DETECTION OF AMPHIBOLE ASBESTOS IN CHRYSOTILE SHEET GASKETS

James L. Hubbard & William E. Longo, Ph.D.

Summary

Analysis of chrysotile containing synthetic rubber sheet gaskets were conducted to determine the presence or absence of amphibole asbestos fibers using a digestion technique. Six separate chrysotile (60 to 80%) gasket samples were prepared using an acid base extraction method then analyzed by transmission electron microscopy (TEM). The results showed that the extraction method removed most of the chrysotile from the gaskets and that tramolite/actinolite fibers were clearly identified in each of these gaskets. Also, anthopyllite and crocidolite fibers were found in two separate chrysotile containing gaskets. These results contrast with earlier analysis of these same gaskets when analyzed by the traditional polarized light microscopy (PLM) method.

Introduction

It has been documented that amphibole contamination (tremolite/actinolite and sometimes anthophyllite) can be found in chrysotile mines located in Canada.(1) The amphiboles are typically found in the non-asbestos serpentine rock that is surrounding the chrysotile fiber veins. Because of the location of the amphibole contaminants in relation to the chrysotile, it is typically not possible to differentially remove only the chrysotile vein deposits and completely avoid the contaminated serpentine rock on such a large-scale mining operation.

It has been suggested that amphibole contaminant concentrations at chrysotile mines are reduced to non-detectable levels by two methods. Areas of amphibole contamination are avoided during mineral extraction by selective mining and the ore is processed in such a way that amphibole contaminants are removed.(1,2,3) The details of how the processing can remove amphibole fibers from the chrysotile have not been explained nor supported by any scientific studies that these investigators could identify. In regards to the selective mining technique, it is unclear if it is being used today at any ongoing mine operations in Canada. However, this type of mining process was most likely not a factor before the late 1980's when some companies were still manufacturing asbestos products such as chrysotile-containing sheet gaskets.

Previous analyses by MAS of chrysotile-containing sheet gaskets using standard EPA asbestos bulk analysis techniques have not detected any tremolite/actinolite contamination in the gasket material.(4,5,6,7,8,9,10) This early MAS work appears to support the proposition that the amphiboles may be removed during processing. However, the lack of amphibole detection for sheet gaskets using the typical PLM technique is also not surprising. The limit of detection for tremolite/actinolite in a material that contains high amounts of chrysotile (70-80%) in a synthetic rubber matrix may be higher than what is normally expected for the PLM method. Additionally, amphibole fibers may be broken up during the milling process and therefore be too small to be seen or identified by PLM (typically operated at 100X). Standard methods now exist to improve detection limits beyond the typical PLM method. Other asbestos-containing polymer products such as VAT with low amounts of chrysotile are now recommended by the EPA to be analyzed by a reduction technique. This procedure removes both the polymer and some of the inorganic fillers in an effort to increase the detection limit of the chrysotile. The residue material is then analyzed by TEM. This method allows for the identification of the small fibers that were typically added to floor tile and overcomes the problem of false negatives when analyzed only by PLM. This technique is sometimes referred to as the Chatfield method. The method uses both high temperature ashing and acid dissolution to remove the interfering material.[10]

Earlier others have addressed this issue concerning the detection of tremolite/actinolite in chrysotile ore and the problems associated with the masking effect of the chrysotile. A chemical extraction method increasing the amphibole detection limit by removing the chrysotile was proposed to address this very problem by Dr. A.A. Hodgson in 1984 at a joint meeting of the Asbestos Research Council and the Asbestos International Association.[11] Addison and Davis published a technique in 1990 to dissolve most of the interfering chrysotile.[12] They reported increasing the amphibole detection limit by a factor of 10 when using X-ray diffraction and an acid/base digestion procedure.

The Addison and Davies method was used only on processed chrysotile ore and not on finished asbestos-containing products such as sheet gaskets. MAS' study investigated the use of the Addison and Davies sample preparation technique on typical chrysotile-containing sheet gaskets to determine if amphibole asbestos was actually a contaminant in the finished material. Tremolite fibers were identified by SEM and quantitative X-ray diffraction was used to determine the amount and type of amphiboles present in chrysotile ore in the Addison and Davies method. MAS' study (Phase I) was conducted to determine if tremolite/actinolite or any other amphibole fibers were present in chrysotile sheet gaskets. TEM was used rather than SEM so individual fibers could be examined and identified more thoroughly. No attempt was made in this study to determine actual amphibole weight percent present in the sheet gasket materials. Future studies will address that issue.

Materials & Methods

Digestion Method – Approximately 10 grams of the sheet gasket sample was placed into a porcelain crucible and heated at 600°C for 15 hours in a muffle furnace (Isotemp Model 184A). The material was allowed to cool. Approximately 2.5 grams of the ashed residue was added to 80 mL of 2N H_2SO_4 in a 250 mL round-bottomed flask fitted with a reflux condenser. The mixture was boiled for one hour and stirred continuously during the process. The mixture was then centrifuged (Dynac II Centrifuge) at 2300 rpm for 30 minutes to collect the remaining residue into a pellet. The residue pellet was refluxed again for another hour in 80 mL of 4N NaOH. The residue was recentrifuged and the residue pellet was resuspended in 10 mL of filtered deionized water (DI). The suspension was recentrifuged as described above and repelleted after a second suspension in DI water. The final pellet was then resuspended in 40 mL of DI water.

A 1 mL disposable pipette was used to add 5 to 20 drops of this suspension to 15 mL of DI water containing 0.025% tetra-sodium pyrophosphate (TSPP). This mixture was then used for the TEM analysis. Reference amphibole standards consisted of tremolite subjected to the above described process and tremolite and crocidolite that were not subjected to the extraction process. A process blank (crucible without sample but exposed to all sample treatments) and a non-asbestos sheet gasket (Garlock Blue Gard) were processed through the acid/base extraction as described above and examined by TEM as controls.

TEM grids from two of the prepared gasket samples (M18549-1 and M18549-7) were sent to Materials and Chemistry Laboratory (MCL) in Oak Ridge, Tennessee for tremolite/actinolite verification for QC purposes.

PLM Bulk Analysis

All gasket samples tested by this procedure were also analyzed by PLM according to the methods described by the Environmental Protection Agency [4,10]. Results of the analysis were reported in area/volume percent.

Electron Microscopy Analysis

A JEOL 1200 EX was used for transmission electron microscopy (TEM) and a Tractor Northern 5500 was used for energy dispersive X-ray analysis (EDXA). Carbon-coated grids were treated with 1% albumen and dried in order to disperse the applied drop mount sample. Five microliters of the final sample was then added to the TEM sample grid and allowed to dry for approximately one hour. Amphibole asbestos fibers were identified by aspect ratio, morphology, energy dispersive X-ray spectrum (EDXA) and electron diffraction patterns (ED). Representative photographs of the amphibole fibers were taken at various magnifications and an ED pattern from each sample was collected, indexed and compared to established literature values.[13]

Results

Amphibole asbestos fibers were detected by TEM analysis in each of the chrysotile-containing sheet gaskets examined in this study. The EDXA and ED patterns were consistent with known amphibole standards. A summary of the results is shown in Table 1. Only chrysotile asbestos was observed in the sheet gaskets by PLM bulk analyses. The results of the PLM analyses are shown in Table 2. No asbestos was detected in the Garlock Blue Gard when this sample was analyzed as a control by both TEM and PLM methods. Also, no asbestos fibers were detected in the process blank.

Table 1
Amphibole Asbestos Types Found in Treated Sheet Gaskets

Sample #	Product Name	Amphibole Type Found
M22785-57	Johns-Manville	Tremolite
M25971-01	Sheet Gasket, MAS Study V	Tremolite/Anthophyllite (1)
M18549-01	Garlock Sheet Gasket	Tremolite
M18549-03	Garlock Sheet Gasket	Tremolite
M18549-07	Garlock Sheet Gasket	Tremolite
M18549-10	Garlock Sheet Gasket	Tremolite/Crocidolite (2)
M22631-02	Garlock Blue Gard Gasket	**ND**
ND = None Detected		
(1) One anthophyllite structure detected		
(2) Amount of crocidolite asbestos approximately equal to the tremolite		

Table 2
PLM Bulk Analysis of Sheet Gaskets

Sample #	Type of Asbestos Detected	Volume Percent
M22785-57	Chrysotile	60%
M25971-01	Chrysotile	80%
M18549-01	Chrysotile	75%
M18549-03	Chrysotile	70%
M18549-07	Chrysotile	70%
M18549-10	Chrysotile	70%
M22631-02	**ND**	**NA**
ND = None Detected		

Conclusion

The Garlock and Johns-Manville chrysotile sheet gaskets as well as the gasket from MAS' Gasket Study V all contained amphibole asbestos fibers (tremolite/actinolite, crocidolite, and a small amount of anthophyllite). Tremolite and actinolite are part of a solid solution series. Depending on the amount of iron detected by EDXA in the fiber, the amphibole fibers can be classified either as tremolite, actinolite or fero-actinolite. The tremolite/actinolite fibers detected and identified during this study were within the tremolite range. The majority of the fibers identified by MCL (see Section 9 of this report) also were within the tremolite range. A small number of tremolite/actinolite fibers analyzed by MCL were iron-rich and therefore classified as actinolite. This small difference in chemistry between tremolite and actinolite is only of academic importance because both tremolite and actinolite asbestos are well known contaminants in chrysotile mines.

We cannot conclude at this time that every Johns-Manville chrysotile gasket contains amphibole contamination because only one gasket was tested in this study. However, we believe this conclusion is plausible for Garlock gaskets. All four Garlock exemplars were found to contain amphiboles. These amphiboles were tremolite/actinolite, crocidolite, and anthophyllite. The crocidolite asbestos was found in Garlock sample M18549-10. The number of crocidolite fibers was similar to the number of tremolite fibers observed in that sample. This observation was only qualitative. An actual number count for mass determination or weight percent may be performed in the future on this sample as well as the others. The source of the crocidolite in the chrysotile gasket may be due to cross-contamination from the manufacturing process at the Garlock plant. That is it's possible that after Garlock finished manufacturing their crocidolite sheet gasket (Garlock Product #7705) that they did not decontaminate the equipment so that when chrysotile gaskets were manufactured with the same equipment there would be some cross contamination. The other possibility is that there is crocidolite contamination in the chrysotile mines as well as tremolite/actinolite contamination. Dr. A. De published a geological survey in a 1961 doctoral thesis showing the Thetford Mine did contain blue fibrous reibeckite (crocidolite)[14]. However, the ultimate source of the crocidolite in the Garlock chrysotile gasket is somewhat moot since these materials are no longer manufactured. The important point is that it was found in a Garlock chrysotile-containing gasket. Therefore, it would be expected to be found in other Garlock chrysotile gaskets as well. Individuals who once worked with Garlock chrysotile gaskets would have the potential for exposure to both tremolite/actinolite and crocidolite.

MAS ran the following samples through the extraction procedure for quality control.

1) Tremolite Standard, NIST 1867[15]
2) Process Blank
3) Garlock Blue Gard, Non-Asbestos Gasket

Tremolite and crocidolite standards that had not gone through the extraction process were compared to the amphibole fibers found in these analysis.[16]

TEM analysis of the tremolite standard demonstrated that the extraction procedure did not change either the chemistry or crystalline structure of the tremolite to any significant degree. Results of this analysis can be found in Section 9 of this report. No asbestos fibers of any type were detected in the process blank and the Garlock Blue Gard gasket. These quality control procedures verified that the tremolite/actinolite, anthophyllite and crocidolite fibers found in the chrysotile-containing gaskets could only come from the chrysotile gaskets and not from any cross-contamination of the glassware, TEM grids, or any other source at this laboratory.

Two treated gasket residue samples already mounted on TEM grids were sent to an independent laboratory to verify that tremolite/actinolite was identified properly at MAS. Samples M18549-1 and M18549-7 were sent to Dr. Robert Stevenson of MCL in Oak Ridge, Tennessee to verify the identities of amphiboles in the two samples. Dr. Stevenson was not told the identity of the suspected amphibole. He was asked to make an independent assessment of the material. Dr. Stevenson's findings are located in Section 9 of this report. The findings confirm MAS' results shown in this report.

The suggestion that tremolite/actinolite asbestos is completely removed during processing of chrysotile ore was not supported by this study. It was demonstrated that chrysotile used in gasket sheet products tested in this study is contaminated with amphibole asbestos fibers. However, it is our belief that a general statement saying all chrysotile-containing products contain tremolite/actinolite would not be appropriate at this time without testing the individual products in questions.

REFERENCES

1) Williams-Jones, E.E., Normand, C., Clark, P., Vali, H., and Martin, F.R., *"Controls of Amphibole Formation in Chrysotile Deposits: Evidence From the Jeffrey Mine, Asbestos, Quebec"* The Health Effects of Chrysotile Asbestos: Contribution of Science to Risk-Management Decisions, Can. Mineral., Spec., Publ. 5, pp. 89-104 (2001).

2) Browne, K., *"Chrysotile Threshold of Risk"* Presented at an International Seminar on: Safety in the Use of Chrysotile Asbestos: Basis for Scientific Based Regulatory Action Havana, Cuba, September 2001.

3) Frank, A.L., Dodson, R.F. and Williams, M.G., *"Carcinogenic Implications of the Lack of Tremolite in UICC Reference Chrysotile"* American J. Ind. Med. 34, 314-318, 1998.

4) Environmental Protection Agency (EPA): Interim Method for the Determination of Asbestos in Bulk Insulation Samples*. EPA-600/M4-82-020, December 1982.

5) Gasket Removal Study I, *"Scraping Wire Brushing and Electric Wire Brushing"*, Materials Analytical Services Report, November 1997.

6) Gasket Removal Study II, *"Scraping and Handwire Brushing"*, Materials Analytical Services Report, April 2000.

7) Gasket Removal Study III, *"Scraping, Handwire Brushing and Electric Wirebrushing"*, Materials Analytical Services Report, May 2000.

8) Gasket Removal Study IV, *"Scraping, Handwire Brushing and Electric Wirebrushing"*, Materials Analytical Services Report, May 2001.

9) Gasket Removal Study V, *"Scraping and Electric Wirebrushing"* Materials Analytical Services Report, May 2001.

10) Environmental Protection Agency (EPA): Method for the Determination of Asbestos in Bulk Building Materials. EPA/600/R-93/116, July 1993.

11) Notes on a meeting between Doctors Elmes, Hodgson, and Browne representing the Asbestos Research Council and Sir Newille Stack, Directory General of the Asbestos International Association to discuss aspects of the problem of tremolite contamination of asbestos fibre (November 22, 1984).

REFERENCES
(continued)

12) Addison, J. and Davis, L.S.T.: *"Analysis of Amphibole Asbestos in Chrysotile and Other Minerals"* Ann. Occup. Hyg. Vol. 34, 2 pp. 159-179, 1990.

13) JCPDS International Centre for Diffraction Data, File Number 13-437, page 1192, 1986.

14) De, A. Pathology of Dikes Enplaced in the Ultramific Rocks of South Eastern Quebec, 1961, Princeton University.

15) Tremolite, Standard Reference Material, NIST 1867, Bulk Asbestos Uncommon (Anthophyllite, Actinolite, and Tremolite), US Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20899.

16) Crocidolite Standard Reference Material, NIST 1866, Bulk Asbestos Common (Chrysotile, Amosite, and Crocidolite), U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20899.