

Invited review
**Chemisorption of organic dyes on chrysotile asbestos and
the toxicity issue**

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ABSTRACT

Asbestos, an extremely useful natural resource, has been studied extensively mineralogically and for industrial application. Its extraction from ores has been greatly improved with respect to safety in the work place. In spite of that, there is a decisive effort in many countries to ban its use on the grounds that it is a toxic substance. This action resulting in drastic decrease in production and the possibility of destroying the industry. The chelation of asbestos with organic dyes seems to be a promising way to abate its toxicity. Dyeing can be done when the fibers are slurred in water at ambient conditions in the same way as textile fibers. © 2001 SDU. All rights reserved.

Keywords: Chemisorption; Organic dyes; Chrysotile asbestos

1. INTRODUCTION

Dyestuffs have been used for many decades to stain cells and microorganisms for identification purposes (Carter and Smith, 1957). They have also been used to identify clay minerals through a color reaction, e.g., montmorillonite gives a blue color with benzidine but illite does not (Dodd, 1955). Reactions like these were exploited by engineers to separate minerals by flotation (Somasundaran and Nagaraj, 1984). For example, Alizarin Red S is more adsorbed on apatite than calcite, hence separation by flotation can be made possible (Fu and Somasundaran, 1986). Fly ash, which is mainly a silicate, is suggested as a cheap material for removal of certain dyestuffs from textile waste water (Khare et al. 1987). Activated charcoal is also used for the same purpose. Dyestuffs are also adsorbed on metallic surfaces to inhibit their corrosion (Makhlouf and Khalil, 1987) and used to color certain metals on which an anodic oxide film has formed (Giles, 1959). This shows the diversified reactions of dyestuffs with materials other than textile fibers-their most important application. In the present communication the reaction of dyestuffs with chrysotile asbestos is reviewed with respect to the toxicity issue.

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2. STRUCTURE OF ASBESTOS

Asbestos is an industrial mineral of great economic importance. It occurs in nature in a variety of forms but the most important is chrysotile which represents more than 90% of the asbestos used; it is a hydrated magnesium silicate, $3\text{MgO}\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$. The given formula, however, represents only the ratio of the components and a more exact formula would be $\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$ (Michaels and Chissick, 1979).

The asbestos fibers that are visible to the naked eye are composed of hundreds of thousands mono-fibers called fibrils in close packed parallel arrangement (Figure 1).



Figure 1. Asbestos fibers under the microscope

The mono-fibers have a tubular shape formed by the rolling up of a sheet composed of hydrated magnesium silicate. This sheet is composed of silica groups in tetrahedral pyramid form linked to each other to form a first layer and conjugated to octahedral groups of hydrated magnesia. The latter groups are bulkier than their conjugate silica groups and the sheet that they form has to curve to accommodate the excess encumbrment of the magnesia.

Lateral crystal growth of the sheet eventually leads to the formation of a tube. A typical fiber consists of 12 to 20 layers rolled up like a scroll (Figure 2).

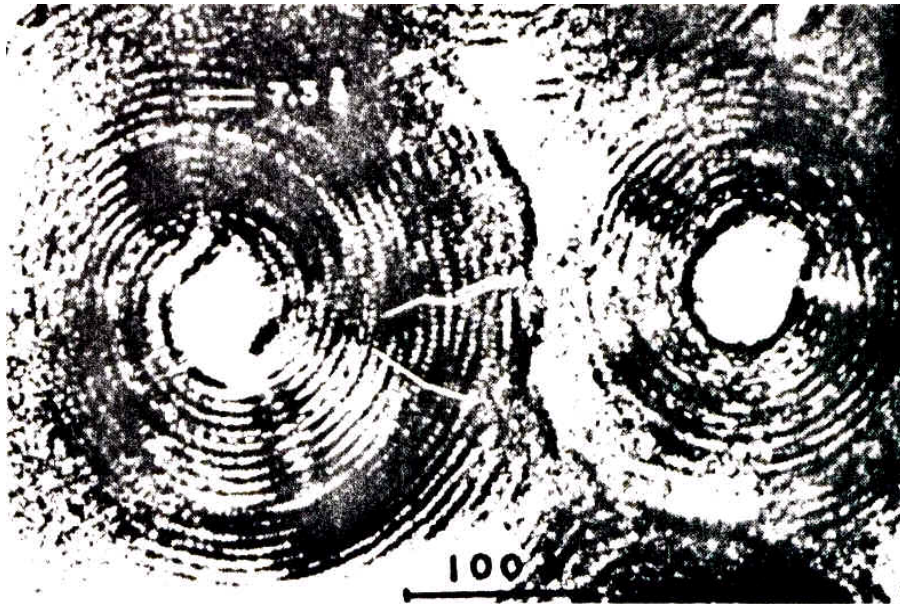


Figure 2. Cross section of fibrils at high resolution electron microscope showing the scroll-like structure

The inner and outer diameters are respectively in the order of 50 to 250Å. The hydration represents about 14% of the mass and is in the form of hydroxyl groups linked to the magnesium and covering the external surface (Figure 3).

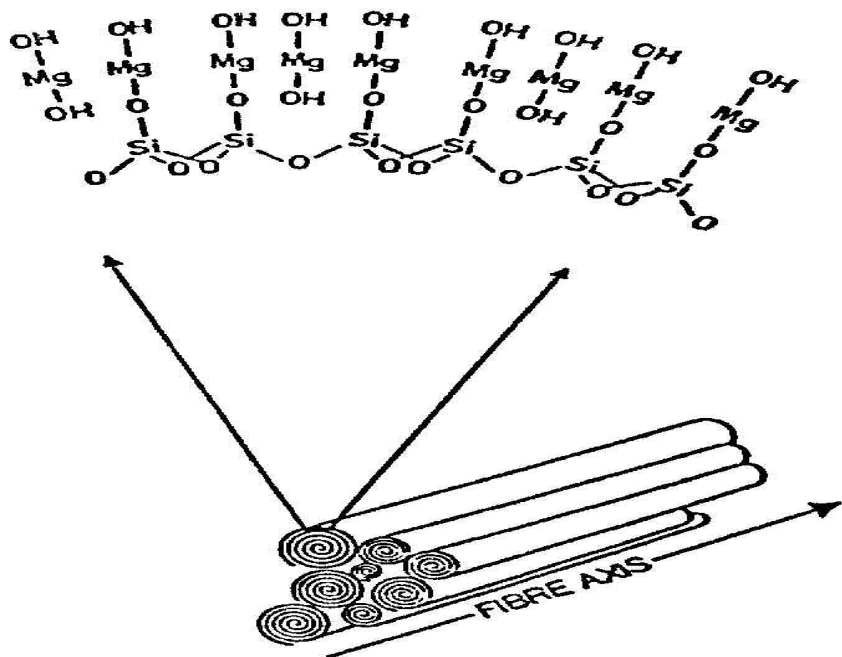


Figure 3. Schematic illustration of the hydrated magnesium silicate sheets rolled in form of scrolls to form an asbestos fiber.

A sliver of chrysotile asbestos with cross section 0.1mm square contains about 20×10^6 fibrils all in parallel orientation. It is possible therefore to strip from asbestos fiber bundle very fine threads, each of which still contains many thousand fibrils. Aqueous suspensions of chrysotile asbestos show a marked alkaline, e.g., 10g suspended in 1 liter of distilled water shows a pH of 9.5 at room temperature. This is due to the reaction:



3. THE TOXICITY ISSUE

Asbestos is claimed by some as a workplace problem that can be adequately addressed with current dust control technology and appropriate practices and not an environmental issue, and by others as a toxic and carcinogenic material that must be banned immediately. It was demonstrated, for example, that heavy smokers in particular are more susceptible to have cancer of the lung; it seems that any fiber lodging in the lung because of its large surface area is capable of adsorbing carcinogenic substances from tobacco smoke. The accumulation of siliceous dust in the lungs may result in causing a disease called silicosis, and this may be cured by surgery. In case of lung cancer due to asbestos, however, this is not possible because the disease spreads rapidly from the lungs to other organs.

As a result of this controversy, the consumption of asbestos in many countries has been decreasing gradually over the past few years, which forced production decline, and in some cases plant shut downs. The industry is looking for substitutes for asbestos, but the long term environmental effects of other minerals or synthetic substitutes that have been proposed are unknown. There are two widely accepted screening toxicity tests for asbestos: hemolytic and cytotoxicity.

- Hemolytic

In these tests red blood cells are left in contact with certain amount of fiber and after various periods of time, the cells are centrifuged; and the hemoglobin content of the supernatant solution is measured using spectrophotometric methods. Usually, 72% of the cells undergo hemolysis when contacted with dry fibers, and 65% when contacted with wet fibers.

- Cytotoxicity

In these tests P 388D₁ cells are incubated with a certain amount of fibers for various periods of time. The number of healthy and dead cells is then measured using Trypan Blue dye. Usually, 81% of the cells die when contacted with dry fibers and 50% when contacted with wet fibers.

While hemolysis is a short-term test in which the membrane stability is involved, cytotoxicity as outlined above gives a global picture of the toxicity of the fibers. Hence, the two tests do not necessarily correlate together since the factors involved are not the same.

4. THE CHELATION OF ASBESTOS

Chrysotile asbestos has the advantage of a large surface area and, unlike activated charcoal, is white in color so that the action of dyes can be followed easily. When a sample of asbestos fibers is agitated at room temperature with an aqueous solution of an organic dye, the fibers become immediately colored. When the colored fibers are separated by filtration, dried and examined by the scanning electron microscope they are homogeneous and contain no precipitates. When boiled with distilled water under reflux condenser, they do not lose their color thus indicating that the dye is chemically bound to the fiber. Table 1 gives the color of the dye solution and the color of the asbestos treated by these dyes.

Table 1
 Color of dye solutions and color of the asbestos treated by these dyes (Habashi, 1992; Awadalla and Habashi, 1990)

	pH of application	Color of dye solution	Color of asbestos
Alizarin	9.5-10	Violet	Blue-violet
	5-6	Brown	Brown
	2-3	Yellow	Yellow
Basic Fuchsin	9.5-10	Purple	Colorless
	5-6	Red rose	Pale red
	2-3	Pale red	Pale red
Brilliant Blue R	9.5-10	Colorless	Blue
	6-7	Blue	Blue
	2-3	Blue	Blue
Brilliant Yellow	9.5-10	Red	Red
	6-7	Orange	Orange
	3-5	Yellow	Yellow
	1-1.5	Green	
Bromocresol Purple *	9.5-10	Precipitate	
	6-7	Violet	Blue
	2-3	Yellow	Yellow
Crystal Violet	9.5-10	Yellow	Yellow
	5-6	Violet	Violet
	2-3	Violet	Violet
Hydroxyquinoline	1-2	Greenish yellow	Greenish yellow
	>2	Yellow	Gray
	9.5-10	Insoluble	--
Malachite Green	6-7	Greenish blue	Pale blue
	2-3	Greenish blue	Pale blue
	9.5-10	Green	Greenish
Methyl Blue	6-7	Colorless	blue
	3-5	Blue	Blue
	2-10	Blue	Blue
Methylene Blue	9.5-10	Pale blue	Blue
Methyl Violet	9.5-10	Pale blue	Blue

continued

	pH of application	Color of dye solution	Color of asbestos
Phenolphthalein*	6-7	Violet	Pale blue
	1-3	Violet	Violet
	9.5-10	Greenish yellow	Violet
Thiazol Yellow G	6-7	Pink	Greenish yellow
	2-3	Colorless	Pink
	9.5-10	Colorless	Pale pink
Trypan Blue	6-7	Red	Colorless
	2-3	Yellow	Yellow
	2-9.5	Orange	Yellow
		Blue	Orange
		Blue	Blue

* Not a dye

The appearance of new peaks in X-ray diffraction patterns and in infrared spectra together with the absence of precipitates supports the view that chelates are formed with asbestos, apparently with its $Mg(OH)_2$ component (Figure 4).

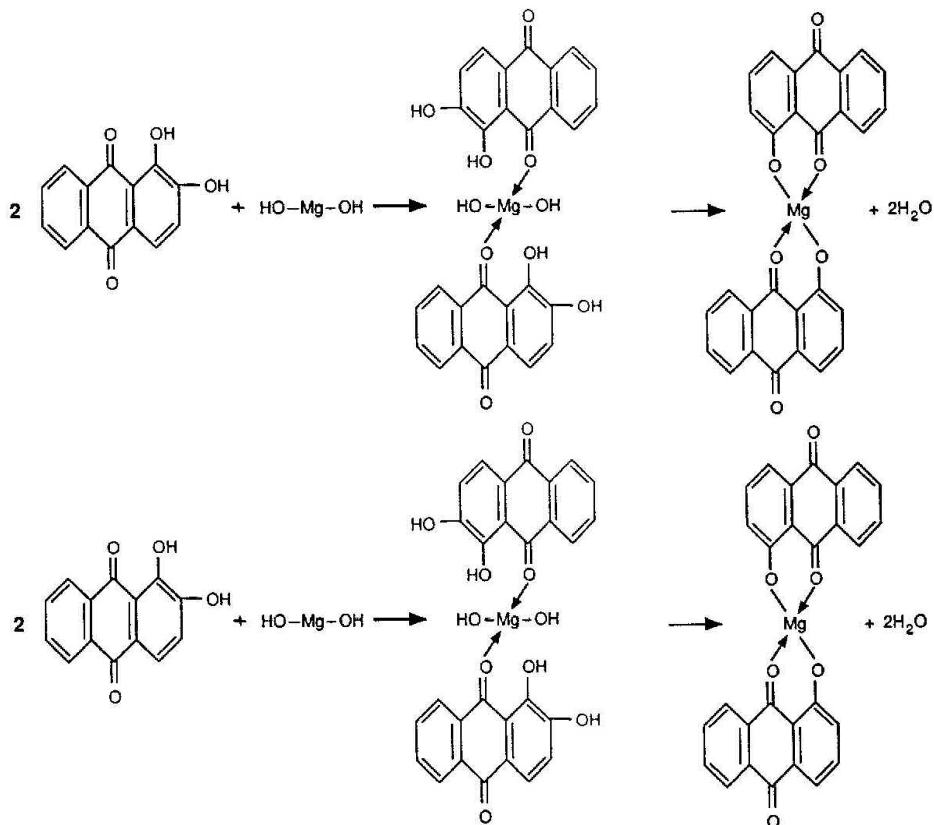


Figure 4. Formation of a chelate between $Mg(OH)_2$ and-top: hydroxyquinoline, bottom: alizarin

This resembles the process of mordant dyeing of textile fibers where $Mg(OH)_2$, $Al(OH)_3$, or $Cr(OH)_3$ are first precipitated on textile fibers then known as "lakes" (Trotman and Trotman, 1948). Some organic compounds, e.g., bromocresol purple and phenolphthalein, although they are not dyestuffs, they color asbestos. They have nearly similar structure and behave nearly the same way towards asbestos. The toxicity of the colored fibers was measured by the tests mentioned earlier and compared with the uncolored sample. It was found that some dyes, e.g., Thiazol Yellow G and Trypan Blue decreased the toxicity of the fibers (Table 2).

Table 2
 Toxicity of chelated asbestos (Habashi et al., 1988, 1991)

Chelating	Concentration of chelating agent on asbestos grade 7 RF66, %	Toxicity	
		Hemolysis	Cytotoxicity
None (dry asbestos)	0	72	81
None (asbestos suspended in water)	0	65	50
Thiazol Yellow G	0.2	54	59
	2.0	1	13
	2.1	6	0
	2.5*	6	12
Trypan Blue	4.0	1	4
Brilliant Yellow	0.2	57	85
	0.9	40	74
	1.0	73	14
Methyl Blue	0.5	69	61
	2.0	23	51
	2.4	12	46
Alizarin	0.4	54	40
	2.7	46	57
	3.9*	90	13
	5.3	64	24

* Chelating agent contacted with asbestos at the boiling point.

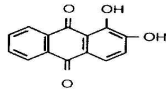
5. CONCLUSIONS

Chrysotile asbestos can be colored by a variety of dyes at ambient conditions like textile fibers forming stable magnesium chelates. Certain dyes render it less toxic as measured by the homolytic and cyto toxicity tests. This is a promising area of research that may lead to the preparation of colored asbestos that is nontoxic. Since the major application of asbestos, about 70%, is in the fabrication of asbestos cement whereby the fibers are slurried in water with Portland cement, the addition of a dye in this step is a simple matter. Colored asbestos is stable with respect to boiling water that suggests a chemical reaction with magnesium hydroxide in the silicate structure.

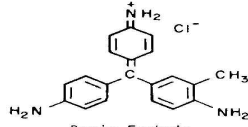
REFERENCES

- Awadalla, F.T., Habashi, F., Reaction of chrysoile asbestos with triphenylmethane dyes. *J. Materials Sci.* 1990, **25**, 87-92.
- Carter, C.F. and Smith, A.L., *Principles of Microbiology*, 1957, Mosby, St Louis.
- Dodd, C.G., In clays and clay technology, Proceedings of the First National Conference. Edited by J.A. Pask and M.D. Turner, Department of Natural Resources Bulletin 169, 1955, pp. 105-111, Division of Mines, San Francisco, California.
- Fu, E. and Somasundaran, P., *Int. J. Min. Processing*, 1986, **18**, 287.
- Giles, C.H., *Chem. Ind.*, 1959, pp. 1400, London.
- Habashi, F. et al., Asbestos fibers modified with organic dyes. *Can. Patent*, 1, 220, 492, 1988.
- Habashi, F. et al., Surface modification of chrysotile asbestos with organic reagents: a preliminary in vitro toxicological study. *Bull. Can. Inst. Min. & Met.*, 1991, **84** (945), 67-79.
- Habashi, F., Dyeing of asbestos fibers. *Textile Chemist & Colorist*, 1992, **24** (4), 23-25.
- Khare, S.K. et al., *J. Chem. Tech. & Biotech.*, 1987, **38**, 99.
- Makhlouf, M.Th. and Khalil, Z.H., *J. Chem. Tech. & Biotech.*, 1987, **38**, 89.
- Michaels, L. and Chissick, S.S. (editors), *Asbestos*, vols 1 and 2, 1979, Wiley, New York.
- Somasundaran, P. and Nagaraj, D.R., In reagents in the mineral industry. Edited by M.J. Jones and R. Oblatt, Institution of Mining and Metallurgy, 1984, pp. 209-19, London.
- Trotman, S.R. and Trotman, E.R., *The bleaching, dyeing, and chemical technology of textile fibers*, 1948, Giffin, London.

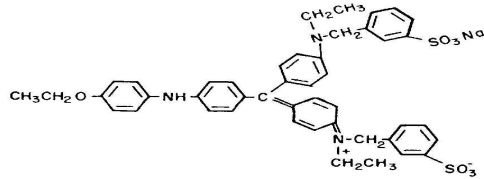
Appendix 1. Structure of the dyes used



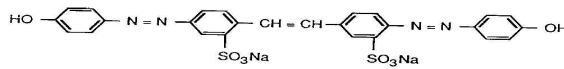
Alizarin



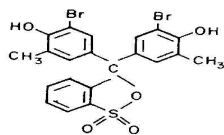
Basic Fuchsin



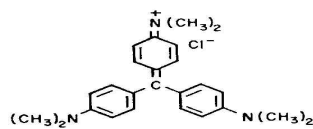
Brilliant Blue R



Brilliant Yellow



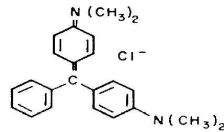
Bromocresol Purple



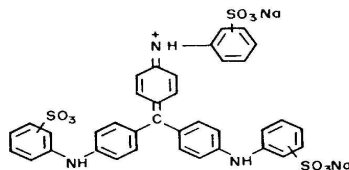
Crystal Violet



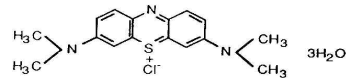
8- Hydroxyquinoline



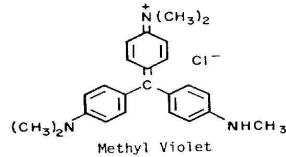
Malachite Green



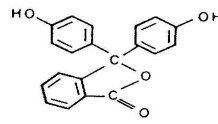
Methyl Blue



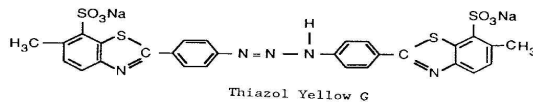
Methylene Blue



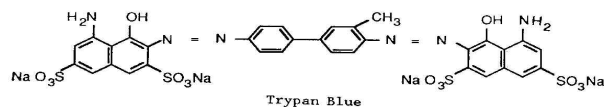
Methyl Violet



Phenolphthalein



Thiazol Yellow G



Trypan Blue