PLAINTIFF'S EXHIBIT

DOW-678

ASBESTOS IN WATER IN THE CHLOR-ALKALI INDUSTRY

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 airborne asbestos was of serious concern, and that some measures for control of industrial exposure to airborne asbestos were good engineering procedures, housekeeping, and careful air monitoring by the industrial hygienist. Since then, airborne asbestos hazard control has been the topic of a Public Health Service manual, a NIOSH Criteria Document, and an EPA national emission standard.

Today I wish to focus attention on the analysis of asbestos in water samples, to briefly summarize and comment on health effects of exposure to water-borne asbestos, 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.

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Analysis of Asbestos in Water Samples

Asbestos is a generic term for a number of hydrated silicates which, when crushed or processed, separate into fibrils. There are many asbestos minerals although only six are of commercial importance. Chrysotile, a serpentine mineral which accounts for 95% of the world's production, is the form used in the chlor-alkali industry. A summary of the chemical and physical properties of asbestos is provided in Appendix B.

Microscopy is the technique of choice for the analysis of asbestos because it provides a direct measurement of the number of fibers per unit volume (expressed here in millions of fibers per liter, MFPL), the parameter of greatest toxicological significance. Conversion to units of weight per unit volume can be made if the particle dimensions are known. 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.(*) 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.

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

Asbestos level in microgram/liter = 0.0023 ($\overline{\ell}$) ($\overline{M}$FPL)

where $\overline{\ell}$ is the mean fiber length. This assumes a fiber density of 2.55 g/ml, a solid particle with a diameter of 340 angstroms, and a solution density of 1 g/ml. The calculation is reasonably accurate for samples encountered in chlor-alkali manufacture, but may not be applicable to those involving fibers of different density and diameter.

To resolve these complicating factors, D. R. Beaman of our Midland Analytical Laboratories has developed a quantitative method which includes fiber identification, based on the simultaneous measurement of morphology, crystal structure and chemistry. Beaman uses a transmission electron microscope equipped with selected area electron diffraction and an energy dispersive spectrometer. 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. Although the results are believed to be accurate within only a factor of two or three, this is by far the most reliable method for determination of asbestos in liquid samples. A detailed description of the method, submitted for publication, will be provided in preprint form upon request.

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 contained some mineral fibers. Much of this is probably of natural origin. 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 United States (2,3).

Underground water sources may also be subject to natural contamination but the available data are very limited (2).

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 in the Ottawa area of Canada, which contributes to fiber levels in local surface waters (4), indicates that wind may play an important role in the dispersal of asbestos.

~~Unusually high levels of~~ Asbestos in unfiltered drinking water from Lake Superior at Duluth, Minnesota, ~~have~~ been attributed to discharge taconite tailings into Silver Bay, Minnesota (7). Reported levels are 1 - 30 million fibers per liter (MFPL). Concentrations of asbestos fibers in water in 22 Canadian communities reported by Kay (5,6) vary from 0.14 to 3.87 MFPL. An earlier study (4) of tap water from three major Canadian cities gave values between 2.0 and 4.4 MFPL. One sample of drinking water drawn from a small lake in the asbestos mining region of Quebec showed 172 MFPL (4).

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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 (4). These levels are very low, corresponding 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 (2). 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	Asbestos Levels Mean Length Microns	Mg/l
Crude Caustic ("cell effluent")			
Unfiltered	20,000	2	0.09
Filtered	200	<1	<0.0005
50% Caustic	3,000	4	0.03
Wastewater Effluent	90	4	0.0007
Steam Condensate (partially derived from caustic evaportors)	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 will be discussed later.

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The level in cell effluent, 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.

Preliminary experiments to improve the filtration of cell effluent resulted in 99% removal of asbestos by fiber count and over 99.5% removal on a weight basis. Work is in progress to optimize the conditions for fiber removal by this technique.

Toxicity 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, and insulation. 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 (10) 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. concluded that if asbestos workers smoke cigarettes, the increase in risk is "tremendous." 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 observations, both OSHA and EPA have promulgated standards for airborne asbestos.

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Stanton and Wrench (11, 12), at the National Cancer Institute, designed a study to determine the carcinogenicity of various sizes of asbestos and fiberglas particles when applied to the pleura of rats. There was a definite relationship between carcinogenicity and size. Fibers <3 microns in diameter and >20 microns in length were more carcinogenic than fibers with diameters >3 microns regardless of length or less than 20 microns in length regardless of diameter.

Selikoff et al (10) have recently summarized epidemiological data from asbestos insulation workers in the United States. His studies 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.(12), chrysotile asbestos fibers were fed 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.

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 reported their findings (13) to the Director of the International Agency for Research on Cancer (a division of the World Health Organization). As part of their report, they state, "such evidence as there is does not indicate any risk from asbestos fibers present in water, food, beverage, or drugs."

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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 shows that process streams and products from diaphragm cell chlor-alkali plants are contaminated with asbestos, but average fiber lengths are short (below 5 microns).

3. Most of the asbestos can be removed from crude caustic ("cell effluent") 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 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 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. Asbestos contamination originating from diaphragm cell operations has not been shown to be a health hazard, nevertheless, common prudence dictates the need to develop methods for controlling the release 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 human ingestion of short fiber asbestos.

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REFERENCES

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

2. M. Kuschner, R. Lee, G. G. Robeck, J. R. Rossum, M. A. Schneiderman, E. W. Taylor, and G. W. Wright, American Water Works Association Journal, p. 1 (September 1974).

3. H. L. Olson, American Water Works Association Journal, p. 515 (September 1974).

4. H. M. Cunningham and R. Pontefract, Nature, 232, 322 (1971).

5. G. H. Kay, Canadian Journal of Water Pollution Control, 111, 33 (1973).

6. G. H. Kay, American Water Works Association Journal, p. 513 (September 1974).

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

8. B. Biles and T. R. Emerson, Nature, 219, 93 (1968).

9. R. R. Merliss, Science, 173, 1141 (1971).

10. I. J. Selikoff, E. C. Hammond, and H. Seidman, Insulation Hygiene Progress Reports 6, (Fall, 1974).

11. M. F. Stanton and C. Wrench, Journal of the National Cancer Institute, 48, 797 (1972).

12. M. F. Stanton, Journal of the National Cancer Institute, 52, 633 (1974).

13. P. Gross, R. A. Harley, L. M. Swinburne, J. M. G. Davis, and W. B. Greene, Archives of Environmental Health, 29, 341 (1974).

14. Advisory Committee Report, British Journal of Industrial Medicine, 30, 180 (1973).

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