ASBESTOS IN WATER IN THE CHLOR-ALKALI INDUSTRY

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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 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 propertie 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 greate

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 findin to the Agency Director. As part of their report (12), they stat "such evidence as there is does not indicate any risk from asbes fibers present in water, food, beverage, or drugs."

Analysis of Asbestos in Water

Microscopy is the technique of choice for the analysis of asbesto 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.

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

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

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.

Sample	MFPL	Mean Asbestos Levels Mean Length Microns	ppm (w/·
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 fiber 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 contair 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 inge of small amounts of asbestos (particularly short fiber a as a risk to man.

Recommendations

1. An industry-wide cooperative program should be initiated to standardize analytical techniques for the determinati of asbestos fibers in liquid samples and to develop a simplified method, e.g. atomic absorption, for routine us The Chlorine Institute might serve as a focal point for t activity.

2. Each chlor-alkali producer using asbestos diaphragms shou carry out a survey to determine the distribution of asbes 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 proce uses no separator.

In a typical diaphragm cell, saturated brine is fed to the anod compartment of the cell, then flows through the diaphragm to th cathode compartment where sodium hydroxide is formed. Flow through the diaphragm is maintained by a differential brine hea During operation, hydrogen and sodium hydroxide form at the cat 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 causti soda together with the depleted brine leaves the cell as a dilu solution of sodium hydroxide and sodium chloride, known in the industry as "cell effluent" or "cell liquor." More concentrate solutions of caustic soda are obtained by evaporation of the ce liquor, whereupon sodium chloride crystallizes from solution.

The asbestos diaphragm is formed by vacuum drawing asbestos fro 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 its relatively good chemical and temperature resistance. Also, unlike other materials, it tends to help regulate the electrolyt 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-alkal 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, frictic 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 an 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 (antigor lizardite) are also usually present, as are small quantities of brucite and magnetite. The remaining five minerals classified as asbestos--amosite, anthophyllite, tremolite, actinoli 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	Refract Inde
Chrysotile	$Mg_3Si_2O_5(OH)_4$	2.4 - 2.5	1.49 -
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	2.9 - 3.2	1.60 -
Actinolite	$Ca_2(Mg,Fe^{2+})_5Si_8O_{22}(OH)_2$	3.0 - 3.5	1.62 -
Anthophyllite	$Mg_7Si_8O_{22}(OH)_2$	2.9 - 3.5	1.60 -
Amosite	$(Mg,Fe^{2+})_7Si_8O_{22}(OH)_2$	2.6 - 3.0	1.66 -
Crocidolite	$Na_2Fe_3^{2+}Fe_2^{3+}Si_8O_{22}(OH)_2$	3.0 - 3.5	1.69 -