

APPENDIX I

0641688

TASK ORGANIZATION REPORT
EPA Contract No. 03-01-5915
October 14, 1980
(Revised October 20, 1980)



TASK 32 - STUDY PROTOCOL FOR THE COLLECTION AND ANALYSIS OF VERMICULITE AND RELATED SAMPLES FOR THE EVALUATION OF FIBER CONTENT WITH EMPHASIS ON ASBESTIFORM FIBERS

I. Background

In December 1978, the vermiculite industry submitted information to the EPA regarding health problems experienced by employees who were processing asbestos-contaminated vermiculite. The original submission indicated that bloody pleural effusions had been detected in 4 of 350 employees; symptomatology and clinical findings in the employees were similar to those found in individuals with asbestos-related diseases. Subsequent follow-up studies by the Occupational Safety and Health Administration (OSHA) revealed an even higher prevalence of health problems among the employees.

Vermiculite is a hydrated magnesium-iron-aluminum silicate which has been mined in the U.S. since 1929. W. R. Grace & Company ("Grace") produces most of the 300 thousand tons consumed domestically. After mining, vermiculite is usually processed to remove impurities; however, all contaminants are not removed. Such is the case with the vermiculite from the Grace Libby Montana mine which historically has had at least 1% tremolite asbestos remaining as a contaminant in their vermiculite. Recent technical advances have reportedly reduced the levels of tremolite.

Information has been received which suggests that the three major domestic deposits in Montana, South Carolina, and Virginia contain asbestiform minerals. Authorities in geology have expressed the opinion that all vermiculite mines may be contaminated with asbestiform minerals, including the South African mine which claims to be free of asbestiform minerals.

Although vermiculite may contain fibrous materials, the health effects from vermiculite itself are unknown at this time. A priority review of asbestos-contaminated vermiculite, completed by the Office of Testing and Evaluation in June 1980, suggested that the asbestos in vermiculite may be responsible for the reported adverse health effects and it concluded that certain information gaps need to be filled before an indepth risk assessment on vermiculite could be initiated.

Several projects have been initiated to fulfill the information gaps and complete the preregulatory analysis on vermiculite. A control options analysis has been initiated to determine regulatory strategy to control asbestiform mineral-contaminated vermiculite and a substitutes analysis is in preparation to evaluate replacements for vermiculite products. Work has also been initiated on a materials balance to show the mass flow of vermiculite along with the release of any associated asbestiform mineral and the development of a mineralogy profile with a sampling and analysis protocol of vermiculite is underway to characterize the fibrous materials within vermiculite.

From the available information on the composition of vermiculite, it seems there is the possibility that contamination of vermiculite does occur. For example, in their comments and response to the Consumer Product Safety Commission and the Environmental Protection Agency's joint-effort Announced Notice of Proposed Rulemaking on asbestos, Grace explains that the inadvertent mineral contaminant form (tremolite), which is generally associated with vermiculite appears in a fibrous and nonfibrous form. This type of information suggests that it may be difficult to assess the magnitude of the contamination of the vermiculite.

Therefore, the objective of this protocol is to specify the sampling and analysis procedure to determine the composition of vermiculite, particularly the amount of asbestiform minerals present in the vermiculite. This will provide the needed information on the risk to the population exposed to asbestiform minerals from vermiculite at each of the various stages of its commercial distribution. Included in the protocol will be an indepth analysis of the asbestiform fibers present in the vermiculite. The protocol will address:

1. The selection, collection, and analysis of bulk samples of:
(a) raw vermiculite ore samples from the four major vermiculite mines in the U.S and from the ports of entry; (b) beneficiated vermiculite ore samples from the four major vermiculite mines in the U.S. and from the ports of entry; and (c) exfoliated vermiculite ore samples from a representative number of exfoliation plants in the U.S. The exfoliation plants where sampling will occur will be statistically chosen by Exposure Evaluation Division (EED) to include all the major sources of vermiculite.

2. The selection, collection, and analysis of air samples taken at sites associated with (a) the handling of raw vermiculite ore at the four major vermiculite mines in the U.S.; (b) the beneficiation of vermiculite ore at the four major vermiculite mines in the U.S.; and (c) the exfoliation of vermiculite ore from a representative number of exfoliation plants in the U.S. The exfoliation plants where sampling will occur will be statistically chosen by EED.

II. Preparation for Sampling

A. Inventory and Preparation of Supplies

1. All necessary equipment for sampling bulk vermiculite and air will be gathered and inventoried.

2. Filters to be used for the collection of airborne particles will be assembled and labeled before samples are obtained.

3. Calibration of the pumps will be performed prior to their shipment to the sampling site.

4. All supplies will be packed and shipped to the vermiculite sampling site at least 2 days in advance of the arrival of the crew.

5. Replicate prenumbered sample identification labels will be prepared for field application to sample containers and the field notebook.

B. Site Investigation

1. Survey site - Upon arrival at the site, the crew chief and other designated persons will survey the site to determine the location of the facility, its boundaries, and the locations of various operations within the facility.

2. Select sampling points - The crew chief and other designated persons will select appropriate points for the collection of ore samples and airborne particulates. Officials of the host plant will be invited to participate and assist in the survey and selection of sampling points.

III. Sampling

A. Bulk Material

1. Basis for selection of protocol - No American Society for Testing Materials (ASTM) method was found that is directly applicable to this situation. The following related methods are used for guidance.

a. American National Standards Institute (ANSI)/ASTM D 75-71 (1978) Standard Methods of Sampling Aggregates.

b. ASTM Designation: D 2234-72 Standard Methods for Collection of a Gross Sample of Coal.

c. ANSI/ASTM E 105-58 (1975) Standard Recommended Practice for Probability Sampling of Materials.

d. ASTM Designation: C 702-72 Standard Methods for Reducing Field Samples of Aggregate to Testing Size.

e. ASTM Designation: C 516-75 Standard Specifications for Vermiculite Loose Fill Insulation.

f. BS 812 (British Standards Institution) Methods for Sampling and Testing of Mineral Aggregates, Sands and Fillers.

g. Other Considerations - The minimum quantity of any sample should be 5 to 10 times the anticipated analytical needs. The analytical needs will vary with particle size and range from approximately 40 g for fine material to 1,000 g for 25-mm particle size. Therefore, sample size minimums should range from 400 g to 10 kg.

Each sample may consist of a composite of individual sampling increments representing different times and/or locations. Increments will be sampled and stored separately with a composite made under laboratory conditions by combining representative fractions of each increment.

2. Samples to be collected - The objective of sampling is to obtain samples that are representative of the operations or sites. It is anticipated that properties of the materials of similar types will vary with time, operation and specific mine site origin. Therefore, to obtain representative samples, it is necessary that composite samples be prepared of a given sample type from individual sample increments, each representing a specific sample time or site. It is likely that a historical sample collection is maintained (by the mine company) from several operation points within the facility. If these historical samples are available, it would be helpful to obtain selected increment samples for both the preparation of a time averaged composite and a comparison of present to past conditions.

The number of increment samples to be collected must depend on the variability of the sample and availability of increment sources, with a decision made by an experienced sampler depending upon increment availability and proper sampling procedures. All decisions will be documented with copies sent to the EPA task manager.

The following sample types will be collected, except where specific operational conditions dictate variations from these sample categories. Any variations from these sample categories will be documented and copies will be sent to the EPA task manager.

a. Raw ore

(1) A bulk sample of the raw vermiculite ore before crushing representing different parts of the mine.

(2) A bulk sample of the raw vermiculite ore after crushing for beneficiation.

(3) A bulk sample of dust from the dust collection equipment where such equipment exists.

(4) A water sample from washings and dust control operations.

b. Beneficiated ore

(1) A bulk sample of each of five grades of beneficiated vermiculite ore.

(2) A bulk sample of ore from one to three intermediate beneficiation processing steps.

(3) A bulk sample of dust from dust collection equipment.

(4) A water sample from washing and dust control operations.

c. Exfoliated material

(1) A bulk sample of each of five grades of exfoliated vermiculite ore.

(2) A bulk dust sample from dust collection equipment and other appropriate related material.

B. Air Samples

1. General considerations - Airborne particulate samples will be collected at designated points inside and outside the plant boundaries. The sampling will generally follow the EPA method described in Electron Microscope Measurement of Airborne Asbestos Concentrations - A Provisional Methodology Manual, EPA-600/2-77-178, Revised June 1978. This method uses polycarbonate 0.4 μ m Nucleopore filters when possible, but allows for the use of cellulose acetate (Millipore) filters.

There are advantages and disadvantages to the use of either Nucleopore or Millipore filters. The sample collected on the smooth polycarbonate (Nucleopore) surface has poor retention efficiency and the sample may be lost or redistributed during transport. The cellulose acetate (Millipore) filters requires an ashing procedure and reconstitution on a polycarbonate filter for TEM analysis. Ashing and reconstitution is an extra step in the procedure but has the potential advantage of eliminating interfering organic matter and provides the opportunity to adjust the filter loading for optimum particle analysis. This reduces the need of multiple time sampling to obtain a range of filter loadings. Asbestos contamination has been reported in some lots of both Nucleopore and Millipore filters.

The current consensus of leaders in the field is to favor the use of Millipore filters for the type of sampling and transport that will be required on this program.

The potential presence of asbestos fibers in the filters themselves will require careful attention to the selection and analysis of filter blanks and field blanks.

2. Control blanks

a. Filter blanks - Four filters from each package of 100 filters, one from each box of 25, will be selected by random numbers as filter blanks. The four filters will be quartered and one-fourth of each combined as a composite sample.

b. Field blanks - One of every 10 filters will be a field blank, subjected to all processing conducted with an actual air sample except for the sampling itself.

3. Sampling procedure - All sampling, fixed and personal, will be taken using 37 mm 0.45 μ m Millipore filters backed with 5 μ m Millipore filters and a Millipore support pad. The sampling rate will be approximately

2 liters/min with the exact rate determined periodically throughout the sampling period by the use of calibrated flow meters.

Sampling will be scheduled for 8 hr (or longer for ambient and background samples). However, if the flow is found to reduce during sampling, indicating that the filter is loaded, sampling will be stopped and the time and flow rate recorded.

4. Air samples to be collected - Personal air zone samples and fixed samples located at targeted areas will be taken. The use of personal samples will depend on the individual work patterns and on the cooperation of the host company. When possible, individuals at each work station will be equipped with personal samplers.

When possible, air samples will be taken which correspond to the bulk samples (Section III-A-2). The following air samples will be taken. Any variation from these sampling locations will be documented.

a. Air samples taken from the raw ore operations.

- (1) An air sample at the mine during mining.
- (2) An air sample at the crushing operation.
- (3) Air samples around the mining facility.
- (4) Air samples downwind of dusty operations.
- (5) Air samples along shipping lanes.

(6) An air sample as a background control within the geographic region.

b. Air samples taken from the ore beneficiation operations. (Where mining and beneficiation are at the same general location, several of the samples may be the same.)

(1) An air sample at each of selected work stations in the beneficiation operation.

- (2) Air samples around the beneficiation plant.
- (3) Air samples downwind from dusty operations.
- (4) Air samples along shipping lanes.

(5) An air sample as a background control within the geographic region.

c. Air samples taken from the exfoliation operation.

(1) An air sample from each of selected work stations in the exfoliation operations.

(2) Air samples around the exfoliation plant.

(3) Air samples downwind from dusty operations.

d. A meteorological station will be installed on-site to collect air speed and direction data throughout the sampling period.

IV. Sample Handling

A. Bulk Samples

The increment samples will be shipped to a central laboratory. Each increment sample will be divided by appropriate procedures (riffle divided or cone and quarter). Part of each increment will be retained and the remainder combined with other appropriate increments to form a composite sample. The composite will be mixed and split (riffle or cone and quartered) to provide appropriate split analytical samples. The composite samples will be properly designated and submitted for analyses.

B. Air Samples

1. Special handling - When sampling is completed, the filter cartridge will be turned to a position with the filter horizontal and the collection surface up, the cartridge disconnected from the pump and the inlet and exit holes plugged. This horizontal filter position will be maintained during transport and storage. The cartridge will be placed in a special container for transport to MRI.

2. Each filter will be divided and hand carried to different laboratories to provide for replicate analysis.

V. Sample Analysis

A. Bulk Sample Analysis

The analysis protocol for the bulk vermiculite samples will include parallel approaches which, to a degree, support one another. However, because of the great differences in the detection limits of the different methods, the justification of some approaches is their simplicity as preliminary screening procedures rather than their sensitivity. X-ray diffraction and optical microscopy of the unfractionated samples are examples of simple procedures with limited sensitivity. These methods may serve to identify some samples with gross quantities of asbestiform minerals and eliminate the need for continued analysis.

1. Unexfoliated raw and beneficiated ore

- a. Examine the sample as received with low power (30X) stereomicroscopy for quantities of visible fibers.
- b. If no fibers are found, proceed to step f.
- c. If fibers are visible, determine if they are free and not attached to the vermiculite particles and are in a weighable quantity. If not, proceed to step e; otherwise continue.
- d. Make a density separation, remove (hand pick) the non-asbestos material from the fraction, and weigh the asbestiform fibers.
- e. Identify the asbestiform mineral by appropriate means (PLM, TEM, SEM, SAED, XRD, or EDXA). Proceed to step f if additional analysis is needed.
- f. Exfoliate the sample by heating for 3 to 6 sec at 800°C and proceed to 2.

2. Exfoliated vermiculite - Steps a and b below are conducted in parallel. Examination of the unfractionated sample will have a low sensitivity for asbestos but will complement the overall procedure.

a. Examination of unfractionated sample

- (1) Grind the sample using a mortar and pestle. Sieve the sample with a 140 U.S. series equivalent sieve.
- (2) Regrind the fraction that does not pass the screen. Any material that still does not pass through the 140 sieve is primarily vermiculite and mica and contains a greatly reduced asbestos content.
- (3) Examine the ground material by XRD for total amphiboles.
- (4) Examine the ground material by PLM for asbestos fibers.

b. Examination of fractionated (asbestos-enriched) samples - An important feature of the analytical procedure to achieve high microfiber detection sensitivity is the fractionation of the sample to remove much of the interfering vermiculite, thereby greatly enriching whatever asbestiform fibers that may be present. The basis of fractionation is the floatation on water of the exfoliated vermiculite and the wetting and sinking of the asbestos and other fibers. This assumes that a proportionally high fraction of the fibers are not physically attached to the vermiculite particles. This is a reasonable assumption but one that will be verified by the examination of representative samples of the fraction that floats.

Start with a sample quantity depending on particle size,

<u>Particle Size</u>	<u>Sample Size</u>
1 mm	10 g
5 mm	50 g
10 mm	100 g
25 mm	250 g

and proceed as follows:

(1) Float separation - Place sample in water; vermiculite will float; released asbestos will sink. Skim off vermiculite and discard.*

(2) Disperse heavy material with ultrasonic treatment. Remove an aliquot during treatment for a preliminary PLM examination and for TEM analysis. Double dilution may be necessary to obtain proper grid loading.

(3) Examine preparation by PLM as a preliminary parallel examination.**

(4) Prepare TEM grid by EPA carbon-coated Nucleopore filter technique.

(5) Fiber count - Determine chrysotile and total amphiboles. Count 100 fibers of chrysotile or amphiboles or 10 grids of 200-mesh screen. Determine limit of detection and count more grids if necessary.

(6) Identify specific amphiboles using SAED or zone axis selected X-ray diffraction.

3. Miscellaneous bulk samples

a. Dust samples

(1) A preliminary examination of the dust sample will be made by optical microscopy including PLM for the identification of gross quantities of asbestiform fibers. If gross quantities of fibers are identified, the quantities will be estimated and the analysis terminated.

(2) If the sample is not adequately characterized by PLM, a portion of the sample will be dispersed in water and filtered for EM analysis.

* Selected samples will be examined to verify the absence of asbestos in this fraction.

** If PLM examination reveals a gross quantity of identifiable asbestiform fibers, the quantity should be estimated and the analysis terminated.

b. Wash water samples - The solids present will be dispersed in the water and aliquots filtered for appropriate optical and EM analysis.

B. Air Samples

The analysis of air samples will basically follow that specified in the EPA document, "EPA-600/2-77-178, Revised June 1978, Electron Microscope Measurement of Airborne Asbestos Concentrations - A Provisional Methodology Manual."



APPENDIX II

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SAMPLING POINTS

I XTRANSFER POINT

- 1) OPERATOR (4:30)
- 2) ROCK GATE CONTROL AREA OR OUTSIDE CONTROL ROOM OVER ORE BELTS
- 3) SIDE OF SCREEN
- 4) OTHER SIDE OF SCREEN BY THE STAIRS
- 5) BOTTOM FLOOR ON SWITCH BOX OR CONCRETE WALL

II X O.S.&E.

- 1) ED GASTON- BELT MAN (3:30)
- 2) = AIR SYSTEM
- 3) = AIR SYSTEM (NOTE WHETHER STACKER OR RECLAIMER SIDE)

III X MILL OPERATORS (ALL LEAVE AT 3:30)

- 1) ~~SKIP~~ OPERATOR
- 2) BOTTOM FLOOR OPERATOR (UTILITY)
- 3) MIDDLE FLOOR OPERATOR (NO. 1)
- 4) UPPER FLOORS OPERATOR (5-10) NOTE WHETHER HE'S CHANGED SCREENS (NO. 2)
- 5) CONTROL ROOM OPERATOR

IV X MILL TEST LAB

- 1) RICHARD FIELDS (LAB ASSAYER)
- 2) MINE TESTER
- 3) MILL TESTER

V X MILL FLOORS (1-10)

NOTE WHETHER ORE SPILLED ON ANY FLOOR, AIR PURIFIERS RUNNING, AIR PURIFIERS CLEAN, WHETHER OVERHEAD DOORS ARE OPEN.

PLACE 2 SAMPLES ON 4th FLOOR: ON FIRE STATION, OR SCREEN AREA OR OUTSIDE LAB AREA

VI X DRYER BAGHOUSE (1-4)

II X SCREENING PLANT OPERATORS

- 1) OPERATOR (3:00)
- 2) SHUTTLE TRUCK DRIVER (3:00)
- 3) HAUL TRUCK- KENWORTH (2:00)
- 4) TEST LAB- JOHN CRAVER (4:30)
- 5) RAY CARLSON- LOADOUT



Butte, Montana
406/723-8075

0641699
Pocatello, Idaho
208/237-2763

III XSCREENING PLANT

- 1) FLOORS (1-6)
- 2) BELT HOUSE
- 3) CONTROL ROOM

IX EXPORT

- 1) KENNY FREDRICKS- DRIVES FOR EXPORT OR SCREENING PLANT (2:30)
- 2) DALE VINSON- FOREMAN
- 3) BAG STACKER
- 4) BAGGING ROOM

X MINE PERSONNEL

- 1) DRILLS (DO BOTH IF RUNNING)
- 2) DOZER
- 3) LOADER
- 4) GRADER
- 5) MOBILE TEST LAB (4:30)
- 6) PIT HAUL TRUCKS

APPENDIX III

Personal Samplers

LIBBY

- 1) Front end loader operator MINE #1
- 2) Shuttle driver SAGIN PLANT 2
- 3) Operator -- at transfer point 145 OPERATING 11/23 1
- 4) Pit haul truck driver 1
- 5) Blending & Storage bldg worker #2 mill operator 1
- 6) Mine taster ("popcorn" man) 1
- 7) Bottom floor operator, mill 1

Stationary Samplers

- 1) Screening operation (upwind) 2
- 2) " " downwind 2
- 3) " " " 2
- 4) ~~Bagging Operation downtown (inside bldg) -- 2 1:00 OPERATING 11/23 PM~~
- 5) Top bench NE side downwind (?) 2 SAMPLERS. 1
- 6) NW of tailings pond on road (crosswind?) -- 2
- 7) SE of mine along road (crosswind?) 2
- 8) Carnoy creek road SW of mine (upwind?) 2

Depends on wind direction day of sampling

Stationary Samplers (concluded)

- 9) ~~Transfer point NE side~~ 1
- 10) Control point upwind and off mine property 2
- 11) Across river at hopper car loading site 2
- 12) ~~Officer/hoghouse area~~
Filter house (back of house) 1

Meteorological Stations

- 1) Screening operation
- 2) Top bench NE side (downwind)

	<u>MINE</u>	<u>SCREENING</u>
Pierman	6	1
Erc	6	6

APPENDIX IV

Sampling Points

4 November, 1980.
Grace, Enmore, SC

A. Mill1. personnel

- a. lab
- b. mill feed operator (MONITOR 2)

2. point

- a. upper floor level of mill

B. Effoliation1. personnel

- a. bagger
 - b. bagger
 - c. bagger
 - d. forklift operator
- } one each operating line

2. point

- a. office of effoliation plant

C. Perimeter1. point

- a. upwind
- b. downwind (2)
- c. exhumed (?)
- d. control