Journal of Occupational and Environmental Hygiene

ISSN: 1545-9624 (Print) 1545-9632 (Online) Journal homepage: http://www.tandfonline.com/loi/uoeh20

Assessing occupational erionite and respirable crystalline silica exposure among outdoor workers in Wyoming, South Dakota, and Montana

Catherine Beaucham, Bradley King, Karl Feldmann, Martin Harper & Alan Dozier

To cite this article: Catherine Beaucham, Bradley King, Karl Feldmann, Martin Harper & Alan Dozier (2018): Assessing occupational erionite and respirable crystalline silica exposure among outdoor workers in Wyoming, South Dakota, and Montana, Journal of Occupational and Environmental Hygiene, DOI: 10.1080/15459624.2018.1447116

To link to this article: https://doi.org/10.1080/15459624.2018.1447116

Publisher: Taylor & Francis

Journal: *Journal of Occupational and Environmental Hygiene*

DOI: https://doi.org/10.1080/15459624.2018.1447116

Assessing occupational erionite and respirable crystalline silica exposure among outdoor workers in Wyoming, South Dakota, and Montana

Catherine Beaucham[1,*], Bradley King[1], Karl Feldmann[1], Martin Harper[2,3], Alan Dozier[1]

[1]National Institute for Occupational Safety and Health, Cincinnati, OH

[2]Zefon International, Inc., Ocala, FL

[3]Department of Environmental Engineering Sciences, University of Florida, Gainesville, FL

[*]Corresponding Catherine Beaucham: cbeaucham@cdc.gov.

ABSTRACT

Erionite is a naturally occurring fibrous mineral found in many parts of the world, including the western United States. Inhalational exposure to erionite fibers in some localities is associated with health effects similar to those caused by asbestos exposure, including malignant mesothelioma. Therefore, there is concern regarding occupational exposures in the western United States. Currently there are no standard sampling and analytical methods for airborne erionite fibers, as well as no established occupational exposure limits. Due to the potential adverse health effects, characterizing and minimizing exposures is prudent. Crystalline silica also occurs naturally in areas where erionite is found, principally as the mineral quartz. Work activities involving rocks containing quartz and soils derived from those rocks can lead to exposure to respirable crystalline silica (RCS). The typically dry and dusty environment of the western United States can increase the likelihood of exposures to aerosolized rocks and soils, but inhalation exposure is also possible in more humid conditions. In this case study, we describe several outdoor occupational environments with potential exposures to erionite and RCS. We describe our method for evaluating those exposures and demonstrate: (1) the occurrence of occupational exposures to airborne erionite and RCS, (2) that the chemical make-up of the erionite mineral can be determined, and (3) that effective dust control practices are needed to reduce employee exposures to these minerals.

Key words

Erionite, mineral fiber, mesothelioma

INTRODUCTION

Erionite is a naturally occurring fibrous zeolite mineral, first described by Eakle.[1] Erionite has three different compositions: Calcium (erionite-Ca), Sodium (erionite-Na), or Potassium (erionite-K) as determined by the predominant element.[2,3] During the Cenozoic era, volcanoes in the western United States produced large volumes of glassy silica-rich volcanic ash, which was deposited or washed into alkaline salty lakes. This glassy ash was later dissolved by water and recrystallized as zeolites, including erionite.[4] Erionite was first described in this type of rock in Nevada and Wyoming and erionite has now been identified in weathered ash layers in sedimentary rocks and some volcanic rocks in Washington, Oregon, California, Nevada, Idaho, New Mexico, Colorado, Utah, Arizona, Montana, Wyoming, North Dakota, and South Dakota.[5,6] Some of the rock formations in the western United States known to contain erionite include the Wagon Bed, White River, and Arikaree.[7] The Wagon Bed rock formation is located in Wyoming, while the White River and Arikaree formations are found throughout the Custer-Gallatin National Forest (CGNF) in Montana and South Dakota, as well as in Wyoming. The formations in CGNF are believed to be of similar age and occurrence as formations in the Killdeer Mountains of North Dakota, 75 miles away. Fort Union, a non-erionite bearing rock formation, is frequently layered just below the Arikaree formation.

When aerosolized and inhaled, erionite fibers have been associated with health effects similar to those typically seen with exposure to asbestos, including malignant mesothelioma.[8–10] The International Agency for Research on Cancer has determined that there is sufficient evidence to classify erionite as carcinogenic to humans, and that it can cause mesothelioma.[11] This determination was made primarily because of extensive exposure, toxicological, and epidemiological studies of villagers in the Cappadocia region of Turkey.[12-14] An equivalent situation has not yet been identified in the United States. Although case reports suggest the occurrence of pulmonary fibrosis and mesothelioma among people who live and work in areas of the western United States or Mexico where erionite occurs, these reports did not provide details of how the minerals were identified.[9,15,16] A study of North Dakota quarry and road workers found a few cases of pleural changes, but the long-term health implications are unknown.[17] Nevertheless, because erionite is considered to present potential risks for cancer and other adverse health effects, it is important to minimize or eliminate exposure.

In contrast to asbestos, erionite mineral fibers do not have established occupational exposure limits (OELs). The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for asbestos of 0.1 fibers greater than 5 micrometers (μm) in length per cubic centimeter of air (f/cc). The REL is based on a personal sample collected over any 100-minute period at a flow rate of 4 liters per minute according to the NIOSH Manual of Analytical Methods 7400. It is known, however, that cancers can still occur with exposures at or below this limit.[18] In 1990, NIOSH revised the REL to include other elongated mineral particles that meet the same length (> 5 μm) and aspect ratio (3:1 length:width) definition of asbestos, and were collected using NIOSH Method 7400 or equivalent (e.g., NIOSH Method 7402).[18,19] The revised definition of airborne asbestos fibers did not explicitly encompass elongated mineral particles from other micro-fibrous minerals (e.g., erionite) that are known to be associated with health effects similar to those caused by asbestos.[19] Researchers Jurinski and Juriniski proposed a control limit of 0.0007 fibers of erionite per cubic centimeter of air.[20] This limit was based on the theory that employees were non-occupationally exposed to environmental erionite throughout their lifetimes. However, non-occupational exposures typically are not considered when developing OELs, and no regulatory or consensus organization has adopted this proposed control limit.

Another mineral frequently found in continental geological environment is quartz, a form of crystalline silica. Quartz is the most common mineral in the Earth's crust. The same kinds of activities that can aerosolize erionite can also aerosolize crystalline silica. Occupational exposure to airborne respirable crystalline silica (RCS) has been associated with silicosis, lung cancer, and other airway diseases.[21] Several OELs for airborne RCS have been established. The new Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) for respirable crystalline silica of 0.05 milligrams per cubic meter of air (mg/m^3), averaged over an 8-hour period, was not in effect at the time of our evaluations.[22] We compared our respirable crystalline silica results to the PEL that was in existence at the time. NIOSH recommends an exposure limit of 0.05 mg/m³, as a time-weighted average (TWA) for up to a 10-hour work day, to reduce the risk of developing silicosis, lung cancer, and other adverse health effects.[23] The American Conference of Governmental Industrial Hygienists (ACGIH®) Threshold Limit Values (TLV®) for quartz is 0.025 mg/m³, as an 8-hour TWA.[24] It is not known if there are any synergistic or additive effects of combined exposures to erionite and RCS.

In 2013 and 2014, two U.S. federal government agencies submitted health hazard evaluation requests to NIOSH. The requestors were concerned about potential erionite exposures to the agencies' employees who work outdoors in areas known or suspected to have erionite. In response to the requests, we evaluated erionite exposures over four site visits in three states: Wyoming, South Dakota, and Montana. We evaluated exposures during tasks involving dirt road maintenance and forestry activities in lands known or suspected to have erionite mineral fibers. Because of the widespread occurrence of quartz, we also evaluated potential exposures to RCS. The site visits took place in October 2012, July 2013, August 2013, and September 2014. We visited areas near Lander, Wyoming in October 2012 and areas near Worland and Cody, Wyoming in August 2013. Two visits were made to the CGNF in North Dakota and Montana in July 2013 and September 2014. This paper presents information about employees' work tasks, the locations and rock formations where the task were performed, the sampling methodology we used to evaluate airborne concentrations of erionite and RCS, and our sampling results. Our objectives were to collect air, bulk rock, and soil samples to: (1) assess employee exposure to erionite and RCS during work tasks, (2) develop an approach to more accurately detect and measure erionite in air samples, and (3) recommend ways to protect employees working in areas that potentially have erionite.[25,26]

Descriptions of Work Tasks Evaluated

Dirt Road Maintenance

Because of use and weather conditions, dirt roads are susceptible to potholes, ruts, erosion, and poor drainage, and require regular maintenance. Employees use road bladers/graders to smooth the road surface, fill in surface irregularities with loose material and aggregate, and improve water drainage across the road surface. During road blading/grading, considerable quantities of road dust are aerosolized, particularly when the dirt roads are dry.

To improve water drainage near roadways and help reduce water erosion of roads following heavy rains, metal or plastic culverts are installed below the road, where necessary. Because the culverts fill with sediment and other debris, periodic cleaning or replacement is also done. In addition, roadside drainage ditches are also periodically cleared of obstructions to ensure proper water flow. Backhoes are typically used during these tasks (Figure 1).

Cattle Guard Replacement

Some of the land is used for cattle grazing, requiring cattle guards to be placed where roads cross fence lines. A cattle guard is a transverse grid of metal bars placed in a shallow ditch. Employees use a backhoe to dig the ditches where the guards will be placed (Figure 2). Cattle guards can become clogged with weeds and brush and must be cleaned periodically.

Parking Lot and Campground Maintenance

Agency employees maintain boat launches for river access by applying aggregate to parking lots and boat launch ramps. Aggregate can be aerosolized as it is dumped and spread onto the ground. Other campground maintenance activities included using push and riding lawnmowers to cut the grass and operating weed trimmers.

Tree Thinning and Vegetation Reduction

Tree thinning is a process of removing slower growing or defective trees to create more space between trees which reduces forest fire risk and the ability of a fire to spread rapidly. Felling is the process of downing individual trees, while bucking is the process of cutting a felled and de-limbed tree into logs. Excessive vegetative growth is also cleared using a masticator attached to a Bobcat®. The masticator grinds woody vegetation into wood chips that are deposited onto the forest floor. The masticator cuts down and grinds up whole standing trees in a single, continuous process. During mastication activities, the operator remained inside of the closed vehicle cab of the Bobcat.

Digging Fireline

A fireline is a 6 inch to 3 feet wide break in fuel (e.g., grasses, trees, shrubs) made by cutting, scraping, or digging to remove all plant debris to reduce the spread of fires. Firelines can be made by mechanized equipment such as bulldozers, but are more commonly made using hand tools (Figure 3).

Push Pit Reclamation

An agency employee used a Bobcat to backfill shallow push pits, which had been dug in the late 1950’s and early 1960’s for uranium exploration, but had not been refilled. A different employee spread grass seed on the newly filled-in pit. Two additional employees monitored the area for radioactivity and other safety concerns. We observed the refilling of one of these pits.

Geological Rock Evaluation

Agency geologists evaluated the mineral content of geologic rock formations through microscopic examination or chemical analysis in a laboratory. Prior to analysis, bulk rock samples were mechanically pulverized. The powdered rock was poured into a container on a down draft table and then dried.

Spraying Invasive Species

One of the agencies used universal terrain vehicles to search for invasive plant species in pastures off the main roads. Employees sprayed invasive plants with an herbicide mixture and then with a blue dye to indicate it had been treated.

Geographic Locations

The October 2012 site visit took place in the Fort Union formation outside of Lander, Wyoming. Although the Fort Union Formation is not known to have erionite fibers, it is frequently layered underneath the Arikaree Formation. Because the formations are exposed to weathering, the agencies were concerned that erionite could have washed down from the Arikaree Formation into the Fort Union Formation where the employees were grading or blading the road and installing culverts. The August 2013 site visit took place in the Wagon Bed Formation (Figure 4) near Worland and Cody, Wyoming.

The July 2013 and September 2014 visits took place in the following areas: (1) Slim Buttes, (2) Long Pines, (3) East Short Pines, and (4) the Ekalaka Hills in the CGNF. All the work in these areas was done within outcrops of the Arikaree and White River Rock Formations and included exposure to soils from those locations. These locations included the cliffs above the campground at Reva Gap, the Castles area of Slim Buttes, and the Capitol Rock area of Long Pines.

METHODS

Exposure Assessment

During the October 2012 evaluation in Lander, Wyoming, we took air samples for the duration of dust-generating tasks. We did not take air samples during the employees' lengthy commute to and from the worksite. We collected personal breathing zone (PBZ) and area air samples for erionite on 25 millimeter (mm) mixed cellulose ester filters at a flow rate of 1.5 liters per minute. Analysis was done by counting fibers using phase-contrast microscopy (PCM), according to the NIOSH Method 7400.[18] This method estimates airborne fiber concentration (reported as fibers per cubic centimeter of air), but does not speciate the fibers.

We then used transmission electron microscopy (TEM) with energy dispersive spectroscopy (EDS) and magnification of 20,000x or greater to analyze the erionite samples according to NIOSH Method 7402, modified to identify erionite instead of asbestos.[18] This method incorporates EDS to identify the elemental composition of fibers. The composition analysis results were then compared to a library of minerals that included erionite to accurately identify specific mineral fibers. The method also provided the elemental composition of the fiber and determined the erionite fiber concentration as structures per cubic centimeter of air (s/cc). It is difficult to obtain diffraction patterns on zeolites under the electron microscope to confirm their identity through their crystallography.[27]

We attempted to use the criteria outlined by Dogan and Dogan to confirm the presence of erionite in the air samples.[3] To confirm erionite using TEM with EDS, Dogan and Dogan recommended that the fibers have a magnesium content of < 0.8 atoms per unit cell and a balance error (E%) of ≤ 10%. Atomic percentages, not weight percentages, were recommended when computing the balance error formula.

For the analysis of our samples, the E% was determined using the following formula*:

$$E\% = \left[\left(Al+Fe^{3+}\right)-\left(Na+K\right)-2\left(Ca+Mg\right)\right]/\left[\left(Na+K\right)+2\left(Ca+Mg\right)\right]\times 100 \quad \text{Equation 1.}$$

*Note the "minus 2" in the formula, which was accidentally left out of the published Dogan and Dogan paper.[28]

According to subsequent research, the balance error formula is applicable to erionite crystals from vesicles in mafic volcanic lavas but works less well when applied to erionites that have formed in a sedimentary environment.[27,28] Erionite in the rock formations in the areas we visited would have formed in a sedimentary environment; therefore, we determined that the Dogan and Dogan criteria to confirm erionite might not provide sufficient accuracy for these fibers. Additional limitations, which are beyond the scope of this case study, are described in Harper et. al.[27]

For air samples collected during subsequent site visits (July 2013, August 2013 and September 2014), we developed and used the following methodology to confirm erionite fibers. We continued to use TEM analysis according to NIOSH method 7402 to identify and visualize the fibers (Figure 5). Fibers having a length greater than 5 µm, and a length to width aspect ratio greater than 3:1 underwent EDS to identify their chemical composition. Two criteria for confirming a fiber as erionite were: 1) the fiber contained major peaks of silicon and aluminum and minor peaks of calcium, sodium, or potassium, and 2) bulk rock samples collected in the area (described in the following section) confirmed that erionite was present.

Erionite in bulk rock and soil samples has been confirmed using x-ray diffraction (XRD) and polarized light microscopy (PLM) techniques. Erionite fibers are much more highly concentrated in bulk and soil samples compared to air samples and extensive databases on minerals such as erionite in soils and rock formations can be used to confirm the fibers in these types of samples. Therefore, if we identified a fiber in air with the proper chemical makeup but without confirmation of erionite in nearby bulk rock, soil, or road aggregate samples, we would conclude that that fiber in the air sample was not erionite.

We collected the PBZ RCS air samples on pre-weighed 37 mm 5-µm pore size polyvinyl chloride filters with a nylon cyclone at a nominal flow rate of 1.7 liters per minute during the October 2012 visit to Wyoming and the July 2013 visit to the CGNF. During the visit to the CGNF in September 2014 we collected the RCS samples using a BGI cyclone at a nominal flow rate of 4.2 liters per minute. We analyzed all RCS samples according to NIOSH Method 7500; however, we modified the method by wiping the interior walls of the filter cassette with the back side of the sample filter to collect particles on the inside of the cassette walls, as recommended by NIOSH.[18,29]

Bulk Rock and Soil Samples

In 2013, we collected bulk rock and soil samples in the CGNF to determine if erionite was present in the rock formations surrounding the areas where the employees worked. Laboratory personnel gently crushed small amounts of rock or soil samples into a fine powder which was then placed between two glass slides and mounted in a drop of a 1.40 refractive index oil. All of the bulk rock samples were analyzed by PCM followed by XRD analysis.[30] A few of these samples were also analyzed in different laboratories for confirmation of erionite by PLM, XRD, and TEM-EDS.

During the September 2014 visit to the CGNF, we collected 10 bulk soil samples from the specific sites where employees were working using a bulk sampling method for asbestos developed by the U.S. Environmental Protection Agency.[31] Each of these 10 samples was collected as a composite consisting of a total of 50 grams (g) of soil from 30 individual sampling points equidistant from each other and representative of a 1,500-square-foot cell around each worker. We documented the sample collection location within each cell using GPS coordinates. In the laboratory, the sample was homogenized by shaking. From each sample we split two 10-g portions into different containers; the remaining 30 g of soil was not analyzed. One 10-g portion was analyzed by PLM according NIOSH Method 9002, but modified to identify erionite rather than asbestos.[18] The second 10-g portion was analyzed by XRD. Approximately 1 g of the sample was added to a mortar and ground to a fine powder with a pestle. The ground powder was wet sieved through a 45-μm sieve using 2-propanol, which was then evaporated. Approximately 0.5 g of sample powder was placed into an aluminum sample plate, which was then placed in the automated sample changer. A fast, full range XRD scan of the powder was performed to determine the primary sample constituents. Slow scans for selected regions were then done to confirm erionite presence. The sample peak identifications were assigned using the American Mineralogist crystal structure database and Jade 8.0 software.[30]

The bulk samples were also analyzed by a fluidized bed asbestos segregator (FBAS), which concentrates the fibers onto a filter. We blended 1 g aliquots of the soil sample with 19 g of clean sand and mixed them together. We then placed the soil-sand combination in the glass vessel of the FBAS according to a procedure developed by U.S. Environmental Protection Agency researchers and modified at NIOSH.[32,33] Filtered air was passed through the vibrated sample, and a portion of the outlet air was collected on a 25-mm diameter mixed-cellulose ester filter in a conductive plastic cassette. We then examined the filter under PCM. We identified fibers as erionite using their morphology and refractive index, and then counted and measured them. We calculated an estimate of fiber mass per unit area of filter from the dimensions and the density of erionite, and converted the result to a mass per gram of soil concentration using the known area of filter and the air flows through the sample and filter, and a 1% recovery factor consistent with earlier work on asbestos-spiked soils.[32]

RESULTS AND DISCUSSION

Erionite Air Sampling

Erionite fibers were not found in the PBZ air samples collected in WY in October 2012 and August 2013 during road grading/blading, cattle guard replacement, and dumping of aggregate on the boat launch parking lot. None of the bulk rock samples collected near employees' work locations contained erionite. Only two air samples contained fibers that met the 3:1 length to width aspect ratio. They were composed of silicon and aluminum, but without alkalis or magnesium, and therefore were not considered zeolites. We could not confirm if erionite from the Arikaree rock formation was washing down into the Fort Union formation. One air sample, taken while the geologist was grinding rock samples in the minerals lab, contained a zeolite fiber. We were not able to determine if that zeolite fiber was erionite because the fiber was crushed during the sample preparation.

Erionite mineral fibers were found in the PBZ air samples when employees were working in the Arikaree and White River rock formations of the CGNF during our site visits in July 2013 and September 2014. (Table 1) Erionite concentrations ranged from not detected to 0.36 fibers per cubic centimeter (f/cc). The tasks that resulted in the highest airborne erionite concentrations during our July 2013 site visit included operating the masticator in East Short Pines (0.36 f/cc), mowing in the Slim Buttes/Reva Gap campground (0.26 f/cc), digging fireline in Ekalaka Hills with the Pulaski axe (0.11 f/cc), and chainsaw operations in East Short Pines (0.11 f/cc). We returned to the East Short Pines and the Slim Buttes areas in September 2014 to re-evaluate full-shift exposures during the tasks that previously contributed to the highest airborne mineral fiber concentrations. The erionite concentrations during our re-evaluation ranged from 0.009–0.096 f/cc. It was raining and snowing, which likely reduced airborne dust generated during work activities. Erionite exposures could be higher in dry weather.

RCS Air Sampling

We collected 4 PBZ RCS samples during our October 2012 evaluation in WY. No cristobalite or tridymite (less common forms of crystalline silica) were present in the air samples. One employee, operating the backhoe during ditch clearing, was exposed to a respirable quartz concentration of 0.11 mg/m^3, which was above OSHA PEL, the NIOSH REL, and the ACGIH TLV. The quartz content of this air sample was 50%. Another employee who operated the backhoe during culvert replacement had a respirable quartz exposure of 0.04 mg/m^3, which exceeded the ACGIH TLV. The quartz content of this sample was 37%. Although the backhoe had an enclosed cab, the operator kept the cab door open for most of the time. The assistant to the backhoe operator during culvert replacement and the road grader/blader operator had exposures below the minimum quantifiable concentration (0.04 mg/m^3). The road grader/blader had an enclosed cab, and the operator kept the cab door closed most of the time. Sample times ranged from 286–322 minutes and did not include the 1.5-hour drive to and from the worksite. We cannot assume zero exposure during that time-period because the employees were exposed to dust from driving on dirt roads which may have a high silica content. This suggests that employees' respirable crystalline silica exposures could be higher at times. During the August 2013 evaluation in WY we mistakenly sampled the thoracic fraction of dust instead of the respirable fraction and therefore do not include those results.

Respirable crystalline silica was present, but below the minimum quantifiable concentration of 0.03–0.07 mg/m^3, in 30 of the 36 PBZ air samples from July 2013 in the CGNF. RCS was detected in all the PBZ samples collected on employees digging firelines. RCS was also detected on one of the employees operating a chainsaw, the masticator operator, and an employee who was stacking logs. RCS concentrations in the remainder of the PBZ samples were below the minimum detectable concentration of 0.01–0.02 mg/m^3. Quartz was the only form of crystalline silica detected.

Respirable crystalline silica was not detected in any of the 14 full-shift air samples taken in September 2014 in the CGNF. The minimum detectable concentration ranged from 0.002–0.004 mg/m^3. These samples were taken while it was raining and snowing, which likely reduced airborne dust generated during work activities. RCS exposures could be higher in dry weather.

Bulk Rock and Soil Sampling

All bulk rock samples collected in the CGNF in July 2013 when analyzed with PLM contained fibrous minerals such as cellulose but predominantly contained erionite. While visual area estimation indicated a large percentage of erionite, conversion to a weight percentage indicated only around 1%. Some of the bulk rock samples that we collected were compared to reference erionite samples from Rome, Oregon and Karain, Cappadocia, Turkey. Harper et. al.[(27)] describe some of differences in morphology and chemical composition in the erionite that we collected in comparison to the reference samples. Similar to asbestos, differences in composition and morphology may have implications for the toxicity of the fiber.

We split each of the bulk soil samples into three separate groups and analyzed each split by PLM, FBAS/PCM, and XRD. Results are shown in Table 2. The variability in the analytical results is believed to be due to method variability. The bulk soil samples that we collected in September 2014 and analyzed by PLM consisted mostly of particles of calcite, gypsum, quartz, opaque minerals, and cellulose fibers. Most of the fibers seen (8–10%) were cellulose fibers. The percentage of erionite fibers in the soil samples analyzed by PLM ranged from not detectable to approximately 5%. The soil samples collected in the East Short Pines had the highest percentage of erionite.

The soil samples analyzed by a fast qualitative XRD scan (5 to 80 two-theta degrees) identified quartz, clinoptilolite (another zeolite that can crystallize in a needle-like or fibrous form, but which is not considered carcinogenic), alkali feldspar, and calcite. We found zeolites in all samples. In addition, some samples had lower levels of erionite (Table 2), which required further confirmation with a slow scan below 20 two-theta degrees so that erionite could be confirmed in the presence of interfering minerals.

A high purity (80–85%) erionite reference sample was obtained from Rome, Oregon. Two lower concentration erionite reference samples were prepared from the Rome, Oregon, reference erionite material. Reference A contained 0.7% erionite, while reference B contained 5.1% erionite. The reference A sample was created to investigate the limit of detection, while reference B was prepared to investigate the erionite fingerprint and compare it to the bulk soil samples.

We took photographs of representative erionite fibers seen with PLM and PCM after FBAS concentration (Figures 6 and 7). We anticipated the FBAS results would be similar to concentrations seen in the PLM analysis, but with more precision, because of the similarities of the two methods (Table 2).[(33)] Erionite mineral fibers can clearly be seen in both microscopic photographs and can be visually differentiated from other types of fibers. The erionite fibers are long and thick fibers, with a thick appearance of being in bundles.

CONCLUSIONS

We confirmed the presence of erionite mineral fibers in many of the rock formations throughout the CGNF and in the soils where employees were working. We also confirmed that several job tasks that took place in those locations aerosolized dust particles containing erionite and generally low or non-detectable concentrations of RCS. We did not confirm the presence of erionite in bulk rocks or soils during our visits to sites in Wyoming, and none of the PBZ samples contained erionite. However, quartz was detected and some of the PBZ RCS samples from the Lander, Wyoming area exceeded applicable occupational exposure limits for silica.

Our sampling approach for erionite mineral fibers involved the collection of air and soil samples to evaluate both employee erionite exposures and the mineralogy of the fibers. As noted in the introduction, inhalation exposure to erionite is associated with mesothelioma, but not lung cancer (unlike asbestos), in three villages in Turkey, and perhaps one other location in Mexico. Recent work on the toxicity of erionite suggests that the pathway to disease may differ from that of amphibole asbestos,[(34)] and that specific germline mutations predisposing to disease may be involved.[(35)] This could account for the unusual limitation on the geospatial prevalence of erionite-associated disease, which would not be expected given the widespread occurrence of erionite in rocks and soils of the Western States of the USA and it's common use in those areas for road-paving. Erionite is often compared to asbestos, but the toxicity of asbestos is a matter of continued discussion given the various chemistries and structures of the different amphiboles and chrysotile. Erionite is also subject to variation in chemistry and morphology, which is now being intensively researched. In addition, the colocation of minerals such as offretite, another fibrous zeolite, can confound the analysis.

Erionite from the Killdeer Mountains in North Dakota has been tested for toxicity with potentially alarming results[(14)], however a recent re-analysis of the material showed a substantial portion of offretite in the bulk samples.[(36)] Ballirano and Pacella noted that "the similarity of the biological activity of samples of erionite from different locations should be supplemented by further tests carried out on well characterized samples of erionite of dissimilar composition, as well as offretite."[(37)] The recent investigation into methods of characterizing erionite has shown the substantial difficulty involved in analyzing sub-microscopic particles of zeolites.[(27)] Subtle differences in chemistry and morphology were observed between erionites in those samples, and samples from other locations, including Rome, OR; Austin, NV; and Karain, Cappadocia, Turkey, which may have implications for relative toxicity.[(27)] Therefore, careful characterization of erionite is a necessity. In addition, a validated sampling and analytical method specifically for airborne erionite fibers is needed.

Even though there are no regulatory or consensus standards or occupational exposure limits for airborne erionite fibers, the National Toxicology Program has designated erionite to be a known human carcinogen.[(38)] As such, minimizing erionite exposures during dust-generating activities is prudent and characterizing potentially hazardous exposures until an evidence-based OEL is developed remains a necessity. In addition, it has been suggested that genetic factors may contribute to the susceptibility of certain individuals and therefore even low dose exposures to erionite could potentially be harmful.[(39)] Controlling dust exposures to erionite will also be effective in reducing silica exposures.

Following the hierarchy of controls, eliminating or substituting hazardous processes or materials reduces hazards and protects employees more effectively than other approaches. Aggregate containing erionite has been used to construct dirt roads, therefore even if the surrounding rock does not contain erionite, exposures may still occur if the road has been constructed with erionite-bearing aggregate.(40) We recommend against using aggregate known or suspected to contain erionite to build or repair roads.

Engineering controls protect employees effectively without placing primary responsibility of implementation on the employee. Although Carbone et. al.(14) found no difference in erionite concentration whether cars were driven with windows open or closed, we recommend that employees working in areas known or suspected to have erionite containing rock formations keep the windows and doors to the equipment operators' cabs closed when operating equipment or driving down dirt roads and maintain equipment air filters as recommended by the equipment manufacturers. We also recommend that the gaskets and seals surrounding the operators' cabs be changed when signs of age (cracking or wear) or damage occur. Air intake filters should have a Minimum Efficiency Reporting Value (MERV) of 16 and should be part of a powered, pressurized system. The enclosed cab should have the structural integrity to achieve pressurization. The recommended flow rate is 40–140 cubic feet per minute. The filtration efficiency of the recirculation filter should be between a MERV-14 and MERV-16 filter at a flow rate of 200–300 cubic feet per minute.(41)

Administrative controls are used to reduce or prevent hazardous exposures. Employees working in areas known or suspected to have quartz- or erionite-containing rock formations should be educated on the health effects and hazards of RCS and the potential health effects of erionite. They should also be trained on which rock formations typically contain quartz or erionite and which tasks are most likely to expose them to RCS or erionite fibers when carried out in those rock formations. They should also be informed about using dust control techniques, including scheduling tasks that generate the most dust on rainy days or when the soil is damp.

Personal protective equipment may be used until effective engineering and administrative controls are in place. We recommend that employees be provided with clothes and boots that are solely designated for work activities, and that employees not be permitted to wash work clothes at home. Employees who have been working in dusty areas should change into clean clothing before leaving the worksite. Protective clothing and other equipment (chaps, hard hats, and tools) should be washed regularly to remove dust, dirt, and other contaminants.

LIMITATIONS

Limitations of our evaluations include the small number of workers, the limited number of site visits, and the lack of standardized sampling and analytical methods for erionite. We know that erionite is present in many more locations and rock formations than the three we evaluated here. Despite these limitations, we have demonstrated that erionite exposures are occurring in the United States and that the combination of air and bulk soil sampling can be used to quantify employee exposure.

ACKNOWLEDGMENTS

The authors would like to thank Bureau Veritas North America for analytical assistance.

DISCLAIMER

The findings and conclusions in this report are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health. Mention of trades names and or commercial products does not constitutes endorsements or recommendations for use. The authors have no known conflicts of interest in conducting and reporting this research.

REFERENCES

1. Eakle, A.S. Erionite, a new zeolite. *American Journal of Science. 6:* 66–68 (1898).

2. Coombs, D.S., A. Alberti, T. Armbruster, G. Artioli, C. Colella, E. Galli, J. Grice, F. Liebau, J. Mandarino, H. Minato, E. Nickel, E. Passaglia, D. Peacor, S. Quartieri, R. Rinaldi, M. Ross, R. Sheppard, E. Tillmanns, and G Vezzalina: Recommended nomenclature for zeolite minerals: report of the subcommittee on zeolites of the International mineralogical association commission on new minerals and mineral names. *Eur J Miner. 10(5)*:1037–1081 (1998).

3. Dogan A.U. and M. Dogan: Re-evaluation and re-classification of erionite series minerals. *Environ Geochem Health. 30(4)*:355–366 (2008). https://doi.org/10.1007/s10653-008-9163-z

4. Mumpton. F.A. and Ormsby, W.C.: Morphology of zeolites in the sedimentary rocks by scanning electronc microscopy. *Clays and Minerals. 24*: 1–23 (1976).

5. Deffeyes, K.S.: Erionite from Cenozoic tuffaceous sediments, *Central Nevada. American Mineralogist. 44*: 501–509 (1959).

6. Van Gosen, B. T. Blitz, G. Plumlee, G. Meeker, M.P. Pierson: Geologic occurrences of erionite in the United States: an emerging national public health concern for respiratory disease. *Environ Geochem Health. 35(4)*:419–430 (2012).. https://doi.org/10.1007/s10653-012-9504-9

7. USGS (U.S. Geological Survey): Occurrences of erionite in sedimentary rocks of the western United States. Denver, Colorado: U.S. Department of the Interior. 1996. [http://pubs.usgs.gov/of/1996/0018/report.pdf]. Date accessed: September 2015.

8. Carbone M., S. Emri, A. Dogan, I. Steele, M. Tuncer, H. Pass, and Y. Baris: A mesothelioma epidemic in Cappadocia: scientific developments and unexpected social outcomes. *Nat Rev Cancer. 7(2)*:147–154 (2007). doi:10.1038/nrc2068

9. Kliment, C., K. Clemens, and T. Oury: North American erionite-associated mesothelioma with pleural plaques and pulmonary fibrosis: a case report. *Int J Clin Exp Pathol. 2(4)*:407–410 (2009).

10. Rom, W., K. Casey, W. Parry, C. Mjaatvedt, and F. Moatamed: Health implications of natural fibrous zeolites in the intermountain west. *Environ Res. 30(1)*:1–8 (1983).

11. IARC: IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans. Lyons, France: World Health Organization, International Agency for Research on Cancer, pp. 311–316 (2004). [http://monographs.iarc.fr/ENG/Monographs/vol100░C/index.php].

12. Baris, Y.I., A.A. Sahin, M. Ozesme, I. Kerse, E. Ozen, B. Kolacan, M. Altinörs, and A. Göktepeli: An outbreak of pleural mesothelioma and chronic fibrosis pleurisy in the village of Karain Urgup in Anatolia. *Thorax. 33(2)*:181–192 (1978). https://doi.org/10.1136/thx.33.2.181

13. Baris YI, Grandjene P [2006]. Prospective study of mesothelioma mortality in Turkish villages with exposure to fibrous zeolite. *J Natl Cancer Inst. 98(6)*:414–417. https://doi.org/10.1093/jnci/djj106

14. Carbone M, Baris I, Bertino P, Brass B, Comertpay S, Dogan AU, Gaudino G, Jube S, Kanodia S, Partridge CR, Pass HI, Rivera ZS, Steele I, Tuncer M, Way S, Yang H, Miller A [2011]. Erionite exposure in North Dakota and Turkish villages with mesothelioma. *PNAS.* 108(33):13618–13623. https://doi.org/10.1073/pnas.1105887108

15. Ilgren EB, Ortega BM, Castro LJ, Loustaunau G, Fuentes A [2008░a]. A reconnaissance study of a potential emerging Mexican mesothelioma epidemic due to fibrous zeolite exposure. *Indoor Built Environ. 17(6)*:496–515.

16. Ilgren EB, Pooley FD, Larragoitia JC, Talamantes M, Navarrete GL, Krauss E, Brena AF [2008]. First confirmed erionite related mesothelioma in North America. *Indoor Built Environ 0(0)*:1–2. https://doi.org/10.1177/1420326X08099908

17. Ryan P, Dihle M, Griffin S, Partridge C, Hilbert T, Taylor R, Adjei S, Lockey J [2011]. Erionite in road gravel associated with interstitial and pleural changes – An occupational hazard in western United States. *JOEM. 53(8)*:892–898. https://doi.org/10.1097/JOM.0b013e318223d44░c

18. NIOSH [2017]. NIOSH manual of analytical methods (NMAM). 4th ed. Schlecht PC, O'Connor PF, eds. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication 94--113 (August 1994); 1░st Supplement Publication 96--135, 2░nd Supplement Publication 98--119; 3rd Supplement 2003--154.

19. NIOSH [2011]. Current intelligence bulletin 62: asbestos fibers and other elongate mineral particles: State of the science and roadmap for research. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No 2011--159. [http://www.cdc.gov/niosh/docs/2011-159/pdfs/2011-159.pdf].

20. Jurinski J and Jurinski N [1997]. A proposed control limit for exposure to airborne erionite fibers. *Appl Occup Environ Hyg. 16(6):*429–434. http://dx.doi.org/10.1080/1047322X.1997.10389532

21. NIOSH [2002]. NIOSH hazard review: health effects of occupational exposure to respirable crystalline silica. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 2002--129. [http://www.cdc.gov/niosh/docs/2002-129/].

22. OSHA [2017]. OSHA permissible exposure limits for silica. U.S. Department of Labor, Occupational Safety and Health Administration. [https://www.osha.gov/silica/index.html]

23. NIOSH [2010]. NIOSH Pocket guide to chemical hazards. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 2010--168░c, http://www.cdc.gov/niosh/npg/.

24. ACGIH [2015]. 2015 TLVs® and BEIs®: threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

25. NIOSH [2014]. Health hazard evaluation report: evaluation of erionite and silica exposure during dirt road maintenance. By Beaucham C, Harper M, King B. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, NIOSH HHE Report No. 2012-0141-3320.

26. NIOSH [2015]. Health hazard evaluation report: evaluation of erionite and silica exposure during forestry activities. By Beaucham C, Harper M, King B, Dozier A. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, NIOSH HHE Report No. 2012-0061-3244.

27. Harper M, Dozier A, Chouinard J, Ray R [2017]. Analysis of erionite from volcaniclastic sedimentary rocks and possible implications for toxicological research. American Minerologist. *102*(8):1718–1726. http://dx.doi.org/10.2138/am-2017-6069

28. Dogan M [2012]. Quantitative characterization of the mesothelioma-inducing erionite series minerals by transmission electron microscopy and energy dispersive spectroscopy. *Scanning. 34(1)*:37–42. doi/10.1002/sca.20276/

29. NIOSH [2014a]. NIOSH manual of analytical methods (NMAM). Consideration of sampler wall deposits. Inclusion of material adhering to internal cassette surfaces during sampling and analysis of airborne particles. [http://www.cdc.gov/niosh/docs/2003-154/cassetteguidance.html].

30. Bish DL, Chipera SJ [1991]. Detection of trace amounts of erionite using x-ray powder diffraction: erionite in tuffs of Yucca Mountain, Nevada, and central Turkey. *Clay Miner. 39(4)*:437–445. https://doi.org/10.1346/CCMN.1991.0390413

31. EPA [2013]. Bulk sampling for asbestos. Science and Ecosystem Support Division, Athens, Georgia. SESDGUID-104-R1.

32. Januch J, Brattin W, Woodbury L, Berry D [2013]. Evaluation of a fluidized bed asbestos segregator preparation method for the analysis of low-levels of asbestos in soil and other solid media. *Anal Methods. 5(7)*:1658–1668.

33. Farcas D, Harper M, Januch J, Jacobs T, Sarkisian K, Stetler L, Schwegler-Berry D [2017]. Evaluation of Fluidized Bed Asbestos Segregator to determine erionite in soil. *Environ Earth Sci. 76*: 126. https://doi.org/10.1007/s12665-017-6438-7. (2017)

34. Yanamala N, Kisin ER, Gutkin DW, Shurin MR, Harper M, Shvedova AA [2018]. Characterization of pulmonary responses in mice to asbestos/asbestiform fibers using gene expression profiles. *J. Toxicol. Environ. Health. 81(4):* 67–79.

35. Dogan AU, Baris YI, Dogan M, Emri S, Steele I, Elmishad AG, Carbone M [2006]. Genetic predisposition to fiber carcinogenesis causes a mesothelioma epidemic in Turkey. *Cancer Res. 66*:5063–5068.

36. Saini-Eidukat B, Triplett JW [2014]. Erionite and offretite from the Killdeer Mountains, Dunn County, North Dakota, U.S.A. *American Mineralogist. 99*:8–15.

37. Ballirano P, Pacella A [2016] Erionite-Na upon heating: dehydration dynamics and exchangeable cation mobility. *Sci. Rep. 6*: 22786; doi 10.1038/sreo22786

38. NTP (National Toxicology Program) [2011]. Erionite. Rep Carcinog 12:183–184. http://www.iaff.org/HS/PDF/12th%20Report%20on%20Carcinogens%20-%202011.pdf

39. Emri S [2017]. The Cappadocia mesothelioma epidemic: its influence in Turkey and abroad. *Annals of Translational Medicine. 5*. 239 doi:10.21037/atm.2017.04.06.

40. University of Hawaii Cancer Center [2011]. Cancer-causing mineral found in U.S. road gravel: Erionite in roads may increase risk of mesothelioma. *ScienceDaily*. Retrieved February 8, 2017 from www.sciencedaily.com/releases/2011/07/110725162527.htm

41. Cecala AB, Organiscak JA, Noll JD, Rider JP [2014]. Key components for an effective filtration and pressurization system for mobile mining equipment. *Mining Engineering. 66(1)*:44–50.

Table 1. Task-based PBZ air sample results in the CGNF by location and activity

Location: Activity (Number of employees sampled)	Erionite (f/cc)	Sample duration (minutes)	Sampling date
Slim Buttes/Reva Gap: campground maintenance			
Felling and bucking (11 employees)	Not detected*–0.056	155–233	July 2013
Mowing (5 employees)	0.012–0.26	54–290	July 2013
Mowing (3 employees)	0.0010–0.0020	296–298	Sept 2014
Seeding push pit (2 employees)	0.0050 and 0.0060	595 and 597	Sept 2014
Safety at push pit (2 employees)	0.0030 and 0.0040	564 and 569	Sept 2014
Bobcat operator (1 employee)	0.009	585	Sept 2014
Long Pines: Universal terrain vehicle operation			
Operator and assistant (4 employees)	0.0077–0.015	302–336	July 2013
East Short Pines: thinning, bucking, felling, mastication			
Chainsaw operation (6 employees)	0.024–0.11	141–225	July 2013
Chainsaw operation (4 employees)	0.012–0.096	516–522	Sept 2014
Masticator (1 employee)	0.36	213	July 2013
Masticator (1 employee)	0.015	501	Sept 2014
Log stacker (1 employee)	0.061	214	July 2013
Skid loading (1 employee)	0.078	164	July 2013
Driving (1 employee)	0.013	496	Sept 2014
Ekalaka Hills (Digging fireline)			
Pulaski axe† (2 employees)	0.025 and 0.11	204 and 206	July 2013
Combi shovel † (2 employees)	0.081 and 0.026	203 and 321	July 2013
Rogue hoe† (2 employees)	0.016 and 0.057	218 and 324	July 2013
McLeod rake† (1 employee)	0.0081	320	July 2013

*Not detected means no fibers were seen after counting 100 TEM grids.

†These are the names of the tools that the employees used while digging fireline.

Table 2. Erionite soil sample results, September 2014

Task Description	Latitude	Longitude	Elevation (feet)	PLM erionite (%)	FBAS/PCM erionite (%)	XRD erionite (%)
East Short Pines						
Masticating	45°22.629′N	103°43.366′W	3915	5	5.1	10
Masticating	45°22.710′N	103°42.906′W	3986	3	3.9	10
Sawing	45°22.612′N	103°43.168′W	3946	<1	1.0	5
Masticating	45°22.683′N	103°42.630′W	3940	<1	1.3	1
Sawing	45°22.618′N	103°43.195′W	4051	<1	1.4	2
Slim Buttes						
Mowing	45°31.559′N	103°10.714′W	3301	2	2.5	6
Mowing	45°31.684′N	103°10.613′W	3342	3	4.2–4.6	7
Mowing	45°31.887′N	103°10.711′W	3299	ND*	0.1	4
Mowing	45°31.852′N	103°10.719′W	3347	ND	0.1	7
Push pit	45°34.965′N	103°11.918′W	3632	ND	ND	4

*ND means not detectable.

Figure 1. Backhoe in use during culvert replacement.

Figure 2. Cattle guard replacement.

Figure 3. Employees using hand tools to dig fireline.

Figure 4. The topmost white layer of the Wagon Bed formation could potentially contain erionite. Photo of Hawkes Butte, near Worland, Wyoming.

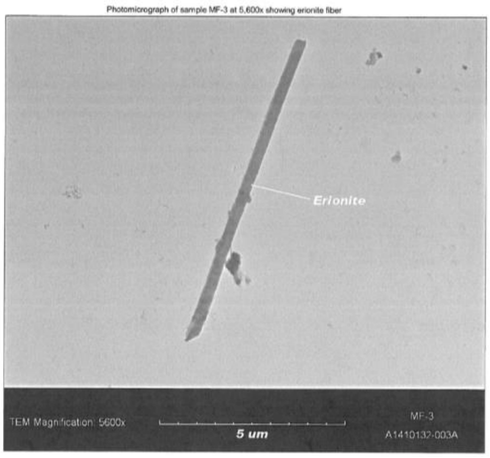

Figure 5. Erionite fiber under TEM.

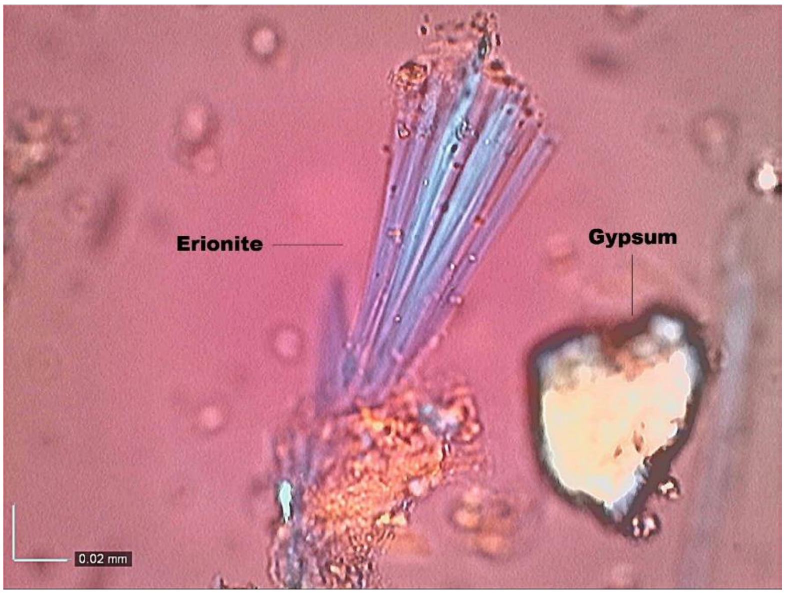

Figure 6. Photograph collected using Polarized Light Microscopy.

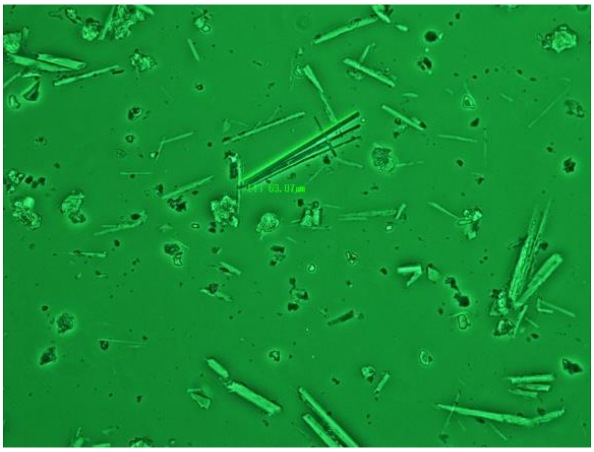

Figure 7. Photograph collected using Phase Contrast Microscopy after Fluidized Bed Asbestos Segregator concentration.