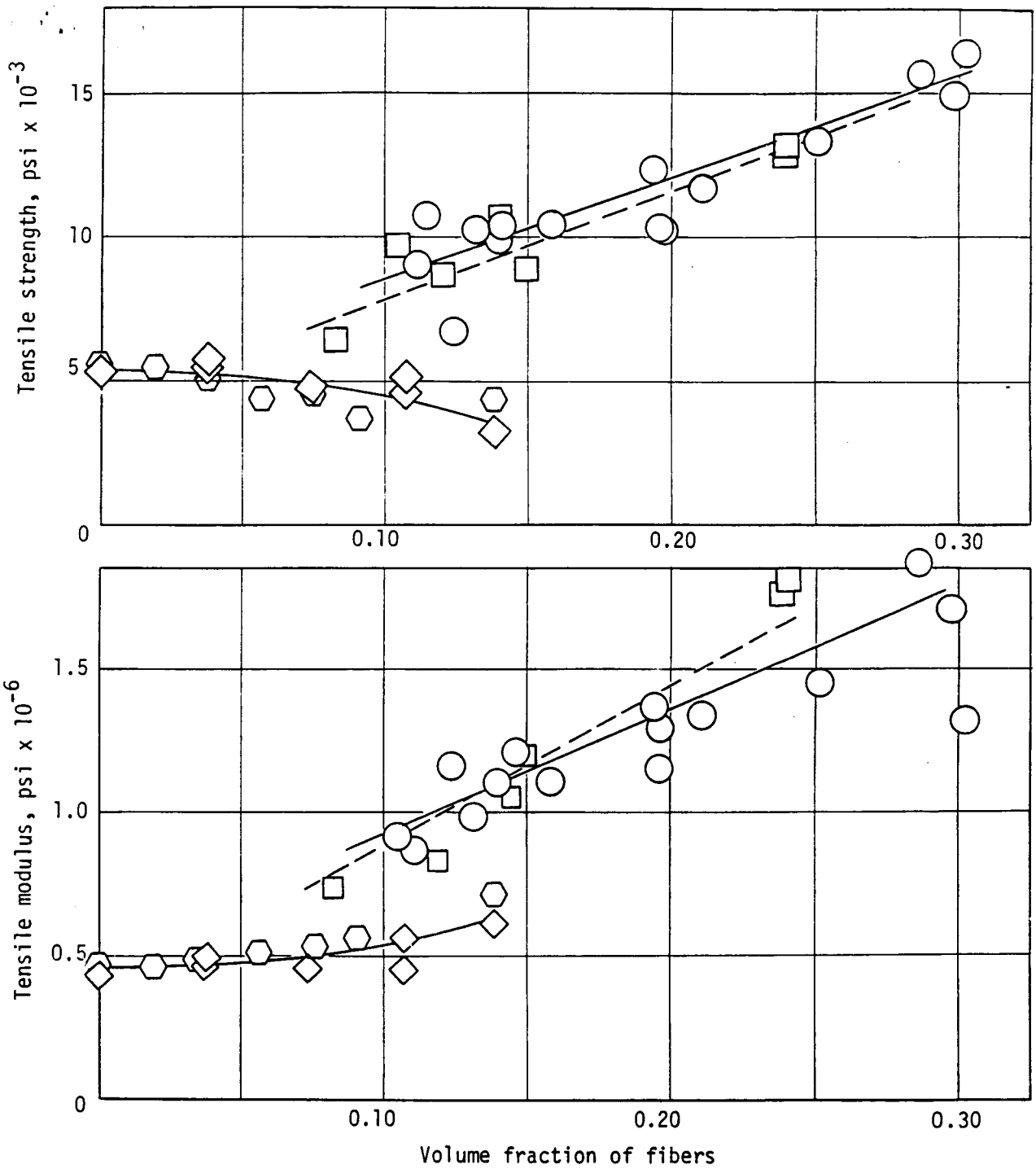


FIGURE 62 - MECHANICAL PROPERTIES OF ASBESTOS-POLYSTYRENE COMPOSITES

- COF-25 asbestos
- COF-25 asbestos with 15 pha stearic acid
- COF-25 asbestos incorporated on rolls
- COF-25 asbestos with 15 pha stearic acid, incorporated on rolls

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The composites made by mixing asbestos into polystyrene on the 2-roll mill show the typical behavior - slight increases in modulus and slight decreases in tensile strength.

The wetting problems can be expected to be solved in the near future. However, if colloidal asbestos fibers are to be used successfully for reinforcing plastics, new technology must be developed for incorporating effectively fine particulates into plastics.

DISCUSSION

Fibrils of chrysotile are tubular in shape, made by groups of sheets rolled into a helical configuration around a central core. Each sheet consists of two layers, one brucite and one silica. The curvature is such that the brucite is always on the outside, so surface properties are determined primarily by the brucite layer of the outside sheet of the fibril. Massive flakes of Coalinga ore have an open texture with no matter filling the spaces between the fibrils. This distinguishes it from cross-fiber asbestos which does have an amorphous, inorganic material between the fibrils. This difference in texture makes Coalinga asbestos relatively easy to process into a colloidal product compared to asbestos from other ore bodies. The holes in the fibrils seem to be filled with amorphous matter of the density and nearly the same composition as chrysotile itself.

The main chemical impurities in the lattice seem to be about 0.05 mole per cent of alumina in the silica layer and about 0.12 mole per cent of iron oxide in the brucite layer.

The diameter of the fibrils is about 260 Å and the majority of the fibrils range in length from 2 to 20 microns, with a guess of about 5 microns as the average length. The surface area is about 65 m^2/g both for liberated asbestos and for flakes of ore, which demonstrates the openness of the flake texture. The fibrils are felt to have a tensile strength of about a million psi and fiber bundles of cross-fiber asbestos have been measured with strengths up to 800,000 psi. The tensile modulus has been measured to be 23×10^6 psi. The fibers keep most of their strength until about 500°C, when some surface dehydration starts, and at 550°C all of the structural water (13 per cent by weight of the crystal) is given off, eventually leaving a weak, amorphous fibril.

Chrysotile is generally recognized as being the most alkali-resistant and the least acid-resistant of the asbestos minerals. In water at pH 4 to 12, the magnesium concentration is between 10^{-5} and 10^{-4} moles per liter, and the silica concentration is about 10^{-5} moles per liter. In strong acids, below pH 1, all of the brucite can be leached out at room temperature, leaving behind a weak silica skeleton somewhat pseudomorphic after the original fiber. At high temperatures, significant acid attack can occur at somewhat higher pH values.

The zpc of Coalinga asbestos is at pH 10.8 while that of Quebec cross-fiber asbestos is higher, approximately pH 11.8, possibly due to the effect of the amorphous matter occurring between the fibrils. Asbestos is positively charged below pH 10.8, but no reliable and reproducible evidence that it becomes negatively charged at pH values greater than 10.8 has been found for Coalinga asbestos. Negative zeta potentials are reported for Quebec cross-fiber asbestos at pH values greater than 11.8.

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The maximum number of positively charged sites on asbestos is about 90 micromoles per gram, which means that the average site occupies 120 square Angstroms of area. The area of a surface brucite group is about 8 square Angstroms, so at most only 1/15 of the surface hydroxyl groups are capable of being positively charged sites.

Negatively charged sites probably also occur - about 20 to 30 micromoles per gram of asbestos. These could be associated with impurities or with edges of sheets in the structure which are exposed on the fibril surface. Some may exist also on the ends of the fibers or partly in the tubes themselves. The net surface charge is always the difference between the number of positively charged sites and the number of negatively charged sites. At the zpc, there are either equal numbers of positive and negative sites, or there are no charged sites on the surface at all. The number of actual positively charged sites increases as the pH is decreased from 10.8 to 3. However, at any pH value studied up to pH 12, all of the latent sites are available for ion exchange with anions which have a strong affinity for the asbestos surface. Salts of anions which show no significant affinity for individual surface sites are the alkali acetate salts, alkali acrylate salts, and alkali methyl sulfonate salts. These are classed as indifferent electrolytes. In their presence, a diffuse layer of anions develops, which extends from the surface of the particle for some distance into the solution. Other inorganic ions show varying amounts of affinity for the surface sites and tend to neutralize their electrical character. Divalent anions, such as sulfate ions, are particularly detrimental to the surface charge. These specifically adsorb, preventing the development of an extensive space charge around asbestos particles in water.

The density of positively charged sites at the asbestos surface can be increased at least by 20 per cent by treatment of asbestos suspensions with aluminum salts. Other multivalent cations, such as thorium, are also effective for this purpose. The mechanism of this reaction is felt to be precipitation and adsorption of hydroxyl complexes of the cations.

The basic and cationic surface of chrysotile can be modified to be less basic and less cationic by treatment with sodium silicate solutions. A layer of silica, comprising 5 to 7 per cent by weight, is placed on the asbestos by the treatment. The silica-treated asbestos can be made permanently anionic and acidic in surface properties by adding a small amount of aluminum salt to the suspension after the silica treatment process. If more aluminum salt is added, the silica-treated asbestos surface reacts essentially with all of it and then it can become cationically charged again at a high addition level. Other multivalent cations, such as those of titanium and thorium salts, are also effectively abstracted from solution by the silica-treated asbestos.

The asbestos has hydrophilic wetting characteristics but it can be made completely hydrophobic by treatment with anionic surfactants whose hydrocarbon portions contain over 12 carbon. Alkyl sulfonates and fatty acids have worked satisfactorily.

Anionic water-soluble polymers adsorb irreversibly on asbestos. Some adsorb in quantities large enough to reverse the particle surface charge from positive to negative and cause dispersions of their suspension. Non-anionic polymers interact less and additions of cationic polymers only increase the viscosity of asbestos suspensions.

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All applications of asbestos fibers depend upon three basic properties:

1. Cationic surface charge in water.

2. Small-size, fibrous shape.

3. Extremely strong fiber.

Furthermore, the surface properties of the fibers can be changed quite readily so that the strong fibers can be used in applications where the intrinsic surface properties are not suitable.

The most obvious applications for chrysotile fiber are:

1. Interaction with anionic particulates in water, which includes most colloidal materials.

2. Thickening aqueous systems, and thickening non-aqueous systems with modified products.

3. Reinforcing.

The purpose of interacting other particulates with asbestos fibers is to prevent aggregation of the particulates into large masses. Even under the most unfavorable conditions, a very dense mass of fibers is not formed due to the tendency of the fibers to make a haystack-like structure. Thus, if discrete particles are uniformly spread along each fiber and are strongly attached to the fiber, the problem of distributing the particulates uniformly throughout a system becomes the relatively easier one of mixing the coated fibers into the system. An advantage applying primarily in paper manufacture is that titania-coated fibers are more effectively retained in the paper than are the titania particles themselves. A possible source of problem with particle-coated fibers is that the fluffy, dry flocs of fibers entrain much air and, in some instances, may carry this into the suspension with them. The entrained air may be difficult to remove, especially from viscous liquids or suspensions.

The excellent thickening by Coalinga asbestos fibers could be predicted from their large number per unit weight, their rigidity, and their highly elongated shape. The first prerequisite for a practical asbestos product for thickening is that the fibrils be liberated extremely well, resulting in a maximum number of fibrils per gram of asbestos. To a first approximation the volume of influence of each individual fiber will be a sphere with a diameter equal to the fiber length. Based on the dimensions of the fiber quoted earlier, the over-all volume occupied by one gram of fully liberated fibrils would be about 17 liters if there were no overlaps of the volumes of influence of each fiber. In practice, the asbestos is not fully liberated and the spheres of influence for each fiber must overlap considerably before a complete network of fibers is obtained. However, significant thickening is often achieved in liquids with additions in the order of 1 weight per cent (1 gram in 0.1 liter).

There is a second requirement needed for thickening other than the purely geometrical one of being able to form a physical network of touching fibers. This is that there must be a "force of sticking" or net attraction between fibers in close contact. In aqueous suspensions, there are two significant forces: (1) electrical forces of repulsion due to like charges on the particles,(2) van der Waal's

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forces of attraction which are intense at distances of a few Angstroms but fall off rapidly with increasing distance. One component of the latter, the London dispersion force, acts between all matter, so an attractive force always exists between two bodies. When the electrical repulsion force dominates between particles, the suspension is described as dispersed. Little thickening is obtained in dilute dispersions and these have nearly Newtonian flow characteristics.

As the electrical repulsion forces are reduced by decreasing the charged densities on the fibers, a position is reached in which close to a balance occurs between the repulsion and attractive forces, and a gel results, which consists of a network of touching particles. Viscosity becomes high, a yield point is found, and the flow is plastic in nature. When the attractive forces predominate, it might be expected that the suspension should be the most viscous, but this is not the case. Particulates become visible in the suspension and the flow is pseudoplastic. No yield point is found and the viscosity often is less than that obtained in the gelled state. It seems that the strong attraction causes enough aggregation so that the number of flow units is drastically reduced, resulting in a lower apparent viscosity.

High viscosities are obtained only at low shear rates since high shear forces break down the structure and line up the particles in the direction of flow. Thus, resistance to flow in the fluid is minimized and the apparent viscosity becomes very low.

In non-polar liquids, significant repulsion due to electrical charges on the particles does not exist, so the only means of reducing viscosity is by forming a coating around the fibers which prevents them from achieving intimate enough contact for van der Waal's forces to bind them together. This is done by adsorbing a surfactant on the fiber. The hydrocarbon portion of the surfactant solvates, forming a coating of surfactant chains and physically adsorbed solvent molecules. It is ironic that some affinity between the fiber surface and the solvent is needed to develop maximum thickening by the fibers. Otherwise, the attraction between fibers is so strong that relatively dense aggregates form and rapidly settle. However, too much affinity between fiber and solvent results in dispersion and is also undesirable for the attainment of high viscosities. Once liberated fibrils are present in a liquid, control over the balance between the attractive forces and those causing separation of the fibrils is the key to achieving good thickening.

The requirements for a reinforcing fiber are superior mechanical strength, an adequate l/d ratio, and a wettable surface. Asbestos fibers with tensile strengths approaching one million psi and l/d ratios averaging in the order of 200 seem suitable physically. However, they are hydrophilic and there is difficulty in wetting them with organic polymers.

Organic polymers and resins are inherently low energy density materials with low surface tensions. A thermodynamic rule of wetting is that low-energy materials will always wet high-energy surfaces because a lower-energy interface is formed, reducing the over-all energy of the system. Most dense inorganic substances, including asbestos, are high-energy materials so they should be wet by polymers. The difficulty is that the hydrophilic asbestos surfaces have a high affinity for water, adsorbing it strongly on their most active sites, and the adsorbed water forms a low-energy surface. This contaminated surface is no longer readily wetted by polymers. Adsorbed surfactants on the surface reduce

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the affinity for water but a close-packed monolayer of surfactant is itself a low-energy surface and is not wetted spontaneously by polymers. The problem remains of finding a practical and inexpensive wetting agent. Perhaps it can be based on a surfactant terminated at one end by an anionic group and at the other end terminated by an alkyl halide, as suggested by Shafrin and Zisman (67).

The chemical wetting problem probably can be solved with some additional effort. A more difficult task will be to devise a mechanical system for effectively and cheaply incorporating many fibers, up to 10^{14} per gram for asbestos, into a viscous polymer phase. If the fibers are evenly distributed in the matrix of a composite, they will be at an average distance of a couple hundred Angstroms from each other. Each particle starts by being surrounded by air which must be first displaced by the polymer and then excluded from the suspension made even more viscous by the asbestos addition. To achieve high loadings of asbestos in polymer it definitely is necessary to have chemical dispersing conditions present so that the fibrils have an inherent tendency to separate.

In the laboratory, it has been possible to make composites of asbestos in polystyrene by starting with dispersions of asbestos in styrene monomer and polymerizing the styrene in place around the fibrils. In spite of the fact that the fibrils are randomly oriented in three dimensions, the mechanical properties of the composites at room temperature have been tripled over those of the pure polystyrene. It seems certain that the relative properties at elevated temperatures should be better yet. The benefits from such enhanced properties will be available once a practical process is invented to incorporate these relatively cheap asbestos whiskers successfully into polymers.

S. Chwastiak

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REFERENCES

1. Deer, Howie, and Zussman, "Rock Forming Minerals," Vol. 3, Sheet Silicates, Wiley and Sons, Inc. (1962)

2. Editors, "Chrysotile Fibers - Filled or Hollow Tubes," Chem. & Eng. News, p. 34, Sept. 30, 1963

3. Pundsack, F. L., "The Properties of Asbestos.II The Density and Structure of Chrysotile," J. Phys. Chem. 60, pp. 361-364 (1963)

4. Naumann, A. W., and Dresher, W. H., "The Morphology of Chrysotile Asbestos as Inferred from Nitrogen Adsorption Data," Am. Mineralogist 51, pp. 711-725 (1966)

5. Whittaker, E.J.W., reported in Reference 2

6. Martinez, E., and Comer, J. J., "The Concentration and Study of the Interstitial Material in Chrysotile Asbestis," Am. Mineralogist 49, pp. 153-157 (1964)

7. Yada, K., "Study of Chrysotile Asbestos by a High Resolution Electron Microscope," Acta Crystallographica 23, 5, pp. 704-707 (1967)

8. Yada, K., Private Communication to F. A. Mumpton, April 12, 1968

9. Frazier, S. E., Bedford, J. A., Hower, J., and Kenney, M. E., "An Inherently Fibrous Organosilicon Polymer," Inorganic Chemistry 6, 9, pp. 1693-1696 (1967)

10. Mumpton, F. A., and Thompson, C. S., "Mineralogy of the Coalinga Asbestos Deposit," Research Report No. 65-50, Union Carbide Mining and Metals Division, Niagara Falls, New York, dated December 3, 1965

11. Dickson, G. L., "The Effects of Water Washing on the Brightness of High-Purity Asbestos," Memorandum to W. L. Carrick, Union Carbide Chemicals and Plastics Division, Niagara Falls, N.Y., dated Sept. 27, 1968

12. Ingalls, B. L., "The Optical Properties of Selected High-Purity Asbestos and Titanium Dioxide Products," Report of Project No. 885-28-2-60, File No. 9, Union Carbide Chemicals and Plastics Division, Niagara Falls, N.Y., dated March 8, 1968

13. Fripiat, J. J., and Faille, M. D., "Surface Properties and Texture of Chrysotile," Proceedings of the Fifteenth Conference on Clays and Clay Minerals, pp. 305-320

14. Medalia, I. M., "Morphology of Aggregates 1. Calculation of Shape and Bulkiness Factors; Applications to Computer Simulated Random Flocs," Preprints of Papers, 41st Nat. Coll. Symp., J. of Coll. and Interface Sc., pp. 107-118 (1967)

15. Sutherland, D. N., J. Coll. Sc. 22, p. 300 (1966)

Union Carbide trial exhibit Union Carbide 127: Properties of Colloidal Chrysotile Asbestos from the Coalinga Regi... Published by AsbestosClaims.Law
ACL Doc 19976 · Page 108 of 112 **asbestosclaims.law/library/19976/108**

16. Lapple, C. E., "Particle-Size Analysis and Analyzers," Chem. Eng., p. 149-156, May 20, 1968

17. Buttignol, V. and Gerhart, H. L., "Polymer Coatings, Pigment Dispersion - Annual Review," Ind. and Eng. Chem. 60, No. 8, pp. 68-79 (1968)

18. Dresher, W. H., Naumann, A. W., and Olsen, R., "A Study of the Mechanical Factors Influencing the Defiberillation of Asbestos," Research Report 64, Union Carbide Nuclear Div., Tuxedo Park, New York, dated Nov. 11, 1964

19. Markiewicz, E. J., "Asbestos Analysis Procedures," Union Carbide Chemicals and Plastics Div., Niagara Falls, N.Y., dated August 14, 1967

20. Faust, G. T., and Fahey, J. J., "The Serpentine Group Minerals," U.S.G.S. Prof. Papers 384A, 92 pp. (1962)

21. Yang, J. C., "The System Magnesia-Silica-Water Below 300°C," J. Am. Ceram. Soc. 43, 10, pp. 542-549 (1960)

22. Yang, J. C., "The Growth of Synthetic Chrysotile Fiber," Am. Mineralogist 46, pp. 748-752 (1961)

23. Naumann, A. W., and Dresher, W. H., "The Influence of Sample Texture on Chrysotile Dehydroxylation," Am. Mineralogist 51, pp. 1200-1211 (1966)

24. Martinez, E., "The Effect of Particle Size on the Thermal Properties of Serpentine Minerals," Am. Mineralogist 46, pp. 901-912 (1961)

25. Koetting, J. D., Progress Reports, Union Carbide Nuclear Div., Research Center, Tuxedo Park, N. Y., periods ending Feb. 15 through Sept. 15, 1964

26. Sinclair, W. E., "Asbestos, Its Origin, Production and Utilization," 2nd Ed., Mining Publications, Ltd., Salisburg House, London, 1959

27. Parks, G. A., and de Bruyn, P. L., "The Zero Point of Charge of Oxides," J. Phys. Chem. 66 (1962)

28. Luce, R. W., and Parks, G. A., "Solubilities and Surface Properties of Some Magnesium Silicates," Research in Mineral Engineering, Progress Report 66-2, Dept. of Mineral Engineering, Stanford Univ., dated Nov., 1966

29. Sillen, L. G., "Stability Constants of Metal-Ion Complexes," Chem. Soc. (London), p. 754 (1964)

30. Pundsack, F. L., and Reimschussel, G., "The Properties of Asbestos III Basicity of Chrysotile Suspensions," J. Phys. Chem. 60, pp. 1218-1222 (1956)

31. Orowan, E., Z. Physics 89, p. 634 (1934)

32. Wronski, J. P., "Fibers and Whiskers as Reinforcement," Asbestos, pp. 2-10, August 1968

33. Mehan, R. L, Sutton, W. H. and Herzog, J. A., "A Review of the Method of Measuring the Strength of Whiskers and Their Role in Reinforcing Ductile Metal Matrices," A.I.A.A. J. 4, 11, pp. 1889-1898 (1966)

Union Carbide trial exhibit Union Carbide 127: Properties of Colloidal Chrysotile Asbestos from the Coalinga Regi... Published by AsbestosClaims.Law
ACL Doc 19976 · Page 109 of 112 asbestosclaims.law/library/19976/109

34. Sears, G. W., "Ultimate Strength of Crystals p. 862 (1961)

35. Zukowski, R., and Gaze, R., "Tensile Strength of Asbestos," Nature 183, 4653 pp. 35-37 (1959)

36. Martinez, E., and Zucker, G. L., "Asbestos Ore Body Minerals Studied by Zeta Potential Measurements," J. Phys. Chem. 64, pp. 924-926 (1960)

37. Overbeek, J.Th.G., "Quantitative Interpretations of the Electrophoretic Velocity of Colloids," Chapter in Advances in Colloid Science, Vol. III, H. Mark and E.J.W. Verwey, Interscience Publishers, Inc., 1950

38. Abramson, H. A., Mayer, L. S., and Gorin, M. H., "Electrophoresis of Proteins," Reinhold Publishing Co. (1942)

39. Long, R. P., and Ross, S., "The Effects of the Overlap of Double Layers on Electrophoretic Mobilities of Polydisperse Suspensions," J. Coll. and Interface Sc. 26, 4, pp. 434-445 (1968)

40. Naumann, A. W., Progress Report, Union Carbide Nuclear Co., Tuxedo Park, N. Y., dated Sept. 15, 1963

41. Naumann, A. W., and Dresher, W. H., "Colloidal Suspensions of Chrysotile Asbestos: Specific Ion Effects," J. Phys. Chem. 70, pp. 288-291 (1966)

42. Grahams, D. C., "The Electrical Double Layer and the Theory of Electrocapillarity," Chemical Review 41, 3, pp. 411-501 (1947)

43. Overbeek, J.Th.G., "Donnan - E.M.F. and the Suspension Effect," J. Coll. Sc. 8, p. 593 (1953)

44. Li, H. L., "Adsorption of Organic and Inorganic Ions on Quartz," Sc. D. Thesis, M.I.T. (1958)

45. Verney, E.J.W., and Overbeek, J.Th.G., "Theory of the Stability of Lyophobic Colloids," Elsevier Publishing Co., N.Y., 1948

46. Matijevic, E., Levit, A. B., Janauer, G. E., "Coagulation and Reversal of Charge of Lyophobic Colloids by Hydrolyzed Metal Ions," J. Coll. and Interface Sc., 28, 1, pp. 10-18 (1968)

47. Shedlovsky, L., Ross, J., and Jacob, C. W., "The Effect of Certain Impurities on the Surface and Interfacial Tension of Aqueous Solutions of Sodium Sulfonate," J. Coll. Sc. 4, 25 (1949)

48. Jones, J. H., "General Colorimetric Method for Determination of Small Quantities of Sulfonated or Sulfated Surface Active Impurities," J. Assoc. Official Agri. Chemists, 28, p. 398 (1945)

49. Naumann, A. W., "Properties of Asbestos Suitable for Use in Cellulosic Paper," Tappi 48, 8, pp. 87A-89A (1965)

50. Dresher, W. H., Progress Report, Union Carbide Nuclear Co., Tuxedo Park, N. Y., dated April 15, 1963

Union Carbide trial exhibit Union Carbide 127: Properties of Colloidal Chrysotile Asbestos from the Coalinga Regi... Published by AsbestosClaims.Law
ACL Doc 19976 · Page 110 of 112 asbestosclaims.law/library/19976/110

51. Graham, D., "The Characterization of Physical Adsorption Systems III The Separate Effects of Pore Size and Surface Activity Upon the Adsorbent Capacities of Activated Carbon," J. Phys. Chem. 59, p. 896 (1955)

52. Braswell, E., "Evidence for Trimerization in Aqueous Solutions of Methylene Blue," J. Phys. Chem. 72, 7, pp. 2477-2482 (1968)

53. Michaelis, L., "Aggregation of Dyes, Reversible Polymerization and Molecular Aggregation," J. Phys. Chem. 54, 1 (1950)

54. Dresher, W. H., Progress Report, Union Carbide Nuclear Co., Tuxedo Park, N. Y., dated April 15, 1963

55. Naumann, A. W., and Dresher, W. H., "Colloidal Suspensions of Chrysotile Asbestos: Surface Charge Enhancement," J. Coll. and Interface Sc. 27, 1, pp. 133-140 (1968)

56. Matijevic, E., and Kolak, N., "Coagulation of Lyophobic Colloids by Metal Chelates," Preprints of Papers, 41st Nat. Coll. Symp., J. Coll. and Interface Sc., pp. 155-164 (1967)

57. Byrne, R. E., and Chwastiak, S., "The Chemical Modification of UCC Chrysotile Asbestos I Silica Modification for Viscosity Control," Report of Project No. 885-28-2-52, Union Carbide Chemicals and Plastics, Niagara Falls, N. Y., dated July 11, 1967

58. Lagerström, G., "Equilibrium Studies of Polyanions III Silicate Ions in $NaClO_4$ Medium," Acta Chemica Scandinavia 13, pp. 722-736 (1959)

59. Chwastiak, S., and Park, K., "Thickening UCAR Latexes with Asbestos Products," Report of Project No. 697-N29, File No. 10, Union Carbide Chemicals and Plastics, Niagara Falls, N. Y., dated March 6, 1968

60. Dickson, G. L., "Modified High-Purity Asbestos: The Evaluation of Silica-Treated Asbestos and Silica-Alumina Treated Asbestos as Paper-Making Additives," Interim Report, Union Carbide Chemicals and Plastics, Niagara Falls, N. Y., dated March 21, 1967

61. Mumpton, F. A., Chwastiak, S., and Park, K., "Properties of Union Carbide's Chrysotile Asbestos," Informal Report, Union Carbide Chemicals and Plastics, Niagara Falls, N. Y., dated May 31, 1967

62. Park, K., "Interaction of Water-Soluble Polymers with Chrysotile Asbestos, Rheological Studies," Report of Project No. 885-28-2-52, File No. 6, Union Carbide Chemicals and Plastics, Niagara Falls, N. Y., dated Dec. 29, 1967

63. Park, K., "The Thickening of Polyester Resins by R-G244 and R-G144," Union Carbide Report in preparation

64. Robinson, McDonald, Pask, J. A., and Fuerstenau, D. W., "Surface Charge of Alumina and Magnesia in Aqueous Media," J. Am. Ceram. Soc. 47, 10, pp. 516-520 (1964)

Union Carbide trial exhibit Union Carbide 127: Properties of Colloidal Chrysotile Asbestos from the Coalinga Regi... Published by AsbestosClaims.Law
ACL Doc 19976 · Page 111 of 112 **asbestosclaims.law/library/19976/111**

65. Parks, G. A., "The Isoelectric Points of Solid Oxides, Solid Hydroxides, and Aqueous Hydroxo Complex Systems," Chem. Rev. 65, p. 177 (1965)

66. Bryne, R. E., "UCC-Resin-Grade 144 Asbestos, A Whisker Reinforcement for Thermoplastic Resins," Report of Project No. 885-28-2-56, File No. 2, Union Carbide Chemicals and Plastics, Niagara Falls, N. Y., dated Aug. 25, 1967

67. Shafrin, E. G., and Zisman, W. A., "Preparation and Wettability of Terminally Chlorophenyl-Substituted Carboxylic Acid Films," A.C.S. Preprint of Organic Coatings and Plastics Chemistry 27 (2), pp. 11-26 (1967)

Union Carbide trial exhibit Union Carbide 127: Properties of Colloidal Chrysotile Asbestos from the Coalinga Regi... Published by AsbestosClaims.Law
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