

CHARACTERIZATION OF SAND PROCESSED FOR USE IN HYDRAULIC
FRACTURE MINING

by

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of the requirements for the Master of Science
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MASTER'S THESIS

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has been approved by the Examining Committee for
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To my husband Jason, who occasionally reminded me that eating and sleeping was more important than science, and to my mother Cindy who was a constant source of support.

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ABSTRACT

Each hydraulic fracturing well uses up to 5,000 tons of silica-containing sand, or proppant, during its operational lifetime. Over one million wells are currently in operation across the continental United States. The resulting increase in demand resulted in the production of 54 million metric tons of sand for use as hydraulic fracturing proppant in 2015.

The goal of this study was to evaluate exposure ratios to respirable crystalline silica during a variety of occupational tasks. Workers performing tasks associated with mining, processing, and transport of proppant. Sand samples were aerosolized in an enclosed chamber. Bulk and respirable samples were submitted to a commercial lab for silica analysis. An exposure ratio was calculated by comparing respirable dust concentrations to the current occupational safety regulations.

Higher concentrations of respirable dust and a higher exposure ratio (3.2) were observed when raw sand was the generation source, whereas processed dust contained higher percentages of respirable crystalline silica but resulted in a lower exposure ratio (0.5). When vibration was introduced prior to aerosolization, concentrations tended to increase as vibration times increased, resulting in an increase of the associated exposure ratio (2.3). Results of the study indicate that workers in sand mines and workers exposed to proppant that has undergone low-frequency vibration are at increased risk of exposure to respirable crystalline silica compared to workers who are exposed to proppant that has not undergone vibration.

PUBLIC ABSTRACT

Each hydraulic fracturing well uses up to 5,000 tons of silica-containing sand, or proppant, during its operational lifetime. Over one million wells are currently in operation across the continental United States. The resulting increase in demand resulted in the production of 54 million metric tons of sand for use as hydraulic fracturing proppant in 2015.

The goal of this study was to determine whether mining, processing, and transport facilities handling proppant sand create a comparison between risk of exposures to crystalline silica and respirable dust. Samples of unprocessed, or “raw” sand, and processed sand were aerosolized in an enclosed chamber. Respirable dust samples were collected from the chamber and subjected to gravimetric and x-ray diffraction analysis.

Percentage of silica composition was compared between bulk and respirable samples from the same sand type. In order to simulate potential respirable particle production from stress during transport, some processed sand samples were submitted to low frequency vibration before being aerosolized.

Higher concentrations of respirable dust were observed when raw sand was the generation source, whereas processed dust contained higher percentages of respirable crystalline silica at lower concentrations of respirable dust. When vibration was introduced prior to aerosolization, concentrations tended to increase as vibration times increased. Results of the study indicate that workers in sand mines and workers exposed to proppant that has undergone low-frequency vibration are at increased risk of exposure to respirable crystalline silica compared to workers who are exposed to proppant that has not undergone vibration.

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INTRODUCTION

Overview

Hydraulic fracturing is the process by which oil and natural gas is extracted from narrow fissures in shale or limestone formations. The process begins when a well is drilled vertically one to two miles below the surface of the earth, then horizontally for five to ten thousand feet. Multiple horizontal wells may be drilled in multiple directions for each vertical well. Water, trace amounts of proprietary chemicals, and a material known as a proppant are pumped into the well to expand the fissures at high pressures. The proppant widens the fissures and holds them open so that the oil or natural gas may be retrieved from the rock formation (WIDNR, 2012). Thousands of tons of proppant may be used at a single well. Sand high in silica content is a desirable proppant due to the natural tendency of the mineral to form round grains uniform in size and shape and with high crush resistance. The desirable mineral is mined by the ton, processed for use as a proppant, and transported to hydraulic fracturing mines all around the country (MEQB, 2013).

Proppant sand mines can operate around the clock for eight to nine months out of the year and the average mine will produce approximately 900,000 tons of sand a year. Mining companies provide financial incentives to landowners by offering mineral rights fees and stipends of \$1.50-3 per ton of sand. These incentives can create a conflict within the community when the same mines fail to meet environmental quality standards or permanently alter the landscape, even after reclamation efforts (Pearson, 2013).

Until 2012, silica sand used as a proppant accounted for approximately 18% of sand mined for industrial use (Benson & Wilson, 2015). By 2014, demand for proppant

sand accounted for 72% of U.S. silica sand production, resulting in 54 million metric tons of sand used as hydraulic fracturing proppant (USGS, 2015). Seventy percent of this sand was mined in Wisconsin. The preferred sandstone deposits in Wisconsin are the St. Peter Formation and Cambrian-age sandstone formations (Figure I-1). Cambrian-age sandstone formations may refer to as the Jordan, Wonewoc, and Mt. Simon formations (WIDNR, 2012). Silica sand is the most common type of proppant in use at hydraulic fracturing wells, accounting for 85% of the proppant market. The other options for proppant include resin-coated sand and manufactured ceramic proppant. Silica sand remains the most common because it is plentiful and easy to produce (Benson & Wilson, 2015).

Once the raw sand has been mined, it must be processed to meet the American Petroleum Institute (API) specifications for proppant. This may be done at the same site where the sand was mined, or the sand may be transported to a processing site. Raw sand is sieved to remove fine particles (defined as particles less than 105 μm), leaving only coarse particles of pre-determined size ranges. The size ranges are identified by the number of holes per square inch in the sieve mesh and is often referred to by the primary and secondary sieves used to establish this size range. In order to meet API standards, 90% of the finished product must fall within the specified particle range. The most widely used grain size is referred to as “20/40” and grains in that category fall between 0.42 to 0.84 mm in diameter (MEQB, 2013).

As of this study, Wisconsin does not require additional regulation of sand mines beyond current state regulations for nonmetallic mining operations. Nonmetallic mining operations have a number of environmental permits that must be filed before operation

can begin. Some of these environmental permits are based on controlling air quality around the mines (WIDNR, 2015). One major air emission of a sand mine is the release of what is termed “fugitive dust” which is particulate matter generated during the mining, blasting, processing, and transport of sand (Pearson, 2013). Since Wisconsin sand is prized for the high silica content, it is reasonable to expect that this fugitive dust will also have some silica content.

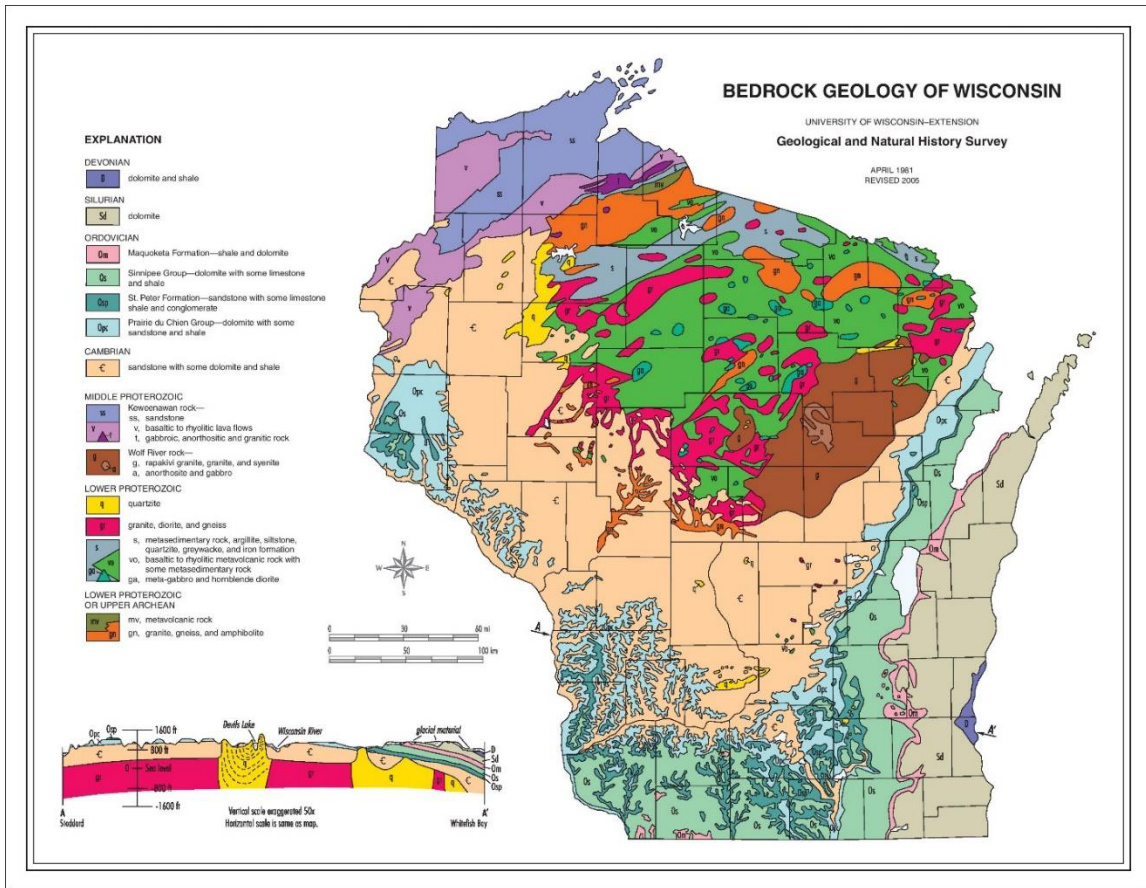


Figure I-1. Bedrock composition of Wisconsin (WGNHS, 1981). Sandstone from the Cambrian age (C) and St. Peter Formation (Osp) provides ideal material for proppant sand (Benson & Wilson, 2015).

Like other nonmetallic mining operations in Wisconsin, proppant sand mines are required to monitor their facilities for fugitive dust emissions (WIDNR, 2015). The mining facilities collect air quality samples to measure the amount of particulate matter less than 10 μm in diameter (PM_{10}) to comply with National Ambient Air Quality Standards for particle pollution (EPA, 1990). It is important to monitor PM_{10} because the smaller particles have an increased deposition rate in the tracheobronchial and alveolar regions of the lungs (Hinds, 1999). However, there are no additional requirements for monitoring of particulate matter less than 2.5 μm in diameter ($\text{PM}_{2.5}$) which have an increased deposition rate in the tracheobronchial and alveolar tissues of the lung compared to PM_{10} . There are also no monitoring requirements for transportation facilities, despite the fact that transportation is also a source of fugitive dust. While some states do impose additional monitoring requirements when crystalline silica is known to be present, Wisconsin is not one of them.

While the Great Lakes area provides a plentiful source of proppant sand, it does not contain significant natural gas or oil deposits. As a result, proppant sand mines tend to be established in close proximity to highways and railways, to allow for ease of transport once the material has been mined (Pearson, 2013). The highest number of hydraulic fracturing wells in the nation is in Texas, with Oklahoma a close second (Gallegos & Varela, 2014). Figure I-2 contains a distribution map of hydraulic fracturing well sites in the continental United States. The wells pictured were in operation between the years 2000-2010.

The increased consumption of proppant sand is a result of technologies which have allowed for multistage horizontal drilling at each hydraulic fracturing well, as well

as the stimulation of older wells. An average well may be expected to consume between 4,000-5,000 tons of proppant, roughly equivalent to 40-50 train car loads. The amount of proppant used per well site can be expected to increase as fracking technology advances, which means a potentially increased exposure to workers at hydraulic fracturing wells (Benson & Wilson, 2015).

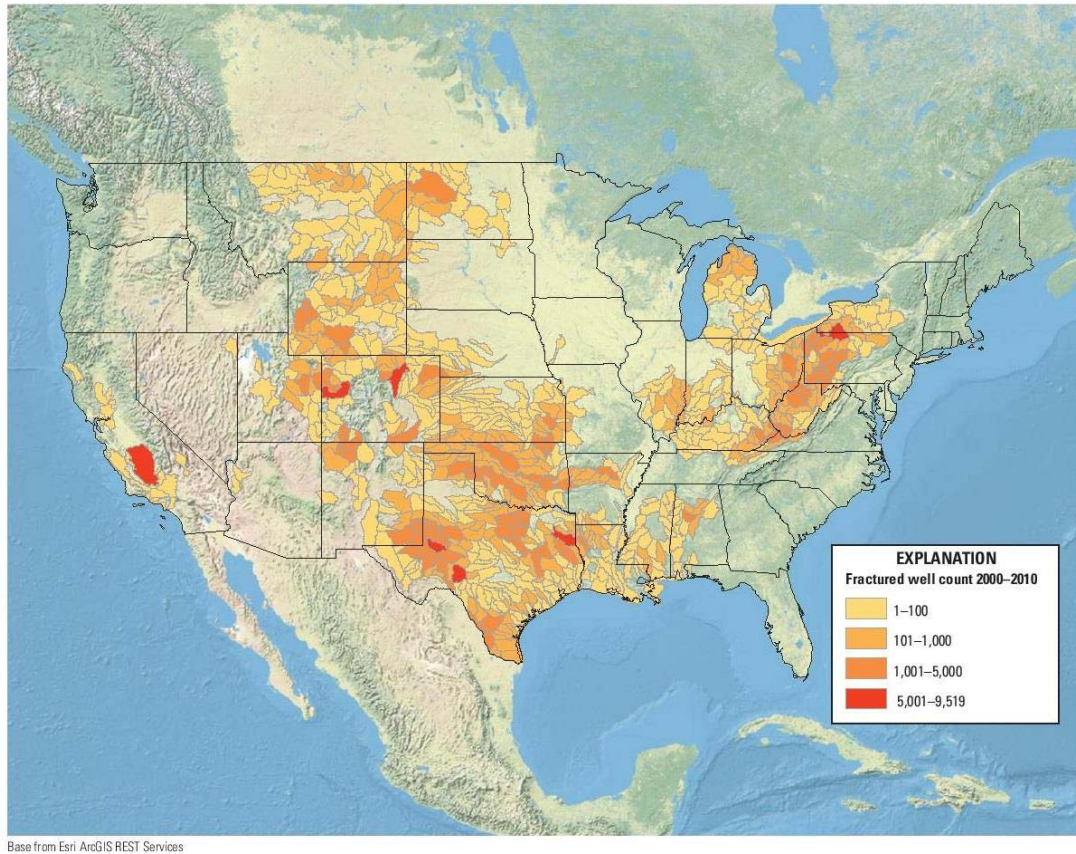


Figure I-2. Distribution of hydraulic fracturing wells from 2000-2010 according to U.S. Geological Survey hydrologic unit. (Gallegos & Varela, 2014)

Health Effects

Silica sand's desirable qualities for proppant use are due to the high quartz (silicon dioxide) composition of the sand, also known as crystalline silica (Benson & Wilson, 2015). Since 2000, the U.S. Department of Health and Human Services' National Toxicology Program has considered respirable crystalline silica (RCS) to be a known human carcinogen (NTP, 2014). Exposure to RCS is known to cause silicosis, which is a disease characterized by the formation of small nodules in the lungs and fibrosis (NIOSH, 2002). Normally the lungs protect themselves from foreign debris by using macrophages that engulf and digest the material (Bhattacharjee & Paul, 2016). Damage incurred by silicosis is permanent, and there are no effective treatments currently available to reverse progression of the disease (Wagner, 1997).

There are three categories of silicosis, all dependent on exposure concentrations and duration to RCS. Chronic silicosis occurs when a worker is exposed at low concentrations for more than 10 years, accelerated silicosis can occur after 5-10 years of exposure to a higher concentration, and acute silicosis can develop after mere weeks or months of exposure when the concentration is extremely high (NIOSH, 2002). Epidemiologic data indicates that chronic silicosis may continue to progress even if the worker is no longer exposed to crystalline silica (NIOSH, 2002; Wagner, 1997).

The ultimate mechanism which causes cellular injury preceding silicosis is not fully understood, though several mechanisms have been proposed (NIOSH, 2002). The inability of macrophages to digest silica particles may be related to the creation of reactive oxygen species. Freshly fractured silica releases free radicals which consume molecular oxygen and form peroxides. This reaction can happen within minutes of the

particle being introduced to lung tissue (Ding et al., 2002). Silica may also disrupt developmental communication between cells, leading to abnormal regeneration of damaged tissues (Perkins et al., 2016).

Epidemiological data suggests that exposure to crystalline silica may increase mortality in other diseases. The Centers for Disease Control and Prevention has found an increased incidence of tuberculosis mortality in workers exposed to silica (CDC, 1995). Workers who are exposed to silica also have an increased risk of lung cancer, with the risk rising as exposure duration or concentration rises (NTP, 2014). Silicosis may also progress beyond the lungs. Particles that migrate beyond the lungs are often found in regional lymph nodes, where they result in inflammation and the creation of nodules or calcification-like scarring in the lymph nodes. There is less definitive evidence for a possible connection between silica exposure and scleroderma, rheumatoid arthritis or systemic lupus erythematosus (ATS, 1997).

Occupational Standards

Acute silicosis became a matter of public concern in the 1930s after 764 workers died from the disease while cutting the Hawks Nest tunnel in West Virginia. An additional 1,500 workers developed acute silicosis after the tunnel was completed. The development of the disease was attributed to exposure to high concentration of silica dust with little to no controls implemented to mitigate exposure. The public outcry resulted in a rush of laws being passed to incorporate silicosis into workers compensation laws. A few years after the Hawks Nest incident, silicosis was considered a disease that afflicted workers in poorly controlled environments. No thought was given to chronic exposure until the 1970s, when a large number of workers performing sand blasting for oil

companies were diagnosed with silicosis (Thomas & Kelley, 2010). Around the same time, the Occupational Safety and Health Administration (OSHA) established the Permissible Exposure Limit (PEL) for crystalline silica (OSHA, 2016a).

Until March 26, 2013, the Mining Safety and Health Administration (MSHA) and OSHA shared the same standard for an 8 hour workplace exposure limit (OSHA, 2016b). MSHA calculates the PEL by taking into account the percentage of silicon dioxide in respirable dust (MSHA, 2006). The formula for calculating the PEL for RCS is calculated using the following equation when at least one percent of crystalline silica is present:

$$\frac{10 \text{ mg/m}^3}{\%SiO_2 + 2} \text{ (MSHA, 2006) [Equation 1]}$$

Using this formula, if a worker was exposed to RCS with a 99% quartz content (the quartz content which high quality proppant sands are advertised as) the highest allowable concentration a worker could be exposed to over an 8 hour work day would be 0.1 mg/m³. Should lower percentages of silica be present, the allowable 8 hour work day PEL would increase to a maximum of 3.3 mg/m³. However NIOSH has set a Recommended Exposure Limit (REL) of 0.05 mg/m³ (NIOSH, 2011) while ACGIH has set a Threshold Limit Value at 0.025 mg/m³ (ACGIH, 2013). Both the REL and TLV are fixed values independent of the percentage of silica content in the respirable dust. In 2013, OSHA proposed an update to reduce the current PEL for crystalline silica to 0.05 mg/m³, to match the REL suggested by NIOSH (OSHA, 2013).

Unfortunately, the Permissible Exposure Limit (PEL) for RCS may not be sufficient to protect the worker. At least 1 in 100 workers will still develop silicosis if exposed at the PEL over the entirety of their working career (NIOSH, 2002). Meanwhile, a study of Vermont granite workers suggests that even the lower limit recommended by NIOSH may not be enough to protect workers. An exposure-response study of Vermont granite workers showed that 45 years of exposure to RCS at a concentration of 0.05 mg/m³ results in a risk of adverse health effects such as silicosis and lung cancer equal to 27 out of 1,000 workers (Attfield & Costello, 2004). This ratio is well above the 1 out of 1,000 workers that OSHA considers an acceptable risk.

Potentially Exposed Worker Population

Ultimately, workers may encounter proppant sand as an occupational hazard in four different employment areas: industrial sand mining, processing of sand for proppant use, transport of proppant sand, and use of proppant sand at hydraulic wells. In 2014, approximately 197,000 employees worked in Oil and Gas Extraction for 9,800 establishments, compared to the Industrial Sand Mining category, where 5,200 employees worked for 188 establishments (BLS, 2015).

Census results for employees in the Industrial Sand Mining category may be responsible for mining or processing the sand originating in the Wisconsin and Minnesota bedrock. Meanwhile, employees in the Oil and Gas Extraction may come into contact with proppant sand if they work at a hydraulic well. There is no separate census category specifically oriented to workers employed at hydraulic wells. The census data aggregates all employees who work in support roles for the mining industry, regardless of which

category they may support, and as a result there is no data for support employees who work directly for Oil and Gas Extraction or Industrial Sand Mining.

Health and safety regulations for employees in Industrial Sand Mining categories would fall under the Mining Safety and Health Administration (MSHA), however workers who are employed in onshore Oil and Gas Extraction or transport proppant sand would fall under the Occupational Safety and Health Administration (OSHA) (Witter, Tenny, Clark, & Newman, 2014). Since transport of proppant sand may be contracted out to a variety of shipping companies, there are no data available on what percentage of workers may be exposed to occupational hazards from the material during transport.

Despite the rapid increase in sand production for proppant use, little exposure data exists for workers mining sand. Steenland and Sanderson (2001) calculated mortality rates of lung cancer among industrial sand workers based on personal breathing zone samples collected from 1974-1995, well before the recent increase in production in the past three years. They found increased risk of lung cancer in workers with less than six months of exposure and in workers with 10 or more years of exposure (Steenland & Sanderson, 2001).

Attfield and Costello (2004) led a closely comparable study of RCS exposure on Vermont granite workers mentioned previously, however that study covers mortality data from 1940-1999. Even if any kind of parallel could have been drawn between the Vermont granite workers and Wisconsin silica sand miners the exposure could hardly be considered relevant considering the dramatic increase in production of proppant sand in the past couple of years.

On the other hand, Esswein, Breitenstein, Snawder, Kiefer, and Sieber (2013) published a recent study of worker exposure to RCS exposure that was conducted at hydraulic fracturing wells. The study found 83.8% of workers were exposed to concentrations above the ACGIH TLV, 68.5% of the workers were exposed to concentrations above the NIOSH REL, and 51.4% of workers were exposed above the OSHA PEL. Some worker exposures exceeded the PEL by factors of 10 or more. Many of the workers listed in the study with exposures above the TLV had job titles tied to transportation such as “Sand Truck Driver” and “Pump Truck Operator.” If these workers are employees of a transportation company hired to move sand to the hydraulic fracturing site, the study demonstrates a potential exposure of transportation employees to RCS. At the time of this paper, no data were available for workers who were exposed to RCS during transport of proppant sand.

Transportation of Proppant

The railway is the primary form of transportation for the proppant once it has been processed, however material may also be transported by truck or barge (WIDNR, 2012). Proppant sand may see multiple transfer points before it arrives at the final destination (Benson & Wilson, 2015). Proppant sand will likely undergo mechanical stress during transfer from one transportation site to another, depending on the material transfer method. The proppant sand may be transferred pneumatically, or via a belt mover (Esswein, Breitenstein, Snawder, Kiefer, & Sieber, 2013). However, all proppant sand will be exposed to some level of vibrational energy as it is transported by railway or highway.

Understanding the mechanical energy that proppant sand is exposed to before use is important because each time mechanical energy is introduced, a potential change to the proppant size distribution may also be introduced if the energy is stronger than the proppant's resistance to change. Proppant sand would be exposed to force from shear by the sand particles rubbing up against each other or the sides of the shipping container. This could potentially cause smaller particles to break off from larger ones, thereby changing the size distribution of the proppant and even creating fine particles small enough to be inhaled. Taslagyan, Chan, and Morgenstern (2015) found that vibrational energy had a negative impact on shear strength of soil. The study did not focus on proppant sand, nor did it state the source of the soil or mineral composition. However, the study also tested glass beads, which could be assumed to have a silica composition similar to proppant sand. The study also used a vibration frequency of 140 Hz (Taslagyan, Chan, & Morgenstern, 2015).

There is no single frequency to which a truck bed or railway car will resonate at during transport. The speed at which the vehicle is traveling and the type of surface it is traveling on will influence the vibrational stress imparted to the material being transported. The range of frequencies which most material being transported tends to be low, with trucks traveling on highway transmitting a frequency between 0-50 Hz (Segel, Gillespie, Schneider, & Campbell, 1981), and a rail car transmitting between 0-30 Hz (Tomioka & Takigami, 2015).

Given the addition of vibrational stress has a negative impact on the shear strength of sand, and that proppant sand will be transported long distances via methods which generate vibrational energies, there is a logical progression of thought that

proppant sand transported to its final destination will have its physical properties altered by the act of transportation. This could be a potential factor contributing to the high RCS exposures seen by Esswein et al. in the exposure study conducted on hydraulic fracturing well workers.

Study Aims and Hypothesis

The overall goal of this study was to determine the characteristics of sand mined for use as a hydraulic fracturing proppant and identify circumstances which might result in an increased exposure of respirable dust to the worker. The significant increase in demand for sand as a proppant in the past five years has led to a boom in industrial sand mining sites, especially in the Great Lakes area (Benson & Wilson, 2015). The research associated with this thesis was associated with three specific aims.

Specific Aim 1: Compare exposure risk to RCS between freshly mined (or “raw”) sand and sand that has been processed for use as a hydraulic fracturing proppant.

Hypothesis: there will be no change in concentration between raw sand and proppant.

Specific Aim 2: Characterize differences in silica composition between bulk samples of raw and proppant sand. A sub-aim was to determine whether the silica composition of respirable dust samples differed from that of the bulk sand types. Hypothesis: percentage composition of crystalline silica is not related to particle size.

Specific Aim 3: Characterize changes in exposure risk to RCS when processed sand undergoes vibrational stress to simulate transport of materials. Hypothesis: respirable dust concentrations will not change as processed sand undergoes additional stress similar to material transport.

CHARACTERIZATION OF SAND PROCESSED FOR USE IN HYDRAULIC FRACTURE MINING

Introduction

Hydraulic fracturing has been used to extract oil and natural gas since 1947. Nearly seventy years of progress have allowed new wells to be drilled to even deeper depths, with more horizontal shafts per well. Not all states require companies to report when new wells are drilled. This means the 278,000 wells reported in the contiguous U.S. from 2000 to 2010 are most likely an underestimation of the actual number of wells currently in operation (Gallegos & Varela, 2014).

Each well requires several tons of proppant to create a slurry that props open fissures and allows oil or natural gas to be extracted. Newer wells may require as much as 9,000 tons of sand during their operational lifetime. As technology progresses, older wells may be reopened after their operational expectancy has expired. Therefore it is not inconceivable to imagine that wells in operation now may be reopened at a later time (Gallegos & Varela, 2014).

Sand high in silica content is the most desirable proppant material as it is cheap and relatively easy to procure from the natural sandstone formations in the Midwest. The demand for sand as a proppant hovered around 5% of U.S. sand production until 2005, when demand—and therefore production—began to increase. Demand for sand as a fracturing proppant now accounts for more than 70% of the sand market, which has seen a corresponding increase in production more than triple the tonnage produced prior to 2005 (Figure II-1).

Characteristics of ideal proppant sand include round, spherical grains with a high silica content, 95% silica or greater is preferred. Sand is referenced by the U.S. Standard Sieve Series sizes used to achieve a uniform grain size. For instance, a sand noted as “20/40” has been sieved so that the material falls through a sieve pan with a mesh size of 20 but does not fall through the sieve pan with a mesh size of 40. This results in sand with grain diameters between 0.42-0.84 mm. In the past, 20/40 has been the preferred proppant type for hydraulic fracturing wells, however 40/70 proppant type (grains with a diameter between 0.21-0.42 mm) has become more popular in recent years.

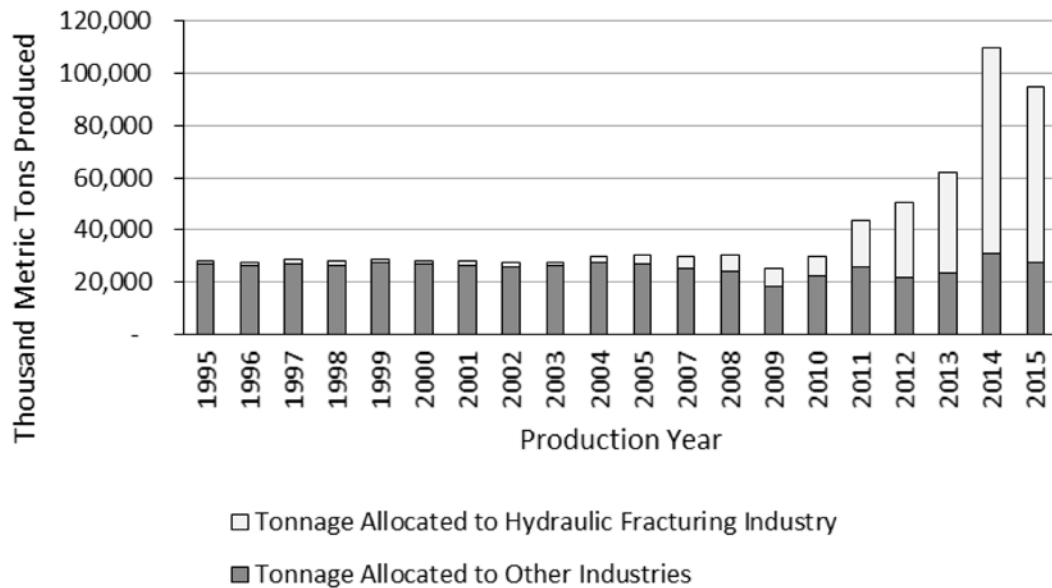


Figure II-1: Total sand and gravel produced in the US for industrial purposes and percentage allocated for use in hydraulic fracturing from 1995-2015. Numbers obtained from annual reports compiled by the US Geological Survey organization. (USGS, 2015)

Despite the smaller grain size of 40/70 proppant, they are still too large to be considered a respiratory hazard, as aspiration into the respiratory tract does not begin

until particles approach 0.1 mm in size for a standard density particle (Hinds, 1999). However this does not address the possibility of RCS particles being present during the extraction of sand from the formation, or respirable particles being generated between where the proppant is sized to when the proppant arrives at the hydraulic fracturing well. The process by which the sand is extracted from the sandstone formation may create respirable dust and logically, RCS since silica-containing sand is the target material in question. After the raw sand is removed from the sandstone formation, it is then sieved into designated grain sizes. Once the sand has been processed for use as a proppant, it is shipped by a combination of rail, truck, and barge to the destination hydraulic fracturing well (MEQB, 2013). The results of a study by Esswein et al. (2013) revealed that the majority of workers at participating hydraulic fracturing wells were exposed to RCS at levels above the TLV and some workers were exposed to concentrations over 10 times the PEL. The change in shear strength of sand particles that have been vibrated may have contributed to the high exposure levels seen in this study. No similar study has been conducted for workers at sand mines since the increase in proppant sand production.

Material transported by rail or truck will be constantly exposed to low-frequency vibration between 0-50 Hz (Segel et al., 1981; Tomioka & Takigami, 2015). The exposure to vibration has the potential to change the size distribution of proppant sand after it has been processed, reintroducing fine particles after they have been removed. Sand exposed to vibration at 140 Hz experiences a negative effect on shear strength (Taslagyan et al., 2015). Shear strength is the strength of a material against structural failure, and is usually produced by sliding a material parallel to the plane of force.

Proppant sand experiences shear force when sand particles rub against each other or the sides of the shipping container.

The high levels of exposure to workers at hydraulic fracturing wells is concerning for two reasons: exposure to RCS is known to cause silicosis, an irreversible obstructive lung disease, and freshly fractured silica particles are especially damaging to lung tissue due to their production of free radicals (Ding et al., 2002; NIOSH, 2002) . Whereas the sieving process is intended to remove all grains less than 0.1 mm, the high levels of exposure to workers at hydraulic fracturing wells may indicate that either the sieving process is not efficient at removing the small particles, or that grains of silica are fracturing during transport and creating fractured particles of respirable size that have an increased risk of inducing silicosis.

This study was designed to address the gap in published exposure studies for workers involved in production of sand used as a proppant. Respirable dust samples were collected and analyzed for crystalline silica content. Three conditions were simulated to correspond to three different worker categories: workers mining sand which has not had fine particles removed (referred to here as “raw sand”), workers who handle sand after it has been processed for use as a proppant (referred to here as “proppant”) and workers who may be exposed to proppant as it is transported from the processing site to the hydraulic fracturing well (referred to here as “vibrated proppant”).

The specific aims were as follows: (1) compare exposure risk to RCS between freshly mined (or “raw”) sand and sand that has been processed for use as a hydraulic fracturing proppant, (2) characterize differences in silica composition between bulk samples of raw and proppant sand with a sub-aim to determine whether the silica

composition of respirable dust samples differed from that of the bulk sand types and (3) characterize changes in exposure risk to RCS when processed sand undergoes vibrational stress to simulate transport of materials.

Methods

Aim 1

Methods associated with the first aim of this research involved aerosolizing sand from bulk samples into a small (5 L), enclosed chamber from which respirable dust samples could be obtained. Sand used in this study consisted of both “raw” sand from a sand mine and the processed “proppant” sand. The raw sand provided for the study originated from the Upper Cambrian Jordan formation in Wisconsin and is a type of sand known in the fracking industry as “Northern White”. Proppant sands were donated to the University of Iowa for experimental use by a proppant sand distributor. Table II-1 describes proppant types used in this study and assumed particle sizes.

Table II-1. Proppant sand types used in Aim 1 and associated grain diameters.

Product Mesh Size (holes per square inch)	20/40	30/50	40/70	100M
Grain Diameter (mm)	0.42 to 0.84	0.30 to 0.60	0.21 to 0.42	>0.15

To aerosolize the sand, 20 g of sand was placed in an acoustical dry aerosol generator/elutriator (ADAGE) system (Thorne, 1994). Dried, filtered, and compressed air flowed through the ADAGE system at 2.5 liters per minute (LPM) into an enclosed chamber (Figure II-2). Five samples of respirable dust from raw sand and each proppant type were collected with an aluminum cyclone operating in accordance with the NIOSH Manual of Analytical Methods, method 7500. A total of 25 samples were collected on 5 μm polyvinyl chloride (PVC) filters at 2.5 LPM using an SKC AirChek sampling pump

(Model 22PCXR4, S/N 634006, SKC Inc, Eighty Four, PA) Flow of the sampling pump was calibrated before and after sample collection period with a Gilibrator calibrator (S/N 1103045, Sensidyne, St Petersburg, FL). Concentration of sand in the chamber was actively monitored with a photometer (personal DataRAM, Model 1200, S/N 6044, Thermoscientific, Waltham, MA) during the same sampling period. Results were logged every 30 seconds over the course of the sampling period. An auto-zeroing sequence was run on the photometer before each use.

During the first aim of the study, samples were sent to the Wisconsin Occupational Health Lab (WOHL) for gravimetric and silica analysis. Filters were weighed before sample collection on a microbalance (Mettler Toledo XP-26, S/N 112122649, Mettler-Toledo LLC, Columbus OH) in the University of Iowa Pulmonary Toxicology Facility. Volume of air passing through the filter and pre-sample filter weights were provided to the Wisconsin Occupational Health Laboratory (WOHL) along with the samples. Personnel in the WOHL weighed filters and reported the mass difference between pre- and post-sample filter weights and sampled concentration. WOHL personnel also conducted an x-ray powder diffraction (XRD) analysis and reported percentage silica composition of respirable dust samples, as well as sampled concentration of RCS.

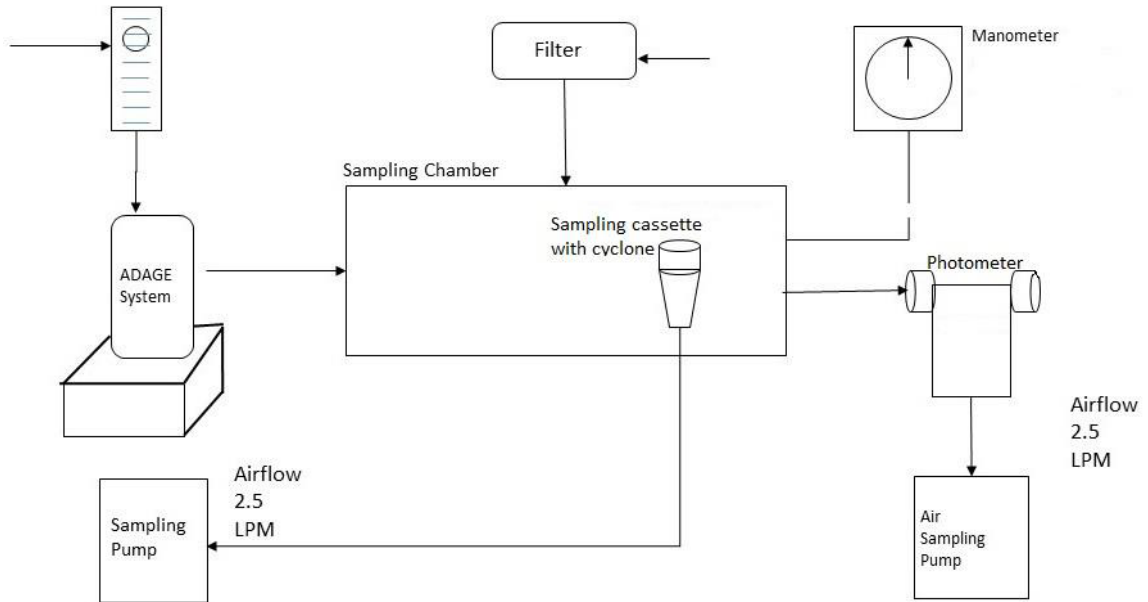


Figure II-2. Chamber schematic for collection of respirable dust samples.

Aim 2

For the second aim of this study, a particle sieve analysis was conducted to determine the size distribution of particles for each sand type. One hundred grams of each proppant sand type was applied to wire mesh sieves (sizes 100, 60, 40, and 18) available in the University of Iowa Pulmonary Toxicology Facility.

Eight bulk samples of sand were submitted to the WOHL for silica analysis. The samples of sand submitted for analysis were: 5 g each of sieved raw sand (sieve sizes: 18/40, 40/60, 60/100, >100) and 5 g each of proppant (sieve sizes: 20/40, 30/50, 40/70, 100M). Respirable dust samples were also analyzed using Scanning Electron Microscopy (SEM) at the University of Iowa's Central Microscopy Research Facility using Energy Dispersive X-ray Spectroscopy (EDS). The results from silica analysis of

bulk samples were compared to silica analysis results of respirable dust reported by the WOHL in Aim 1 using descriptive statistics.

Aim 3

In the third aim of this study, 20 g of sand was placed in the ADAGE system and exposed to vibration prior to aerosolization. Five samples of 20/40 sand was exposed to vibration at 35 Hz for 15 minutes prior to being aerosolized, and 5 samples of 20/40 sand was exposed to vibration at 35 Hz for 30 minutes prior to being aerosolized.. This vibration frequency was chosen to represent to the low-frequency vibrations experienced during transport by rail or highway. Dried, filtered, and compressed air passed through the ADAGE system at 2.5 LPM into the same chamber used in Aim 1. Results of previous samples collected using the 20/40 proppant type in Aim 1 were used as a baseline measurement for a comparison of peak and average chamber concentrations. Concentration of sand in the chamber was also monitored and logged every 10 seconds with a photometer during the same sampling period. A dilution equation was created using regression analysis on the photometer data, using a log-normal scale. The dilution equation follows the format seen in Equations 2 and 3 (Stewart, Herrick, Horowitz, Labato, & Shapiro, 2005). Number of air changes per hour (N changes) is calculated using the air flow through the chamber (Q) and the volume of the chamber (V). The dilution equation calculates the concentration of a substance in the chamber (C_t) given the initial concentration (C_o), number of air changes per hour (N changes) and elapsed time in hours (t).

$$N \text{ changes} = \frac{Q * 60}{V} \text{ (Equation 2)}$$

$$C_t = C_o e^{-t N \text{ changes}} \text{ (Equation 3)}$$

In this scenario, air flow through the chamber remained a constant 5 LPM. The volume of the sampling chamber was 5 L, resulting in 60 air changes per hour. Since air flow through the chamber remained constant, the dilution ventilation equations calculated using the photometer data reflect the residence time in air of the proppant sand once aerosolized.

Filters were weighed before and after sample collection on a microbalance (Mettler Toledo XP-26, S/N 112122649, Mettler-Toledo LLC, Columbus OH) in the University of Iowa Pulmonary Toxicology Facility. The performance of the microbalance was checked with calibration weights prior to each use. During performance checks, 0.005 mg was the greatest difference observed between calibration weight and reported weight. For the purposes of this study, this value was considered to be the precision of the instrument.

Two exposure ratios were calculated for each respirable dust sample. The first exposure ratio was calculated by dividing the chamber concentration by the current MSHA PEL, which is dependent on the percentage of silica in the sample.

$$\frac{10 \text{ mg}/\text{m}^3}{\%SiO_2 + 2} \text{ (MSHA, 2006)} [Equation 1]$$

The second exposure ratio was calculated using the current OSHA PEL of 0.05 mg/m³, as the PEL is a fixed value regardless of the silica content. As chamber concentration values are laboratory simulations and not directly representative of worker exposure, an exposure ratio will provide a comparison of study results relative to both respirable dust concentration and RCS.

Results

Aim 1

Respirable dust concentrations produced by aerosolizing raw sand were 18 times higher than concentrations produced by proppant sand (Table II-2). In contrast, the percentage of silica in respirable dust produced by proppant sand was 3.3 times higher than percentages of silica in raw sand (Table II-2).

Table II-2. Comparison of concentration and silica composition percentages of respirable dust samples.

	Arithmetic Mean of Respirable Dust Concentrations (mg/m ³)	Silica Composition (%)
Raw (n=5)	4.06 (SD = 2.20)	5.7 (SD = 4.2)
Proppant (n=7)	0.22 (SD = 0.17)	19.0 (SD = 6.7)

Real-time chamber concentrations were recorded with the photometer during sample collection (Figure II-3). A regression equation was calculated for each proppant type using the data logged from the time the chamber reached peak concentration to when the photometer first recorded a concentration at or below 0.02 mg/m³.

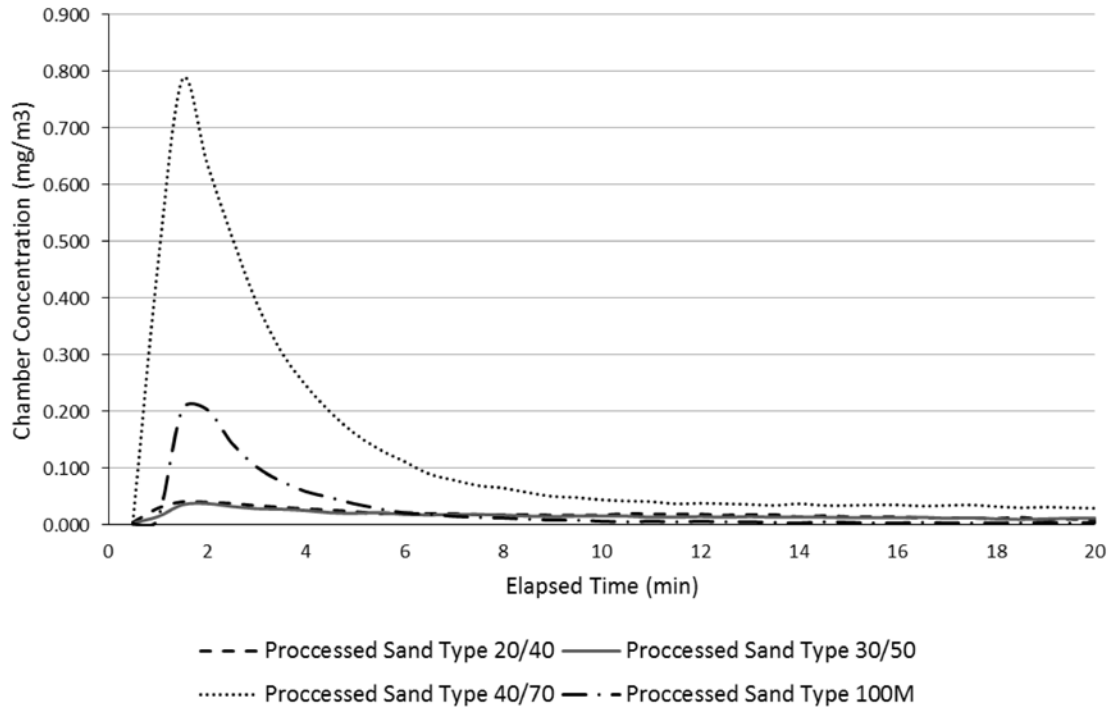


Figure II-3. Real-time chamber concentrations of aerosolized proppant as monitored by a photometer.

Based on the grain sizes of the proppant sands, proppant type 100M was expected to generate the greater peak concentration. The greater concentration seen in proppant type 40/70 was unexpected, and may indicate that fine particles were not effectively removed from the sand source during processing.

Aim 2

A sieve analysis was conducted for each proppant type to determine particle size distribution (Figure II-4). Proppant types 20/40 and 30/50 had similar particle size distribution. Proppant type 100M showed the greatest distribution range, with particles ranging from 0.425 mm to smaller than 0.15 mm. Proppant types 40/70 and 100M were the only types to have detectable weights of particles less than 150 μ m.

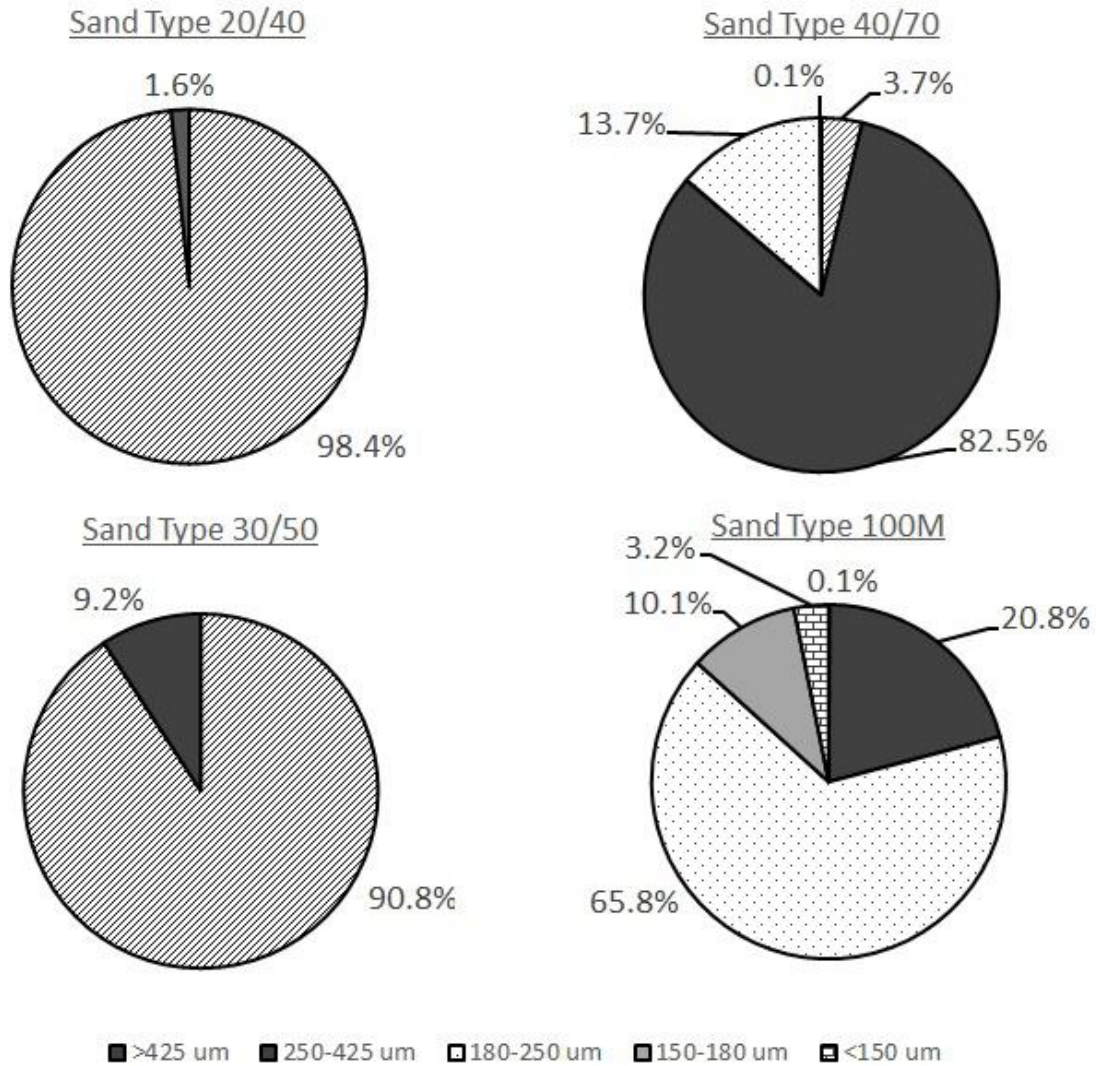


Figure II-4. Particle size distribution results for 20/40, 30/50, 40/70, and 100M proppant types.

Figure II-5 displays a comparison of percentage silica composition in samples of raw and proppant sand. With the exception of respirable dust samples, silica percentages remained high, although not at the ideal 95-99% range desired for proppants. Silica percentages in raw sand ranged from 59-88% while proppant sand ranged from 67-85% in the same size range.

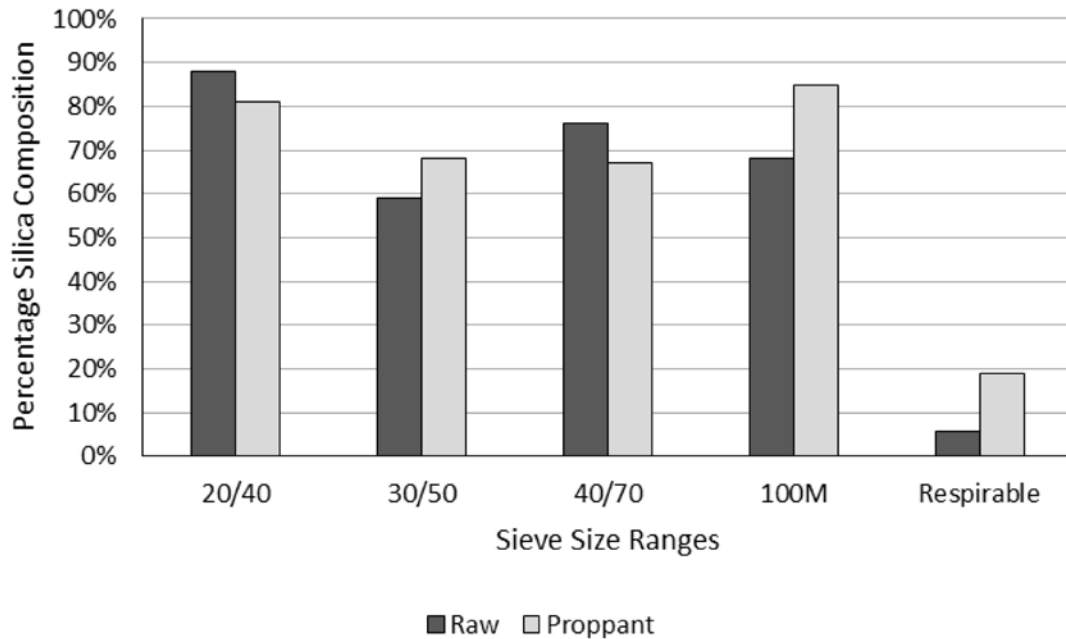


Figure II-5. Percentage of silica in raw sand, proppant sand, and respirable dust.

Figure II-6 is a photograph taken by the SEM and EDS analysis on a sample collected from raw sand. The accompanying EDS analysis of particle 1 is representative of the EDS analyses conducted on the remaining particles in the top of the figure. The raw sand particles contain aluminum, potassium, silicon, and oxygen. EDS analysis of proppant sand contained the same chemical composition.

Aim 3

When low-frequency vibration was introduced to sand before aerosolization and sample collection, average concentration of respirable dust tended to increase. However as vibration time increased the variability in measured concentrations also increased (Figure II-7). Results from samples collected during Aim 1 from 20/40 proppant were used as a baseline measurement for visual comparison. The introduction of a pre-sample vibration time of 15 minutes resulted in an average concentration of 0.55 mg/m^3 (SD=0.17), 10 times higher than the baseline concentration of 0.05 mg/m^3 (SD=0.07). Introducing a pre-sample vibration time of 30 minutes resulted in an average concentration of 1.09 mg/m^3 (SD=0.96), 20 times higher than the baseline concentration.

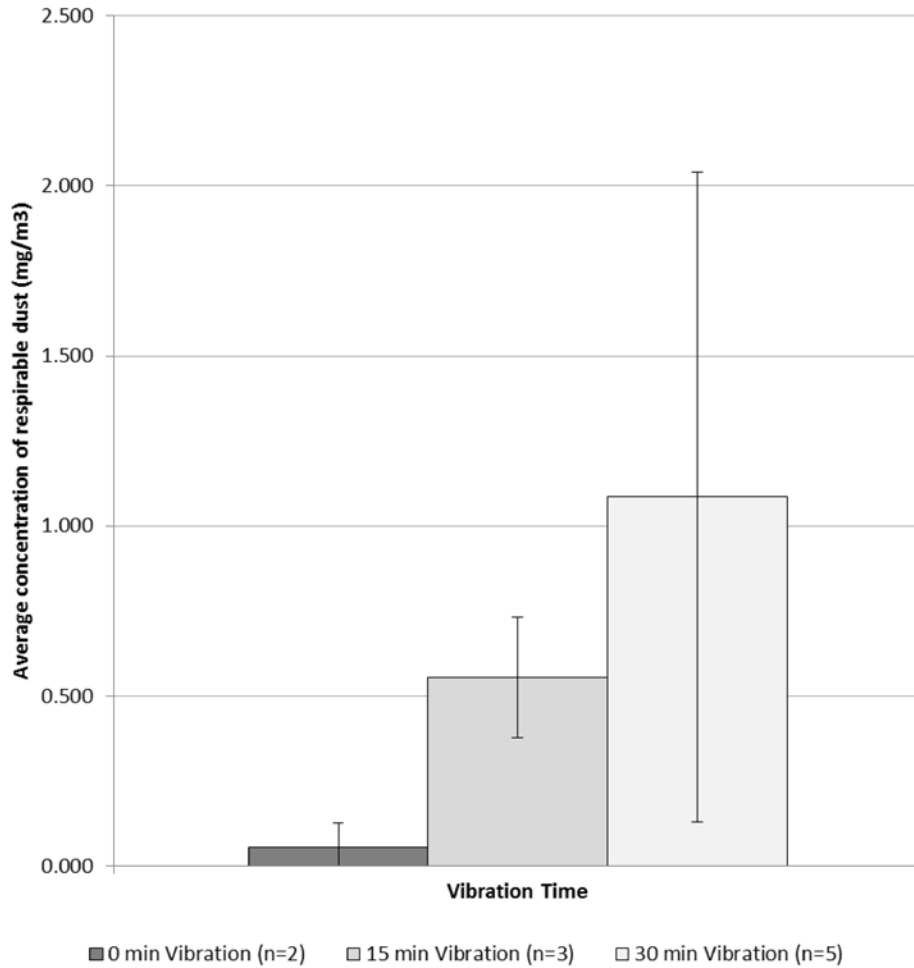


Figure II-7. Respirable dust concentrations of 20/40 proppant with vibration time before aerosolization. Error bars represent standard deviation in sample population.

The introduction of low-frequency vibration also increased the time it took for the aerosolized dust to settle (Figure II-8). Logged data from Aim 1 was used as the baseline for comparison in settling time. Conditions in the chamber were considered settled when the aerosolized dust concentration measured less than 0.02 mg/m³.

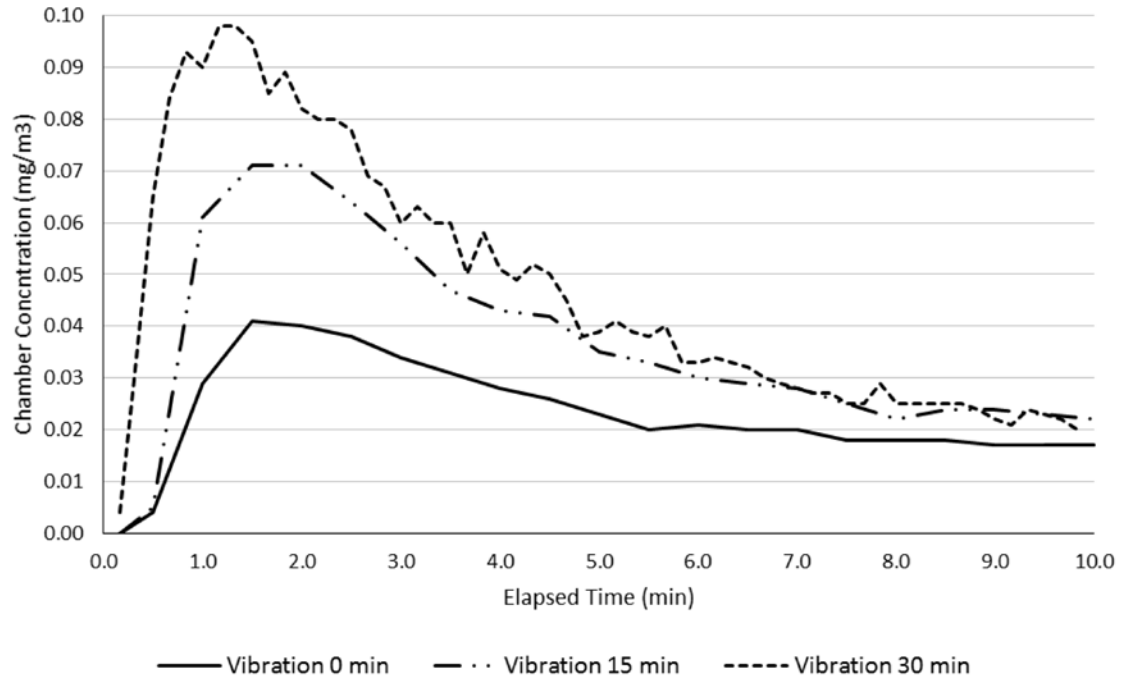


Figure II-8. Chamber concentration readings logged by photometer after vibration is introduced.

Table II-3 lists the dilution ventilation equations modeled for proppant type based on the length of time the sample vibrated prior to aerosolization. The residence time of aerosolized proppant increased when samples were exposed to 30 minutes of vibrational stress. This means that vibrating proppant sand for 30 minutes or more will increase the residence time of proppant sand particles once they become airborne.

Table II-3. Regression equations to calculate time for aerosolized proppant to settle after exposure to vibration.

Vibration Time	Regression Equation	R ² value
No Vibration	$C_t = 0.039e^{-17.2t}$	R ² = 0.94
15 minutes	$C_t = 0.067e^{-17.2t}$	R ² = 0.92
30 minutes	$C_t = 0.099e^{-34.5t}$	R ² = 0.97

Two exposure ratios were calculated using average gravimetric respirable dust concentrations from three different conditions: raw sand, proppant, and vibrated proppant

(Table II-4). The gravimetric concentrations were divided by either the current MSHA or OSHA PEL.

Table II-4. Comparison of chamber concentrations, percentage silica composition, and effects in ratio of time-weighted allowance and concentration by sand type.

	Concentration (mg/m ³)	% Silica	MSHA PEL (mg/m ³)	MSHA Exposure Ratio	OSHA Exposure ratio
Raw sand	4.06 (SD = 2.20)	5.7 (SD = 4.2)	1.30	3.2	82.0
Proppant	0.22 (SD = 0.17)	19.0 (SD = 6.7)	0.48	0.5	4.4
Vibrated (15 min)	0.56 (SD = 0.18)	19.0 (SD = 6.7)	0.48	1.2	11.1
Vibrated (30 min)	1.09 (SD = 0.96)	19.0 (SD = 6.7)	0.48	2.3	21.6

Proppant sand was the only type with an MSHA exposure ratio to chamber concentration ratio below 1 (0.5), while raw sand and vibrated proppants had ratios ranging from 1.2 to 3.2. In contrast, once the OSHA PEL of 0.05 mg/m³ was incorporated into the exposure ratio, all exposure ratios exceeded one, with the exposure ratio for mined sand rising to 82.0, almost four times greater than the next highest exposure ratio of 21.6 seen in proppant sand that had been exposed to low-frequency vibration for 30 minutes.

Discussion

The results of this study are intended to develop a risk comparison of potential environments in which workers handling proppant may be exposed to crystalline silica. Raw sand exposure ratios reflect relative risk to workers exposed to mined sand before it is processed. This may include workers at sand mines, or workers at processing sites before the sand is processed. Proppant exposure ratios reflect relative risk to workers exposed to proppant sand that has not experienced vibrational stress, and vibrated

proppant exposure ratios reflected relative risk to workers who are exposed to proppant which has undergone at least 30 minutes of vibrational stress.

In Aim 1, the initial hypothesis was that there would be no difference in respirable dust concentration between raw sand and proppant. Respirable dust concentrations produced by aerosolizing raw sand were almost 80 times greater than the concentrations generated by proppant. Of the four proppant types, the type that would be most likely to generate higher concentrations of respirable dust was 100M, as that type is composed of smaller particles. However the logged data from the photometer revealed that the 40/70 type produced the highest concentration. This finding may indicate that the process used to create this proppant type did not adequately remove the fine particles from the final product.

In Aim 2, it was hypothesized that particle size would not influence silica content. Bulk analysis of raw sand ranged from 59-88%, with a corresponding 5% silica content in respirable samples of the same material. Meanwhile, proppant sand produced a similar range in bulk samples (67-85%) with a respirable sample silica content average of 19%. EDS analysis and bulk silica analysis of sand showed mineral elements consistent with a feldspathic sandstone, or a feldspar-containing sandstone, which can be found in western Wisconsin. Typically, “Northern White” sand is considered a premium proppant, with an assumed silica content greater than 95% (Benson & Wilson, 2015). This is higher than the values seen in the bulk sand analysis, and much higher than the silica analysis conducted on respirable dust. This suggests that small particles of bulk sand were not derived from fracturing of silica quartz grains, but some other rock type. The addition of

aluminum and potassium to create a feldspathic sandstone may result in a material that is more friable than pure silica and may be the major contributor to respirable particles.

In Aim 3 it was hypothesized that respirable dust concentrations would not change when samples were vibrated prior to being aerosolized. When the proppant is introduced to low-frequency vibration prior to sampling for respirable dust, chamber concentrations showed a positive trend, although as vibration time increased so did the range in concentration. Of interest is the tendency for aerosolized dust to stay airborne for longer periods of time. While there is no change in residence time between proppant sand not exposed to vibrational energy and proppant sand exposed to at least 15 minutes of vibrational energy, once samples were exposed for 30 minutes, the residence time increased to twice that of other levels. The difference in suspension times may be due to energy from vibration creating smaller particles that remain airborne for longer periods of time.

A exposure ratio greater than one indicates that when all other conditions are the same, the worker has a high relative risk of exposure to RCS from the sample source. The PEL for respirable dust without crystalline silica is 5 mg/m^3 . If silica is present, the PEL decreases as the percentage of silica increases and can range from 0.01 mg/m^3 to 3.33 mg/m^3 . The change in PEL for the raw sand demonstrates how even low concentrations of silica will alter the allowable exposure level. Meanwhile, the higher ratio seen in the vibrated processed sand demonstrates how a lower concentration may still present a hazard when the silica content is high.

The respirable dust concentrations for all three scenarios exceeded limits recommended by NIOSH and ACGIH. When the same exposure ratio is calculated for

the OSHA PEL, the exposure ratio becomes directly proportional the chamber concentration. This is because the OSHA PEL is a fixed value based on a presence/absence of silica, rather than trying to incorporate the percentage of silica present.

The raw sand produced the highest exposure ratios, indicating that when all conditions are otherwise controlled, raw sand carries the greater risk of exposure to RCS. The lowest exposure ratios were found in proppant sand, however the longer proppant was exposed to vibration, the higher the exposure ratio became. The low-frequency vibration represents vibration energy imparted to proppant as it travels by truck or rail. The results of this study indicate that the longer proppant is exposed to this energy, and therefore the greater distance it is transported, the greater potential risk of exposure to RCS becomes to the worker.

Limitations

Of the 31 samples submitted to the WOHL for gravimetric and silica analysis, only nine samples had reported results above the reporting limit for respirable dust or RCS. WOHL has a reporting limit of 53 µg for respirable dust and 10 µg for RCS. Samples below the reporting limit were excluded from analysis.

Gravimetric analysis of respirable dust samples tended to have a wide range of results, resulting in a large standard deviation. Some variability between samples may be present that was not accounted for in laboratory conditions. Samples with a mass difference equal to or less than the precision of the microbalance were not included in the results and analysis, resulting in a smaller sample size than anticipated. Therefore,

statistical analysis of sample results was not feasible. Analysis of results was limited to trends and exposure ratio calculations.

Conclusions

Aerosolization of raw sand produced the highest concentrations of respirable dust, but contained the lowest percentage of silica. Proppant produced the lowest concentrations of respirable dust, but had silica percentages that averaged four times higher than that of raw sand. Real-time monitoring of chamber concentrations showed that airborne particles peaked quickly, then tended to settle within 10 minutes after initial suspension. When vibration was introduced to samples before aerosolization, the suspension time increased accordingly.

The highest exposure ratios were seen in raw sand, whether the current MSHA PEL or the OSHA PEL was used. Exposure ratios in vibrated proppant increased as the vibration time prior to sampling increased. Analysis of vibrated proppant samples indicates that the length of vibration may affect the exposure ratio to RCS. Based on the results of this study, workers exposed to raw sand at industrial sand mines are at the highest relative risk of exposure to crystalline silica, followed by workers who are exposed to proppant which has traveled long distances by highway or rail. Workers who are exposed to proppant which has not yet been transported are at the lowest relative risk for exposure to crystalline silica.

CHAPTER III: CONCLUSIONS

Aerosolized sand was studied in a controlled setting to characterize differences between raw sand, processed sand used as proppant, and proppant which was exposed to low-frequency vibration. Chamber concentrations were monitored and logged during the sampling period using a photometer. Respirable dust samples were collected on a PVC filter using an aluminum cyclone filter and subjected to a gravimetric analysis in the University of Iowa Pulmonary Toxicology Facility. Respirable dust samples and bulk samples were sent to the Wisconsin Occupational Health Laboratory for silica analysis by x-ray diffraction. Gravimetric and silica analysis results were used to calculate relative exposure ratios for raw sand, proppant, and vibrated proppant.

This study observed respirable particles generated from 20 grams of sand, while the actual product is mined, processed, and shipped in units of millions of metric tons per year. The vibration time in this study was limited to 30 minutes with the intention of demonstration that the introduction of vibration increased the risk of exposure to RCS. The goal of this study was not to replicate a realistic exposure scenario for the worker, but rather establish a relationship between different scenarios in order to anticipate future risk.

Raw sand produced the highest concentrations of respirable dust, but contained the lowest percentage of silica. Proppant produced the lowest concentrations of respirable dust, but had silica percentages that averaged four times higher than that of raw sand. Real-time monitoring of chamber concentrations showed that airborne particles tended to peak quickly, then settle within 10 minutes after initial suspension.

The percentage of silica in bulk samples (59%-88%) did not reflect that found in respirable samples (5%-19%). The particle size distribution of the proppant types did not always correspond to the ability of the proppant to generate respirable dust. Silica content of respirable samples were lower than bulk samples of the same material. An Energy Dispersive X-ray Spectroscopy analysis showed mineral composition similar to feldspathic sandstone. The lower silica content in respirable samples may be due to other, less durable minerals fracturing and creating smaller particles instead of silica.

Respirable dust concentrations produced by proppant increased when low-frequency vibration was introduced to the samples before aerosolization. Respirable dust concentrations from vibrated proppant did not exceed concentrations from raw sand under the conditions of this study. Real-time monitoring of chamber concentrations revealed that as time exposed to vibration increased, the suspension time of airborne particles increased. When samples were exposed to vibrational energy for 30 minutes, the residence time of airborne particles was twice that of samples which had not been exposed to vibrational energy or were exposed for periods less than 30 minutes.

The highest exposure ratios were seen in raw sand, whether the current MSHA PEL or the OSHA PEL was used. Exposure ratios in vibrated proppant increased as the vibration time prior to sampling increased. Analysis of vibrated proppant samples indicates that the length of vibration may affect the exposure ratio to RCS. Based on the results of this study, workers exposed to raw sand at industrial sand mines are at the highest relative risk of exposure to crystalline silica, followed by workers who are exposed to proppant which has traveled long distances by highway or rail. Workers who

are exposed to proppant which has not yet been transported are at the lowest relative risk for exposure to crystalline silica.

This study provides several potential avenues for further research. (1) While silica sand is the most common type of proppant, other forms of proppant are in use. Similar vibration studies could be conducted on other forms of proppant to characterize other proppants and compare the results to silica sand. (2) Only one vibration frequency was used in this study. Proppant sand may generate different concentration profiles when exposed to a range of low-frequency vibrations. (3) In this study, proppant sand was vibrated for zero, 15, or 30 minutes prior to aerosolization. Meanwhile, proppant may travel for hours or days before it reaches its final destination. Increasing the exposure time to low frequency vibration has the potential to further define the relationship between transportation of proppant and generation of RCS.

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APPENDIX: ADDITIONAL DATA COLLECTION METHODS

Loading the filters

Of the first round of samples submitted to WOHL for analysis, the majority returned results below the limit of detection (LOD). A report of filter weights was provided, though the numbers were not given on official documentation. The LOD for respirable dust analysis was 53 µg. Further samples collected after the initial round attempted a mass weight on the filter of at least 100 µg.

Tube Swaps

A photometer was connected to the chamber to monitor real-time aerosol concentrations during the sampling period. After observing behavior of sand in the chamber (Figure II-3), it became clear why sample results were below the limit of detection. The assumption was that of a steady-state concentration, rather than one that decayed over time. All respirable dust samples collected after this point had corresponding photometer log data.

Samples which returned results below LOD were re-sampled while switching ADAGE elutriator tubes. Each sampling period was 120 minutes long, during which elutriator tubes were alternated every 10 minutes, with 20 g of sand in each tube, for a total sand weight of 240 g. The elutriator tubes were made of two different materials; one was aluminum and the other PVC. The difference in materials is reflected in the peaks of the photometer log data (Figure A-1).

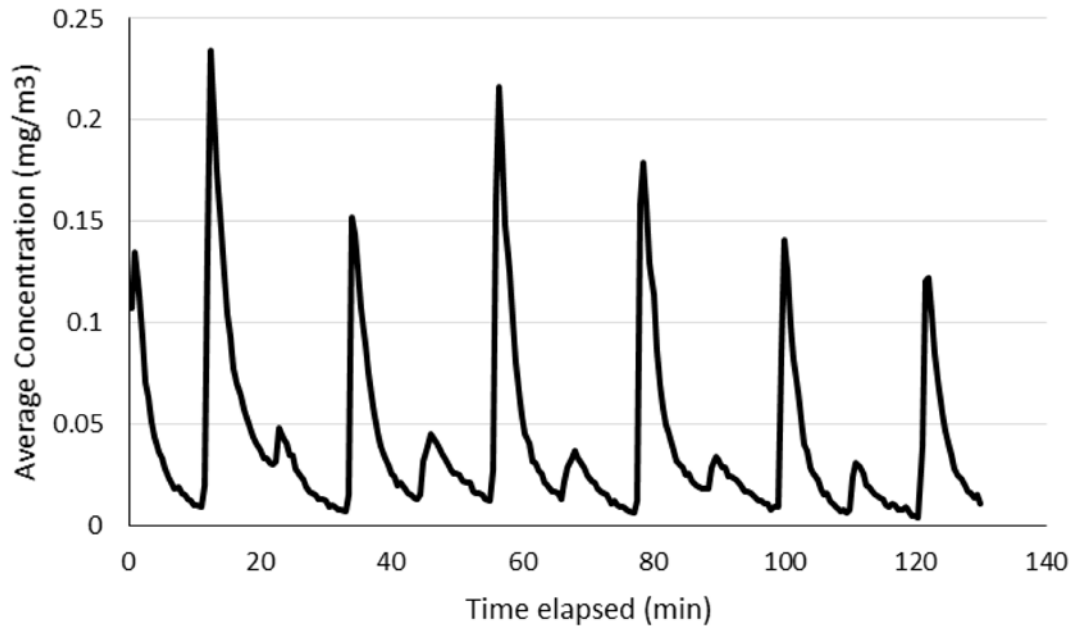


Figure A-1. Real-time chamber concentrations logged by photometer while ADAGE elutriator tubes were swapped every 10 minutes.

A trial run with a gravimetric analysis conducted by the University of Iowa Pulmonary Toxicology Facility resulted in a filter mass difference equal to the target weight of 100 µg, however of the six samples sent to WOHL for analysis, all were below LOD for respirable dust and crystalline silica.

Mimicking Transportation

Different methods were tested to try and find the best way to simulate proppant sand being transported across the country.

Steel or Glass Beads

Initial attempts to mimic energy created by transport involved adding steel or glass beads to the sand being aerosolized in the ADAGE system. The theory was that the

beads would create a situation similar to proppant sand particles colliding with the sides of transportation vehicles. Sieve analysis results showed a difference in particle distribution before and after aerosolization in the ADAGE system (Figure A-3), however the method was not deemed a suitable simulation of transportation stress.

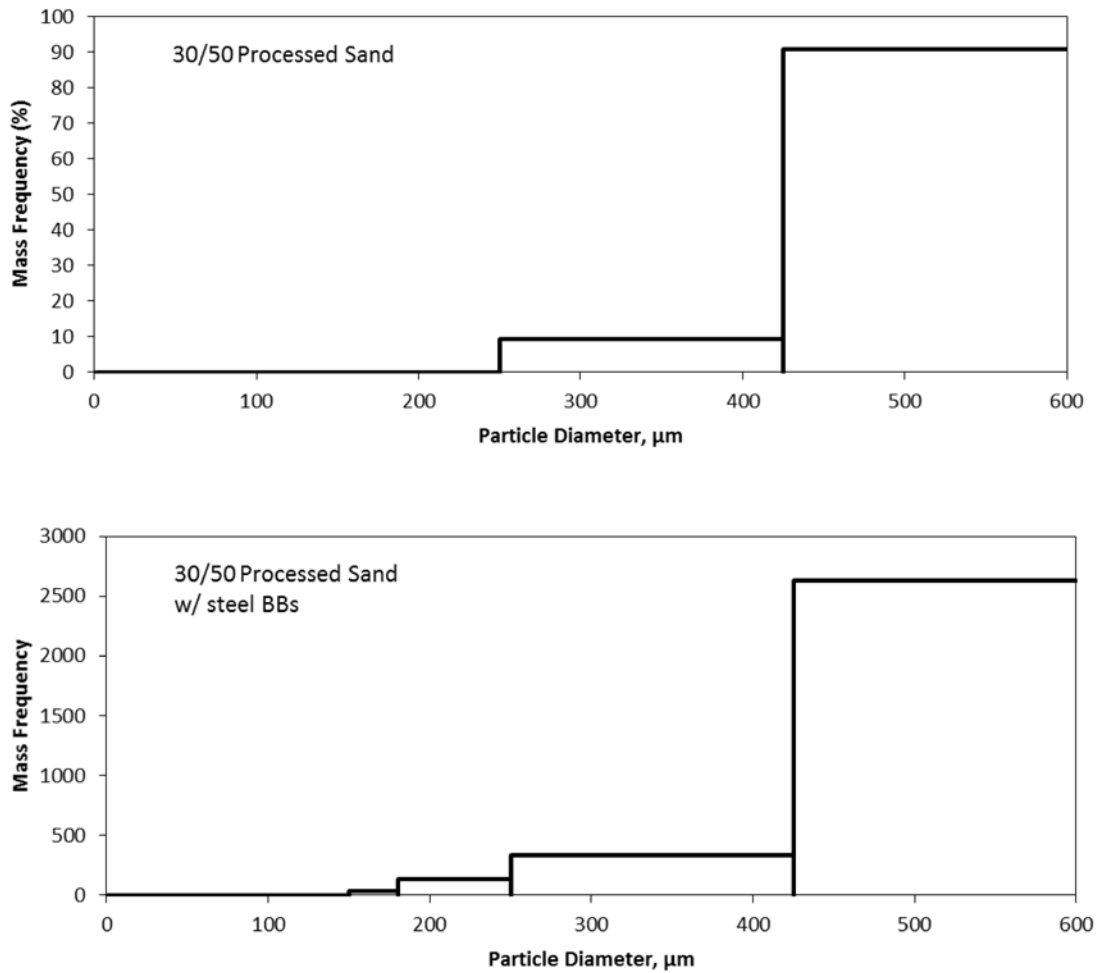


Figure A-2. Comparison of 30/50 proppant sand particle size distribution before and after adding steel beads to the ADAGE elutriator tube.

Dust Feeder

We attempted to create a chamber environment with a steady state concentration through using a dust feeder that would provide a constant flow of proppant sand into the ADAGE elutriator tube. Two diameters of augers were used; the larger auger could not supply dust at a rate needed to create the chamber concentration required, while the smaller auger altered the particle size distribution and concentration characteristics beyond what was anticipated. Table A-1 provides a comparison of peak and average chamber concentrations with and without the dust feeder and small auger. While an increase in proppant aerosolization is desired, the scale of change seen when using the small auger was deemed too drastic to be comparable to transportation mechanics.

Table A-1. Comparison of photometer readings between sand added directly to the ADAGE elutriator tube and sand added to the tube over time with a dust feeder.

Proppant	Dust Feeder		No Dust Feeder	
	Peak (mg/m ³)	Avg (mg/m ³)	Peak (mg/m ³)	Avg (mg/m ³)
30/50	8.154	5.412	0.040	0.008
40/70	7.409	2.776	0.786	0.056
100M	0.935	0.378	0.277	0.008

Vibrating Proppant for 60 min

Vibration of proppant in the ADAGE elutriator tube prior to aerosolization seemed to be the best method available to simulate transport. The initial plan had samples vibrated at 15, 30, and 60 minutes, with the concept being that any changes between vibration times could be plotted on a linear or exponential scale.

What we found in the photometer logs of the 60 minute vibration time samples was that data recorded was similar to 30 minute vibration times (Figure A-3). At this

point in time, we decided any further study of vibration time and the effect on respirable dust concentration was beyond the scope of this study.

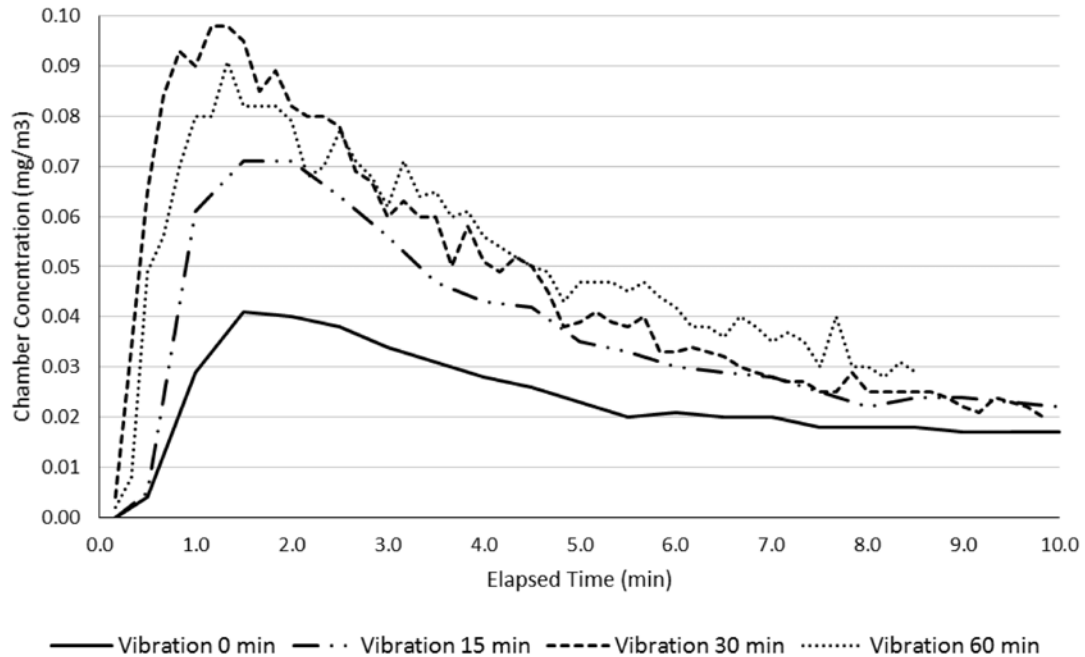


Figure A-3. Real-time chamber concentrations logged by photometer when proppant had been exposed to vibration prior to aerosolization.

Dilution Ventilation Equations by Proppant Type

Dilution ventilation equations were calculated for photometer data plotted in Figure II-3, using Equations 2 and 3 referenced in the text. Table A-2 contains dilution ventilation equations calculated using methods described for Aim 3. The expectation was that residence time would increase as the grain diameters associated with proppant types decreased. The proppant types are listed in descending order of grain diameter, however the residence times do not display a corresponding increase. Since the expected trend did

not hold true for two of the four proppant types (40/70 and 100M), the regression equations were considered not reliable enough to include in the main text of the study.

Table A-2. Regression equations to calculate time for aerosolized proppant to settle

Proppant Type	Regression Equation	R ² value
20/40	$C_t = 0.034e^{-17.2t}$	R ² = 0.94
30/50	$C_t = 0.025e^{-27.8t}$	R ² = 0.80
40/70	$C_t = 0.725e^{-3.38t}$	R ² = 0.94
100M	$C_t = 0.356e^{-2.37t}$	R ² = 0.98