

DOW CHEMICAL U.S.A.



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Mr. John Fisher
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Dear Mr. Fisher:

Over the past few years Dow has been exploring new means of identifying impurities in our products. At the Chlorine Institute Meeting February 5, 1975, in New Orleans, Dr. R.J. Moolenaar of Dow will present the attached report which discusses one of our latest advancements in analytical technology. This new method has provided us with previously unavailable information on minute quantities of asbestos fibers in caustic soda.

At most, our scientists believe that only trace quantities of asbestos may exist in products as a result of contacting caustic. Medical authorities have stated they do not view the ingestion of small amounts of asbestos(particularly short fiber asbestos as these are) as a health risk.

As part of our continuing product stewardship program, we are revealing details of this research and notifying directly those in industry and government who might be interested in the subject.

Because you might be reading about this work in the trade press, I thought you would be interested in seeing a copy of the paper as it was presented. We have enlisted the assistance of Bill Nelson, Research and Development Group Leader in

my department, to help answer any questions you and others in your company might have about this new research. Please feel free to contact Bill at 517/636-5528 or 636-3170.

Very truly yours,

J. T. Rodth

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E-02168

ETC 15797

ASBESTOS IN WATER IN

THE CHLOR-ALKALI INDUSTRY

Presented at

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

February 5, 1975

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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 gastro-intestinal 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 th 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."

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, $\overline{M}$FPL). 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 $\overline{M}$FPL 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.

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*The formula for conversion of $\overline{M}$FPL to a weight per unit volume basis is the following:

$$\text{Asbestos level in milligram/liter} = 2.3 \times 10^{-6} \; (\overline{\ell}) \; (\overline{M}\text{FPL})$$

where $\overline{\ell}$ 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.

Erosion from outcroppings of serpentine- or amphibole-containing rock by streams will transport fibers into potable water supplies. Regions of the Unites 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:

Sample	MFPL	Mean Asbestos Levels Mean Length Microns	ppm (w/v)
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.

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.

REFERENCES

1. C. G. Kramer, "Asbestos and Health," presented at the Chlorine Institute, Inc., Fourteenth Chlorine Plant Managers' Seminar, New Orleans, Louisiana, February 3, 1971.

2. "Occupational Exposure to Asbestos." U.S. Department of Health, Education and Welfare, Public Health Service, Health Services and Mental Health Administration, National Institute for Occupational Safety and Health, 1972.

3. Federal Register 37, No. 202, 22142 (1972).

4. Federal Register 39, No. 125, 23543 (1974).

5. Federal Register 38, No. 66, 8820 (1973).

6. I. J. Selikoff, E. C. Hammond, and H. Seidman, Insulation Hyg. Progr. Rep. 6, No. 3 (Fall 1974).

7. I. J. Selikoff, E. C. Hammond, and J. Churg, J. Amer. Med. Ass. 204, 104 (1968).

8. P. Gross, R. A. Harley, L. M. Swinburne, J. M. G. Davis, and W. B. Greene, Arch. Environ. Health 29, 341 (1974).

9. P. Gross, Arch. Environ. Health 29, 115 (1974).

10. M. F. Stanton and C. Wrench, J. Nat. Cancer Inst. 48, 797 (1972).

11. M. F. Stanton, J. Nat. Cancer Inst. 52, 633 (1974).

12. Advisory Committee Report, Brit. J. Ind. Med. 30, 180 (1973).

13. M. Kuschner, R. Lee, G. G. Robeck, J. R. Rossum, M. A. Schneiderman, E. W. Taylor, and G. W. Wright, J. Amer. Water Works Ass. 66 (9), Part 2, p. 1 (1974).

14. H. L. Olson, J. Amer. Water Works Ass. 66 (9), 515 (1974).

15. H. M. Cunningham and R. Pontefract, Nature, 232, 332 (1971).

16. P. M. Cook, G. E. Glass, and J. H. Tucker, Science, 185, 853 (1974).

17. G. H. Kay, Water and Pollut. Contr. (Toronto) 111 (9), 33 (1973).

18. G. H. Kay, J. Amer. Water Works Ass. 66 (9), 513 (1974).

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 predominently 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	$Mg_3Si_2O_5(OH)_4$	2.4 - 2.5	1.49 - 1.57
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	2.9 - 3.2	1.60 - 1.65
Actinolite	$Ca_2(Mg,Fe^{2+})_5Si_8O_{22}(OH)_2$	3.0 - 3.5	1.62 - 1.68
Anthophyllite	$Mg_7Si_8O_{22}(OH)_2$	2.9 - 3.5	1.60 - 1.66
Amosite	$(Mg,Fe^{2+})_7Si_8O_{22}(OH)_2$	2.6 - 3.0	1.66 - 1.70
Crocidolite	$Na_2Fe_3^{2+}Fe_2^{3+}Si_8O_{22}(OH)_2$	3.0 - 3.5	1.69 - 1.71

The ideal chemical composition of chrysotile approximates 44% MgO, 43% SiO_2, and 13% H_2O, 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 H_2O 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 (Mg_2SiO_4) and/or enstatite ($MgSiO_3$).

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 7.3A.

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).

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 m^2/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.

REFERENCES

(1) P. B. Meijer and W. E. DeKoning-Pierens, TNO Nieuws 27, 661 (1972) (Eng.).

(2) F. A. Mumpton, Siemens Review XLI, 75 (1975).

(3) W. C. McCrone and I. M. Stewart, American Laboratory 6 (4), 13 (1974); Y. Julian and W. C. McCrone, The Microscope 18, 1 (1970).

(4) E. J. W. Whittaker and F. J. Wicks, Amer. Mineral. 55, 1025 (1970).

(5) M. S. Badollet, Can. Mining Met. Bull. No. 468, 237 (1951).

(6) J. P. Schelz, Thermochimica Acta 8, 197 (1974).

(7) L. A. Drobyshev and Ya. Ya. Govorova, Kristallografiya 16, 544 (1971) (Russ.).

(8) K. Yada, Acta Cryst. 23, 704 (1967).

(9) D. V. Rosato, "Asbestos, Its Industrial Applications." Reinhold Publishing Corp., New York, 1959, p. 43.

(10) R. G. Keenan and J. R. Lynch, Amer. Ind. Hyg. Ass., J. 31, 587 (1970).

(11) J. A. Gadsden, J. Parker, and W. L. Smith, Atmos. Environ. 4, 667 (1970).

(12) K. Goodhead and R. W. Martindale, Analyst (London) 94, 985 (1969).