

A Fiber Characterization of the Natural Zeolite, Mordenite: A Potential Inhalation Health Hazard

Dale J. Stephenson , Charles I. Fairchild , Roy M. Buchan & Maxine E. Dakins

To cite this article: Dale J. Stephenson , Charles I. Fairchild , Roy M. Buchan & Maxine E. Dakins (1999) A Fiber Characterization of the Natural Zeolite, Mordenite: A Potential Inhalation Health Hazard, *Aerosol Science & Technology*, 30:5, 467-476, DOI: [10.1080/027868299304507](https://doi.org/10.1080/027868299304507)

To link to this article: <https://doi.org/10.1080/027868299304507>



Published online: 30 Nov 2010.



Submit your article to this journal [↗](#)



Article views: 292



View related articles [↗](#)



Citing articles: 7 View citing articles [↗](#)



A Fiber Characterization of the Natural Zeolite, Mordenite: A Potential Inhalation Health Hazard

*Dale J. Stephenson, Charles I. Fairchild, Roy M. Buchan,
and Maxine E. Dakins*

INDUSTRIAL HYGIENE PROGRAM, ROCKY MOUNTAIN CENTER FOR OCCUPATIONAL
AND ENVIRONMENTAL HEALTH, UNIVERSITY OF UTAH, 75 SOUTH 2000 EAST,
SALT LAKE CITY, UT 84112-5120 (D.S.), LOS ALAMOS NATIONAL LABORATORY,
ENVIRONMENT, SAFETY AND HEALTH DIVISION, INDUSTRIAL HYGIENE AND SAFETY
GROUP, RESEARCH AND DEVELOPMENT SECTION, MS K499, LOS ALAMOS,
NM 87545 (C.F.), COLORADO STATE UNIVERSITY, COLLEGE OF VETERINARY MEDICINE
AND BIOMEDICAL SCIENCES, DEPARTMENT OF ENVIRONMENTAL HEALTH,
OCCUPATIONAL HEALTH AND SAFETY SECTION, 133 ENVIRONMENTAL HEALTH
BUILDING, FT. COLLINS, CO 80523-1681 (R.B.), UNIVERSITY OF IDAHO,
ENVIRONMENTAL SCIENCE PROGRAM, 1776 SCIENCE CENTER DRIVE,
IDAHO FALLS, ID 83402 (M.D.)

ABSTRACT. Interest in mordenite as an inhalation hazard arose when it was discovered that the mineral exists in the subsurface of Yucca Mountain, NV, the site of a federally proposed nuclear waste repository. During preliminary geologic investigations at Yucca Mountain, workers performing air coring (dry-drilling) operations were potentially exposed to aerosols of mordenite. Mordenite is also increasingly used in industrial applications, such as cation exchange, molecular absorbency, and reversible dehydration. Concern that the fibrous nature of mordenite may present an inhalation hazard is supported by the "Stanton Hypothesis," which states that the carcinogenicity of any fiber type depends upon dimension and durability rather than physicochemical properties. To date, little scientific literature is available on the inhalation health hazards of mordenite. This study initiates research in this area.

Mordenite specimens collected from different geologic localities were analyzed macroscopically and microscopically. Mineral verification was performed using energy dispersive x-ray and x-ray diffraction analysis. Fibrous aerosols were generated to simulate aerosols created during air coring operations. Anderson cascade impactors were used to obtain aerosol mass median aerodynamic diameters. Electron microscopy of nucleopore filters allowed for individual aerosol fibers to be morphologically sized and applied to the Stanton Hypothesis for mesothelioma induction. Physical fiber dimensions were used to calculate aerodynamic diameters and to estimate pulmonary deposition. Results obtained from this study indicate that under similar conditions of aerosolization, using similar mordenite materials, inhalation of mordenite fibers could produce substantial deep-lung deposition.

INTRODUCTION

Mordenite is an aluminosilicate zeolite mineral. Like all natural zeolites, it is characterized by crystallographic chains of linked SiO_4 tetrahedra. Their unique structural and chemical properties (ion exchange, reversible dehydration, acid and heat stability, and molecular absorbency) make all zeolites favorable to a wide variety of commercial applications ranging from waste-effluent treatment to paper production (Mumpton 1976).

Little scientific data exists documenting human exposure to mordenite minerals. An exposure to environmental zeolites was brought to the world's attention when Baris et al. (1978) reported an outbreak of mesothelioma in 2 villages in the Cappadocia region of Turkey. In another case of potential environmental zeolite exposure, Casey et al. (1981) treated a patient with extensive parenchymal and pleural fibrosis who resided and worked in an area rich in zeolite deposits. A similarly fibrous zeolite, erionite, has been shown to produce pleural tumors in rats (Wagner et al. 1985; Johnson et al. 1984; Maltoni et al. 1982; and Suzuki 1982).

Increased scrutiny is being placed upon a fiber's dimensional characteristics and the role they play in the induction of pulmonary disease. A fiber's aerodynamic diameter is known to be a major factor in predicting the degree and anatomical location of pulmonary deposition. Stanton et al. (1981) formed a hypothesis stating that the carcinogenicity of all fibers depends upon dimension and durability rather than physicochemical properties. Stanton and Layard (1977) devised size categories that correlate fiber dimension with the probability of pleural mesothelioma in rats.

Scientific evidence suggests that mordenite may be an inhalation health hazard. Industrial applications involving zeolites make occupational exposure to aerosolized fibers a possibility. This was exemplified during air coring operations at Yucca Mountain, NV (the site of a federally proposed nuclear waste repository).

Thus, air coring was simulated in a mechanical aerosolization process.

All analyses concentrated on the dimensional, aerodynamic, and depositional aspects of mordenite fibers. This characterization was undertaken to identify similarities between mordenite and other known disease-inducing fibers. No direct evidence was found implicating mordenite fibers in pulmonary disease or carcinogenesis. This study is intended to raise awareness of this fibrous mineral and set the foundation for future scientific studies.

METHODS

Fibrous evaluation of mordenite samples was performed by macroscopic and microscopic inspection. Based upon the prevalence of fibers seen during scanning electron microscopic (SEM) evaluations, 3 mordenite specimens (Bucoda, WA, [BU]; Eagle Eye, AZ, [EE]; and Yucca Mountain, NV, [YU]) were chosen to be aerosolized in a specially designed aerosol generation system (Figure 1).

Aerosolization was by mechanical disintegration of fibrous material using a Dremel, high-RPM, moto-tool drill. Mordenite minerals were verified by quantitative x-ray diffraction using the Reference Intensity and Rietveld Methods. Mineral densities were determined by triplicate measurements using helium pycnometry (Model MVP-1 Multipycnometer, Quantachrome Corporation, Sysosset, NY).

Four aerosol collection devices were used, 2 Anderson 1 ACFM Ambient Particle Sizing Samplers and 2 nucleopore filter samplers. One vacuum pump provided flow and aerosol mixing within the collection chamber. The Anderson impactor collection surfaces were Gelman, 76-mm polypropylene filters. These filters were weighed using a Mettler AE260 Microbalance having a gravimetric sensitivity of $\pm 10 \mu\text{g}$. The nucleopore, 0.2- μm , 25-mm filters were housed in Gelman, 25-mm Delrin in-line filter holders and were used to acquire scanning electron photomicrographs.

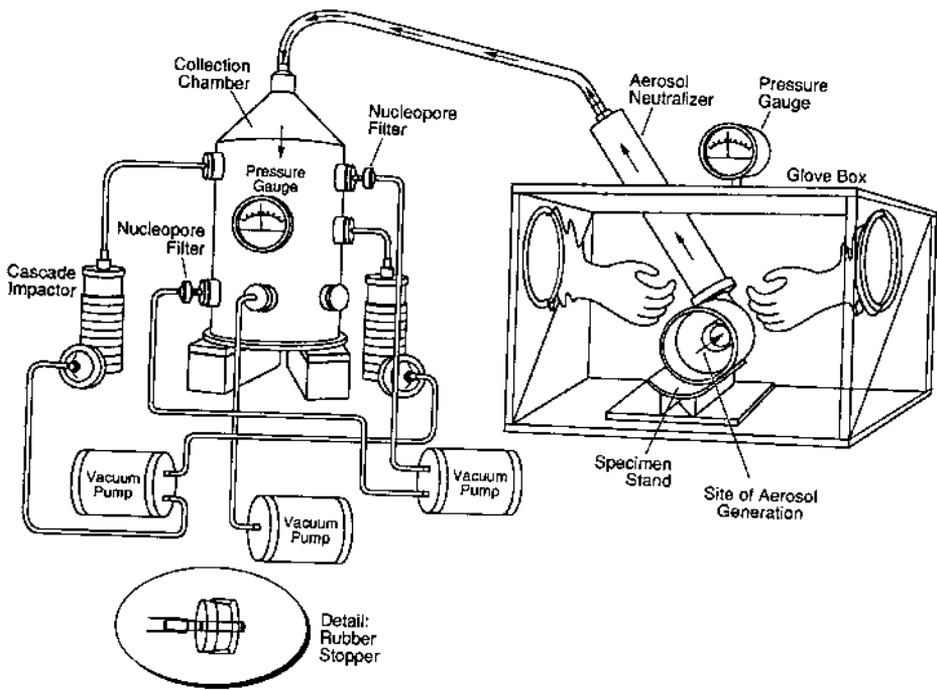


FIGURE 1. Aerosol generation and collection system.

Five, 2 min, aerosol sampling runs were performed. Two runs were performed on each of the BU and EE specimens. One run was performed on the YU specimen. Flow rates during each run were 28.3 L/min for each particle size sampler, 2 L/min for each nucleopore filter sampler, and 18 L/min for the vacuum pump associated with aerosol chamber mixing. Between each run, the aerosol generation system and impactor samplers were washed and air dried to avoid cross contamination. All impactor stages were analyzed between runs using a Wild Heerbrug M8 stereo-light microscope to confirm that no significant interstage fiber losses occurred.

Gravimetric analysis of cascade impactor filters was used to calculate mass median aerodynamic diameters (MMAD) and associated geometric standard deviations (GSD). Respirable mass fractions were estimated as a function of

MMAD and GSD using respirable mass fraction curves developed by Moss and Ettinger (1970). These curves used the American Conference of Governmental Industrial Hygienists (1969) definition of respirable dust.

Mordenite fibers collected on nucleopore filters were morphologically sized using SEM. A Bausch & Lomb measuring magnifier (1000x) was used to obtain size measurements directly from photomicrographs using NIOSH reference method 7402 for analyzing asbestos fibers (1989). Fiber length, width, and aspect ratio were noted, up to a fiber count of 1000. SEM evaluation of the YU specimen yielded 9 fibers in 200 fields. Given the low statistical confidence obtainable from such a small sample size, fibers from the YU specimen were not sized. All sized fibers were applied to Stanton and Laryard's (1977) dimensional categories. Using the

dimensional characteristics of sized fibers, aerodynamic diameters were calculated using formulas developed by Stober (1972).

Derived fiber aerodynamic diameters were used to estimate regional pulmonary aerosol deposition according to Stahlhofen et al.'s (1989) deposition equations. Estimation of fiber deposition was performed for the extra-thoracic, thoracic, and alveolar regions. Formulae were based on typical respiratory parameters exhibited during physical work (a respiratory flow rate of $750 \text{ cm}^3\text{s}^{-1}$ and a tidal volume of 1000 cm^3) and mouth breathing. Nasal deposition was assumed to be negligible and was not estimated.

RESULTS

MMADs for each aerosol run are shown in Figures 2–4.

All MMADs were within the respirable range ($< 10 \mu\text{m}$) and all, except 1, were within or close to the size range noted for maximum alveolar deposition efficiency ($2\text{--}4 \mu\text{m}$). Application of MMADs and associated GSDs to Moss and Etinger (1970) curves gave estimates of aerosol respirable mass fractions. Respirable mass is defined as the ability of particulate mass to penetrate to the gas-exchange region of the lung. Half of the estimates were over 50% and 7 of 10 were over 40%, indicating that a relatively high

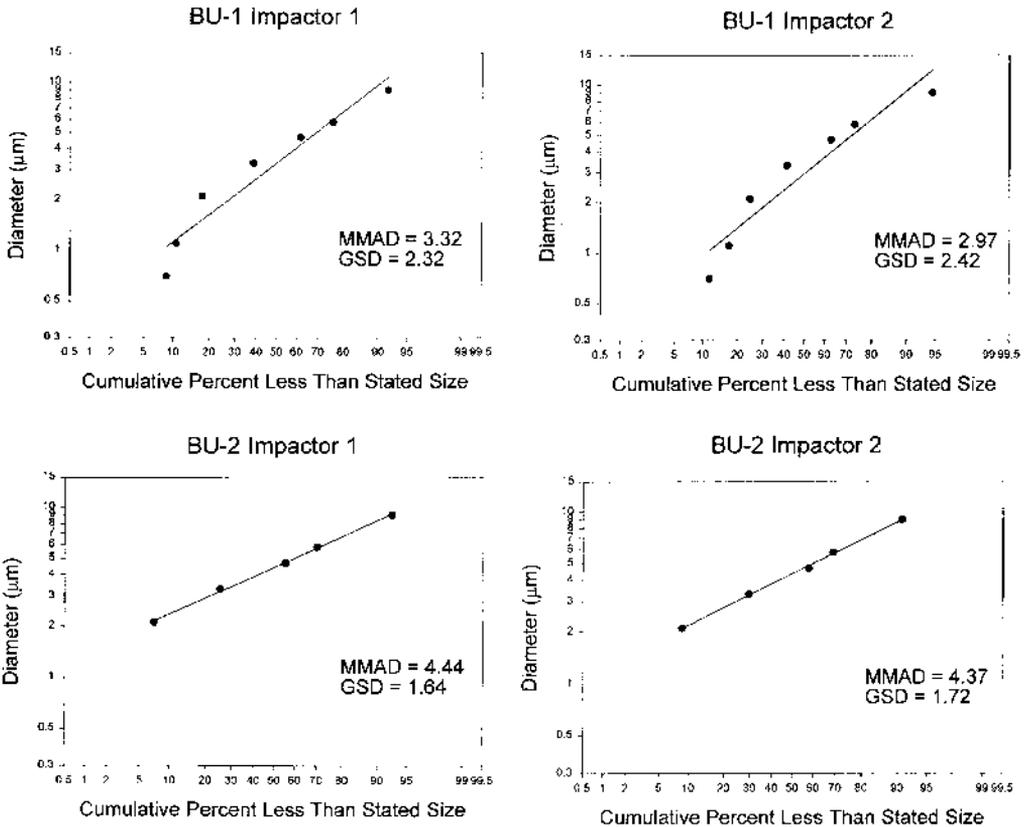


FIGURE 2. Impactor characterization of BU aerosols.

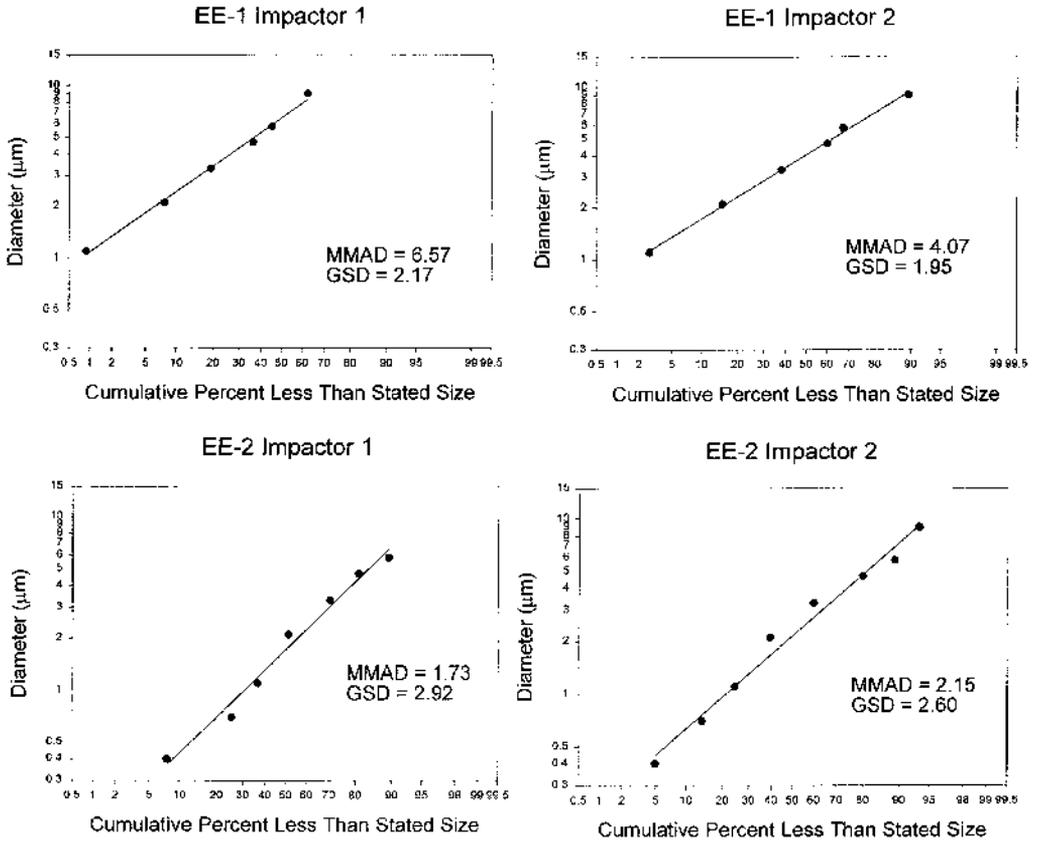


FIGURE 3. Impactor characterization of EE aerosols.

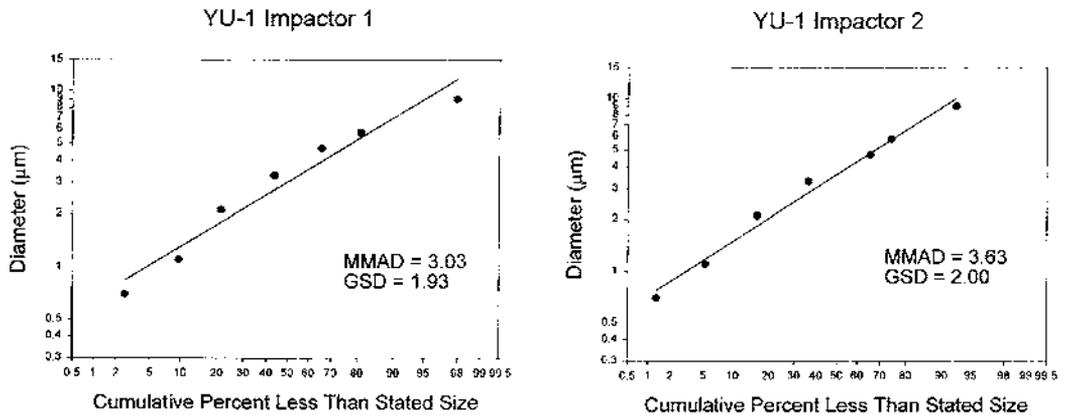


FIGURE 4. Impactor characterization of YU aerosol.

TABLE 1. Aerosol respirable mass fractions.

Aerosol ID	MMAD (μm)	GSD	Respirable Mass Fraction ^a
BU-1(#1) ^b	3.32	2.32	0.52
BU-1(#2)	2.97	2.42	0.58
BU-2(#1)	4.44	1.64	0.39
BU-2(#2)	4.37	1.72	0.39
EE-1(#1)	6.57	2.17	0.26
EE-1(#2)	4.07	1.95	0.42
EE-2(#1)	1.73	2.92	0.69
EE-2(#2)	2.15	2.60	0.64
YU-1(#1)	3.03	1.93	0.57
YU-1(#2)	3.63	2.00	0.48

^aBased on extrapolation from respirable mass fraction curves developed by Moss and Ettinger (1970).

^bNumbers in parentheses designate impactor number.

percentage of each mordenite aerosol would potentially penetrate to the alveolar region of the lung (Table 1).

Fiber length, diameter, and aspect ratio distributions were assumed to be lognormal and are described using their geometric means (GM) and GSD for each morphological feature in Table 2.

TABLE 2. Fiber morphology.

	Mineral Specimen	
	Bucoda, WA	Eagle Eye, AZ
FIBER DIAMETER		
Geometric Mean (μm)	0.74	0.55
Geometric Standard Dev.	1.67	1.43
FIBER LENGTH		
Geometric Mean (μm)	7.42	5.40
Geometric Standard Dev.	2.39	2.25
FIBER ASPECT RATIO		
Geometric Mean (μm)	9.98	9.94
Geometric Standard Dev.	2.41	2.12

Application of measured fiber lengths and widths to the dimensional categories developed by Stanton and Layard (1977) demonstrated that for the BU aerosol, 65% of sized fibers fell into the 4 categories associated with the highest risk

for inducing pleural mesotheliomas. For the EE aerosol, 57% of sized fibers fell into the same high-risk categories (Table 3).

Fiber aerodynamic size distributions (Figures 5 and 6) followed a lognormal probability model.

The number of fibers having aerodynamic diameters of 1.5–4 μm was compiled. The compilation showed that 63.1% of the BU aerosol and 23.6% of the EE aerosol have fibers that fall within this range of enhanced alveolar deposition efficiency.

Application of calculated aerodynamic diameters to Stahlhofen's (1989) equations yielded pulmonary deposition estimates for the BU and EE specimens (Table 4).

These estimates show a large percentage of each distribution (BU: 37.5%; EE: 38.6%) depositing in the alveolar region, suggesting that inhalation of such aerosols could produce substantial deep-lung deposition.

DISCUSSION

Macroscopic analysis of mordenite specimens yielded insight into their relative fibrous nature. The EE and BU specimens were visibly fibrous. In contrast, the YU specimen showed no visible indication of fibrous material.

TABLE 3. Number of fibers corresponding to Stanton and Layard's (1977) fiber dimensional categories.

Bucoda, WA Specimen			
Fiber Diameter (μm)	Fiber Length (μm)		
	> 4	> 4 - 8	> 8
> 4	—	—	4(-.38) ^a
> 1.5-4	—	25(-.24)	45 (.13)
> 0.25-1.5	273 (.01)	283 (.45)	356 (.68)
> 0.25	5 (.20)	5 (.63)	4 (.80)

Eagle Eye, AZ Specimen			
Fiber Diameter (μm)	Fiber Length (μm)		
	> 4	> 4 - 8	> 8
> 4	—	—	1(-.38)
> 1.5-4	—	3(-.24)	4 (.13)
> 0.25-1.5	416 (.01)	297 (.45)	273 (.68)
> 0.25	4 (.20)	1 (.63)	1 (.80)

^aPercentages in parentheses are correlation coefficients associated with the probability of inducing pleural sarcomas in rats (Stanton and Layard, 1978).

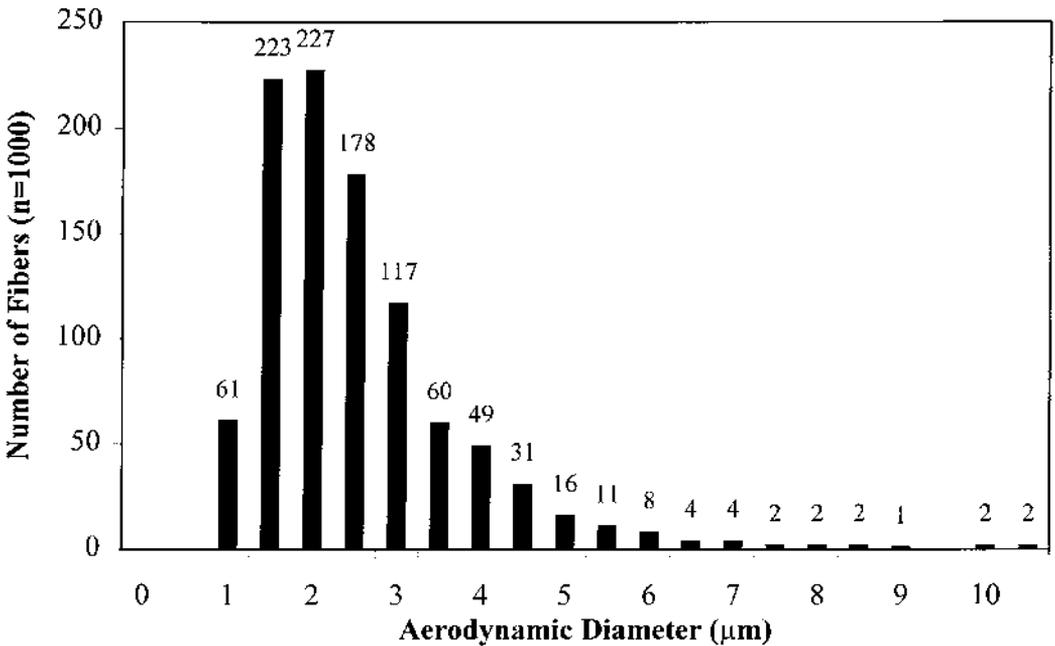


FIGURE 5. BU fiber aerodynamic diameter distribution.

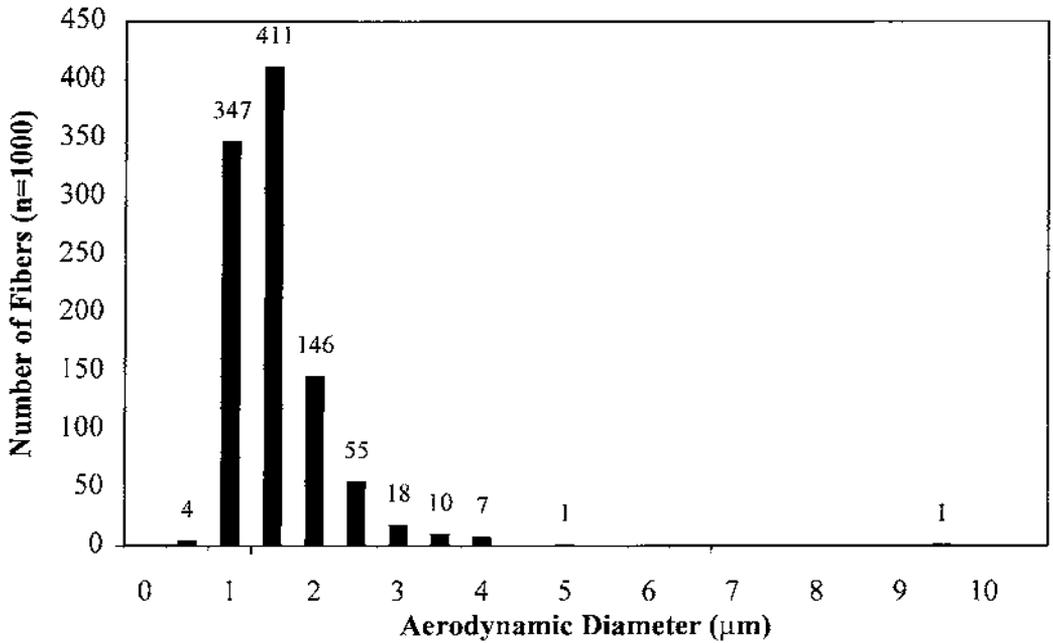


FIGURE 6. EE fiber aerodynamic diameter distribution.

TABLE 4. Regional fiber deposition.

Interval Maximum (μm)	Fiber Frequency		Regional Percent Deposition					
	Specimen ID		Extra-Thoracic		Thoracic		Alveolar	
	BU	EE	BU	EE	BU	EE	BU	EE
0.4	0	1	0	0	0	0	0	0
0.5	0	0	0	0	0	0	0	0
0.6	1	3	0	0	0	0	0	0
0.7	6	2	0	0	0	0	.001	0
0.8	13	24	0	0	0	.001	.003	.005
0.9	18	22	0	0	.001	.001	.004	.005
1.0	23	45	0	0	.001	.002	.007	.011
2.0	448	699	.005	.009	.059	.092	.182	.284
3.0	294	160	.014	.007	.077	.042	.126	.068
4.0	109	32	.013	.004	.042	.012	.038	.011
5.0	47	10	.010	.002	.021	.004	.011	.002
6.0	19	0	.006	0	.009	0	.003	0
7.0	8	1	.004	0	.003	0	0	0
8.0	6	0	.003	0	.002	0	0	0
9.0	4	0	.003	0	.001	0	0	0
10.0	4	1	.003	.001	.001	0	0	0
Totals	1000	1000	.051	.023	.217	.154	.375	.386

Scanning electron photomicrographs of the EE and BU specimens showed many acicular, symmetrical fibers. Unlike macroscopic results, microscopic analysis of the YU specimen revealed many small (diameters < 0.25- μ m), curly, hair-like fibers.

Aerosolization and collection of the YU specimen provided few fibers for analysis. One explanation for the lack of YU fibers is that the degrading action of the Dremel moto-tool drill bit modified their morphologic features, thus the resultant aerosolized material did not fit the NIOSH definition of a fiber. This is an important finding in terms of occupational exposure to such aerosols.

Energy-dispersive x-ray analysis showed that the major elemental constituents of the mordenite specimens were silica and aluminum. Quantitative x-ray diffraction analysis (XRDA) proved that mordenite was the major mineral phase in each specimen.

CONCLUSIONS

The differences found in the fibrous nature of collected mordenite specimens and possible fiber degradation of the YU specimen during aerosolization are likely to be a function of the mineral's specific geologic processes of formation. Investigation of the influence of geologic etiology on fiber growth was beyond the scope of this study, but does warrant further scientific investigation.

The study results show that aerosolizing analogous mordenite materials can produce fibers capable of deep-lung penetration and deposition:

- 90% of the MMADs range from 1.73–4.44 μ m;
- 43% of fiber aerodynamic diameters are between 1.5–4 μ m;
- 70% of the respirable mass fractions are over 40%;
- alveolar deposition estimates for the BU and EE aerosols of 38% and 39%, respectively.

The capability of deep-lung penetration and deposition, combined with the relatively large per-

centages of the sized fibers falling within high-risk categories for mesothelioma induction, supports the claim that mordenite is a potential inhalation health hazard.

Aerosol generation was intended to simulate air-coring operations in an occupational setting. However, a laboratory simulation does not provide an exact replication. In an effort to ensure collection of sufficient amounts of fibers for experimental analysis, highly concentrated aerosols were generated. It is likely that aerosols generated during this experiment provide a conservative estimate of those generated in an occupational setting.

RECOMMENDATIONS

No inhalation data exists to substantiate the above findings. These study results should raise awareness of potential health hazards connected with inhalation of mordenite aerosols. The primary recommendation from this study is that investigation of the health implications of this fibrous mineral be continued. In light of what was found with the YU specimen in this study, aerosol inhalation studies should be conducted using mordenite minerals found in the subsurface of Yucca Mountain. Additional follow-ups could include a chronic, animal inhalation study and a fiber solubility study. Such toxicological studies would help to determine the true inhalation health hazard of mordenite fibers with respect to deposition in the pulmonary system.

References

- American Conference of Governmental Industrial Hygienists (1969). *Threshold Limit Values of Airborne Contaminants for 1969*. Cincinnati, OH.
- Baris, Y. I., Sahin, A. A., Ozesmi, M., Kerse, I., Ozen, E., Kolacan, B., Altinors, M., and Goktepe, A. (1978). An Outbreak of Pleural Mesothelioma and Chronic Fibrosing Pleurisy in the Village of Karin/Urgup in Anatolia, *Thorax* 33:181–192.
- Casey, K. R., Moatamed, F., and Shigeoka, J., et al. (1981). Demonstration of Fibrous Zeolite in Pulmonary Tissue, *Amer. Rev. Respir. Dis.* 123:98.
- Johnson, N. F., Edwards, R. E., Munday, D. E., Rowe, N., and Wagner, J. C. (1984). Pluri Potential Na-

- ture of Mesothelioma Induced by Inhalation of Erionite in Rats, *Br. J. Exp. Path.* 65:377-388.
- Maltoni, C., Minardi, F., and Morisi, L. (1982). Pleural Mesotheliomas in Sprague-Dawley Rats by Erionite: First Experimental Evidence, *Env. Res.* 29:238-244.
- Moss, R. O., and Ettinger, E. J. (1970). Respirable Dust Characteristics of Polydispersed Aerosols, *Amer. Ind. Hyg. Assoc. J.* 31:546-547.
- Mumpton, F. A. (1976). Natural Zeolites: A New Industrial Mineral Commodity. In *Natural Zeolites: Occurrence, Properties, Utilization of Natural Zeolites*, edited by L. B. Sand and F. A. Mumpton. Pergamon Press, New York, pp. 3-24.
- NIOSH Manual of Analytical Methods, Method 7402 (1989). Asbestos by TEM. *National Institute for Occupational Safety and Health* Issue 1.
- Stahlhofen, W., Rudolf, G., and James, A. C. (1989). Intercomparison of Experimental Regional Deposition Data, *J. of Aer. Med.* 2:285-308.
- Stanton, M. F., and Layard, M. (1977). The Carcinogenicity of Fibrous Minerals. In *Proceedings of the Workshop on Asbestos*. National Bureau of Standards, Publication 506, Gaithersburg, MD, pp. 143-151.
- Stanton, M. F., Layard, M., Tegeris, A., Miller, E., May, M., Morgan, E., and Smith, A. (1981). Relation of Particle Dimension to Carcinogenicity in Amphibole Asbestos and other Fibrous Minerals, *J. Natl. Cancer Inst.* 67:965-975.
- Stober, W. (1972). Dynamic Shape Factors of Nonspherical Aerosol Particles. In *Assessment of Airborne Particles*, edited by T. T. Mercer, P. E. Morrow, and W. Stober. Charles C. Thomas, Springfield, IL, pp. 249-288.
- Suzuki, Y. (1982). Carcinogenic and Fibrogenic Effects of Zeolites: Preliminary Observation, *Env. Res.* 27:433-445.
- Wagner, J. C., Skidmore, J. W., Hill R. J., and Griffiths, D. M. (1985). Erionite Exposure and Mesothelioma in Rats, *Br. J. Cancer* 51:727-730.

Received July 23, 1998; accepted December 31, 1998.