

## **Examining Play Sand Products for Asbestos Contamination**

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In 1986, a letter in a medical journal generated concern with asbestos contamination in play sand; a play-sand product made from crushed calcsilicate rock contained from 2 to 4 percent tremolite asbestos (Germine 1986). As a result, a variety of play-sand products were tested by suppliers and by private and government laboratories. A workshop was sponsored in February 1987 by the Northeast Regional Environmental Public Health Center at the University of Massachusetts (Amherst) to discuss the findings of the various private, federal and state agencies. A majority of participants concluded that tremolite was present in some crushed-stone sand products but only as massive or cleavage fragments. In the summer of 1987, asbestos-contaminated play sand received renewed media coverage when Dr. Gerald Abraham of the Upstate Medical Center in Syracuse, NY reported tremolite fiber contamination in another brand of play sand. Dolomitic limestone from the Gouverneur, NY area was being crushed for various products (limestone, marble chips), and a certain size fraction was being marketed as play sand. This product also contained tremolite, a silicate byproduct of the metamorphosis of its parent carbonate mineral (Brinsmade, 1905). The manufacturer voluntarily withdrew all play sand from the market and the New York State Department of Health issued an advisory on the product.

This paper presents our analyses of play-sand products for asbestos and discusses the difficulties inherent in this task and in assessing health hazards associated with such contamination.

### **MATERIALS AND METHODS**

Calcsilicate sand products were scrutinized for asbestos by a variety of methods. Samples were analyzed by polarized-light microscopy (PLM) using both the two-step visual estimation method (Webber et al., 1982) and the EPA point-counting technique (USEPA 1982). PLM analyses were done on samples as received, after dissolution in hydrochloric acid and after sifting through a 200-mesh screen. These preparations were also analyzed qualitatively by scanning electron microscopy (SEM) with energy-dispersive x-ray spectroscopy (EDX) at 500x and 5000x magnifications. Large grains were separated from finer particles by

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aqueous sedimentation. 10 g of sample were poured into a beaker containing 50 ml of 0.1- $\mu\text{m}$ -filtered water and this was ultrasonicated for 2 min. Following a 60-sec settling period, the top 45 ml was decanted to a clean beaker. An additional 45 ml of filtered water was added to the original beaker and another 2-min ultrasonication followed. After a 60-sec settling period, another 45 ml was decanted to the beaker holding the original 45 ml of decanted water. This cycle was run a total of five times, yielding 225 ml of decanted water with the sample's fine particles. This was ultrasonicated for 2 min and then an aliquot (10 or 20  $\mu\text{l}$ ) was withdrawn and added to 15 ml of filtered water and filtered through a 25-mm diameter, 0.1- $\mu\text{m}$ -pore polycarbonate (PC) filter. These filters were prepared for SEM and TEM analysis by techniques described below.

A third set of analyses attempted to duplicate the results reported by Abraham in a letter and videotape (personal communication). Abraham poured his sand within a glove box and collected the resultant dust for analysis by SEM. Since details of that procedure were not specified, we initiated a pilot study to determine the time required for the large, non-respirable fraction to settle out. Subsamples of 50 or 100 g were poured from a height of 45 cm into a petri dish in the bottom of a glove box to generate visible dust. Samples of the suspended dust were collected at different time intervals on mixed-cellulose ester (MCE) and PC filters, which were subsequently prepared for analysis by both SEM and transmission electron microscopy (TEM). This study revealed that 60 min was appropriate for allowing the non-respirable fraction to settle out.

All MCE filters were analyzed by phase-contrast microscopy according to the 7400 "A" Method (USNIOSH 1987). For SEM analysis, MCE filters were collapsed in acetone and then carbon-coated. PC filters were simply carbon coated. Horizontal and vertical dimensions of all particles were measured within random fields of view at 2000x or 4000x after calibrating screen measurements with NBS SRM 484d. Counting was terminated at 50 particles for each filter. Estimated volume ( $\mu\text{m}^3$ ) for each particle was calculated by multiplying its horizontal by its vertical dimensions and then multiplying this product by half the shorter of the two dimensions. Since the densities of dolomite, calcite and tremolite, the dominant minerals in the samples, are between 2.7 and 3.25  $\text{pg}/\mu\text{m}^3$ , the mass of each particle measured was determined by multiplying its volume by 3.0  $\text{pg}/\mu\text{m}^3$ . Airborne particulate ( $\text{no.}/\text{cm}^3$ ) and mass concentrations ( $\text{ng}/\text{m}^3$ ) were calculated by:

$$\text{no.}/\text{cm}^3 = \frac{P \times 855 \text{ mm}^2/\text{filter}}{F \times V \times 10^3 \text{ cm}^3/\text{liter}} \quad \text{and} \quad \text{ng}/\text{m}^3 = \frac{M \times 855 \text{ mm}^2/\text{filter} \times 10^{-3} \text{ ng/pg}}{F \times V \times 10^3 \text{ m}^3/\text{liter}}$$

where P = Total number of particles counted, F = Total filter area examined ( $\text{mm}^2$ ), V = Volume of air sampled (liters), and M = Total mass of particles counted (pg). Mass concentrations were also calculated for only those particles with masses less than 24.5 pg (the mass of a 2.5- $\mu\text{m}$  sphere with a density of 3.0). This eliminated the biasing effect on mass concentrations caused by a few large (nonrespirable) particles.

For TEM analysis, 200-mesh London finder-grid mounts were prepared from MCE filters by the collapsed-filter method (Burdett and Rood, 1983)

and from PC filters by the Jaffe wick procedure (Yamate et al., 1984). For each sample, five grid squares chosen at random (Webber 1987) from two grid preparations were analyzed at 20,000x magnification for a total analysis area of .01 mm<sup>2</sup>. Based on electron-diffraction (ED) patterns from particles with aspect ratios >3, particles were classified as chrysotile or amphibole asbestos or nonasbestos. EDX were collected from certain particles to characterize elemental composition. Lengths and widths were measured on calibrated circles on the viewing screen. Airborne concentrations were calculated according to Yamate et al. (1984).

## RESULTS AND DISCUSSION

For the sake of convenience, "fiber" will refer to fragments that have aspect ratios >3 and essentially parallel sides. Our use of "fiber" does not imply the flexibility, frayed ends and extreme elongation associated with commercially defined "asbestos".

Four different samples of the Gouverneur product and two different samples of a second product were analyzed for fibers (Table 1). Only 20 to 25% of the non-Gouverneur samples (B2 and B3) dissolved when placed in HCl, indicating that carbonates were not the dominant minerals. Of the 3200 points counted on the two samples by PLM, 1.3% were particles with aspect ratios >3 and only 0.2% had aspect ratios >5. These were generally blade-like and had oblique extinction ranging from 6 to 22°. Based on this extinction and refractive indices near 1.620, these were identified as tremolite cleavage fragments. None of these had the highly elongated morphology or parallel extinction typical of asbestiform amphiboles. Carbonate minerals dominated the Gouverneur sand - only 2 to 19% of the original sample remained after HCl treatment. Of the 2400 points counted on samples B4 and B5, less than 1% were particles with aspect ratios >3 and only 0.13% had aspect ratios >5. These elongated particles shared the same characteristics as the tremolite fragments in the non-Gouverneur play sand. No asbestiform minerals were detected by PLM.

Table 1. Sources of crushed play-sand products.

<u>Sample</u>	<u>Product Source</u>	<u>Collector</u>
B1	Gouverneur, NY	NYSD Health
B2	Bellmore, NY	NYSD Law
B3	Great River, NY	NYSD Law
B4	Gouverneur, NY	NYSD Health
B5	Gouverneur, NY	Concerned Citizen
B6	Gouverneur, NY	Dr. J. Abraham

Samples B2, B3 and B4 were prepared by the waterborne suspension method for analysis by SEM. (Insufficient material in B6 prevented waterborne preparation of this sample.) In scans at 2000x magnification, no fibers were detected in these samples. Fifty fields of view were scrutinized at 1000x and 10,000x magnification for Sample B4. At 1000x, 14 elongated particles were detected, most with aspect ratios much smaller than 10 and with tapering or blade-like morphology. At 10,000x, one suspicious particle was detected, a 3-µm rod with an aspect ratio of 13.

Two Gouverneur samples (B4 and B6) were prepared by the 60-min glove-box suspension technique. Dust was not visible after the 60-min sedimentation period but mass concentrations were still in the double- and triple-digit  $\mu\text{g}/\text{m}^3$  range (Table 2), typical of dirty urban-industrial environments. Respirable ( $<2.5 \mu\text{m}$ ) particle concentrations in B6 ranged from 11 to 240  $\mu\text{g}/\text{m}^3$  but mean concentrations from B4 and B6 were in surprisingly good agreement.

Samples B4 and B6 were markedly different in their fiber contents, however. No fibers were observed by SEM in any of the B4 glove-box preparations but fibers were detected in 6 of 8 preparations from B6. Fibers as detected in the 6 samples by SEM ranged from 0.009 to 0.14 fibers/ $\text{cm}^3$  (f/ $\text{cm}^3$ ) and from 5 to 520  $\text{ng}/\text{m}^3$ . On a mass basis, this ranged from 0.0069 to 0.32 % of the respirable fraction and, by extrapolation, from 10 ppt to 3 ppb of the mass of poured sand. Fibers on all filters ranged from 9.9 to 1200  $\text{ng}/\text{m}^3$  and composed a maximum of 1.2% of the respirable size fraction.

Fibers were not detected by TEM in any of the glove-box preparations of B4 but were detected in all 8 preparations from B6. TEM results were similar to the results from SEM on a mass basis and on a fiber concentration basis when only fibers  $>5\mu\text{m}$  were considered (Table 3). TEM's superior resolution, however, revealed many more fibers (1.1 to 14.3 f/ $\text{cm}^3$ ) than SEM. On a numerical basis, chrysotile was the most abundant fiber, generally present as short but thick unit fibrils (Figure 1). In contrast, the amphibole fibers constituted most of the fiber mass because of their much larger size. Tremolite was the dominant type, with Si, Mg and Ca the major elements identified by EDX. A variety of ED patterns were observed along the 5.3 Å layer lines from these amphiboles. Some yielded highly symmetrical patterns with discrete points, typical of cleavage fragments, while others yielded patterns with streaking and irregularly spaced points along the layer lines, as expected from crystallized asbestiform amphiboles (Hutchison et al., 1975). Some Mg-only silicate fibers may have been the "talcoles" found in Gouverneur's fibrous talc (Virta, 1985).

PCM analysis did not reveal elevated fiber levels, with airborne concentrations ranging from 0 to 0.06 f/ $\text{cm}^3$ . Even when TEM-determined fiber concentrations were limited to fibers  $>5\mu\text{m}$ , the definition of a NIOSH fiber, TEM concentrations were much higher than PCM concentrations. This discrepancy was probably due to the inferior resolution of PCM, of the fibers longer than 5  $\mu\text{m}$  detected by TEM, the thickest one was only 0.2  $\mu\text{m}$ , barely resolvable by PCM.

These results reveal the inadequacy of light microscopy in detecting fibers in sand samples. The long thin fibers (the most hazardous according to some carcinogenicity models e.g., Stanton et al., 1981) are not visible by PLM or PCM. Even SEM was unable to detect the very thin fibers that were ultimately resolved by TEM.

Future preparation methods will have to be tightly controlled if fiber contamination is to be quantitated. Waterborne suspensions are probably most appropriate due to the containment of product during separation and

Table 2. SEM analyses of airborne suspensions of crushed play-sand products

Sample	Bulk Source	Filter*	Volume (l)	Total Particles per cm <sup>3</sup>	Geometric Mean Diameter $\mu\text{m}$	Respirable Particles $\mu\text{g}/\text{m}^3$	Fibers $\text{f}/\text{cm}^3$	Fibers $\text{ng}/\text{m}^3$	Fibrous Percent of Respirable Particles
A1	B4	0.4P	128.	11.	1.4	57.	0.	0.	0.
A2	B4	0.8C	143.	14.	1.1	46.	0.	0.	0.
A3	B4	0.22C	18.4	7.6	1.4	59.	0.	0.	0.
A4	B6	0.4P	105.	29.	1.2	138.	0.14	300.	0.22
A5	B6	0.8C	176.	22.	0.82	72.	0.009	5.	0.0069
A6	B6	0.22C	36.6	3.5	1.3	11.	0.	0.	0.
A7	B6	0.8C	59.2	34.	0.68	100.	0.089	170.	0.17
A8	B6	0.6P	52.4	97.	0.68	240.	0.10	350.	0.15
A9	B6	0.4P	37.8	128.	0.54	160.	0.093	520.	0.32
A10	B6	0.8C	193.	50.	0.54	67.	0.018	35.	0.053
A11	B6	0.22C	18.1	14.	0.80	46.	0.	0.	0.

\*P=Polycarbonate, C=Cellulose Ester

Table 3. Results of TEM analysis of airborne asbestos from crushed play-sand samples B4 and B6.

Sample	All Fibers $\frac{f}{cm^3}$ $\frac{ng}{m^3}$	>5 $\mu m$ Long $\frac{f}{cm^3}$ $\frac{ng}{m^3}$	Chrysotile $\frac{f}{cm^3}$ $\frac{ng}{m^3}$	Amphibole $\frac{f}{cm^3}$ $\frac{ng}{m^3}$	Mean Aspect Ratio		Mean Length $\mu m$		Fibrous Percent of Respirable Particles
					Chrys.	Amph.	Chrys.	Amph.	
A2	0.	0.	0.	0.	-	-	-	-	0.
A3	0.	0.	0.	0.	-	-	-	-	0.
A4	7.3	470.	6.8	120.	16.	130.	0.78	6.5	0.34
A5	2.7	340.	2.2	230.	17.	27.	1.1	2.2	0.47
A6	5.2	9.9	5.2	9.9	14.	-	0.47	-	0.091
A7	1.1	1200.	0.76	2.5	12.	9.4	0.52	3.0	1.2
A8	1.7	450.	1.5	9.0	21.	80.	0.88	17.	0.19
A9	1.9	44.	1.7	2.5	11.	8.6	0.37	1.6	0.027
A10	1.8	450.	1.1	17.	13.	29.	0.74	3.8	0.68
A11	14.	140.	14.	130.	12.	100.	0.58	2.2	0.29

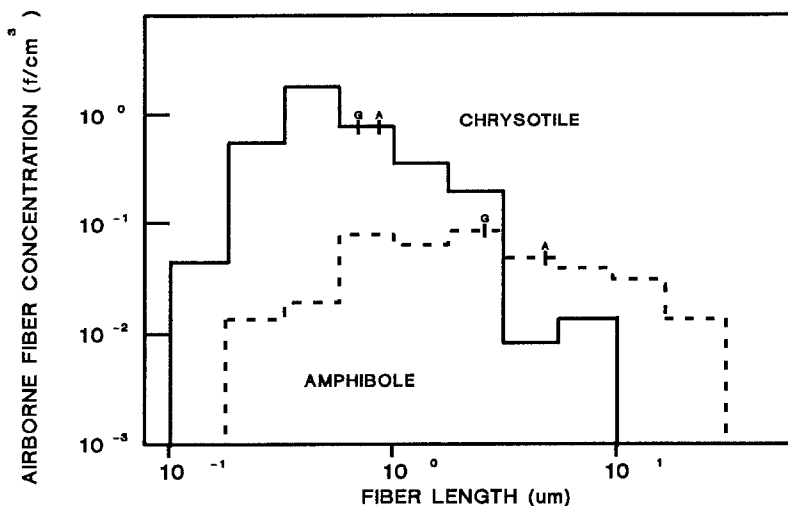


Figure 1. Mean fiber length distribution in B6 versus airborne concentration as determined by TEM in 8 particulate air samples collected in the glove box. G=Geometric mean, A= Arithmetic mean.

filtration steps. If widescale product sampling is required, a stratified analytical scheme should be devised. The first step would be simple PLM analysis of the sand. If the sand contains no amphibole, serpentine or other minerals associated with these, analysis could be terminated. This would eliminate further analysis of true quartz beach sand. The second step for samples with suspicious minerals would be waterborne suspension, sedimentation and separation. TEM analysis of this would provide mass per mass quantitation of product contamination. Finally, for samples with contamination as determined by TEM analysis, a glove-box experiment could be undertaken to semi-quantitatively assess the types of fibers likely to become airborne. In any instance, even such careful examination will have limited reliability because of bag-to-bag variability of the same product, as exemplified by the disparate results of B4 and B6; these were samples of the same product, bought at the same store but at different times.

Although tremolite asbestos is not a common asbestos type, there is evidence that it poses a hazard when inhaled. Davis et al. (1985) stated that tremolite was "the most dangerous dust that we have studied," - more hazardous even than crocidolite, based on their inhalation/injection studies with mice. They qualified that statement with the caveat that their tremolite "contained ~95% by mass of pure fibrous tremolite." Similarly, very long, high-aspect-ratio tremolite was shown to markedly increase mesothelioma in laboratory animals and cell cultures while less fibrous tremolite did not (Wagner et al., 1982). Fibrous tremolite has been related to excess mesothelioma in chrysotile workers who were exposed to

tremolite-contaminated ore (Churg 1988). Exposure to tremolite in residential stucco has apparently led to increased mesothelioma in one region of Turkey (Baris et al., 1988). Magee et al. (1986) cite a case of a 41-year man old who apparently developed mesothelioma after he was exposed as a child to tremolite-contaminated chrysotile ore. Interestingly, the tremolite fibers in his lung tissue were as long as crocidolite and amosite fibers associated with mesothelioma in other studies but were much thicker, not the high-aspect ratio fibers typically associated with elevated carcinogenicity (Stanton et al. 1981).

Assuming that tremolite fibers in some size categories are hazardous when inhaled, it remains difficult to draw conclusions about the hazards of the airborne concentrations in the present study. Airborne fiber concentrations within the glove box were higher than ambient background levels we've measured, typically 0-0.1 f/cm<sup>3</sup> and 0-5 ng/m<sup>3</sup>. We've measured airborne asbestos concentrations that exceeded the maximum concentration (1200 ng/m<sup>3</sup>) in the present study in only one instance, when a chrysotile-backed floor had been sanded in a house. The presence of the few long amphibole fibers is cause for concern. The extended latency period of asbestos-related diseases and the decades of life remaining to children, the group most likely to be exposed to play sand, increase the probability of ensuing asbestos-related diseases. The dimensions of the tremolite fibers we measured were the long, high-aspect ratio fibers typically associated with increased carcinogenicity (Stanton et al. 1981). Additionally, we should be concerned about fibers up to several  $\mu$ m in diameter, those that probably settled out during the 60-min period, because these wider, though of smaller aspect ratio, fibers may also promote mesothelioma (Magee et al., 1986).

These question of hazard should be viewed in perspective of the sand itself and the environment. The glove-box experiment created a worst-case scenario, i.e., aggressive disturbance in an enclosed environment with no air currents to scatter fibers. How quickly would ppb fibers disperse in outdoor sandboxes due to wind and rain? Are fibers tracked indoors on clothing and shoes?

Fortunately, the Gouverneur sand product that contained tremolite fibers has been removed from the market. Should similar products be discovered, difficult decisions will have to be made about sampling/analysis strategies and "safe" levels of exposure.

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