

FROM: G. O. PRATT



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TO: DR. M. D. Solwell - 29

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ASBESTOS IN WATER IN
THE CHLOR-ALKALI INDUSTRY

B.L.

Presented at

The Chlorine Institute, Inc.
Seventeenth Chlorine Plant Managers' Seminar
New Orleans, Louisiana

February 5, 1975

D. R. Beaman, F. P. Boer, C. T. Lichy
R. J. Moolenaar, F. W. Spillers,
O. C. Taylor, and D. M. Young

The Dow Chemical Company

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H. W. F.

ASBESTOS IN WATER IN THE CHLOR-ALKALI INDUSTRY

R. J. Moolenaar, Dow Chemical U.S.
Midland, Michigan

(Presented at The Chlorine Institute, Inc.
Seventeenth Chlorine Plant Managers' Seminar
New Orleans, Louisiana, February 5, 1975)

Introduction

Dr. Charles Kramer, a physician in Dow's Medical Department, addressed the Fourteenth Plant Managers' Seminar at the 1971 Chlorine Institute meeting on the topic "Asbestos and Health" (1). He clearly pointed out that exposure to air-borne asbestos was of serious concern, and that control of industrial exposure to air-borne asbestos was essential. Good engineering procedures, good housekeeping, and careful monitoring of the workroom air were recommended as aids in the control. Since then, air-borne asbestos hazard control has been the topic of a NIOSH criteria document (2), an OSHA standard (3,4), and an EPA national emission standard (5).

Today I wish to focus attention on asbestos in water; to summarize briefly and comment on health effects of exposure to water-borne asbestos, to discuss the analysis of asbestos in water, and to review results obtained in the determination of asbestos levels in diaphragm cell chlor-alkali process streams. For those not acquainted with the use of asbestos in the chlor-alkali industry, a brief description is supplied in Appendix A. The chemical and physical properties of asbestos are summarized in Appendix B.

Health Effects of Asbestos

The health hazards associated with prolonged inhalation of asbestos have been established beyond reasonable doubt. Chronic effects have been found in workers involved in asbestos mining, milling, textile manufacture, and in the insulation industry. The most obvious is asbestosis, a condition not seen in the general population, characterized by breathing difficulties, wheezing, clubbed fingers (caused by oxygen deficiency) and cyanosis (blueness of the skin).

Cancer of the respiratory tract has also been attributed to prolonged asbestos inhalation. This has been discussed in several publications, most recently by Selikoff and co-workers (6) who studied cancer risk of insulation workers in the United States. They found an incidence of lung cancer about six times that expected in the general population. Selikoff et al. (7) concluded that if asbestos workers smoke cigarettes, the risk is greatly increased. Another form of cancer associated with

asbestos is mesothelioma, a very rare form of tumor in the general population. Mesotheliomas most commonly associated with asbestos occur in the linings of the lung and of the abdominal cavity. As a result of these and other observations, both OSHA and EPA have promulgated standards for control of exposure to air-borne asbestos.

Epidemiological data from asbestos insulation workers in the United States (6) also showed increased incidence of gastrointestinal cancer in exposed workmen compared with that expected in the general population. The asbestos exposure to the GI tract is thought to arise from nasal and throat clearing mechanisms, whereby about 90% of the dust inhaled is swallowed.

On the other hand, animal feeding studies have not confirmed this effect, even where amounts fed were extraordinarily large. In studies reported by Gross et al. (8), chrysotile asbestos fibers were fed to rats in food (5% of food weight) for 21 months. There were no deaths in this group and at autopsy no lesions could be found either grossly or microscopically. Another study was reported wherein groups of rats were fed asbestos mixed in butter at levels to provide 5-10 mg/rat weekly for 16-18 weeks. After six months, some rats were killed to assess pathological changes while the others were allowed to survive until they died a natural death. No increased incidences of tumors were observed. Other studies have shown similar results.

Very short fibers may not present a significant health hazard. Thus, Gross (9) concluded from his own experiments and from evidence in the literature that short-fibered asbestos dust, i.e. shorter than 5 microns, is incapable of causing fibrosis or cancer. Studies conducted at the National Cancer Institute by Stanton and Wrench (10) suggest that the carcinogenicity of asbestos and fibrous glass is primarily related to the structural shape of these materials rather than to physicochemical properties, and that fiber size is of critical importance. In a recent editorial, Stanton (11) claims that when the pleura of rats are exposed to asbestos, fibers less than 3 microns in diameter and longer than 20 microns are far more carcinogenic than fibers with diameters exceeding 3 microns (regardless of length) or shorter than 20 microns (regardless of diameter).

These views are consistent with the OSHA standard for air-borne asbestos which is concerned only with those fibers greater than 5 microns in length and a length to diameter ratio of 3 or greater.

The widespread distribution of asbestos in potable water, foods, and beverages has prompted concern over the effects of ingested asbestos. However, in 1973, the Advisory Committee on Asbestos Cancer of the International Agency for Research on Cancer (a division of the World Health Organization) reported their findings to the Agency Director. As part of their report (12), they state: "such evidence as there is does not indicate any risk from asbestos fibers present in water, food, beverage, or drugs." 409677 0297

Analysis of Asbestos in Water

Microscopy is the technique of choice for the analysis of asbestos because it gives information on fiber dimensions, and also it provides a direct measurement of the number of fibers per unit volume (expressed here in millions of fibers per liter, MFPL). These two parameters appear to be of prime importance in assessing the human physiological response to asbestos fibers. The data may also be converted to a weight basis if desired.* For particle sizes of interest in the chlor-alkali industry, 1 MFPL corresponds to about 0.01 microgram per liter or 0.00001 ppm (w/v). In most water samples of interest the concentration of asbestos is very low, the fibers have small diameters (0.034 - 0.7 microns) and the length to diameter ratio is usually less than 300. Such samples also contain other solids, some of which appear to be fibrous in the microscope, but are not asbestos. In fact, in our studies we have seen samples where the asbestos content ranged from 0-100% of the total fiber content.

To resolve these complicating factors, Dr. D. R. Beaman and D. M. File of our Midland Analytical Laboratories, have developed a quantitative method which includes fiber identification, based on the simultaneous measurement of morphology, crystal structure and chemical composition. They use a transmission electron microscope equipped with selected area electron diffraction and an energy dispersive spectrometer. The fiber concentrations are corrected for losses encountered during sample preparation and for ambiguities in the selected area electron diffraction patterns. Even with this sophisticated array of equipment (costing up to \$150,000), the time required for analysis of a single sample is about eight hours. Furthermore, the method is tedious - in samples with low fiber concentration, up to 2000 fields of view are counted to provide statistical significance. The results are believed to be accurate to within a factor of two or three, and this is by far the most reliable method currently available for the determination of asbestos in liquid samples. A detailed description of the method has been submitted for publication.

Levels of Asbestos in Water

Asbestos is ubiquitous. It has been widely found in natural waters throughout the North American continent. Literature reports indicate most waters examined so far contain some mineral fibers. Much of this is probably of natural origin.

*The formula for conversion of MFPL to a weight per unit volume basis is the following:

$$\text{Asbestos level in milligram/liter} = 2.3 \times 10^{-6} (\bar{L}) (\text{MFPL})$$

where $\bar{L}$ is the mean fiber length in microns. This assumes a fiber density of 2.5 g/ml and a solid particle with a diameter of 340 angstroms.

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Erosion from outcroppings of serpentine- or amphibole-containing rock by streams will transport fibers into potable water supplies. Regions of the United States known or believed to contain serpentine or amphibole minerals include a large portion of the mountainous regions of the Eastern and Western States (13,14). Underground water sources may also be subject to natural contamination but the available data are very limited (13).

Further distribution of asbestos into regions where serpentine or amphibole minerals are not indigenous can occur through transport by the wind. The presence of asbestos in melted snow, which contributes to fiber levels in local surface waters (15), indicates that wind may play an important role in the dispersal of asbestos.

Amphibole fibers in unfiltered drinking water from Lake Superior at Duluth, Minnesota, have been attributed to discharge of taconite tailings into the lake (16). Reported levels are 1 - 30 million fibers per liter (MFPL). Concentrations of asbestos fibers in water in 22 communities reported by Kay (17,18) vary from 0.1 to 3.9 MFPL. An earlier study (15) of tap water from three major cities gave values between 2.0 and 4.4 MFPL. One sample of drinking water drawn from a small lake in an asbestos mining region showed 170 MFPL (15).

Levels of 2 to 12 MFPL found in beers, sherries, ports, vermouths, and soft drinks have been attributed to the extensive use of asbestos in filtration processes (15). These levels correspond to only about 0.0001 mg asbestos in one bottle of beer.

Comparison of results from one study to another will be fraught with uncertainty until analytical methods are standardized. Analytical techniques differ considerably from one laboratory to another. Within the present state of the art, it is questionable whether any analysis based solely on electron microscopy is accurate to better than an order of magnitude (14). Finally, direct comparison of data for samples containing different asbestos minerals is intrinsically difficult.

Asbestos in Chlor-Alkali Process Streams

The above findings allow us to view in perspective the levels of asbestos encountered in diaphragm cell process streams and products. Our measurements, based on very limited sampling, have given the following results:

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<u>Sample</u>	<u>MFPL</u>	Mean Asbestos Levels	
		<u>Mean Length</u> <u>Microns</u>	<u>ppm (w/v)</u>
Cell Liquor			
Unfiltered	40,000	6	0.6
Filtered	400	1	0.001
50% Caustic	3,000	3	0.02
Wastewater Effluent	150	4	0.001
Steam Condensate (partially derived from caustic evaporators)	200*	-	-

*Determined by electron microscopy alone, with no chemical analysis or structure confirmation.

The distribution of fiber lengths is fairly broad, but very few fibers longer than 20 microns have been observed. The significance of the short average fiber lengths was discussed above.

The level in cell liquor, the product stream coming directly from the electrolytic cells, is by far the highest. Some of the fibers are returned to the cells with the salt precipitated during the evaporation process. Surprisingly, some fibers apparently are entrained in the steam from caustic evaporation. The implications of this observation will depend on the disposition of evaporator steam, which undoubtedly varies with manufacturing location.

Filtration of cell liquor resulted in 99% removal of asbestos by fiber count and over 99.9% removal on a weight basis. Work is in progress to optimize the conditions for fiber removal by this technique.

Conclusions

1. An analytical method has been developed which provides both positive identification and quantification of asbestos fibers in water. It is reliable but tedious and slow for routine use.
2. Results from very limited sampling show that process streams and products from diaphragm cell chlor-alkali plants contain asbestos, but average fiber lengths are 6 microns or less.
3. Most of the asbestos, especially the longer fibers, can be removed from cell liquor by filtration.

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4. Asbestos of natural origin or dispersed through man's activities is found in drinking water, beverages, food, and drugs.
5. Health authorities have stated they do not view the ingestion of small amounts of asbestos (particularly short fiber asbestos) as a risk to man.

Recommendations

1. An industry-wide cooperative program should be initiated to standardize analytical techniques for the determination of asbestos fibers in liquid samples and to develop a simplified method, e.g. atomic absorption, for routine use. The Chlorine Institute might serve as a focal point for this activity.
2. Each chlor-alkali producer using asbestos diaphragms should carry out a survey to determine the distribution of asbestos in his liquid effluent streams and products.
3. Water-borne asbestos originating from diaphragm cell operations has not been shown to be a health hazard; nevertheless, prudence dictates the need to develop methods for controlling the level of asbestos in products, process streams, and water effluents.
4. Medical and toxicological experts in government, academia and industry should cooperate to develop a better understanding of the effects of the ingestion of short fiber asbestos by human beings.

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APPENDIX A

USE OF ASBESTOS IN THE MANUFACTURE OF CHLORINE AND CAUSTIC SODA

The bulk of the chlorine and caustic soda produced in North America is by the electrolysis of sodium chloride brine using either the diaphragm cell process or the mercury cell process. The diaphragm process uses an asbestos separator between the anode side of the cell and the cathode side. The mercury process uses no separator.

In a typical diaphragm cell, saturated brine is fed to the anode compartment of the cell, then flows through the diaphragm to the cathode compartment where sodium hydroxide is formed. Flow through the diaphragm is maintained by a differential brine head. During operation, hydrogen and sodium hydroxide form at the cathode and chlorine forms at the anode. The two gases, chlorine and hydrogen, bubble up through the liquid on either side of the diaphragm and are removed from the top of the cell. The caustic soda together with the depleted brine leaves the cell as a dilute solution of sodium hydroxide and sodium chloride, known in the industry as "cell effluent" or "cell liquor." More concentrated solutions of caustic soda are obtained by evaporation of the cell liquor, whereupon sodium chloride crystallizes from solution.

The asbestos diaphragm is formed by vacuum drawing asbestos from a slurry directly on to the cathode, which is normally made of woven steel wire or punched steel plate.

The chlorine cell diaphragm serves several purposes:

1. Prevents mixing of the acid side of the cell (anolyte) with the basic side (catholyte).
2. Prevents mixing of the chlorine and hydrogen gas which can form explosive mixtures.
3. Prevents the hydroxyl ion, formed at the cathode, from migrating to the anode, which would cause discharge of oxygen and oxidation of the anode surface.

Asbestos has been valued as an excellent diaphragm material due to its relatively good chemical and temperature resistance. Also, unlike other materials, it tends to help regulate the electrolytic process by changing its actual porosity with changing electrical current loads and changing acid/basic conditions.

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APPENDIX B

CHEMICAL AND PHYSICAL PROPERTIES OF ASBESTOS

The term asbestos designates certain naturally-occurring inorganic fibers belonging to the amphibole and serpentine groups of minerals. It also designates an important industrial commodity which is heat resistant, chemically resistant, and capable of being spun into flexible yarn. These unique properties make asbestos an exceptionally useful material, and consumption in the United States has risen rapidly to the 800,000 ton per year level. Its application in the chlor-alkali industry represents just one of over 300 industrial uses of asbestos, which include very large volumes consumed in asbestos cement, floor tiles, asbestos paper, asbestos textiles, friction materials, and gaskets (1). The chlor-alkali industry uses less than 1% of the total asbestos produced.

Chrysotile is the most important commercial form of asbestos and is the form generally used in the chlor-alkali industry. It is a member of the serpentine group of phyllosilicates. It is usually mined from large bodies of serpentinite rock, where it occurs in cross- or slip-fiber veins (2). These veins vary in thickness from a fraction of a millimeter to several centimeters. Non-fibrous varieties of serpentine minerals (antigorite, lizardite) are also usually present, as are small quantities of brucite and magnetite. The remaining five minerals classified as asbestos--amosite, anthophyllite, tremolite, actinolite, and crocidolite--belong to the amphibole group of inosilicates. Together the amphibole forms of asbestos account for less than 5% of commercial production. Consumption in the chlor-alkali industry is also predominantly of chrysotile asbestos, although crocidolite (or "blue asbestos") has occasionally been used.

Asbestos minerals have quite different elemental compositions, and show significant differences in specific gravity and refractive index (3) as seen below:

Mineral	Empirical Formula	Specific Gravity	Refractive Index
Chrysotile	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	2.4 - 2.5	1.49 - 1.57
Tremolite	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	2.9 - 3.2	1.60 - 1.65
Actinolite	$\text{Ca}_2(\text{Mg}, \text{Fe}^{2+})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	3.0 - 3.5	1.62 - 1.68
Anthophyllite	$\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	2.9 - 3.5	1.60 - 1.66
Amosite	$(\text{Mg}, \text{Fe}^{2+})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	2.6 - 3.0	1.56 - 1.70
Crocidolite	$\text{Na}_2\text{Fe}_3^{2+}\text{Fe}_2^{3+}\text{Si}_8\text{O}_{22}(\text{OH})_2$	3.0 - 3.5	1.69 - 1.71

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The ideal chemical composition of chrysotile approximates 44% MgO, 43% SiO₂, and 13% H₂O, although small amounts of other elements such as iron, aluminum, and nickel may substitute for magnesium in the structure (2,4). Chrysotile will decompose under severely acid conditions (5), whereby essentially all the MgO and H₂O are dissolved, as indicated by a 56% weight loss, leaving² behind a silica skeleton. Amphibole forms of asbestos possess superior resistance to acid.

Chrysotile also decomposes at elevated temperatures (6,7) and exhibits an intense dehydroxylation endotherm at approximately 650°C and an exotherm at 820°C which is believed to be associated with the formation of forsterite (Mg₂SiO₄) and/or enstatite (MgSiO₃).

The nature of chrysotile bears an important relationship to its atomic structure. Together with the other serpentine minerals, lizardite and antigorite, chrysotile is classed as a phyllosilicate or "sheet-like" silicate. All three minerals are considered polymorphs of the same basic chemical composition, and are built up of similar, infinite, two-dimensional sheets. Each individual sheet consists of a silicate layer and a magnesium hydroxide layer, with an overall thickness of 7.3Å.

A small, but important, difference in the preferred lattice spacing of the silicate and magnesium hydroxide layers appears to cause the wide variations in morphology of serpentine minerals. In chrysotile, the strain caused by this difference is relieved when several adjacent sheets "curl up" to form the hollow tube structure that constitutes an individual chrysotile filament. High resolution electron micrographs of chrysotile fibers in cross-section have shown both the multiple spiral pattern and the characteristic hollow center of this structure very clearly (8). The three known varieties of chrysotile are related to the manner in which these spirals form. Clino-chrysotile, the most common type, curves around the a axis of its monoclinic unit cell. In ortho-chrysotile, the unit cell is orthorhombic, but curvature remains around a. A rarer form, parachrysotile, also has an orthorhombic unit cell but is curved about the b axis.

Antigorite and lizardite must relieve the same strain, but they do so by quite different mechanisms: antigorite forms a "wavy" sheet structure with a very long unit cell repeat, while lizardite generally contains other elements that substitute within the silicate or magnesium hydroxide layers in a manner that equalizes the lattice spacings. It is interesting to note that, although the differences in morphology between the filament structure of chrysotile and the plate-like or lath-like habit of antigorite or lizardite are conspicuous, the similarities in structure on the atomic scale make it relatively difficult to distinguish these serpentine minerals from each other by X-ray powder diffraction (2).

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The characteristic morphology of chrysotile fibers can be observed with the transmission electron microscope, an important aid in their identification. The interior cavity of a chrysotile fiber is usually visible and has an average inner diameter of 80-100Å. However, a hollow center is not always seen (8), and amorphous material may be observed within the interior of the filaments (2). Outer diameters of chrysotile fibers range from 150 to 1000Å. The mean diameter is about 340Å in the industrial samples we have examined, but other reports (2,8) cite mean diameters from 250 to 500Å. The narrowness of its individual filaments gives rise to one of the most important physical properties of chrysotile asbestos, namely, its very high specific surface area which can be in excess of 10 m²/g. Fibers of the amphibole varieties of asbestos are considerably larger in cross-section (9).

The ratio of length to diameter, known as the aspect ratio, may be quite large for individual chrysotile fibrils. Aspect ratios of several hundred are normal for most vein materials, but very short fibers with aspect ratios of 5 to 10 may be found in the serpentinite matrix of many ore bodies (2). Mean aspect ratios in samples related to the chlor-alkali process range from about 30 to over 400, corresponding to average lengths up to about 15 microns. Obviously, any processing which tends to shear or grind the asbestos will both increase the number of fibers and decrease their aspect ratio.

Chrysotile may occur either as individual fibrils or as bundles of fibrils. Since the diameters of single chrysotile filaments are only a fraction of the wave length of visible light, individual fibers cannot be resolved visually, even with the best optical microscope. The measurement of chrysotile by optical methods is therefore confined to material which may occur as bundles or other filamentary masses.

The electron microscope is by far the most useful instrument for identification and quantification of individual chrysotile fibers. With an instrument equipped with accessories for selected area electron diffraction and energy dispersive X-ray spectroscopy, the morphological data can be supplemented with the diffraction pattern and quantitative elemental identification applied to individual particles. When somewhat larger quantities are involved, a successful analytical technique--atomic absorption spectroscopy (10), infrared spectroscopy (11), X-ray diffraction (12), differential thermal analysis (6), optical microscopy/index of refraction (3)--can be devised by exploiting some of the characteristic chemical and physical properties discussed above.

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Analysis of Asbestos in Water

Microscopy is the technique of choice for the analysis of asbestos because it gives information on fiber dimensions, and also it provides a direct measurement of the number of fibers per unit volume (expressed here in millions of fibers per liter, MFPL). These two parameters appear to be of prime importance in assessing the human physiological response to asbestos fibers. The data may also be converted to a weight basis if desired.* For particle sizes of interest in the chlor-alkali industry, 1 MFPL corresponds to about 0.01 microgram per liter or 0.00001 ppm (w/v). In most water samples of interest the concentration of asbestos is very low, the fibers have small diameters (0.034 - 0.7 microns) and the length to diameter ratio is usually less than 300. Such samples also contain other solids, some of which appear to be fibrous in the microscope, but are not asbestos. In fact, in our studies we have seen samples where the asbestos content ranged from 0-100% of the total fiber content.

To resolve these complicating factors, Dr. D. R. Beaman and D. M. File of our Midland Analytical Laboratories, have developed a quantitative method which includes fiber identification, based on the simultaneous measurement of morphology, crystal structure and chemical composition. They use a transmission electron microscope equipped with selected area electron diffraction and an energy dispersive spectrometer. The fiber concentrations are corrected for losses encountered during sample preparation and for ambiguities in the selected area electron diffraction patterns. Even with this sophisticated array of equipment (costing up to \$150,000), the time required for analysis of a single sample is about eight hours. Furthermore, the method is tedious - in samples with low fiber concentration, up to 2000 fields of view are counted to provide statistical significance. The results are believed to be accurate to within a factor of two or three, and this is by far the most reliable method currently available for the determination of asbestos in liquid samples. A detailed description of the method has been submitted for publication.

Levels of Asbestos in Water

Asbestos is ubiquitous. It has been widely found in natural waters throughout the North American continent. Literature reports indicate most waters examined so far contain some mineral fibers. Much of this is probably of natural origin.

*The formula for conversion of MFPL to a weight per unit volume basis is the following:

$$\text{Asbestos level in milligram/liter} = 2.3 \times 10^{-6} (\bar{L}) (\text{MFPL})$$

where $\bar{L}$ is the mean fiber length in microns. This assumes a fiber density of 2.5 g/ml and a solid particle with a diameter of 340 angstroms.

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Erosion from outcroppings of serpentine- or amphibole-containing rock by streams will transport fibers into potable water supplies. Regions of the United States known or believed to contain serpentine or amphibole minerals include a large portion of the mountainous regions of the Eastern and Western States (13,14). Underground water sources may also be subject to natural contamination but the available data are very limited (13).

Further distribution of asbestos into regions where serpentine or amphibole minerals are not indigenous can occur through transport by the wind. The presence of asbestos in melted snow, which contributes to fiber levels in local surface waters (15), indicates that wind may play an important role in the dispersal of asbestos.

Amphibole fibers in unfiltered drinking water from Lake Superior at Duluth, Minnesota, have been attributed to discharge of taconite tailings into the lake (16). Reported levels are 1 - 30 million fibers per liter (MFPL). Concentrations of asbestos fibers in water in 22 communities reported by Kay (17,18) vary from 0.1 to 3.9 MFPL. An earlier study (15) of tap water from three major cities gave values between 2.0 and 4.4 MFPL. One sample of drinking water drawn from a small lake in an asbestos mining region showed 170 MFPL (15).

Levels of 2 to 12 MFPL found in beers, sherries, ports, vermouths, and soft drinks have been attributed to the extensive use of asbestos in filtration processes (15). These levels correspond to only about 0.0001 mg asbestos in one bottle of beer.

Comparison of results from one study to another will be fraught with uncertainty until analytical methods are standardized. Analytical techniques differ considerably from one laboratory to another. Within the present state of the art, it is questionable whether any analysis based solely on electron microscopy is accurate to better than an order of magnitude (14). Finally, direct comparison of data for samples containing different asbestos minerals is intrinsically difficult.

Asbestos in Chlor-Alkali Process Streams

The above findings allow us to view in perspective the levels of asbestos encountered in diaphragm cell process streams and products. Our measurements, based on very limited sampling, have given the following results:

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<u>Sample</u>	<u>MFPL</u>	Mean Asbestos Levels	
		<u>Mean Length Microns</u>	<u>ppm (w/v)</u>
Cell Liquor			
Unfiltered	40,000	6	0.6
Filtered	400	1	0.001
50% Caustic	3,000	3	0.02
Wastewater Effluent	150	4	0.001
Steam Condensate (partially derived from caustic evaporators)	200*	-	-

*Determined by electron microscopy alone, with no chemical analysis or structure confirmation.

The distribution of fiber lengths is fairly broad, but very few fibers longer than 20 microns have been observed. The significance of the short average fiber lengths was discussed above.

The level in cell liquor, the product stream coming directly from the electrolytic cells, is by far the highest. Some of the fibers are returned to the cells with the salt precipitated during the evaporation process. Surprisingly, some fibers apparently are entrained in the steam from caustic evaporation. The implications of this observation will depend on the disposition of evaporator steam, which undoubtedly varies with manufacturing location.

Filtration of cell liquor resulted in 99% removal of asbestos by fiber count and over 99.9% removal on a weight basis. Work is in progress to optimize the conditions for fiber removal by this technique.

Conclusions

1. An analytical method has been developed which provides both positive identification and quantification of asbestos fibers in water. It is reliable but tedious and slow for routine use.
2. Results from very limited sampling show that process streams and products from diaphragm cell chlor-alkali plants contain asbestos, but average fiber lengths are 6 microns or less.
3. Most of the asbestos, especially the longer fibers, can be removed from cell liquor by filtration.

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4. Asbestos of natural origin or dispersed through man's activities is found in drinking water, beverages, food, and drugs.
5. Health authorities have stated they do not view the ingestion of small amounts of asbestos (particularly short fiber asbestos) as a risk to man.

Recommendations

1. An industry-wide cooperative program should be initiated to standardize analytical techniques for the determination of asbestos fibers in liquid samples and to develop a simplified method, e.g. atomic absorption, for routine use. The Chlorine Institute might serve as a focal point for this activity.
2. Each chlor-alkali producer using asbestos diaphragms should carry out a survey to determine the distribution of asbestos in his liquid effluent streams and products.
3. Water-borne asbestos originating from diaphragm cell operations has not been shown to be a health hazard; nevertheless, prudence dictates the need to develop methods for controlling the level of asbestos in products, process streams, and water effluents.
4. Medical and toxicological experts in government, academia and industry should cooperate to develop a better understanding of the effects of the ingestion of short fiber asbestos by human beings.

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APPENDIX A

USE OF ASBESTOS IN THE MANUFACTURE OF CHLORINE AND CAUSTIC SODA

The bulk of the chlorine and caustic soda produced in North America is by the electrolysis of sodium chloride brine using either the diaphragm cell process or the mercury cell process. The diaphragm process uses an asbestos separator between the anode side of the cell and the cathode side. The mercury process uses no separator.

In a typical diaphragm cell, saturated brine is fed to the anode compartment of the cell, then flows through the diaphragm to the cathode compartment where sodium hydroxide is formed. Flow through the diaphragm is maintained by a differential brine head. During operation, hydrogen and sodium hydroxide form at the cathode and chlorine forms at the anode. The two gases, chlorine and hydrogen, bubble up through the liquid on either side of the diaphragm and are removed from the top of the cell. The caustic soda together with the depleted brine leaves the cell as a dilute solution of sodium hydroxide and sodium chloride, known in the industry as "cell effluent" or "cell liquor." More concentrated solutions of caustic soda are obtained by evaporation of the cell liquor, whereupon sodium chloride crystallizes from solution.

The asbestos diaphragm is formed by vacuum drawing asbestos from a slurry directly on to the cathode, which is normally made of woven steel wire or punched steel plate.

The chlorine cell diaphragm serves several purposes:

1. Prevents mixing of the acid side of the cell (anolyte) with the basic side (catholyte).
2. Prevents mixing of the chlorine and hydrogen gas which can form explosive mixtures.
3. Prevents the hydroxyl ion, formed at the cathode, from migrating to the anode, which would cause discharge of oxygen and oxidation of the anode surface.

Asbestos has been valued as an excellent diaphragm material due to its relatively good chemical and temperature resistance. Also, unlike other materials, it tends to help regulate the electrolytic process by changing its actual porosity with changing electrical current loads and changing acid/basic conditions.

APPENDIX B

CHEMICAL AND PHYSICAL PROPERTIES OF ASBESTOS

The term asbestos designates certain naturally-occurring inorganic fibers belonging to the amphibole and serpentine groups of minerals. It also designates an important industrial commodity which is heat resistant, chemically resistant, and capable of being spun into flexible yarn. These unique properties make asbestos an exceptionally useful material, and consumption in the United States has risen rapidly to the 800,000 ton per year level. Its application in the chlor-alkali industry represents just one of over 300 industrial uses of asbestos, which include very large volumes consumed in asbestos cement, floor tiles, asbestos paper, asbestos textiles, friction materials, and gaskets (1). The chlor-alkali industry uses less than 1% of the total asbestos produced.

Chrysotile is the most important commercial form of asbestos and is the form generally used in the chlor-alkali industry. It is a member of the serpentine group of phyllosilicates. It is usually mined from large bodies of serpentinite rock, where it occurs in cross- or slip-fiber veins (2). These veins vary in thickness from a fraction of a millimeter to several centimeters. Non-fibrous varieties of serpentine minerals (antigorite, lizardite) are also usually present, as are small quantities of brucite and magnetite. The remaining five minerals classified as asbestos--amosite, anthophyllite, tremolite, actinolite, and crocidolite--belong to the amphibole group of inosilicates. Together the amphibole forms of asbestos account for less than 5% of commercial production. Consumption in the chlor-alkali industry is also predominantly of chrysotile asbestos, although crocidolite (or "blue asbestos") has occasionally been used.

Asbestos minerals have quite different elemental compositions, and show significant differences in specific gravity and refractive index (3) as seen below:

Mineral	Empirical Formula	Specific Gravity	Refractive Index
Chrysotile	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	2.4 - 2.5	1.49 - 1.57
Tremolite	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	2.9 - 3.2	1.60 - 1.65
Actinolite	$\text{Ca}_2(\text{Mg}, \text{Fe}^{2+})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	3.0 - 3.5	1.52 - 1.63
Anthophyllite	$\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	2.9 - 3.5	1.60 - 1.66
Amosite	$(\text{Mg}, \text{Fe}^{2+})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	2.6 - 3.0	1.66 - 1.70
Crocidolite	$\text{Na}_2\text{Fe}_3^{2+}\text{Fe}_2^{3+}\text{Si}_8\text{O}_{22}(\text{OH})_2$	3.0 - 3.5	1.69 - 1.71

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The ideal chemical composition of chrysotile approximates 44% MgO, 43% SiO₂, and 13% H₂O, although small amounts of other elements such as iron, aluminum, and nickel may substitute for magnesium in the structure (2,4). Chrysotile will decompose under severely acid conditions (5), whereby essentially all the MgO and H₂O are dissolved, as indicated by a 56% weight loss, leaving behind a silica skeleton. Amphibole forms of asbestos possess superior resistance to acid.

Chrysotile also decomposes at elevated temperatures (6,7) and exhibits an intense dehydroxylation endotherm at approximately 650°C and an exotherm at 820°C which is believed to be associated with the formation of forsterite (Mg₂SiO₄) and/or enstatite (MgSiO₃).

The nature of chrysotile bears an important relationship to its atomic structure. Together with the other serpentine minerals, lizardite and antigorite, chrysotile is classed as a phyllosilicate or "sheet-like" silicate. All three minerals are considered polymorphs of the same basic chemical composition, and are built up of similar, infinite, two-dimensional sheets. Each individual sheet consists of a silicate layer and a magnesium hydroxide layer, with an overall thickness of 7.3Å.

A small, but important, difference in the preferred lattice spacing of the silicate and magnesium hydroxide layers appears to cause the wide variations in morphology of serpentine minerals. In chrysotile, the strain caused by this difference is relieved when several adjacent sheets "curl up" to form the hollow tube structure that constitutes an individual chrysotile filament. High resolution electron micrographs of chrysotile fibers in cross-section have shown both the multiple spiral pattern and the characteristic hollow center of this structure very clearly (8). The three known varieties of chrysotile are related to the manner in which these spirals form. Clino-chrysotile, the most common type, curves around the a axis of its monoclinic unit cell. In ortho-chrysotile, the unit cell is orthorhombic, but curvature remains around a. A rarer form, parachrysotile, also has an orthorhombic unit cell but is curved about the b axis.

Antigorite and lizardite must relieve the same strain, but they do so by quite different mechanisms: antigorite forms a "wavy" sheet structure with a very long unit cell repeat, while lizardite generally contains other elements that substitute within the silicate or magnesium hydroxide layers in a manner that equalizes the lattice spacings. It is interesting to note that, although the differences in morphology between the filament structure of chrysotile and the plate-like or lath-like habit of antigorite or lizardite are conspicuous, the similarities in structure on the atomic scale make it relatively difficult to distinguish these serpentine minerals from each other by X-ray powder diffraction (2).

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The characteristic morphology of chrysotile fibers can be observed with the transmission electron microscope, an important aid in their identification. The interior cavity of a chrysotile fiber is usually visible and has an average inner diameter of 80-100Å. However, a hollow center is not always seen (8), and amorphous material may be observed within the interior of the filaments (2). Outer diameters of chrysotile fibers range from 150 to 1000Å. The mean diameter is about 340Å in the industrial samples we have examined, but other reports (2,8) cite mean diameters from 250 to 500Å. The narrowness of its individual filaments gives rise to one of the most important physical properties of chrysotile asbestos, namely, its very high specific surface area which can be in excess of $10 \text{ m}^2/\text{g}$. Fibers of the amphibole varieties of asbestos are considerably larger in cross-section (9).

The ratio of length to diameter, known as the aspect ratio, may be quite large for individual chrysotile fibrils. Aspect ratios of several hundred are normal for most vein materials, but very short fibers with aspect ratios of 5 to 10 may be found in the serpentinite matrix of many ore bodies (2). Mean aspect ratios in samples related to the chlor-alkali process range from about 30 to over 400, corresponding to average lengths up to about 15 microns. Obviously, any processing which tends to shear or grind the asbestos will both increase the number of fibers and decrease their aspect ratio.

Chrysotile may occur either as individual fibrils or as bundles of fibrils. Since the diameters of single chrysotile filaments are only a fraction of the wave length of visible light, individual fibers cannot be resolved visually, even with the best optical microscope. The measurement of chrysotile by optical methods is therefore confined to material which may occur as bundles or other filamentary masses.

The electron microscope is by far the most useful instrument for identification and quantification of individual chrysotile fibers. With an instrument equipped with accessories for selected area electron diffraction and energy dispersive X-ray spectroscopy, the morphological data can be supplemented with the diffraction pattern and quantitative elemental identification applied to individual particles. When somewhat larger quantities are involved, a successful analytical technique--atomic absorption spectroscopy (10), infrared spectroscopy (11), X-ray diffraction (12), differential thermal analysis (6), optical microscopy/index of refraction (3)--can be devised by exploiting some of the characteristic chemical and physical properties discussed above.

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DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
CENTER FOR DISEASE CONTROL

f-asker

August 8, 1975

NATIONAL INSTITUTE FOR OCCUPATIONAL
SAFETY AND HEALTH
5600 FISHERS LANE
ROCKVILLE, MARYLAND 20852

Dear Colleague:

This communication is intended to alert you to recently gathered information indicating a potential health hazard for persons exposed to asbestos during the servicing of motor vehicle brake and clutch assemblies.

On July 21, 1975, the National Institute for Occupational Safety and Health convened a meeting of government and university scientists, industry representatives, and labor union officials to discuss the present state of knowledge with respect to this problem. Data was presented by investigators from the Mount Siani School of Medicine in New York City indicating that workers engaged in the maintenance and repair of automobile and truck brake linings are exposed to potentially hazardous levels of airborne asbestos dust. Specific brake servicing operations studied included blow-out of automobile drum brake assemblies, grinding of used truck brake linings, and bevelling of new truck brake linings. Average peak asbestos air concentrations for these three activities based on personal samples taken within ten feet of the operator were, respectively, 10.5, 3.75, and 37.3 fibers (>5 microns in length) per ml. An analysis of samples of brake drum dust revealed that almost all of the asbestos fibers found were shorter than 0.4 microns in length.

Previous studies of the extent of asbestos emissions from automobile brake lining wear showed that only a very small fraction of the original asbestos content of the brake lining is found in brake drum dust (Ref. 1-3). It was presumed that this is due to thermal degradation of the fibers during braking. The present findings indicate that enough asbestos is preserved to produce significant exposures during certain brake servicing procedures.

The full extent of asbestos-related disease in brake servicing personnel is not known at present because this particular occupational group has not been studied systematically up to now. However, a review of the scientific literature on the association between asbestos exposure and mesothelial tumors of the pleura and peritoneum has revealed at least four cases of these rare tumors in persons who were employed in jobs involving automobile brake servicing (Ref. 4-6).

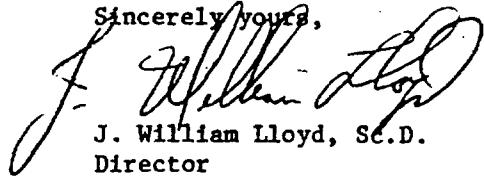
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For your information and guidance, we are enclosing pertinent references, estimates of the population at risk, a NIOSH interim recommendation for brake and clutch servicing procedures, and a copy of the Department of Labor standard covering exposure to asbestos in the work place.

The environmental studies of brake lining servicing operations outlined above together with observations of mesothelial tumors in persons so employed affirms the necessity for instituting and maintaining recommended control measures in this industry so that the health hazards of asbestos are minimized.

Sincerely yours,



J. William Lloyd, Sc.D.
Director
Office of Occupational Health
Surveillance and Biometrics

Enclosures

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ESTIMATES OF THE WORKFORCE POTENTIALLY EXPOSED TO ASBESTOS
IN THE MANUFACTURING AND SERVICING OF BRAKE LININGS AND CLUTCHES

Auto Mechanics	833,535
Garage Workers	67,679
Manufacture (original and rebuilding)	<u>6,657</u>
TOTAL	907,871

SOURCE: Adapted from 1972 Census of Manufacturers, 1972 County Business Patterns, and Census of Population: 1970 Occupation by Industry (all are Department of Commerce, Census Bureau publications)

RECOMMENDED (INTERIM) PROCEDURES FOR
ASBESTOS BRAKE AND CLUTCH SERVICING

The National Institute for Occupational Safety and Health (NIOSH) has research underway concerning dust exposures during brake and clutch servicing. Due to preliminary data demonstrating significant asbestos exposures during presently used brake and clutch servicing techniques, NIOSH has reviewed alternate techniques whereby asbestos exposures are reduced. The following are interim procedures recommended by NIOSH to minimize dust exposures.

1. If possible, an area shall be designated for all brake and clutch repairs. Entrances into this area shall be posted with an asbestos exposure warning sign as follows:

Asbestos
Dust Hazard
Avoid Breathing Dust
Wear Assigned Protective Equipment
Do Not Remain in Area Unless Your Work Requires It
Breathing Asbestos Dust May Cause Asbestosis and Cancer

2. During brake servicing, an air purifying respirator, either single use or with replaceable particulate filter(s), as approved by the Mining Enforcement and Safety Administration (formerly Bureau of Mines) or NIOSH, shall be worn during all procedures starting with the removal of the wheels and including reassembly. During manual clutch servicing, such a respirator shall be worn during removal and cleaning of the clutch, pressure plate and housing assembly and during installation of the new clutch assembly.
3. Dust shall first be cleaned from brake drums, brake backing plates, brake assemblies and clutch assemblies using an industrial type vacuum cleaner equipped with a high efficiency filter system (>99% efficiency for 0.3 μ m diameter aerosols). After vacuum cleaning, any remaining dust shall be removed using a rag soaked in water and wrung until nearly dry. Under no circumstances shall compressed air or dry brushing be used for cleaning.
4. During arcing and riveting operations, an approved respirator, as described in (2) above, shall be worn. Grinding (arc) machines shall be provided with local exhaust ventilation such that worker exposures are maintained at least below the 1976 OSHA asbestos standard (29 CFR 1910.1001).* At a minimum, the dust bag of the arcing machine shall be removed and replaced with the hose of the high efficiency industrial vacuum described in (3) above.

5. Industrial vacuum cleaner bags containing asbestos dust and cloths used for wiping brake and clutch assemblies shall be sealed in plastic bags and labeled with the following warning label printed in letters of sufficient size and contrast to be readily visible and legible:

Caution
Contains Asbestos Fibers
Avoid Breathing Dust
Breathing Asbestos Dust May Cause Asbestosis and Cancer

All asbestos waste shall be disposed of in accordance with the OSHA asbestos regulation, 29 CFR 1910.1001(h). During removal of vacuum bags, an approved respirator, as described in (2) above, shall be worn.

6. All floor cleaning in areas where brakes and clutches are repaired shall be done with the high efficiency industrial vacuum cleaner as described in (3) above. Grinding (arcing) machines shall also be cleaned with such a vacuum cleaner and any remaining dust wiped with a damp cloth. An approved respirator, as described in (2) above, shall be used during this cleaning.
7. Although adherence to the above procedures should minimize any contamination of work clothing, it is required that the appropriate portions of the OSHA regulations on asbestos (29 CFR 1910.1001(d) (3 and 4)) concerning special clothing, change rooms, etc. be followed.

NOTE: Strict adherence to the above procedures should minimize exposures to mechanics during brake and clutch servicing. These are interim recommendations and are subject to revision pending results of ongoing NIOSH research.

- * Section 1910.1001 of the Code of Federal Regulations was formerly Section 1910.93a. This change was noted in the Federal Register, May 28, 1975.

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air, as determined by the method prescribed in paragraph (e) of this section.

(c) *Methods of compliance*—(1) *Engineering methods*. (i) *Engineering controls*. Engineering controls, such as, but not limited to, isolation, enclosure, exhaust ventilation, and dust collection, shall be used to meet the exposure limits prescribed in paragraph (b) of this section.

(ii) *Local exhaust ventilation*. (a) Local exhaust ventilation and dust collection systems shall be designed, constructed, installed, and maintained in accordance with the American National Standard Fundamentals Governing the Design and Operation of Local Exhaust Systems, ANSI Z9.2-1971, which is incorporated by reference herein.

(b) See § 1910.6 concerning the availability of ANSI Z9.2-1971, and the maintenance of a historic file in connection therewith. The address of the American National Standards Institute is given in § 1910.100.

(iii) *Particular tools*. All hand-operated and power-operated tools which may produce or release asbestos fibers in excess of the exposure limits prescribed in paragraph (b) of this section, such as, but not limited to, saws, scorers, abrasive wheels, and drifts, shall be provided with local exhaust ventilation systems in accordance with subdivision (ii) of this subparagraph.

(2) *Work practices*—(i) *Wet methods*. Insofar as practicable, asbestos shall be handled, mixed, applied, removed, cut, scored, or otherwise worked in a wet state sufficient to prevent the emission of airborne fibers in excess of the exposure limits prescribed in paragraph (b) of this section, unless the usefulness of the product would be diminished thereby.

(ii) *Particular products and operations*. No asbestos cement, mortar, coating, grout, plaster, or similar material containing asbestos shall be removed from bags, cartons, or other containers in which they are shipped, without being either wetted, or enclosed, or ventilated so as to prevent effectively the release of airborne asbestos fibers in excess of the limits prescribed in paragraph (b) of this section.

(iii) *Spraying, demolition, or removal*. Employees engaged in the spraying of asbestos, the removal, or demolition of pipes, structures, or equipment covered or insulated with asbestos, and in the removal or demolition of asbestos insulation or coverings shall be provided with respiratory equipment in accordance with paragraph (d) (2) (iii) of this section and with special clothing in accordance with paragraph (d) (3) of this section.

(d) *Personal protective equipment*—(1) Compliance with the exposure limits prescribed by paragraph (b) of this section may not be achieved by the use of respirators or shift rotation of employees, except:

(i) During the time period necessary to install the engineering controls and to institute the work practices required by paragraph (c) of this section;

§ 1910.93a Asbestos.

(a) *Definitions*. For the purpose of this section, (1) "Asbestos" includes chrysotile, amosite, crocidolite, tremolite, anthophyllite, and actinolite.

(2) "Asbestos fibers" means asbestos fibers longer than 5 micrometers.

(b) *Permissible exposure to airborne concentrations of asbestos fibers*—(1) *Standard effective July 7, 1972*. The 8-hour time-weighted average airborne concentrations of asbestos fibers to which any employee may be exposed shall not exceed five fibers, longer than 5 micrometers, per cubic centimeter of air, as determined by the method prescribed in paragraph (e) of this section.

(2) *Standard effective July 1, 1976*. The 8-hour time-weighted average airborne concentrations of asbestos fibers to which any employee may be exposed shall not exceed two fibers, longer than 5 micrometers, per cubic centimeter of air, as determined by the method prescribed in paragraph (e) of this section.

(3) *Ceiling concentration*. No employee shall be exposed at any time to airborne concentrations of asbestos fibers in excess of 10 fibers, longer than 5 micrometers, per cubic centimeter of

(ii) In work situations in which the methods prescribed in paragraph (c) of this section are either technically not feasible or feasible to an extent insufficient to reduce the airborne concentrations of asbestos fibers below the limits prescribed by paragraph (b) of this section; or

(iii) In emergencies.

(iv) Where both respirators and personnel rotation are allowed by subdivisions (i), (ii), or (iii) of this subparagraph, and both are practicable, personnel rotation shall be preferred and used.

(2) Where a respirator is permitted by subparagraph (1) of this paragraph, it shall be selected from among those approved by the Bureau of Mines, Department of the Interior, or the National Institute for Occupational Safety and Health, Department of Health, Education, and Welfare, under the provisions of 30 CFR Part 11 (37 F.R. 6244, Mar. 25, 1972), and shall be used in accordance with subdivisions (i), (ii), (iii), and (iv) of this subparagraph.

(i) *Air purifying respirators.* A reusable or single use air purifying respirator, or a respirator described in subdivision (ii) or (iii) of this subparagraph, shall be used to reduce the concentrations of airborne asbestos fibers in the respirator below the exposure limits prescribed in paragraph (b) of this section, when the ceiling or the 8-hour time-weighted average airborne concentrations of asbestos fibers are reasonably expected to exceed no more than 10 times those limits.

(ii) *Powered air purifying respirators.* A full facepiece powered air purifying respirator, or a powered air purifying respirator, or a respirator described in subdivision (iii) of this subparagraph, shall be used to reduce the concentrations of airborne asbestos fibers in the respirator below the exposure limits prescribed in paragraph (b) of this section, when the ceiling or the 8-hour time-weighted average concentrations of asbestos fibers are reasonably expected to exceed 10 times, but not 100 times, those limits.

(iii) *Type "C" supplied-air respirators, continuous flow or pressure-demand class.* A type "C" continuous flow or pressure-demand, supplied-air respirator shall be used to reduce the concentrations of airborne asbestos fibers in the respirator below the exposure limits prescribed in paragraph (b) of this section, when the ceiling or the 8-hour time-weighted average airborne concentrations of asbestos fibers are reasonably expected to exceed 100 times those limits.

(iv) *Establishment of a respirator program.* (a) The employer shall establish a respirator program in accordance with the requirements of the American National Standards Practices for Respiratory Protection, ANSI Z88.2-1959, which is incorporated by reference herein.

(b) See § 1910.6 concerning the availability of ANSI Z88.2-1969 and the maintenance of an historic file in connection therewith. The address of the American National Standards Institute is given in § 1910.100.

(c) No employee shall be assigned to tasks requiring the use of respirator: if, based upon his most recent examination, an examining physician determines that the employee will be unable to function normally wearing a respirator, or that the safety or health of the employee or other employees will be impaired by his use of a respirator. Such employee shall be rotated to another job or given the opportunity to transfer to a different position whose duties he is able to perform with the same employer, in the same geographical area and with the same seniority, status, and rate of pay he had just prior to such transfer, if such a different position is available.

(3) *Special clothing:* The employer shall provide, and require the use of, special clothing, such as coveralls or similar whole body clothing, head coverings, gloves, and foot coverings for any employee exposed to airborne concentrations of asbestos fibers, which exceed the ceiling level prescribed in paragraph (b) of this section.

(4) *Change rooms:* (i) At any fixed place of employment exposed to airborne concentrations of asbestos fibers in excess of the exposure limits prescribed in paragraph (b) of this section, the employer shall provide change rooms for employees working regularly at the place.

(ii) *Clothes lockers:* The employer shall provide two separate lockers or containers for each employee, so separated or isolated as to prevent contamination of the employee's street clothes from his work clothes.

(iii) *Laundrying:* (a) Laundrying of asbestos contaminated clothing shall be done so as to prevent the release of airborne asbestos fibers in excess of the exposure limits prescribed in paragraph (b) of this section.

(b) Any employer who gives asbestos-contaminated clothing to another person for laundrying shall inform such person of the requirement in (a) of this subdivision to effectively prevent the release of airborne asbestos fibers in excess of the exposure limits prescribed in paragraph (b) of this section.

(c) Contaminated clothing shall be transported in sealed impermeable bags, or other closed, impermeable containers, and labeled in accordance with paragraph (g) of this section.

(e) *Method of measurement.* All determinations of airborne concentrations of asbestos fibers shall be made by the membrane filter method at 400-450 X (magnification) (4 millimeter objective) with phase contrast illumination.

(f) *Monitoring—(1) Initial determinations.* Within 6 months of the publication of this section, every employer shall cause every place of employment where asbestos fibers are released to be monitored in such a way as to determine whether every employee's exposure to asbestos fibers is below the limits prescribed in paragraph (b) of this section. If the limits are exceeded, the employer shall immediately undertake a compliance program in accordance with paragraph (c) of this section.

(2) *Personal monitoring—(1) Samples* shall be collected from within the breathing zone of the employees, on membrane filters of 0.8 micrometer porosity mounted in an open-face filter holder. Samples shall be taken for the determination of the 8-hour time-weighted average airborne concentrations and of the ceiling concentrations of asbestos fibers.

(ii) *Sampling frequency and patterns.* After the initial determinations required by subparagraph (1) of this paragraph, samples shall be of such frequency and pattern as to represent with reasonable accuracy the levels of exposure of employees. In no case shall the sampling be done at intervals greater than 6 months for employees whose exposure to asbestos may reasonably be foreseen to exceed the limits prescribed by paragraph (b) of this section.

(3) *Environmental monitoring—(1) samples* shall be collected from areas of a work environment which are representative of the airborne concentrations of asbestos fibers which may reach the breathing zone of employees. Samples shall be collected on a membrane filter of 0.8 micrometer porosity mounted in an open-face filter holder. Samples shall be taken for the determination of the 8-hour time-weighted average airborne concentrations and of the ceiling concentrations of asbestos fibers.

(ii) *Sampling frequency and patterns.* After the initial determinations required by subparagraph (1) of this paragraph, samples shall be of such frequency and pattern as to represent with reasonable accuracy the levels of exposure of the employees. In no case shall sampling be at intervals greater than 6 months for employees whose exposures to asbestos may reasonably be foreseen to exceed the exposure limits prescribed in paragraph (b) of this section.

(4) *Employee observation of monitoring.* Affected employees, or their representatives, shall be given a reasonable opportunity to observe any monitoring required by this paragraph and shall have access to the records thereof.

(g) *Caution signs and labels.* (1) *Caution signs.* (i) *Posting.* Caution signs shall be provided and displayed at each location where airborne concentrations of asbestos fibers may be in excess of the exposure limits prescribed in paragraph (b) of this section. Signs shall be posted at such a distance from such a location so that an employee may read the signs and take necessary protective steps before entering the area marked by the signs. Signs shall be posted at all approaches to areas containing excessive concentrations of airborne asbestos fibers.

(ii) *Sign specifications.* The warning signs required by subdivision (i) of this subparagraph shall conform to the requirements of 20" x 14" vertical format signs specified in § 1910.145(d)(4), and to this subdivision. The signs shall display the following legend in the lower panel, with letter sizes and styles of a visibility at least equal to that specified in this subdivision.

Legend	Notation
Asbestos -----	1" Sans Serif, Gothic or Block.
Dust Hazard -----	3/4" Sans Serif, Gothic or Block.
Avoid Breathing Dust ---	1/2" Gothic.
Wear Assigned Protective Equipment.	1/4" Gothic.
Do Not Remain In Area Unless Your Work Requires It.	1/4" Gothic.
Breathing Asbestos Dust May Be Hazardous To Your Health.	14 point Gothic.

Spacing between lines shall be at least equal to the height of the upper of any two lines.

(2) **Caution labels**—(1) **Labeling.** Caution labels shall be affixed to all raw materials, mixtures, scrap, waste, debris, and other products containing asbestos fibers, or to their containers, except that no label is required where asbestos fibers have been modified by a bonding agent, coating, binder, or other material so that during any reasonably foreseeable use, handling, storage, disposal, processing, or transportation, no airborne concentrations of asbestos fibers in excess of the exposure limits prescribed in paragraph (b) of this section will be released.

(ii) **Label specifications.** The caution labels required by subdivision (1) of this subparagraph shall be printed in letters of sufficient size and contrast as to be readily visible and legible. The label shall state:

CAUTION
Contains Asbestos Fibers
Avoid Creating Dust
Breathing Asbestos Dust May Cause
Serious Bodily Harm

(h) **Housekeeping**—(1) **Cleaning.** All external surfaces in any place of employment shall be maintained free of accumulations of asbestos fibers if, with their dispersion, there would be an excessive concentration.

(2) **Waste disposal.** Asbestos waste, scrap, debris, bags, containers, equipment, and asbestos-contaminated clothing, consigned for disposal, which may produce in any reasonably foreseeable use, handling, storage, processing, disposal, or transportation airborne concentrations of asbestos fibers in excess of the exposure limits prescribed in paragraph (b) of this section shall be collected and disposed of in sealed impermeable bags, or other closed, impermeable containers.

(i) **Recordkeeping**—(1) **Exposure records.** Every employer shall maintain records of any personal or environmental monitoring required by this section. Records shall be maintained for a period of at least 3 years and shall be made available upon request to the Assistant Secretary of Labor for Occupational Safety and Health, the Director of the National Institute for Occupational Safety and Health, and to authorized representatives of either.

(2) **Employee access.** Every employee and former employee shall have reasonable access to any record required to be maintained by subparagraph (1) of this

paragraph, which indicates the employee's own exposure to asbestos fibers.

(3) **Employee notification.** Any employee found to have been exposed at any time to airborne concentrations of asbestos fibers in excess of the limits prescribed in paragraph (b) of this section shall be notified in writing of the exposure as soon as practicable but not later than 5 days of the finding. The employee shall also be timely notified of the corrective action being taken.

(j) **Medical examinations**—(1) **General.** The employer shall provide or make available at his cost, medical examinations relative to exposure to asbestos required by this paragraph.

(2) **Preplacement.** The employer shall provide or make available to each of his employees, within 30 calendar days following his first employment in an occupation exposed to airborne concentrations of asbestos fibers, a comprehensive medical examination, which shall include, as a minimum, a chest roentgenogram (posterior-anterior 14 x 17 inches), a history to elicit symptomatology of respiratory disease, and pulmonary function tests to include forced vital capacity (FVC) and forced expiratory volume at 1 second (FEV_{1.0}).

(3) **Annual examinations.** On or before January 31, 1973, and at least annually thereafter, every employer shall provide, or make available, comprehensive medical examinations to each of his employees engaged in occupations exposed to airborne concentrations of asbestos fibers. Such annual examination shall include, as a minimum, a chest roentgenogram (posterior-anterior 14 x 17 inches), a history to elicit symptomatology of respiratory disease, and pulmonary function tests to include forced vital capacity (FVC) and forced expiratory volume at 1 second (FEV_{1.0}).

(4) **Termination of employment.** The employer shall provide, or make available, within 30 calendar days before or after the termination of employment of any employee engaged in an occupation exposed to airborne concentrations of asbestos fibers, a comprehensive medical examination which shall include, as a minimum, a chest roentgenogram (posterior-anterior 14 x 17 inches), a history to elicit symptomatology of respiratory disease, and pulmonary function tests to include forced vital capacity (FVC) and forced expiratory volume at 1 second (FEV_{1.0}).

(5) **Recent examinations.** No medical examination is required of any employee, if adequate records show that the employee has been examined in accordance with this paragraph within the past 1-year period.

(6) **Medical records**—(i) **Maintenance.** Employers of employees examined pursuant to this paragraph shall cause to be maintained complete and accurate records of all such medical examinations. Records shall be retained by employers for at least 20 years.

(ii) **Access.** The contents of the records of the medical examinations required by this paragraph shall be made available, for inspection and copying,

to the Assistant Secretary of Labor for Occupational Safety and Health, the Director of NIOSH, to authorized physicians and medical consultants of either of them, and, upon the request of an employee or former employee, to his physician. Any physician who conducts a medical examination required by this paragraph shall furnish to the employer of the examined employee all the information specifically required by this paragraph, and any other medical information related to occupational exposure to asbestos fibers.

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