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Characterization of Nano Particles Released During Asphalt and Concrete Laboratory Activities

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Abstract: Although nanomaterials possess new properties and their industrial application generates promising opportunities in construction, they also present new risks and uncertainties. To quantify the level of risks associated with engineered nanomaterials, research needs to first quantify the level of nanoparticles exposure encountered in different construction activities. Therefore, the objective of this study is to evaluate the potential inhalation exposure risk associated with Hot-Mix Asphalt (HMA) and Portland Cement Concrete (PCC) preparation activities in the laboratory. To achieve this objective, the number concentration, size distribution, surface area, and mass concentration were measured for different activities including dry mixing, wet mixing, pouring, and compaction in an asphalt and concrete laboratory using a Scanning Mobility Particle Sizer (SMPS). Results showed that more than 70% of the particles in the concrete preparation activities were ultrafine particles. In addition, workers in the concrete laboratory were exposed to relatively higher ultrafine particles concentrations than workers in the asphalt laboratory. The majority of the total particle number (49%) released during concrete laboratory activities was in the lowest size category, between 10-30 nm in diameter. Based on the results of this study, further research is needed to understand the negative effects of nanoparticles on the health of workers.

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***Key words**: Construction processes; Exposure risk; Nano materials; Safety.*

Introduction

The growth of using nanomaterials in different products increases the concern for their potential impacts on the environment and on the biological systems. Inhalation of nanoparticles has been associated with adverse health effects that range from myocardial infarction to decrements of lung function among asthmatics. Epidemiological studies have established the relationship between ambient ultrafine particles (less than 100 nanometer in diameter) concentrations and mortality or morbidity of urban populations. These studies indicated that exposure to ultrafine particles may cause pulmonary diseases, cardiovascular health effects and impairment of the immune system. However, the toxicological mechanisms behind these effects are not clear [1-2]. Animal nanoparticles exposure studies also showed that ultrafine particles cause a stronger airway inflammation than similar mass concentrations of larger particles [3]. Epidemiological data also indicated that exposure to ambient ultrafine particles worsens respiratory diseases [4].

Nanoparticle exposure can be from natural, incidental or engineered nanoparticles making risk assessments even more problematic. Naturally occurring nanomaterials such as volcanic ash, ocean spray, magnetotactic bacteria, mineral composites and others exist in our environment. Incidental nanoparticles, sometimes called ultrafine particles, are particles unintentionally produced during an intentional operation. Combustion, welding, metal processing, and emissions from diesel engines are examples of major sources of incidental nanoparticles. Engineered nanoparticles are particles designed and produced intentionally to have a certain structure and size, usually less than 100 nm. Both natural and incidental nanoparticles may have irregular or regular shapes. Engineered nanoparticles most often have regular shapes, such as tubes, spheres, ring, etc. [5-6]. However, the difficulties in distinguishing between engineered and incidental occurring nanoparticles complicate the assessment of exposure to humans and the environment. In order to understand the potential effect of the nanoparticles on the environment, the levels of the natural, incidental, and engineered nanoparticles should be quantified.

Safety in nanotechnology is determined through comprehensive studies that include exposure assessment, determination of metrics, toxicological and epidemiological studies, and life cycle analysis [7]. Studies show that a major route of exposure to ultrafine particles is through the respiratory system [8]. Several factors including size, shape and particulate matter density influence the impact of these particles on different parts of the respiratory system and the amount of time that it takes for them to settle [8]. Thus, exposure measurements that use an appropriate dose metrics such as number, mass and surface area concentration of particles should be considered. Several studies have investigated the toxicity and risk management of nanoparticles based on the different exposure scenarios that may occur during the production and use; however, little is known about nanoparticle exposure from construction activities [2, 6-7, 9-13].

One reason for this trend is that there are currently no national or international standards on measurement techniques for nanomaterials in the workplace. The National Institute for Occupational Safety and Health (NIOSH) established a nanotechnology field research team that identified numerous techniques to measure airborne

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Fig. 1. Sampling Nanoparticles During Mixing Process.

a. Mixing aggregate with asphalt binder b. Compaction

Fig. 2. Sampling Nanoparticles During Mixing and Compaction.

Table 1. Experimental Plan and Test Condition.

Material Type (1)	Task (2)	Task Description (3)
Concrete		
	Dry Mixing	Mixing Aggregate and Cement
	Wet Mixing	Adding Water to the Aggregate and Cement
	Pouring	Pouring the Ready Mix Into the Mold
Asphalt		
	Pouring	Pouring Binder Into the Aggregates
	Mixing	Mixing Binder and Aggregates
	Compaction	Compacting the Ready Mix by Using Gyratory Compactor

nanomaterials with respect to particle size, mass, surface area, number concentration, and composition. One of these measurement techniques is the Nanoparticle Emission Assessment Technique (NEAT) that uses a combination of measurement techniques and instruments to assess potential inhalation exposures in facilities that handle or produce nanomaterials [14]. The following instrumentations are recommended to be used by NEAT for measuring ultrafine particles in workplaces: the Condensation Particle Counter (CPC), Optical Particle Counter (OPC), scanning mobility particle sizer (SMPS), Fast Mobility Particle Sizer (FMPS), and Electrical Low-Pressure Impactor (ELPI). These technologies measure the number, surface area or mass metric directly or indirectly. In addition, Nano-Aerosol Sampler (NAS) can be used to collect nano particles for offline characterization. In order to characterize morphology of the particles and verify the primary size distribution, scanning electron microscopy (SEM) and Transmission Electron Microscopy (TEM) can be used [1]. The objective of this study is to assess the exposure to nanoparticles associated with different asphalt and concrete laboratory activities. To achieve this objective, the number concentration, size distribution, surface area concentration, and mass concentration were measured for different activities including dry mixing, wet mixing, pouring, and compaction in an asphalt and concrete laboratory using a SMPS. SEM and TEM were also used to characterize morphology, geometry, and to verify the primary size distribution of the particles.

Methodology

Sampling Site

Two AMRL accredited asphalt and concrete laboratories, one for asphalt and one for concrete, with 23 m^2 area were used as the test environment in this study. The total particle concentrations and size distributions were independently measured for asphalt and concrete in laboratory environment under different operating scenarios including dry mixing, wet mixing, pouring, and compaction (Figs. 1 and 2). Background levels were measured every day prior to the start of any work and between tasks. The results of the nanoparticle released during each task were compared to background nanoparticles counts of the laboratory indicating that nanoparticles were released. The measuring instruments were located as close as possible to the job activities without disturbing the ongoing work. The experimental plan and testing conditions are summarized in Table 1.

Sampling Strategy

Since nanoparticles naturally exist in the environment and to accurately assess occupational exposure risk, it is important to characterize background nanoparticles before quantifying the nano particles resulting from different laboratory activities. This includes particles that penetrate from outdoors to indoors and particles that are suspended by background activities in the facility. Thus, a preliminary measurement was conducted to quantify additional sources of ultrafine particles. In the first step, the sources of ultrafine emissions in the workplace atmosphere were quantified by measuring particle number, particles concentration, and size distribution. Thus, to determine the nanoparticle concentration level in the laboratory under normal conditions, background data were collected before the start of concrete laboratory activities. Similarly, for asphalt processes, background measurements were taken before the beginning of each task.

Particles Measurements and Characterization

The measured nanoparticles in the workplace were characterized using a CPC and SMPS. Size distributions were measured by a SMPS system, which consists of an electrostatic classifier (TSI Model 3080) and a differential mobility analyzer (DMA, TSI 3081) coupled with CPC (TSI model 3776) (see Fig. 3). Scanning mobility particle sizer brings aerosol to electrostatic equilibrium ensuring

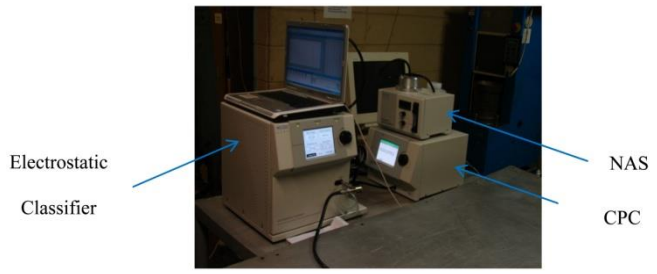

Fig. 3. SMPS System.

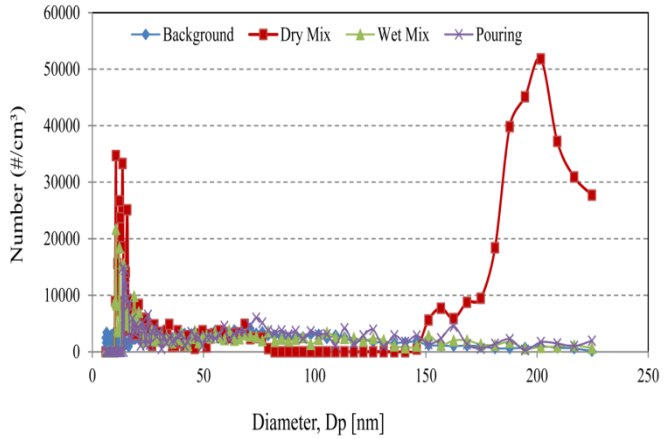

Fig. 4. Size Distribution for Nanoparticles Released During Concrete Construction Activities.

that the aerosol has known charge distribution. The system was operated at 1.5 liter per minute (lpm) of sheath flow rate and 1.5 lpm of aerosol inlet flow rate. The aerosol instrument manager software was used, which is capable of collecting data weighted by number concentration, diameter, surface area, volume, and mass, recorded the SMPS spectrometer data. Particles were collected on silicon nitride grids with 100 nm square membrane using a vacuum pump sample collector set to 7000 V. The collected particles were analyzed by SEM (Model Quanta 3D FEG, FEI Company, USA) and TEM (Model JEOL 100CX) for size and shape.

Results and Discussion

Concrete Laboratory Activities

Particle number size distribution of ultrafine particles was measured by a SMPS during the synthesis process of different tasks including background, dry mix, wet mix, and pouring, see Fig. 4. The total number concentration of the particles was approximately 680000, 313000, and 264000 particles cm^3 during dry mixing, wet mixing and pouring, respectively. Table 2 shows a summary of the total concentration, mean size, and ultrafine particles percentage of each activity. As shown in this table, a higher percentage of ultrafine particles were emitted from wet mixing and pouring respectively, 87% and 81%, while dry mixing had the largest mean size (96.3 nm). However, dry mixing activity emitted a higher number concentration (679331#/cm^3) compared to the other activities. Compared with larger particles, the number of ultrafine particles, which are less than 100 nm is generally larger for all of the tasks. In addition, measurements at the laboratory showed that 90%, 82%, and 69% of the ultrafine particles were smaller than 50 nm in dry mixing, wet mixing, and pouring activities, respectively.

Fig. 5 shows the particle number concentration as measured for the background, dry mixing, wet mixing, and pouring. The average particle concentration during whole process was 4,817 particles per cm^3. Background level as measured prior to process was 2,223 particles per cm^3 and peak concentration was 51,800 particles per cm^3, which was measured during dry mixing process. As shown in Fig. 5, the higher particle concentration was during dry mixing. Subtracting the total number of background particle concentration from the total number concentration of each activity shows that 452593, 87217, and 37406 particles per cm^3 are emitted during dry mixing, wet mixing and pouring, respectively.

Fig. 6 shows the measurements carried during dry mixing, wet mixing and pouring in a box plot. The plot shows the minimum, the 25% percentile, the median value, the 75% percentile and the maximum nanoparticles concentrations. The median of the data is represented by the line in the center of the rectangular box. As shown in Fig. 6, dry mixing had the highest variability in comparison with the other activities. The greater variability is likely to be a result of the spike in nanoparticle emission, which was noted when adding the aggregates. Furthermore, there is no significant difference between the concentration of the nanoparticle released from wet mixing and pouring. In contrary, there is a significant difference between particle concentrations in the dry mixing and wet mixing.

Asphalt Laboratory Activities

Fig. 7 shows the particle number concentration as measured in the background before any activity, pouring, mixing, background after mixing, compaction, and background after compaction. Background level as measured prior to process was 9,436 particles per cm^3, background level after mixing was 11,851 particles per cm^3 and background after compaction was 12,057 particles per cm^3. Peak concentration was 85,500 particles per cm^3, which was during pouring process. As shown in Fig. 7, pouring has the highest concentration. Furthermore, subtracting the total number of

Table 2. Exposure Measurement to Nanoparticles During Concrete Preparation Activities.

Task	Particle Size Measured		Total Concentration	Mean Particle	Ultrafine particle
	Min(nm)	Max (nm)	(#/cm^3)	Diameter (nm)	Percentage (%)
(1)	(2)	(3)	(4)	(5)	(6)
Dry mixing	5.94	224.7	679331	96.3	57
Wet Mixing	5.94	224.7	313955	42.7	87
Pouring	5.94	224.7	264144	58.6	81

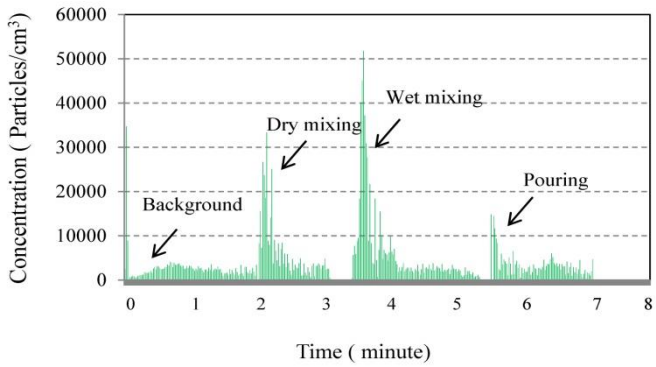

Fig. 5. Particle Number Concentration During Concrete Construction Activities.

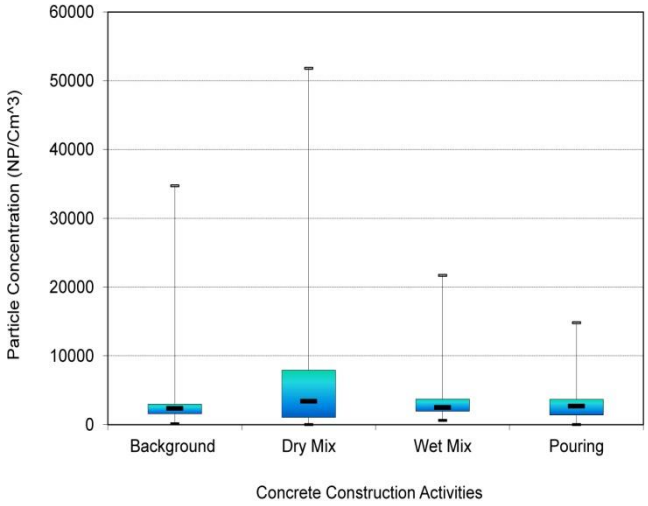

Fig. 6. Concentration of Nanoparticles Released During the Various Concrete Construction Activities.

background particle concentration from the total number concentration of each activity shows that 1,179,000, 459,000, and 155,600 particles per cm^3 are emitted during pouring, mixing, and compaction, respectively.

Table 3 shows the total concentration, mean size, and ultrafine particle percentage for each task separately. As shown in this table, the mean size of pouring and mixing activities is almost the same while compaction has a higher mean size (160 nm). Based on these results, it was determined that the total concentration of pouring and mixing is higher than the total concentration for compaction.

Fig. 8 shows the particle number size distribution of ultrafine particles during background, pouring, mixing, and asphalt compaction. The total number concentration of the particles during pouring, mixing, and compaction was 2×106, 1.28×106, 9.77×105 particles per cm^3, respectively. Ultrafine particles originated mainly

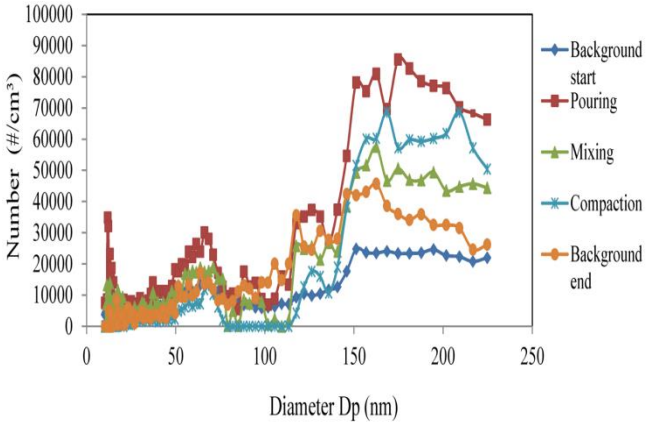

Fig. 7. Size distribution for nanoparticles released during asphalt construction activities.

from pouring and mixing. It is also noted that the concentration of particles in the background after mix and compaction is slightly higher than the background before any activity began. This suggests that some of the ultrafine particles emitted remain in the air after completion of the activities.

The measurements carried during background, pouring, and mixing are presented in a box plot in Fig. 9. The plot shows the minimum, the 25% percentile, the median value, the 75% percentile and the maximum nanoparticles concentrations. Pouring released more nanoparticles in comparison with the nanoparticles released during background, mixing, and compaction.

Nanoparticle Comparison in Concrete and Asphalt Laboratory Activities

Descriptive statistics of particle number concentration per a selected size range released during all concrete activities are summarized in Table 4. This table presents information on the relative contribution of each size range and the total number of concentration. As shown in Table 4, the majority of the total particle number (49%) released during concrete preparation was in the lowest size category, between 10-30 nm in diameter. About 9% of particles fell in the second size category, between 30-50 nm, and 14% of particles between 50-100 nm. In total, 72% of particle number fell in the ultrafine particle fraction with diameter below 100 nm. In contrast, mass concentration had a different pattern. Only 15% of all particles were found in the ultrafine particle fraction. The majority of mass (85%) was found in the larger diameter range between 100-500 nm. About 13% of particle mass was found in the size range between 50-100 nm, and 1% of particles were between 10-30nm.

Table 5 summarizes the descriptive statistics of particle number concentration per a selected size released during asphalt mixing

Table 3. Exposure Measurement to Nanoparticles During Asphalt Preparation Activities.

Task	Particle Size Measured		Total Concentration	Mean Particle	Mean Mass	Ultrafine Particle
	Min (nm)	Max(nm)	(#/cm^3)	Diameter (nm)	(µg/m^3)	Percentage (%)
(1)	(2)	(3)	(4)	(5)	(6)	(7)
Pouring	10.2	224.7	2.00×10^6	121	172	40
Mixing	10.2	224.7	1.28×10^6	122	171.6	40
Compaction	10.2	224.7	9.77×10^5	160	17.8	14

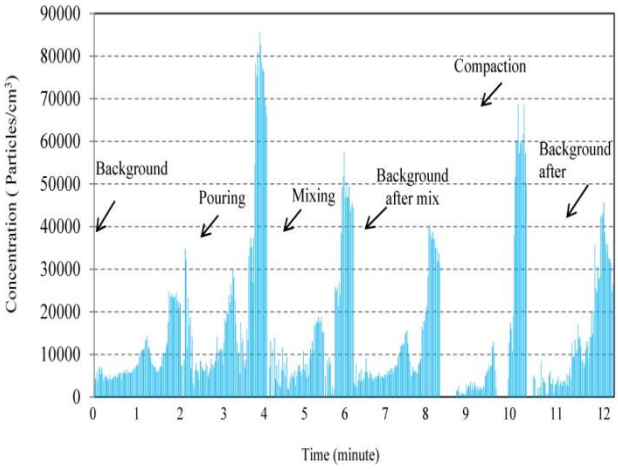

Fig. 8. Particle Number Concentration During Asphalt Construction Activities.

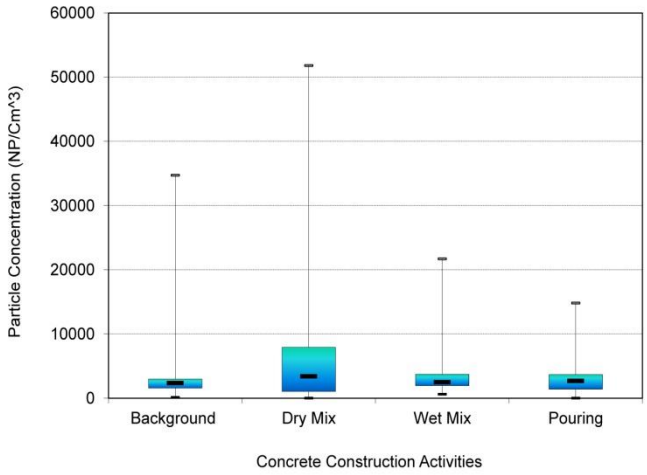

Fig. 9. Concentration of Nanoparticles Released During the Various Asphalt Activities.

Table 4. Particle Concentrations in Concrete Laboratory Activities.

Parameter (1)	Total Concentration (2)	Mean Particle Diameter (3)	Percentage of Total (4)
Number Concentration (Particles/cm^3) – Concrete			
NC $_{10\text{-}30\ nm}$	7.27×10^5	15.9	49
NC $_{30\text{-}50\ nm}$	1.36×10^5	39.7	9
NC $_{50\text{-}100\ nm}$	2.13×10^5	70.4	14
NC $_{100\text{-}300\ nm}$	4.09×10^5	181.2	27
Mass Concentration (µg/m^3) – Concrete			
NC $_{10\text{-}30\ nm}$	1.67	15.8	1.1
NC $_{30\text{-}50\ nm}$	2.7	41.9	1.8
NC $_{50\text{-}100\ nm}$	20.2	77.8	13
NC $_{100\text{-}300\ nm}$	125.6	184.5	83

Table 5. Particle Concentration in Asphalt Mixing Activities.

Parameter (1)	Total Concentration (2)	Mean Particle Diameter (3)	Percentage of Total (4)
Number Concentration (Particles/cm^3) – Asphalt			
NC $_{10\text{-}30\ nm}$	6.48×10^5	17.6	13
NC $_{30\text{-}50\ nm}$	3.72×10^5	40.4	7
NC $_{50\text{-}100\ nm}$	8.53×10^5	77.3	17
NC $_{100\text{-}300\ nm}$	3.20×10^6	173	63
Mass Concentration (µg/m^3) – Asphalt			
NC $_{10\text{-}30\ nm}$	164	21.5	3.2
NC $_{30\text{-}50\ nm}$	4.44	41.5	0.8
NC $_{50\text{-}100\ nm}$	26.3	72.5	5
NC $_{100\text{-}300\ nm}$	480	181	93

laboratory activities. Similar to the concrete analysis, this table includes data obtained from all of the considered asphalt activities. As shown in Table 5, in contrast with concrete, the majority of the total particle number (63%) released during asphalt activities was in the highest size category, between 100-300 nm in diameter. About 13% of particles fell in the first size category, between 10-30 nm, and 17% of particles between 50-100 nm. In total, 37% of particle number fell in the ultrafine particle fraction with diameter below 100 nm. Mass concentration had the same pattern with number concentration in asphalt mixing. Only 9% of all particles were found in the ultrafine particle fraction. The majority of mass (93%) was found in the larger diameter range between 100-500 nm. About 13% of particle mass was found in the size range between 50-100 nm, and 1% of particles were between 10 and 30 nm.

Fig. 10 compares the particle number concentrations released during asphalt and concrete preparation activities. As shown in this figure, the total number particle concentration released during asphalt activities is approximately 3.6×10^6 (NP/cm^3) higher than concrete activities while the percentage of ultrafine particles in concrete is higher than in asphalt activities. The higher percentage of ultrafine particles in concrete is due to the cement used in it. Type I Portland cement was used for this study, which has a particle size distribution of more than 5µm and less than 30 µm [15]. Gypsum and calcium carbonate are also relatively soft minerals, and quickly grind to ultrafine particles [16]. Fig. 11 compares the mass concentration released from asphalt and concrete laboratory activities. As shown in this figure, the total mass concentration released from preparing asphalt is approximately 362 (µg/m^3) higher than the total mass concentration released from preparing concrete. However, the ultrafine particle percentage in concrete is higher than in asphalt activities.

TEM and SEM Characterization Results

To characterize nanoparticles released during asphalt and concrete preparation, the morphology, geometry, shape, surface, composition, and size of these particles need to be identified. To characterize these properties, electron microscope analysis was used. Typical images obtained from SEM and TEM are presented in Figs. 12 and 13. Fig. 12 shows the size, shape, and morphology of the particles collected during asphalt and concrete preparation. SEM images show the spherical shape of the particles with primary particle size less than 400 nm. To get a higher resolution image of the smaller particles, TEM was used. Fig. 13 shows the size, shape, and morphology of the particles collected during asphalt and concrete preparation. As shown in this figure, TEM images show spherical

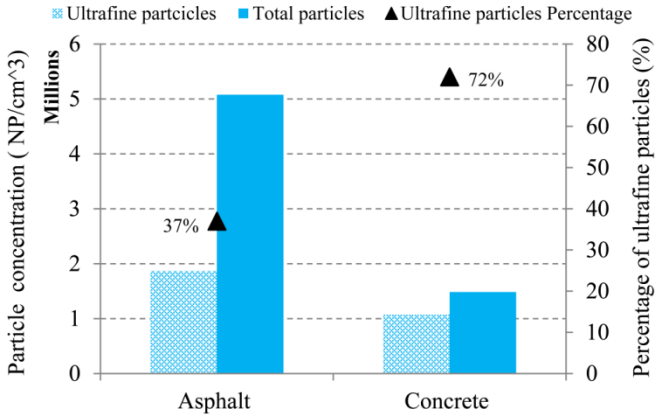

Fig. 10. Particle Concentrations in Asphalt and Concrete Production Activities.

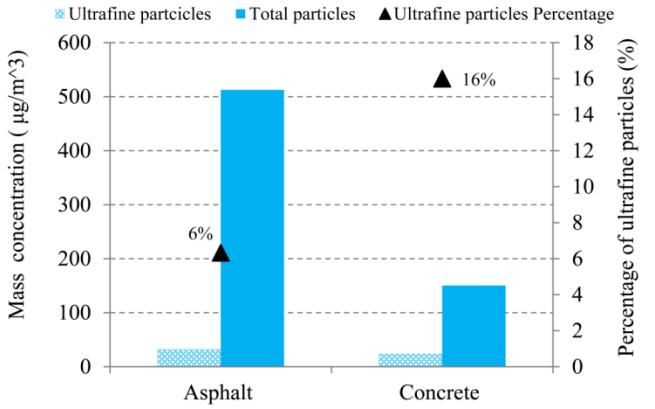

Fig. 11. Mass Concentrations in Asphalt and Concrete Laboratory Activities.

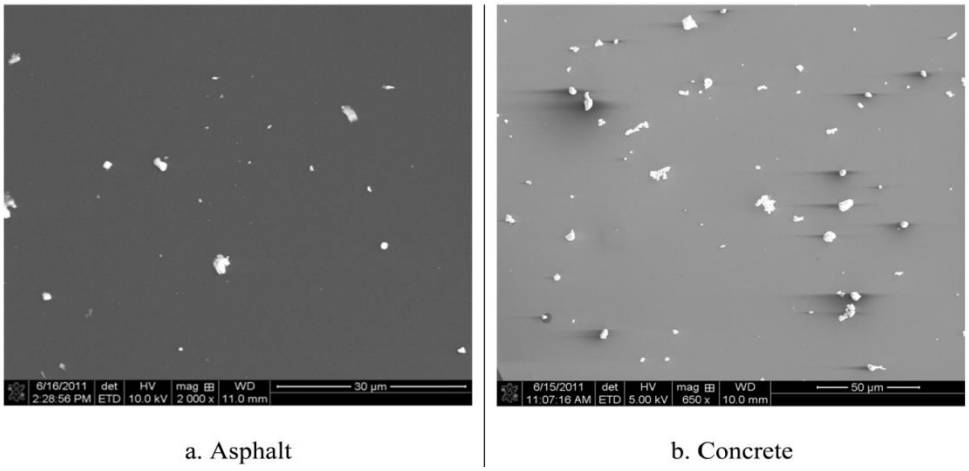

Fig. 12. SEM Images of Particles Collected on Electron Microscope Grids.

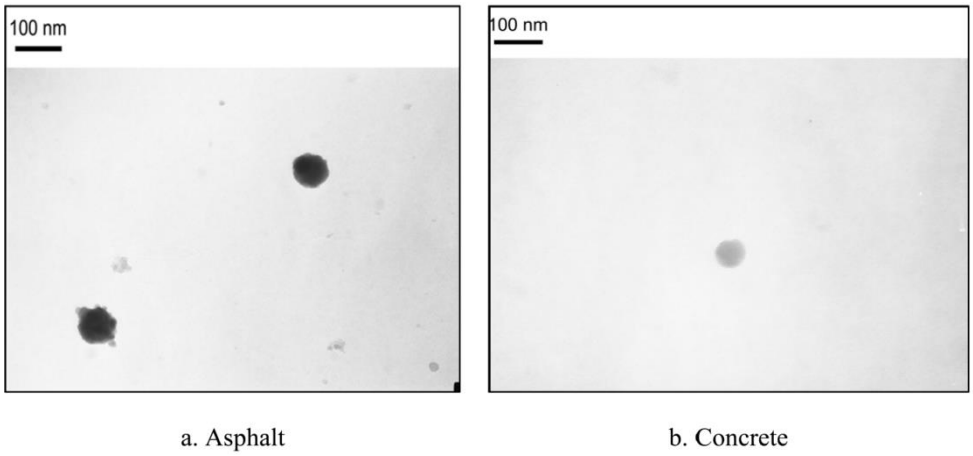

Fig. 13. TEM Images of Particles Collected on Electron Microscope Grids.

particles with primary particle size less than 100 nm. It is noted that several smaller particles were unstable and were destroyed by the electron beam; hence, they were not detected in Fig. 13. The estimated sizes that were obtained by TEM analysis are very similar to the estimate obtained by calculations using SMPS for the experimental study.

Conclusions and Recommendations

Ultrafine particles are increasingly being recognized as a potential threat to human health. Aerosols in workplace environments may come from a wide variety of sources, depending on the type of activity and processes taking place. Measurements from a laboratory in this study showed that more than 70% of the particles in the asphalt and concrete preparation activities were ultrafine particles. Results showed that workers in the concrete laboratory were exposed to relatively higher ultrafine particles concentration than

workers in the asphalt laboratory. However, the majority of the total particle number (49%) released during concrete laboratory activities was in the lowest size category, between 10-30 nm in diameter. Further, the estimated sizes obtained by TEM analysis in the concrete and asphalt workplace study were in agreement with the estimate size obtained by calculations using SMPS for the experimental study. Based on the results of this study, further research is needed to characterize the hazardous nature and possible health effects of the emitted particles.

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