

Release of Crystalline Silica Nanoparticles During Engineered Stone Fabrication

Materials and Methods

1. Materials

A commercially available engineered stone was used for this study. According to the safety data sheet (SDS), this engineered stone was predominantly comprised of crystalline silica (> 70 % by mass) in a resin matrix with additives such as pigments and other minerals.

Crystalline silica content in the aerosol from grinding this engineered stone was quantified with reference to standard reference materials. In XRD and FT-IR methods, the α -quartz calibration plots were generated using SRM 1878 (NIST), SRM 1878b (NIST), and Min-U-Sil 5 (US Silica Company, Berkeley Springs, WV) whereas SRM 1879b (NIST) was used for the cristobalite calibration.

2. Sample Collection

The experimental setup and test chamber was designed for characterizing the generation rate of aerosol from various workplace tasks per the European Standard EN 1093-3. This chamber was used in previous studies to characterize the crystalline silica aerosol from cutting fiber-cement. In this study, aerosol was generated in the test chamber by manually grinding a stack of the engineered stone samples using a hand-held pneumatic angle grinder (GPW-216, Gison Machinery Co., Ltd., Taiwan) equipped with a 10 cm diameter, coarse, diamond grinding cup wheel (Model SIS-4SPCW-SC, Stone Industrial Supplies, Inc., USA). Each test consisted of three cycles comprised of 4 minutes of grinding followed by one minute idling time (a total of 12 minutes of active grinding time and 3 minutes idling time). A total of six tests were conducted as detailed in Table 1. The aerosol was carried downstream to a measurement duct at a controlled and constant

airflow velocity of about 2.26 m/s corresponding to a flow velocity of 0.11 m/s in the chamber in accordance with the European Standard EN 1093-3. The measurement duct contained near-isokinetic sampling probes for sampling and monitoring the aerosol. The sampling bias from these probes was estimated to be $< 10\%$ for particles smaller than $19\ \mu\text{m}$. The number size distribution of the aerosol was measured by an Aerodynamic Particle Sizer (APS) Spectrometer (Model 3321, TSI Inc.). Size fractionated aerosol was collected using a Micro-Orifice Uniform-Deposit Impactor (MOUDI) (Model 110-R, TSI Inc.) that consists of different stages with cut sizes (d_{50}) of $18\ \mu\text{m}$ (pre-cut), $10\ \mu\text{m}$, $5.6\ \mu\text{m}$, $3.2\ \mu\text{m}$, $1.8\ \mu\text{m}$, $1.0\ \mu\text{m}$, $0.56\ \mu\text{m}$, $0.32\ \mu\text{m}$, $0.18\ \mu\text{m}$, $0.10\ \mu\text{m}$, $0.056\ \mu\text{m}$, and $< 0.056\ \mu\text{m}$ (after filter), at a flow rate of 30 lpm. The MOUDI's air flow rate was calibrated by a mass flow meter (Model 4043H, TSI Inc.) before each use. The pressure drops in the MOUDI remained consistent before and during measurements. The impactor nozzles were cleaned using 2-propanol (reagent grade, TSI Inc.) after each test.

Size fractionated calibration samples for XRD/FT-IR were collected using the MOUDI and the Quartz Crystal Microbalance MOUDI (QCM MOUDI, TSI Inc.) as detailed in Table 1. The QCM MOUDI consists of six stages with d_{50} of $0.960\ \mu\text{m}$, $0.510\ \mu\text{m}$, $0.305\ \mu\text{m}$, $0.156\ \mu\text{m}$, $0.074\ \mu\text{m}$ and $0.045\ \mu\text{m}$ at a flow rate of 10 lpm. For FT-IR calibration, additional size-fractionated Min-U-Sil 5 samples with aerodynamic diameters of $0.32\ \mu\text{m}$, $0.56\ \mu\text{m}$, and $1\ \mu\text{m}$ were obtained independently using the Aerodynamic Aerosol Classifier (AAC; Cambustion Ltd, Cambridge, United Kingdom) and NanoSpot Collector (Aerosol Devices Inc., Fort Collins, CO) as detailed in Table 1. The NanoSpot Collector concentrated the sampled aerosol on a small spot for enhanced analytical measurement sensitivity over a shorter sampling time. All filters were conditioned in a humidity-controlled chamber prior to weighing. All gravimetric measurements were performed on an ultra-micro balance (Model XPR6U, Mettler-Toledo). Each filter was pre- and post-weighed

thrice and the difference of the averages was the representative mass of the aerosol/calibration material.

Table 1. Details of generation, sampling, redeposition, and analysis methods for engineered stone aerosol from grinding and calibration samples.

| Material | Generation Method | Sampling Method ^a | Redeposition ^b | Replicates | Analysis Method |
|------------------|------------------------|---------------------------------------|---|------------|--|
| Engineered Stone | Grinding | MOUDI with PVC filter ^c | - | 4 | FT-IR ^g |
| | | MOUDI with aluminum foil ^d | Silver filter ^c | 1 | XRD ^g , O-PTIR ^j |
| | | MOUDI | SEM stubs ^h , TEM grids ⁱ | 1 | SEM, TEM |
| Calibration | | | | | |
| SRM 1878 | Nebulization (aqueous) | QCM | Silver filter ^c | 1 | XRD |
| SRM 1878b | Vortex shaking (dry) | MOUDI | PVC filter ^f | 2 | FT-IR |
| Min-U-Sil 5 | | MOUDI | Silver filter ^c | 1 | XRD |
| | | MOUDI with PVC filter ^c | - | 1 | FT-IR |
| | | AAC | PVC filter ^f | 1 | |
| SRM 1879b | | MOUDI | Silver filter ^c | 3 | XRD |
| | | MOUDI with PVC filter ^c | - | 1 | FT-IR |
| | | MOUDI | PVC filter ^f | 2 | FT-IR |

^aIf specified, filters/foil was mounted on the impactor substrates, else aerosol was sampled directly on the impactor substrates.

^bSubstrates with sampled aerosol were rinsed in 2-propanol (A461-212, Optima LC/MS Grade, Fisher Scientific). The resuspensions were vacuum filtered on the filtration media.

^c47 mm, 5 µm pore size, SKC, Inc.

^d47 mm, TSI Inc.

^e25 mm, 0.45 µm pore, SKC, Inc.

^f25 mm, pore size 5 µm, SKC Inc. The deposition area on these filters was lower than the 47mm PVC filters used for collecting the aerosol from grinding. For calibration, this difference was accounted for by normalizing the mass with the ratio of the deposition areas.

^gMass of the sub-100 nm and sub-micron sized samples was much lower than the micron-sized samples. To minimize the potential particle loss during ashing when sampled on PVC filters as recommended in the NIOSH 7500 and NIOSH 7603 methods, we opted to resuspend the sampled aerosol on aluminum foil in 2-propanol and redeposit on silver filters for XRD. Additionally, we opted to measure the aerosol sampled on PVC filters directly for FT-IR.

^hTransferred to adhesive carbon conductive tabs (PELCO Image Tabs, Ted Pella, Inc.) mounted on SEM pin stubs (Aluminum, grooved edge, Ted Pella, Inc.) before rinsing the substrate in 2-propanol.

ⁱSub-100 nm and sub-micron sized samples suspended in 2-propanol were pipetted onto TEM grids (400 mesh carbon coated Ni or Cu, SPI) and dried under ambient conditions. Micron-sized samples (dry collection) were transferred to the TEM grids using a needle-tip.

^jMeasurements were performed on the same silver filters used for XRD.

3. Sample Analysis Methods

3.1. X-Ray Diffraction (XRD) Measurements

The silver filters with aerosol/calibration samples were mounted onto holders atop a “zero background” backing plate made of silicon single crystal. The crystalline silica content in the size-fractionated aerosol samples was measured using an X-ray diffractometer (Empyrean series 2, PANalytical, The Netherlands). The diffractometer was equipped with a 1.8 kW long fine focus Cu X-ray tube operated at 45 kV and 40 mV, 0.04 rad Soller slit, 10mm mask, 2° anti-scatter slit and ½° divergence slit, Bragg-Brentano HD, and PIXcel 3D detector. XRD measurements were conducted over a 2θ-range from 20° to 40° with 0.02° step size for each sample. During XRD batch measurements, an instrument reference standard (PANalytical, The Netherlands) was analyzed to account for long-term tube drift. The peak intensity of this standard was used as a correction factor following the NIOSH 7500 method. The calibration curves for quartz and cristobalite were obtained by plotting the net height of each primary peak (located at 26.69° 2θ and 22.02° 2θ for quartz and cristobalite, respectively) as a function of the reference material mass on the filter for each size-fractionated sample. The slope from each size-fractionated calibration curve was compared to the mass normalized net XRD peak height from the aerosol samples to quantify the fractional quartz and cristobalite contents.

3.2. Fourier transform Infrared (FT-IR) Spectroscopy Measurements

The PVC filters with aerosol/calibration samples were mounted on FT-IR sample cards (International Crystal Laboratories, Garfield, NJ). The absorbance was measured using an FT-IR spectrometer (Alpha-II, universal sample model, Bruker) with a spectral range of 400 – 4000 cm⁻¹.

¹ at 2 cm⁻¹ resolution. For each sample, the absorption spectrum (averaged over 16 scans) was obtained three times. Since the characteristic FT-IR vibration mode from both silica polymorphs interfere with each other at 800 cm⁻¹ (normally used to quantify the crystalline silica content), distinct signature peaks for quartz and cristobalite according to NIOSH Method 7602 were selected for analysis. The quartz and cristobalite peak heights of the absorbance band at 695 cm⁻¹ (baseline between 680 cm⁻¹ and 710 cm⁻¹) and 625 cm⁻¹ (baseline between 610 cm⁻¹ and 630 cm⁻¹), respectively, were measured. Like the XRD method, size-fractionated calibration curves were prepared and used to determine the quartz/cristobalite content in different size fractions of the aerosol.

3.3. Electron Microscopy

For multi-particle characterization, a Phenom XL (Thermo Fisher Scientific, Waltham, MA, USA) scanning electron microscope (SEM) operated in the low-pressure mode (~1 Pa) at 15 kV acceleration voltage and 1.7 nA probe current with a backscattered electron (BSE) detector and an energy dispersive X-ray spectrometer (EDS) was used. To characterize individual particles at high magnifications, we used a JEOL 2100F (JEOL USA, Peabody, MA) scanning transmission electron microscope (STEM) with a field emission gun, equipped with an EDS detector (X-Max80T, Oxford Instruments America, Concord, MA) and a post-column Gatan Image Filter (GIF) (Tridiem 863, Gatan, Pleasanton, CA). Composition, crystallinity, and local electronic structure of individual silica particles in the samples were examined by EDS, selected area electron diffraction (SAED), and electron energy loss structure (EELS), respectively.

3.4. Optical Photothermal Infrared (O-PTIR) Spectroscopy

An advanced optical photothermal infrared (O-PTIR) spectroscopy microscope (Photothermal Spectroscopy Corp., Santa Barbara, CA) was used to detect the presence of

polymeric resin in the sub-100 nm and respirable size fractions of the aerosol. The O-PTIR microscope is equipped with a tuneable mid-IR quantum-cascade laser (QCL) source (Block Engineering, Southborough, MA) and a 532 nm laser, both collimated through an 40X/0.78N.A. reflective objective (PIKE Technologies, Inc., Madison, WI). O-PTIR spectra were recorded at increments of 0.1 μm along both co-planar axes from a 5 μm x 2.7 μm region on the filter sample (see footnote j in Table 1) in the wavenumber range of 771 – 1881 cm^{-1} at a resolution of 2 cm^{-1} .

4. Comparison of size-fractionated XRD and FT-IR Calibration with literature

The size-fractionated quartz calibration curves for XRD and FT-IR in this study were compared with results from literature studies (Bhaskar et al. 1994; Dodgson & Whittaker, 1973; Edmonds et al., 1977; Foster & Walker, 1984; Gordon and Harris, 1955; Kauffer, 2002; Stacey et al. 2009; Tuddenham & Lyon, 1960; Yabuta and Ohta, 2003). Due to differences in the instruments used in literature, the relative normalized peak height (right-axis) expressed as a percentage was plotted as function of aerodynamic size for comparison with our data. The projected area diameter from microscopy (Gordon and Harris, 1955; Tuddenham & Lyon, 1960) and spherical equivalent diameter (Dodgson & Whittaker, 1973; Edmonds et al., 1977; Foster & Walker, 1984; Kauffer, 2002) were converted to aerodynamic diameter after accounting for the dynamic shape factor (1.36), density (2.65 g/cm^3), and slip correction factor (< 1.08 for particle size $> 1\mu\text{m}$). The reported aerodynamic diameters (Bhaskar et al. 1994; Stacey et al. 2009; Yabuta and Ohta, 2003) were used as is for comparison with our data.

5. Comparison of fractional crystalline silica content in the engineered stone aerosol from size-fractionated XRD and FT-IR Calibrations

A nonparametric statistical test (Kruskal–Wallis ANOVA) was used to compare the fractional crystalline silica content in the engineered stone aerosol across all size fractions based on the size-fractionated XRD and FT-IR calibrations.

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