

How Are The Physical and Chemical Properties of Chrysotile Asbestos Altered by a 10-Year Residence in Water And up to 5 Days in Simulated Stomach Acid?

by Krishna Seshan*

Although there have been a number of studies on the ingestion of asbestos, few studies exist on how the chrysotile asbestos itself is altered by the exposure to the acid stomach environment. This study has found that there are changes in the physical, chemical and surface properties of chrysotile asbestos as a result of exposure to water, strong acids, and simulated gastric juices. It was observed that the charge on the surface (the zeta potential) is changed from positive to negative; the surface becomes silicalike; and the magnesium is lost from the fibers of asbestos upon exposure to water and acid. It was also noted that the smaller the fiber diameter, the faster the loss of the magnesium.

Notable among the changes in physical properties is a change in the refractive index. This means that asbestos exposed to acids or water may not be detectable using the dispersion staining techniques that identify asbestos based on the refractive index. Other physical property changes include the destruction of the gross crystallinity of the fibers. The x-ray diffraction signal disappears when fibers are exposed to acid. However, this study shows that the fibers may still be detected by electron diffraction.

It appears that upon acid exposure, the magnesium ions are leached out, leaving a magnesium-free silica network. A positive ion, possibly the proton (H^+) or the hydronium ion (H_3O^+), replaces the lost magnesium ion.

Introduction

The prevalence of asbestos in drinking water in the United States has been cataloged (1,2), and the effects of magnesium leaching on the biological effects of inhaled asbestos have been studied (3-5). However, no studies have been found that have considered the effects of magnesium leaching in ingested asbestos.

Several mineralogists (6,7) have studied how asbestos changes under heat and pressure, while others (8,9) have studied the surface properties of asbestos fibers. The physical and chemical properties of asbestos have been cataloged (10,11). The optical properties of chrysotile have been studied (12), and dye absorption on chrysotile has been

investigated (13,14). The study summarized here attempted to use these various techniques and tests on asbestos fibers altered by exposure to simulated gastric juices and fibers stored in water for long periods of time. Specific details of the studies can be found in the more comprehensive final report, which will be available from the U.S. Environmental Protection Agency (U.S. EPA) at a future date.

This work impacts two areas. The first is the area of chrysotile identification in the environmental matrix. Acid-treated fibers may not be easily detectable by conventional techniques used for asbestos identification. Second, there is the biomedical implication: What changes in fiber properties caused by exposure to water or gastric juice will alter the biological effects of asbestos? Light and Wei have pointed out the possibility of a connection between surface charge and toxicity (15).

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Materials and Methods

This project studied the changes in the physical, chemical, and surface properties of chrysotile asbestos after exposure to doubly distilled (DD) water for 10 years, 1 N hydrochloric acid for 1/2-hr to 5-day intervals, and to simulated gastric juices for up to 5 days. The simulated gastric juices were produced by adding 2 g of NaCl, 3.2 g of pepsin (hog extract), and 7.0 mL of HCl to a liter of distilled water (16). The pH of the juice was 1.2.

Chrysotile asbestos samples were obtained from three sources: International Union Against Cancer (UICC), National Institute of Environmental Health Sciences (NIEHS), and Globe, AZ.

A variety of tests, including X-ray and electron diffraction, energy-dispersive X-ray analysis, and various surface tests, were performed. The tests may be divided into three main categories: physical, chemical, and surface charge investigations.

Changes in surface charge as a result of acid exposure were determined by the measurement of zeta potential (ZP) (17,18) versus pH. Untreated fibers were compared with those treated in 1 N HCl and those treated in simulated gastric juices. A nitrogen adsorption (19) experiment was performed to determine changes in surface area. Changes in surface were also studied by a dye adsorption method (20).

Physical changes to the fiber after acid exposure were found by measuring the refractive index of the fibers. X-ray and electron diffraction were used to study the differences between acid-treated, water-treated, and untreated fibers.

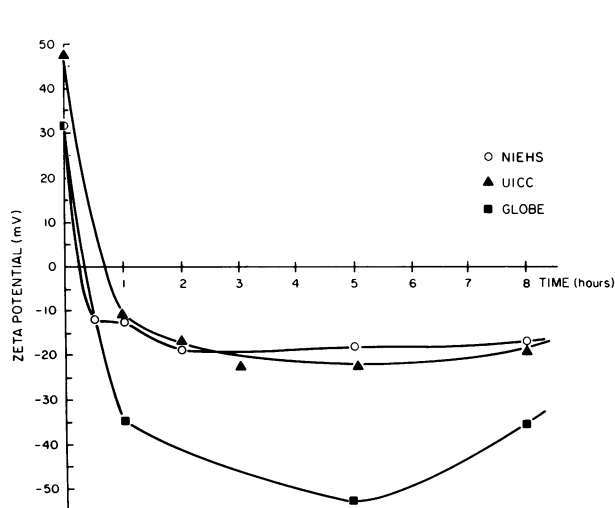


FIGURE 1. Plot showing the variation of zeta potential of chrysotile asbestos fibers during an 8-hr treatment in simulated gastric juice.

Chemical changes to the fiber after acid treatment were studied by performing atomic absorption (AA) analyses of the liquid in which the fibers were treated. The total amount of magnesium lost from the fibers was determined. Energy-dispersive X-ray analysis on individual fibers was performed using a scanning transmission electron microscope (STEM). In this case the Mg/Si ratio, as a function of residence time in acid, was determined.

Results

Upon exposure to simulated gastric juice, the ZP of NIEHS, UICC, and Globe chrysotile asbestos goes from positive to negative in less than 1 hr (Fig.1). Figure 2 shows the results of asbestos exposure to 1 N HCl. In 8 hr the ZP still remained positive. The different results suggest that the NaCl and pepsin have an important part to play in changing surface charge.

ZP-pH measurements can be used to understand surface changes. Figures 3 and 4 compare ZP-pH curves for untreated and 0.1 N HCl-treated chrysotile. The point at which the ZP curve cuts the x-axis, called the zero point charge (ZPC), has moved from a pH of 6.5 for untreated fibers to a pH of 4 for the treated chrysotile. Since chrysotile has a ZPC of 6 and silica has a ZPC of 4, Figures 3 and 4 show that acid exposure has turned the chrysotile surface to a silicalike surface.

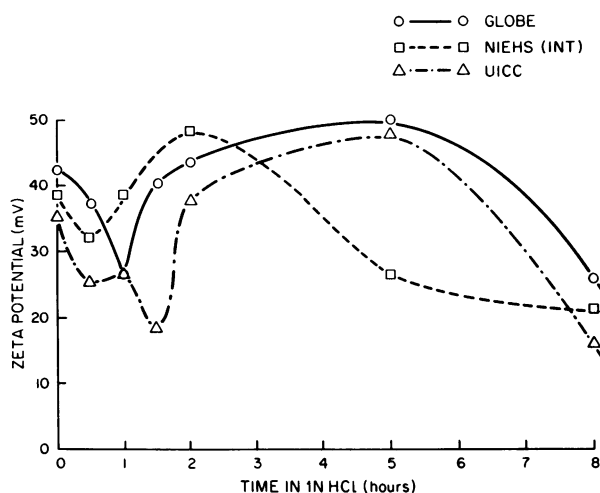


FIGURE 2. Plot showing the variation of zeta potential of chrysotile asbestos from several sources during an 8-hr treatment in 1 N HCl.

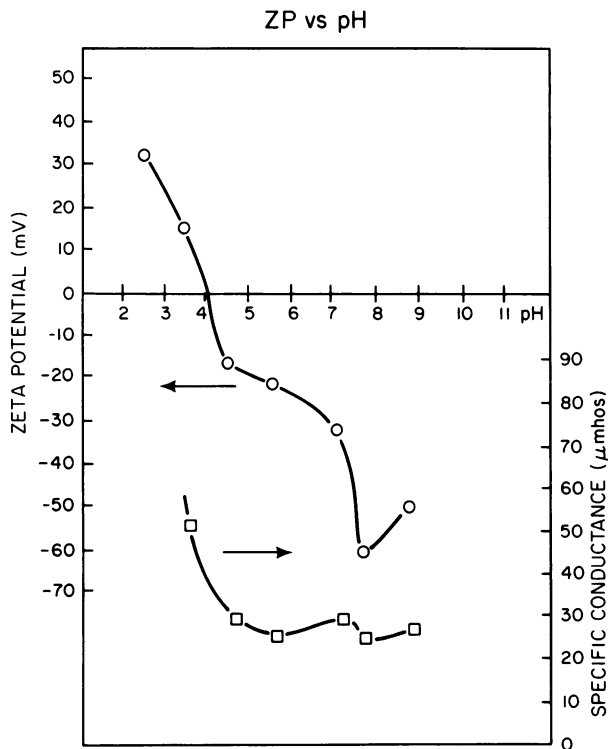
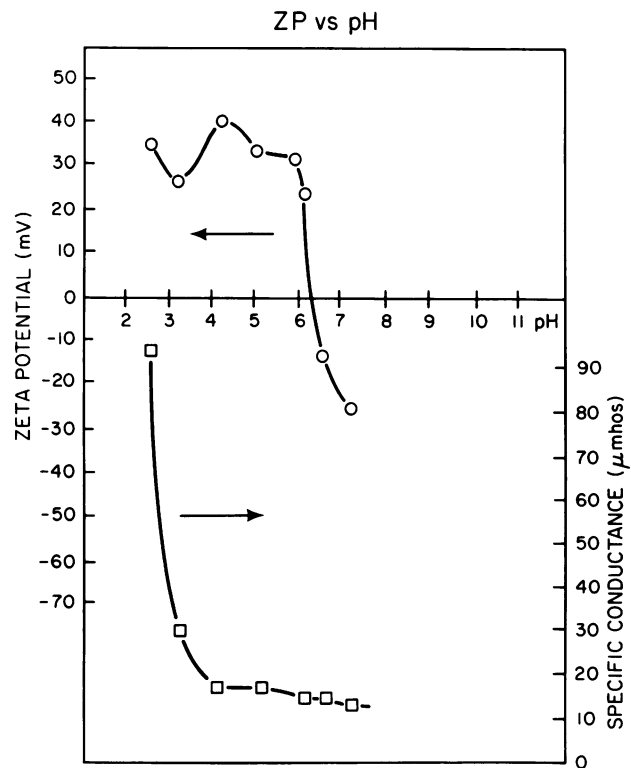


FIGURE 3. Plot showing the variation of zeta potential vs. pH for chrysotile asbestos treated in 0.1 N HCl for 5 days. The specific conductance of the solution is shown at the bottom, for calibration purposes.



UNTREATED CHRYSOTILE ASBESTOS

FIGURE 4. Plot showing the variation of zeta potential vs. pH for chrysotile that has not been treated.

Table 1. Surface area of chrysotile asbestos determined using the nitrogen adsorption technique.

Sample	Treatment	Surface area, m ² /g
Globe (fine)	Untreated	29.55
NIEHS (intermediate)	Untreated	29.76
Globe (fine)	2 hr, 1 N HCl	30.99
NIEHS (intermediate)	2 hr, 1 N HCl	59.82
Globe (fine)	Sonicated	21.21
NIEHS (intermediate)	Sonicated	21.50

Table 1 shows that the surface area of the treated NIEHS chrysotile is about double that of the untreated chrysotile as measured by the nitrogen adsorption experiment. The chrysotile from Globe was not affected by the acid treatment. The difference cannot be attributed to larger fibers in the NIEHS material breaking up into smaller fibers with more surface area because there was no difference in nitrogen adsorption after sonication of both materials.

The results of the dye adsorption measurement of surface area are shown in Figure 5. The HCl is shown to have the greatest effect on the asbestos fibers.

One of the important physical properties that changes upon acid treatment of chrysotile is its refractive index. This change for 1 N HCl and simulated gastric juice treatments is shown in Figure 6. The refractive index decreases from 1.54 for the untreated fiber to 1.44 for the treated fibers. A refractive index of 1.4 is approaching that of the zeolite minerals. This is consistent with the removal of magnesium from the chrysotile, leaving an open framework type of silicate. The result suggests that methods used to identify chrysotile based on its refractive index alone will not be effective in identifying acid-treated fibers.

Acid treatment also destroys the X-ray diffraction pattern of chrysotile. The effect on the X-ray pattern of chrysotile after 3 and 5 days in 1 N HCl is shown in Figure 7. Crocidolite, an amphibole asbestos form, remains unchanged (Fig. 8). The results of an electron diffraction study of acid-treated chrysotile are shown in Table 2. It was observed that after 5 days in 1 N HCl, the electron diffraction patterns lost clarity; this is assumed to be related to the loss of magnesium ions from the fiber.

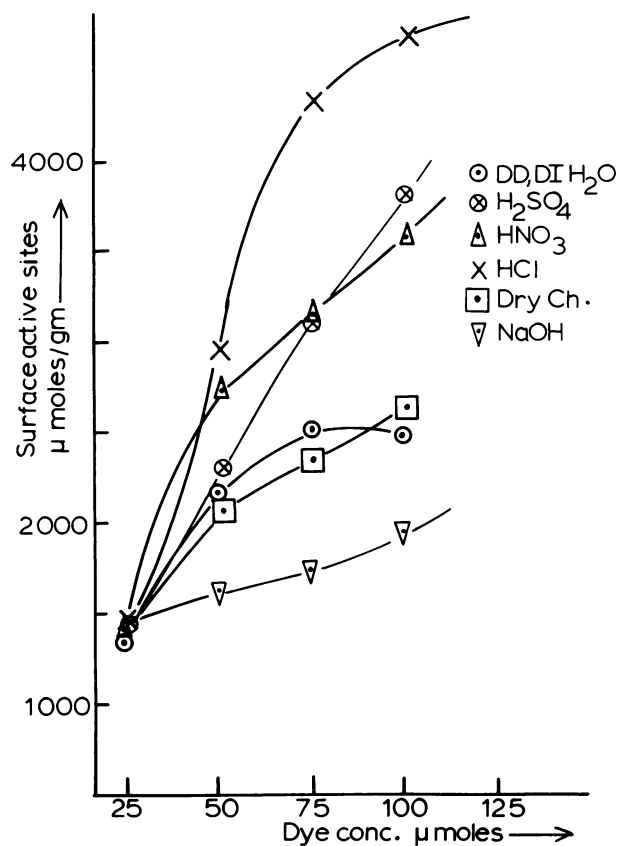


FIGURE 5. Results of surface area measurement using a dye adsorption technique. Chrysotile asbestos from Globe, AZ.

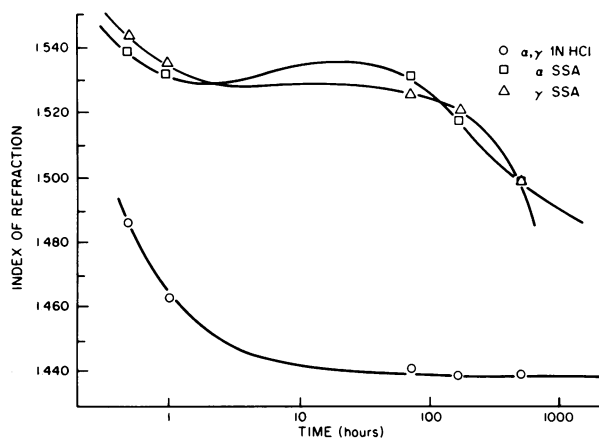


FIGURE 6. Graph showing the refractive index of Globe chrysotile vs. the time treated in 1 N HCl and in simulated gastric juice. α is the refractive index perpendicular to the fiber axis. γ is the index along the fiber axis. Treatment in HCl cause α and γ to become equal and drop to a value of 1.44.

Table 2. Chrysotile fibers identifiable by electron diffraction.^a

Source	Fibers identifiable, %		
	Untreated	30 min, 1 N HCl	5 days, 1 N HCl
UICC	89	67	60
NIEHS	90	80	77
Globe, AZ	92	87	80

^aAt least three layer lines must be visible to be considered identifiable for this test.

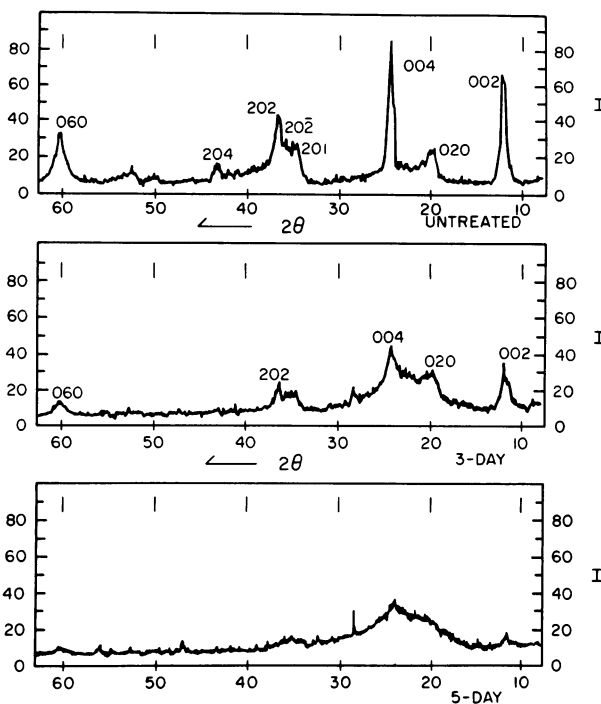


FIGURE 7. X-ray diffractometer trace of intensity vs. 2θ for 1 N HCl-treated chrysotile asbestos.

Chrysotile asbestos has the formula $Mg_3[Si_2O_5](OH)_4$. The results of the AA analysis of the liquid in which the asbestos materials had been placed (Fig.9) leads to the clear conclusion that acid leaches magnesium from chrysotile fibers. The excellent agreement with electron microprobe results of Monchaux et al. (4) may also be seen in Figure 9.

The X-ray microanalysis results shown in Figures 10 and 11 show that the smaller the fiber, the greater the magnesium loss. This implies that the loss of magnesium is from the surface of the fiber rather than from the ends.

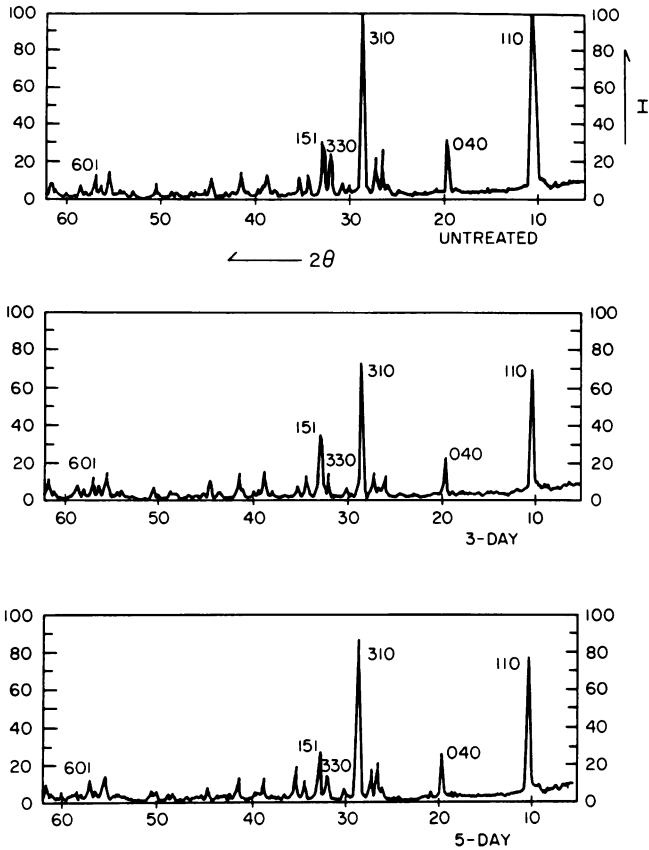


FIGURE 8. X-ray diffractometer trace of intensity vs. 2θ for 1 N HCl-treated crocidolite.

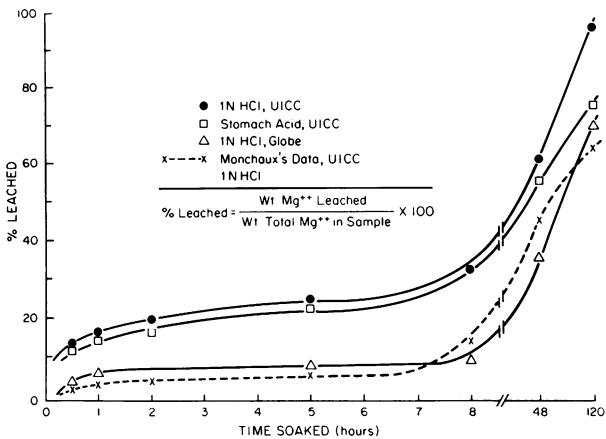


FIGURE 9. Percent magnesium as function of time. Comparison with the results of Monchaux et al. (4).

Discussion

Some of the changes caused by HCl and gastric acid would make it difficult to identify acid-treated fibers. It will be necessary to develop new

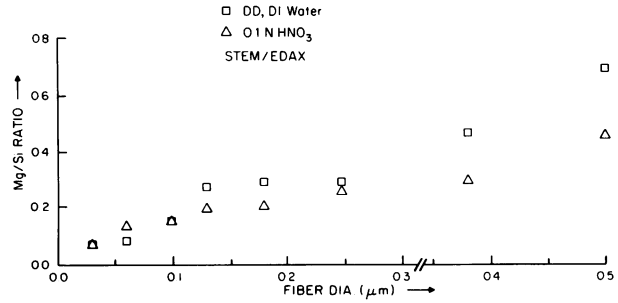


FIGURE 10. Magnesium to silicon ratio vs. fiber diameter for Globe chrysotile in water and in 0.1 N HCl.

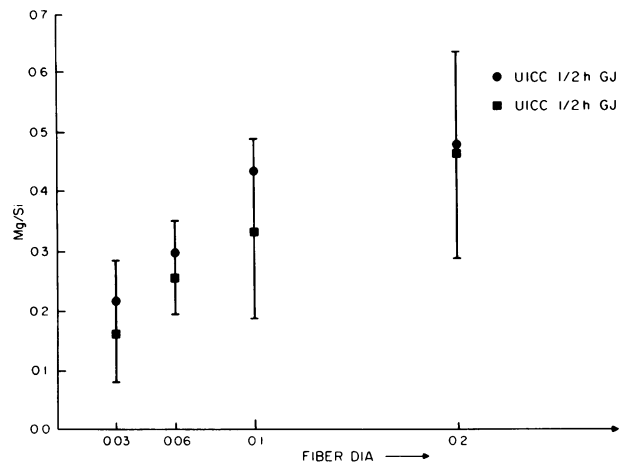


FIGURE 11. Magnesium to silicon ratio vs. fiber diameter for UICC chrysotile treated with simulated gastric juice.

techniques for the optimum identification of fibers after they have been placed in the gastrointestinal tract through ingestion.

The simulated gastric juices used in this study did not contain all components of human stomach acid. The complex organic compounds such as muco- and glycoproteins may play a large part in coating the fibers after they are in the stomach and have a great effect on such parameters as surface charge and magnesium leaching.

Conclusions

Chrysotile asbestos from three sources (UICC, NIEHS, and Globe, Arizona) has been shown to change its physical, chemical and surface properties after exposure to HCl and simulated gastric juice.

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REFERENCES

1. Millette, J. R., and McFarren, E. F. EDS of waterborne asbestos fibers in TEM, SEM, and STEM. *SEM/1976* 9: 451-460 (1976).
2. Millette, J. R., Clark, P. J., Pansing, M. F., and Twyman, J. D. Concentration and size of asbestos in water supplies. *Environ. Health Perspect.* 34: 13-24 (1980).
3. Wagner, J. C., Berry, G., and Timbrell, V. Mesotheliomas in rats after inoculation with asbestos and other materials. *Brit. J. Cancer* 28: 173-185 (1973).
4. Monchaux, G., Bignon, J., Jaurand, M. C., Lafuna, J., Sebastian, P., Masse, R., Hirsch, A., and Goni, J. Mesotheliomas in rats following inoculation with acid leached chrysotile asbestos and other mineral fibers. *Carcinogenesis* 2: 229-236 (1981).
5. Morgan, A., Davies, P., Wagner, J. C., Berry, G., and Holmes, A. The biological effect of magnesium leached chrysotile asbestos. *Brit. J. Exptl. Pathol.* 58: 465-473 (1977).
6. Chen, Y. Y. T. IR studies of acid, bases, heat and pressure on asbestos and structurally related substances. *J. Assoc. Anal. Chem.* 60: 1266-1278 (1977).
7. Choi, I., and Smith, R. W. Kinetic study of the dissolution of asbestos fibers in water. *J. Colloid. Interface Sci.* 40: 253-262 (1971).
8. Fripiat, J. J., and Faille, M. D. Surface properties and texture of chrysotile. *Clays Clay Min.* 15: 305-320 (1966).
9. Holt, P. F., and Clark, S. G. Dissolution of chrysotile asbestos in water, acid, and alkalies. *Nature* 185: 237-253 (1966).
10. Papirer, E., and Roland, P. Grinding of chrysotile in hydrocarbons, alcohol, and water. *Clays Clay Min.* 29: 161-175 (1981).
11. Pundsak, F. L. The properties of asbestos. I. *J. Phys. Chem.* 59: 892-895 (1955).
12. Bloss, F. D. *An Introduction to the Methods of Optical Crystallography.* Holt, Rinehart, and Winston, New York, 1961, p. 59.
13. Gurr, E. *Synthetic Dyes in Biology, Medicine and Chemistry.* Academic Press, London, 1971, pp. 288-291.
14. Markham, M. C., and Wosczyzna, K. Determination of microquantities of chrysotile asbestos by dye adsorption. *Environ. Sci. Technol.* 10: 930-931 (1976).
15. Light, W. G., and Wei, E. T. Surface charge and hemolytic activity of asbestos. *Environ. Res.* 13: 135-145 (1977).
16. U. S. Pharmacopeia. Rockville, MD, 1979, p. 1105.
17. Chowhury, S., and Kitchner, J. A. Zeta potentials of natural and synthetic chrysotiles. *Intern. J. Min. Proc.* 2: 277-285 (1975).
18. Ralston, J., and Kitchner, J. A. The surface chemistry of amosite asbestos, an amphibole silicate. *J. Colloid Interface Sci.* 50: 242-249 (1975).
19. Naumann, A. W., and Drescher, W. H. Colloidal suspensions of chrysotile asbestos: specific ion effects. *J. Phys. Chem.* 70: 288-291 (1966).
20. Rose, H. A. Detection and determination of chrysotile in talc USP. *J. Pharm. Sci.* 63: 268-269 (1974).