DEPARTMENT OF HEALTH AND HUMAN SERVICES Public Health Service

Centers for Disease Control and Prevention
National Institute for Occupational
Safety and Health
Robert A. Taft Laboratories
1090 Tusculum Ave.
Cincinnati, OH 45226-1998

Date: December 4, 2023

Stephen Corkill
Vice President of Operations
Hydrograph Clean Power Inc.
809 Levee Dr. Suite I
Manhattan, KS 66502

Dear Mr. Corkill,

Please find enclosed the final report of the NIOSH visit on August 30th and 31st, 2023 to Hydrograph Clean Power Inc. in Manhattan, Kansas. Thank you again for participating in the NIOSH Industrywide Exposure Assessment Study on Two-Dimensional Nanomaterials and providing us the opportunity to visit. The site visit and subsequent exposure assessment work on graphene was extremely successful. If not for forward-thinking companies such as yours, valuable research would not be conducted.

This final report summarizes our findings and contains recommendations for improving some of your material handling practices and process. The recommendations are based on observations as well as the results of the sampling that we conducted during the visit. I hope that the data will assist you and your company in making improvements at your facility. Please share this report with your employees by posting a visible copy around the workplace. If significant changes are made to the processes at your facility in the future, such as a scale up of production activities or other process upgrades, we would be happy to discuss visiting again to conduct additional sampling. If you have any questions regarding the content of the report or any other general concerns, please feel free to contact me at any time.

Sincerely,

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Enclosure:

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Industrial Hygiene Report
For Graphene Surveys

Hydrograph Clean Power Inc.
Manhattan, Kansas

Prepared by:
Matthew Dahm, MPH, PhD
Seth McCormick, MPH
December 4, 2023

For:
NIOSH-NTP Industrywide Exposure Assessment Study on Two-Dimensional Nanomaterials

Centers for Disease Control and Prevention (CDC)
National Institute for Occupational Safety and Health (NIOSH)
Division of Field Studies and Engineering (DFSE)
Field Research Branch (FRB)
Cincinnati, Ohio USA

PLANT SURVEYED: Hydrograph Clean Power Inc.
809 Levee Drive, Suite I
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FILE NUMBER: 1.06

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SURVEY DATE: August 30, 2023

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National Institute for Occupational Safety and Health site visit report for Hydrograph Clean Power Inc.

Executive Summary

The past decade has witnessed an extraordinary increase in research progress and innovation on ultrathin two-dimensional (2-D) nanomaterials, which offer great potential in numerous applications such as in electronics (conductive inks), energy storage, water remediation, paints and coatings, sensors, lighting, composites, and biomedicine. As the utilization of graphene and other 2-D nanomaterials continues to rise, with greater expansion into industrial applications, the potential for workplace and environmental exposures throughout the life cycle of these materials will successively increase as well.

There are a limited number of animal studies that have investigated the toxicity following pulmonary exposure of graphene, and even fewer studies are available regarding workplace exposures and the development of exposure assessment methodologies. Additionally, there are currently no assigned occupational exposure limits (OELs) specifically available for any type of 2-D nanomaterial, including graphene. Therefore, the objective of this study was to collect information on personal workplace exposures to graphene and other 2-D nanomaterials which can be used to develop relevant exposure assessment methods and inform risk assessors and toxicologists regarding realistic human exposure information and material characteristics which can be used to develop future OELs.

In order to address this deficiency of limited occupational exposure data regarding graphene related materials, a site visit was conducted by NIOSH researchers on August 30-31, 2022, at Hydrograph Clean Power Inc. in Manhattan, Kansas. The focus of this visit was to assess potential exposures to graphene materials during the production of graphene within a combustion reactor, test firing and troubleshooting reactors, disassembling a reactor for maintenance activities, transferring graphene materials, and curing resin/graphene mixtures. Personal and area filter-based samples were collected for the mass concentration of elemental carbon (EC) and transmission/ scanning electron microscopy (TEM/SEM) analysis to assess exposures during the sampled task.

Four operators agreed to participate in the study and were subsequently sampled during their various tasks. Overall, personal exposures collected at the respirable aerosol fraction over the two days of sampling for EC mass, used as a marker for graphene exposure, ranged from a negative value after background correction to 6.75 $\mu g/m^3$. Personal graphene exposures at the inhalable aerosol size fraction collected from the operators ranged from 0.27 to 5.91 $\mu g/m^3$. Corresponding samples were collected for microscopy analysis from every personal and area sample that was also collected for EC analysis. Visual evidence of graphene exposures was confirmed for nearly all samples analyzed by scanning and transmission electron microscopy.

The results from the filter-based samples showed that the potential for airborne exposures to graphene materials does exist. However, since there are no published OELs from recognized public health agencies at this time for graphene, limited published exposure data, and limited animal toxicity information, interpretation of these results is difficult. However, it is good occupational safety and health practice to keep exposures to new and uncharacterized materials as low as reasonably achievable until more information on toxicity is gathered and synthesized.

Process Description

General:

A site visit was conducted on August 30th and 31st, 2023 at Hydrograph Clean Power Inc. in Manhattan, KS. Hydrograph is a primary production facility of a few-layered and multi-layered graphene materials and is currently scaling up production. Hydrograph accepted an invitation to voluntarily participate in the National Institute for Occupational Safety and Health (NIOSH) Industrywide Exposure Assessment Study on Graphene and other Two-Dimensional Nanomaterials (2-D). The aim of this study, with respect to the current report, was to measure exposures to graphene for the employees overseeing graphene production and packaging as well as curing graphene/resin mixtures.

During the site visit, it was observed by NIOSH field staff that four Hydrograph employees had the potential to come into direct contact with graphene on a typical operational day. These four employees were observed performing graphene production tasks as well as post-production tasks such as packaging and developing dispersion techniques for graphene/resin mixtures within its facility. All four Hydrograph employees voluntarily agreed to participate in the research study and were subsequently sampled over two full 8–9-hour work shifts. Several tasks were observed and sampled during the site visit which included the production of graphene within a combustion reactor, test firing and troubleshooting reactors, disassembling a reactor and other maintenance activities, transferring graphene from production containers into smaller packaging for customers, and curing resin/graphene mixtures.

Graphene Production

First, employees conducted system checks by ensuring all pressurized gas connections were secure, checked mechanical parts, and conducted a computer software check before production. Next, a mixture of pressurized gases and reagents were pumped into an enclosed combustion reactor. Once preparations were finished, employees moved to a separate control room to initiate and monitor graphene production. As the graphene was produced, the material would collect in a large metal container beneath the reactor. Once the container was full, it would be replaced with an empty container and production would continue. The graphene materials were produced within an enclosed reactor under vacuum which was located inside a large, ventilated enclosure. Hydrograph had a centralized HEPA filtration system with flexible ducting that could be moved to each reactor to provide ventilation. No personal protective equipment was observed being used during the production tasks.

Graphene Product Transfer

During the two days of sampling, two employees were observed transferring the large metal containers containing graphene from the production reactor into smaller sealed bags weighing between 180 to 500 grams for customers and internal use. A total weight of 13 kilograms of graphene powder was transferred over several hours during the first day and 800 grams were transferred on the second day of sampling. First, the employees turned on a custom-made ventilated enclosure and placed the large container of graphene into the bottom of the enclosure. The employees then prepared several clear plastic bags on a workbench across from the exhaust enclosure. Next, the lid of the container was removed, and the employees used a metal scoop to transfer the graphene into the plastic bags. The plastic bags were then weighed using a scale inside the enclosure and labeled with the product identification and weight. The employees were observed wearing an N-99 filtering facepiece respirator, a lab coat, and nitrile gloves during this task.

Troubleshooting and Maintenance

Throughout the two days of sampling, participants conducted troubleshooting and maintenance tasks intermittently on the reactors. These tasks included disassembling and cleaning a reactor as well as the machining of production equipment. During the first day of sampling, an employee was observed disassembling a test reactor. This was achieved by opening the reactor and using a HEPA shop-vac to remove any remaining graphene materials from the interior. The employee wore nitrile gloves, lab coat, and a N-99 filtering facepiece respirator to complete the disassembly and cleaning task. No personal protective equipment was used during the other troubleshooting and maintenance tasks.

Resin Curing

During both days of sampling, an employee was observed working to cure resin and graphene mixtures in various solvents. The employee did not handle any graphene materials in powder form during these tasks, as they were already mixed in a liquid solvent. All work was completed within a large ventilated walk-in enclosure. Personal protective equipment observed in use included nitrile gloves.

Sampling Overview and Methods

To date, limited exposure data has been collected from the U.S. workforce to determine occupational exposures to any form of 2-D nanomaterial. Additionally, there are no published Occupational Exposure Limits (OEL) for graphene or any other 2-D nanomaterial from recognized public health agencies. Therefore, the objective of this study is to collect information on personal workplace exposures to graphene and other 2-D nanomaterials which can be used to develop relevant exposure assessment methods necessary for future OELs.

Full-shift personal breathing zone (PBZ) and tasked-based area filter samples (AS) were collected for the mass concentration of elemental carbon (EC) as well as scanning and transmission electron microscopy (SEM/TEM) analysis to assess exposures during the previously mentioned task. Samples were collected at both the respirable and inhalable aerosol size fractions. Respirable particles are less than approximately 4 micrometers (µm) in size and when they are breathed in, they can enter the deepest parts of the lung, the alveoli. Inhalable particles are less than approximately 100 µm in size and, when these particles are breathed in, they can deposit in the nose, mouth, windpipe (trachea), and the upper portions of the lung.

Since a very limited amount of 2-D nanomaterial exposure information is currently available in the published literature, it is important to collect both task-based area samples and personal exposure data. Task-based area samples will provide additional insights for exposure assessors and safety and health specialists since they shed light on work practices and processes associated with higher exposures. Full-shift personal exposure measurements are important for extrapolating acute and chronic exposure concentrations for toxicology studies and risk assessments. Table 1 shows in detail the sampling scheme and methods used during the NIOSH visit to Hydrograph. All sampling pumps were calibrated before and after each day of sampling to maintain the proper flow.

Air Sampling- Elemental Mass Analysis:

Personal and area samples were collected for the airborne mass concentration of elemental carbon (EC) at both the respirable and inhalable aerosol size fractions. Personal respirable aerosol collection for EC was performed by using a 25- millimeter (mm) cassette with quartz fiber filters (QFF) attached to a GK 2.69 BGI cyclone (BGI Inc., Waltham, MA, USA) and an Airchek TOUCH sampling pump (SKC Inc., Eighty Four, PA, USA) operating at the cyclone specified flow rate of 4.2 liters of air per minute (lpm). Customized adapters for the GK 2.69 cyclone (BGI Inc.; catalog number 3503) were used to fit the 25-mm cassettes. Additionally, personal inhalable samples were also collected using 25-mm QFFs (SKC Inc.) within a Button Aerosol Sampler (SKC Inc.) with an Airchek TOUCH sampling pump (SKC Inc.) operating at the sampler specified flow rate of 4 lpm.

The airborne mass concentration of EC was measured using the NIOSH Manual of Analytical Methods (NMAM) Method 5040, based on a thermal-optical analysis technique for organic and elemental carbon (OC and EC). Bulk samples consisting of several milligrams of functionalized graphene oxide were collected and analyzed to obtain their thermal profiles. Manual splits were then assigned based on results from the bulk material analyses (Birch et al., 2011; NIOSH, 2006; Dahm et al., 2015). Based on the total mass of respirable/inhalable EC collected on the filter reported from Bureau Veritas North America, the NIOSH contract laboratory, and the sample specific collected air volume, the respirable/inhalable EC mass concentrations were calculated and reported as micrograms per cubic meter ($\mu g/m^3$).

The measurement of EC mass using NMAM 5040 is a non-specific marker for graphene exposure but has been successfully used to assess exposures for other carbonaceous nanomaterials, such as carbon nanotubes and nanofibers. Consequently, to account for potential interferences, daily outdoor and/or indoor background measurements for the airborne mass of EC at the respirable and inhalable size fractions were collected using the same methods as previously stated at the facility. Interferences in NMAM 5040 can be caused by anthropogenic sources such as diesel exhaust, emissions from coal or oil-fired power plants, and the seasonal burning of biomass (Schauer, 2003). Background samples were collected indoors, away from production areas, within the front office area during both days of sampling.

Air Sampling- Electron Microscopy:

Personal breathing zone samples were collected at the inhalable size fraction using 25-mm mixed cellulose ester filters (SKC Inc.) within a Button Aerosol Sampler (SKC Inc.) using an Airchek TOUCH sampling pump (SKC Inc.) operating at the sampler specified flow rate of 4 lpm. SEM analysis of air samples was performed using a Phenom XL Scanning Electron Microscope (SEM) with a backscattered electron (BSE) detector in the low-vacuum mode (~10 Pascals) at 10 kilovolts acceleration voltage and 1.0 nanoampere probe current. Each filter was placed on a glass slide, collapsed with acetone vapor on a hot station, and coated with a thin layer of carbon (thickness of 30nm) as instructed in the modified NIOSH Method 7402 (Birch et al., 2017). The loading level and particle distribution of each sample were determined by analyzing an auto-montaged image stitched from 16 tiles of SEM images taken at a magnification of 530x with the same image settings. The stitched image covers an area of 3.88 mm^2 with ~1 µm resolution. The stitched images were processed and analyzed by MIPAR software (MIPAR. Columbus, OH, USA) to determine particle counts, particle size distribution, and perform feature measurements. Segmented particles for the automated particle counts only include those above 1 µm resolution threshold and without touching the image edges. Transmission Electron Microscopy (TEM) analysis was performed using a JEOL 2100F TEM (JEOL USA, Inc. Peabody, MA, USA). Carbon-coated filters were processed and transferred to calibrated 200 mesh TEM index grids following the modified NIOSH-7402 method (Birch et al., 2017). Each TEM grid was analyzed in TEM and scanning TEM (STEM) modes. Representative images from each of the samples were obtained by bright field (BF) and/or high-angle annular dark-field (HAADF) detectors. In addition, the elemental composition and maps of the particles were determined by energy dispersive x-ray spectroscopy (EDS).

Results

Four participants were recruited and voluntarily participated in the NIOSH exposure study that collected 34 filter-based air samples using a task-based and personal sampling approach to characterize potential exposures during the two days of sampling at Hydrograph. Of the 34 samples collected, 23 were collected at the inhalable and respirable size fractions and analyzed for the mass concentration of EC (15 full-shift PBZ samples, four area samples, and four indoor background samples) while 11 samples were analyzed using TEM at the inhalable size fraction (eight full-shift PBZ samples and three area samples). One personal inhalable sample collected on day one was unable to be analyzed for EC due to incorrect filter media used for collection.

Results for EC samples collected at the facility during the first and second days of sampling are presented in Tables 2 and 3, respectively. These tables provide information on sample locations, controls, personal protective equipment used, the calculated eight-hour time-weighted average concentrations (TWA), and the background-corrected eight-hour TWA concentrations, which is the eight-hour TWA background concentration subtracted from the personal or area eight-hour TWA concentration. The limit of detection (LOD) for the 25-mm filters for NMAM 5040 was 0.2 µg EC/filter and the limit of quantitation (LOQ) was 0.60 µg EC/filter. All sample labels with the same numbers were mounted together during personal or area sampling (e.g., QFFI03, QFFR03, and MCE03).

Indoor background samples were collected during the two days of sampling from the office area located at the front of the building (see sample sets QFF05 in Table 2 & QFF11 in Table 3). The corresponding indoor background EC mass measurements at the inhalable size fraction for the two days of sampling were 0.37 and 0.13 µg/m^3. The EC indoor background concentrations at the respirable size fraction were 0.29 and 0.17 µg/m^3 on days one and two, respectively. Exposures to EC (a surrogate for exposure to graphene) during day one of sampling from the personal aerosol samples collected at the inhalable size fraction ranged from 0.42 to 5.91 µg/m^3 and 0.27 to 2.22 on day two. The personal exposures to EC at the respirable size fraction collected on day one ranged from 0.18 to 6.75 µg/m^3 and one negative value after background correction to 0.34 µg/m^3 on day two.

An area sample was collected at the inhalable and respirable aerosol fractions during the product transferring task on day one and was located directly beside the ventilated enclosure and found EC measurements of 1.36 µg/m^3 and 0.41 µg/m^3 at the inhalable and respirable size fractions, respectively. The area sample collected during day two of sampling was located outside of the ventilated enclosure, near a combustion reactor that was producing graphene and found an EC concentration at the inhalable fraction of 0.22 and 0.10 µg/m^3 at the respirable size fraction.

Samples were also collected for SEM/TEM analysis from all personal and area samples collected. Table 4 provides the automated particle counts and subsequent air concentrations from the SEM analysis. Air concentration ranged from 0.422 to 0.731 particles/cm^3 from samples collected on day one. Air concentrations ranged from 0.514 to 0.659 particles/cm^3 from samples collected on day two. Figure 1 provides a compilation of SEM images of each filter to show particle distribution and loading levels for each sample collected. Figures 2-9 contain representative TEM images from personal and area samples collected during the visit that confirmed the presence of graphene in nearly all the air samples collected.

Discussion

Currently, only a small number of studies have been published in the literature that have assessed occupational exposures to graphene (McCormick et al., 2021). One study was conducted in Korea at two small facilities performing R&D production of limited quantities of graphene as well as benchtop work using graphene (Lee et al., 2016). The study found EC exposures at the two sites between 0.26 and 1.15 µg/m^3. Another exposure study was conducted at a graphene manufacturer in Italy that used a chemical process to thermally exfoliate graphite into graphene and had the production capability to produce up to 30 tonnes per year (Spinazze et al., 2016). Exposures were estimated for the mass concentration of graphene to be between 0.38 to 3.86 µg/m^3. More recent studies have found personal exposures to range between non-detectable concentrations to 5.6 µg/m^3 at the inhalable size fraction (Vaquero et al., 2019; Loven et al., 2020). The representativeness of these exposure concentrations to the industrial levels of production and use expected in the United States is still largely unknown.

Presently, there are no published Occupational Exposure Limits (OEL) for graphene or any other 2-D nanomaterials from recognized public health agencies, making determinations of "high (exposures over an OEL)" vs. "low (exposures below an OEL)" exposures difficult to interpret. However, Lee et al. (2019) conducted a subchronic inhalation study on graphene oxide using a lung dosimetry model with a derived no observed adverse effect level (NOAEL) to provide a recommended minimum safety guideline of 18 µg/m^3 for graphene exposures within workplaces. One of the main aims of this study is to understand the range of exposures to graphene materials currently occurring in U.S. manufacturing. As more site visits are conducted, and additional exposure data are collected as part of this study, more context will be provided to these exposure results regarding how they compare to other U.S. manufacturing and downstream use facilities.

The personal samples collected to assess EC (a surrogate for graphene exposures) at the inhalable aerosol size fraction during the two-day site visit from Hydrograph operators ranged from 0.27 µg/m^3 to 5.91 µg/m^3 while respirable exposures ranged from one negative value after background correction to 6.75 µg/m^3. Nearly all detectable concentrations from the collected personal and area samples were found to be greater than the indoor background samples at both the inhalable and respirable aerosol size fractions. Compared to the previously published inhalable elemental carbon exposure information from other personal samples collected internationally at graphene workplaces, the exposures collected at Hydrograph were roughly comparable to those in the available literature. However, all measurements collected at both the inhalable and respirable aerosol size fractions were below the minimum safety guideline of 18 µg/m^3 for graphene oxide published by Lee et al. (2019).

The highest exposure measured during the two days of sampling occurred on day 1 during the transferring tasks when the finished graphene product was re-packaged into smaller bags. The employee was observed to be very deliberate and methodical with their actions, which likely led to less material being aerosolized and reduced the operator's overall exposure (5.91 µg/m^3 inhalable; 6.75 µg/m^3 respirable). While the negative pressure ventilated enclosure likely reduced graphene exposures, this work area may see further exposure reduction with continuing efforts to increase air velocity within the enclosure. This may provide sufficient airflow to prevent aerosolized graphene from spreading into the employee's personal breathing zones and surrounding work areas. Detailed recommendations to reduce exposures can be found below in the recommendations section.

It is difficult to directly compare the previously published exposure literature with the exposure information collected at this site since the production methods and quantities of graphene handled were likely very different. However, with limited animal toxicity information currently available for the family of graphene materials, it may be prudent to reduce exposures as low as reasonably achievable until more information regarding toxicity is widely published and better understood.

The results provided from the filter-based samples analyzed for EC and by SEM/TEM show that the potential for airborne exposures to functionalized graphene materials does exist. However, based upon our observations during the evaluation and the measured exposure levels, the PPE worn and current engineering controls in place appear adequate. Since there are no published OELs from recognized public health agencies at this time for graphene, limited published exposure data, and limited animal toxicity information on graphene related materials, interpretation of these results regarding human exposure and health effects is difficult at this time. However, it is good occupational safety and health practice to keep exposures to new and uncharacterized materials as low as reasonably achievable until more information on toxicity is better understood and future OELs are developed.

Recommendations

The operators at Hydrograph observed during the NIOSH site visit demonstrated responsible handling of the graphene materials. The enclosed production processes and handling of graphene material within ventilated enclosures are considered best practices to reduce the potential airborne exposures. NIOSH offers a few recommendations for improvement to reduce overall exposures. However, if a change in processes or future scale-up occurs, additional sampling may be necessary to again validate that the exposure controls are functioning properly, and the personal protective equipment worn is adequate.

- On the first day of sampling, an operator was observed using a full-face respirator with facial hair. Facial hair prevents an adequate seal between the respirator and user's face and limits the respirator's ability to filter particulates. The OSHA Respiratory Protection standard, paragraph 29 CFR 1910.134(g)(1)(i)(A), states that respirators shall not be worn when facial hair comes between the sealing surface of the facepiece and the face or that interferes with valve function.
    - Additionally, it is recommended that guidelines for effective respiratory protection programs be followed including storage and maintenance of respirators.
- A trip hazard was observed to be present in the form of flexible duct located in the walkway between the graphene packaging exhaust hood and the main productor reactor. This could pose additional danger in the event of emergency egress. Consider running the flexible duct at a height that allows walking underneath or slightly altering the layout of this area to facilitate clear egress.

    - If production volumes increase and efficacy of existing source capture controls do not remove graphene from the breathing zone as effectively, consider switching to smooth ductwork as opposed to the flexible duct. This could reduce the static pressure, and buildup of graphene over time, potentially improving source capture efficiency and reduce dust accumulation inside the ducts.
- Use safety glasses when working in areas with solvents to prevent incidental splashes into the eyes. Protective eye and face protection devices must comply with the appropriate ANSI standards outlined in 29 CFR 1910.133.
- Consider increasing air velocity and/or reduced open area at the face of the ventilated enclosure used to transfer and package graphene products. This may more effectively prevent aerosolized graphene from spreading to other work areas and reduce the need for respiratory protection.

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Table 1. Sampling Types and Methods used at Hydrograph

Type of Sample	Filter	Size Fraction	Flow Rate (LPM)	Analytical Method
Personal	25 mm QFF	Inhalable	4	NMAM 5040
	25 mm QFF	Respirable	4.2	NMAM 5040
	25 mm MCE	Inhalable	4	NMAM 7402
Area	25 mm QFF	Inhalable	4	NMAM 5040
	25 mm QFF	Respirable	4.2	NMAM 5040
	25 mm MCE	Inhalable	4	NMAM 7402
Background	25 mm QFF	Inhalable	4	NMAM 5040
	25 mm QFF	Respirable	4.2	NMAM 5040
	25 mm MCE	Inhalable	4	NMAM 7402

LPM = liters per minute; QFF = quartz fiber filter; MCE = mixed cellulose ester filter;
NMAM= NIOSH Manual of Analytical Methods

Table 2. Elemental Carbon (EC) Results – Day 1

Sample ID	Type of Sample (PBZ or AS)	Job Title	Sample Location or Tasks Performed	Engineering Controls Present/PPE	Sampling Time (min)	Air Volume (L)	8-Hr TWA EC Concentration (μg/m³)	Background Corrected 8-Hr TWA Concentration (μg/m³) [β]
QFFI05	AS-Inhal	Indoor Background	In office in the back right under a desk ~6 inches off ground	N/A	480	1910.6	0.37	-
QFFR05	AS-Resp				484	2020.0	0.29 [α]	-
QFFI01	PBZ-Inhal	Operator	Office work, test firing chamber, electrode research	Enclosed test chamber	545	2151.1	0.79	0.42
QFFR01	PBZ-Resp				545	2247.9	0.66	0.37
QFFI02	PBZ-Inhal	Operator	Material packaging, test firing/disassembling chamber	Ventilated enclosure for packaging/lab coat, nitrile gloves, N 99 respirator	528	2102.8	6.28	5.91
QFFR02	PBZ-Resp				528	2188.3	7.04	6.75
QFFI03	PBZ-Inhal	Operator	Office work, curing resins	Walk-in ventilated enclosure/nitrile gloves	456	1803.0	1.11	0.74
QFFR03	PBZ-Resp				456	1881.9	0.47	0.18
QFFI04	PBZ-Inhal	Operator	Disassembling & maintenance on chambers, assisting w/ packaging	None/ lab coat, nitrile gloves, N 99 respirator	498	1981.3	3.14	2.77
QFFR04	PBZ-Resp				499	2068.4	1.26	0.97
QFFI06	AS-Inhal	Area sample	Beside ventilated enclosure for packaging, at breathing zone height	Ventilated enclosure	414	1647.5	1.73	1.36
QFFR06	AS-Resp				414	1717.5	0.70	0.41

[α] Sample was between the Limit of Detection and Limit of Quantitation
AS= Area Sample (collected at a fixed position); PBZ= Personal Breathing Zone (sampling cassette fixed to lapel of worker)
Resp.= Sample collected at the respirable size fraction; Inhal= Sample collected at the inhalable size fraction
ND= non-detectable concentration; PPE= Personal Protective Equipment; TWA= Time Weighted Average
[β] (8-hr TWA concentration) – (8-hr TWA indoor background concentrations) = Background corrected 8-Hr TWA Concentration.

Table 3. Elemental Carbon (EC) Results – Day 2

Sample ID	Type of Sample (PBZ or AS)	Job Title	Sample Location or Tasks Performed	Engineering Controls Present/PPE	Sampling Time (min)	Air Volume (L)	8-Hr TWA EC Concentration (µg/m³)*	Background Corrected 8-Hr TWA Concentration (µg/m³) β
QFFI11	AS-Inhal	Indoor background	In office, far back right corner ~ 6 inches off ground	N/A	479	1902.3	0.13 α	-
QFFR11	AS-Resp				479	1969.6	0.17 α	-
QFFI07	PBZ-Inhal	Operator	Office work, reactor programming	None	478	1892.2	0.40	0.27
QFFR07	PBZ-Resp				478	1969.6	0.29 α	0.12 α
QFFI08	PBZ-Inhal	Operator	Test firing/disassembling chamber, trouble-shooting reactor	None	514	2055.7	0.40	0.27
QFFR08	PBZ-Resp				514	2099.2	0.51	0.34
QFFI09	PBZ-Inhal	Operator	Office work, curing resins	Walk-in ventilated enclosure/nitrile gloves	424	1655.3	†	†
QFFR09	PBZ-Resp				424	1750.3	0.16 α	0 ‡
SQFFI10	PBZ-Inhal	Operator	Transferring product, production operations, electrode maintenance	Enclosed production chambers, ventilated enclosure/lab coat, gloves, N 99 respirator	508	1983.0	2.35	2.22
QFFR10	PBZ-Resp				508	2058.2	0.43	0.26
SQFFI12	AS-Inhal	Area sample	~1ft away from operational combustion reactor approximately 5 feet above the ground	Enclosed reaction chamber, ventilated enclosure around reactor	469	1846.2	0.35	0.22
QFFR12	AS-Resp				469	1912.8	0.27 α	0.10 α

α Sample was between the Limit of Detection and Limit of Quantitation
AS= Area Sample (collected at a fixed position); PBZ= Personal Breathing Zone (sampling cassette fixed to lapel of worker)
Resp.= Sample collected at the respirable size fraction; Inhal= Sample collected at the inhalable size fraction
ND= non-detectable concentration; PPE= Personal Protective Equipment; TWA= time weighted average
β (8-hr TWA concentration) – (8-hr TWA indoor background concentrations) = Background corrected 8-Hr TWA Concentration.
†Incorrect sample media used, unable to analyze sample for EC by NMAM 5040.
‡ Negative value after performing background correction, reported as a 0 concentration.

Table 4. Microscopy Automated Particle Counts – Days 1 & 2

Sample ID	Type of Sample (PBZ or AS)	Job Title	Sample Location or Tasks Performed	Sampling Time (min)	Air Volume (L)	Loading Level (count/mm^2)	Concentration per sample (count/cm^3)
MCE05	AS-Inhal	N/A	In office, far back right corner ~ 6 inches off ground	480	1902.72	1233	0.249
MCE01	PBZ-Inhal	Operator	Office work, test firing chamber, electrode research	544	2143.632	2352	0.422
MCE02	PBZ-Inhal	Operator	Material packaging, test firing/disassembling chamber	527	2085.603	3127	0.577
MCE03	PBZ-Inhal	Operator	Office work, curing resins	456	1799.148	2782	0.595
MCE04	PBZ-Inhal	Operator	Disassembling & maintenance on chambers, assisting w/ packaging	499	1974.294	3751	0.731
MCE06	AS-Inhal	Area Sample	Beside ventilated enclosure for packaging, at breathing zone height	414	1636.749	2352	0.553
MCE07	PBZ-Inhal	Operator	Office work, reactor programming	472	1797.376	2534	0.543
MCE08	PBZ-Inhal	Operator	Test firing/disassembling chamber, troubleshooting reactor	501	1957.908	2614	0.514
MCE09	PBZ-Inhal	Operator	Office work, curing resins	424	1652.328	2216	0.516
MCE10	PBZ-Inhal	Operator	Transferring product, production operations, electrode maintenance	508	1973.834	3377	0.659
MCE12	AS-Inhal	Area Sample	~1ft away from operational combustion reactor approximately 5 feet above the ground	469	1831.445	2511	0.528

AS = Area Sample (collected at a fixed position); **PBZ** = Personal Breathing Zone (sampling cassette fixed to lapel of worker); **Resp**.= Sample collected at the respirable size fraction; **Inhal.**= Sample collected at the inhalable size fraction; **8-hr TWA**= 8 Hour Time Weighted Average Concentration;

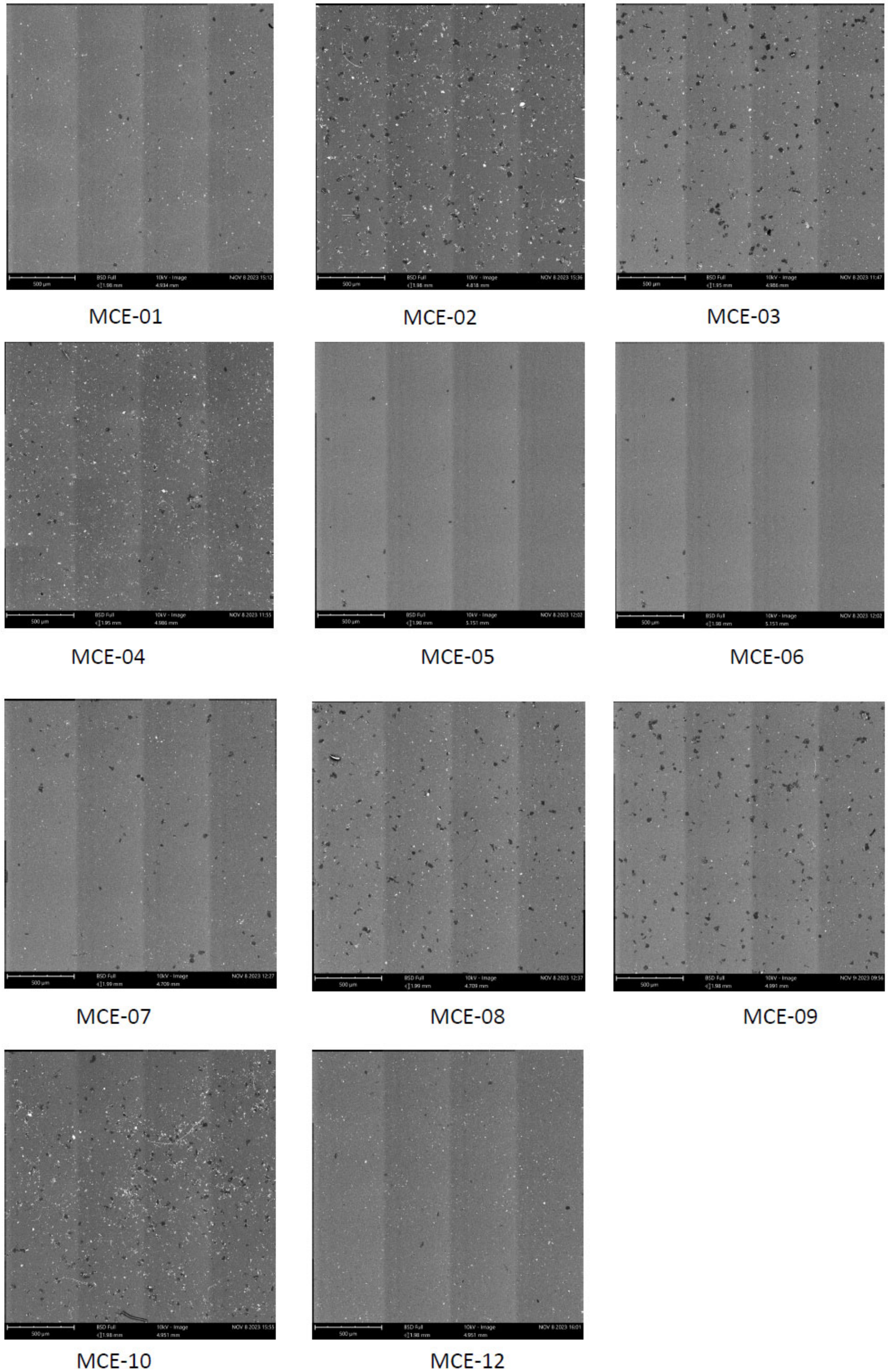

Figure 1. Stitched SEM images to show particle loading over entire filter for 11 personal and area air samples described in Table 4.

Figures 2-9. TEM images of representative particles over entire filter for 9 personal and area air samples described in Table 4.

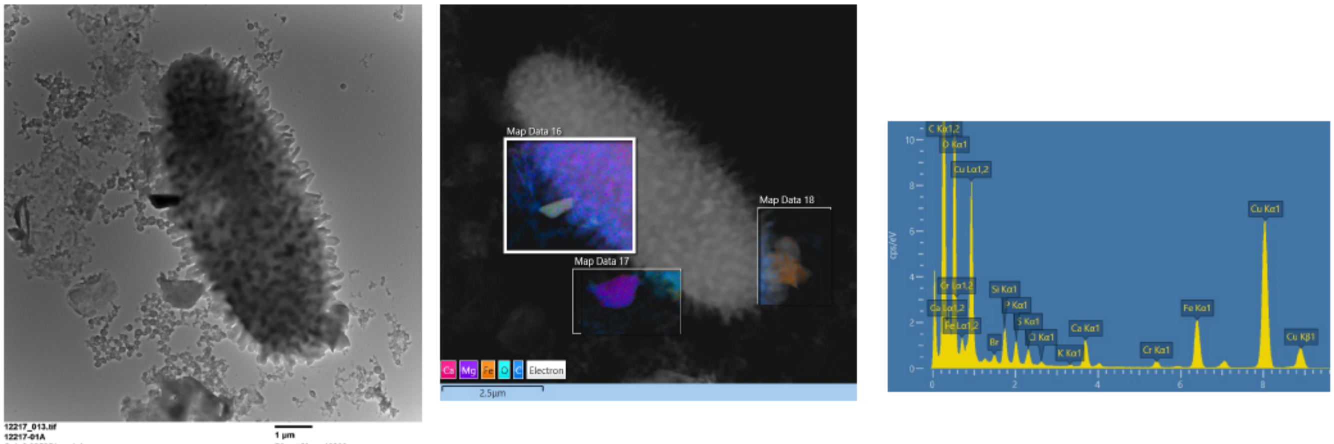

Figure 2. Carbon structure with Ca, Mg, and Fe particles observed from MCE01 collected from a worker performing electrode research on day 1.

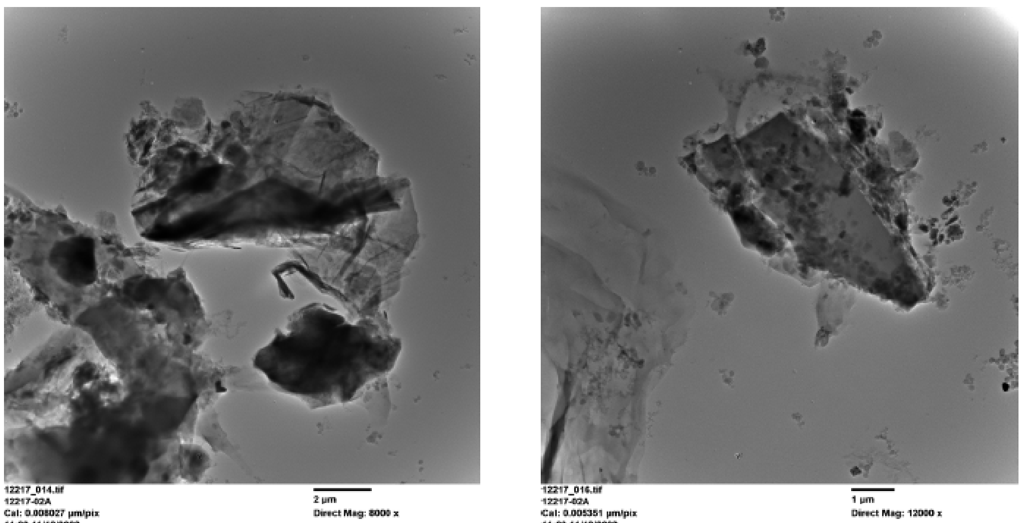

Figure 2. Graphene particles observed from MCE02 collected from a worker transferring material and test firing a reactor on day 1.

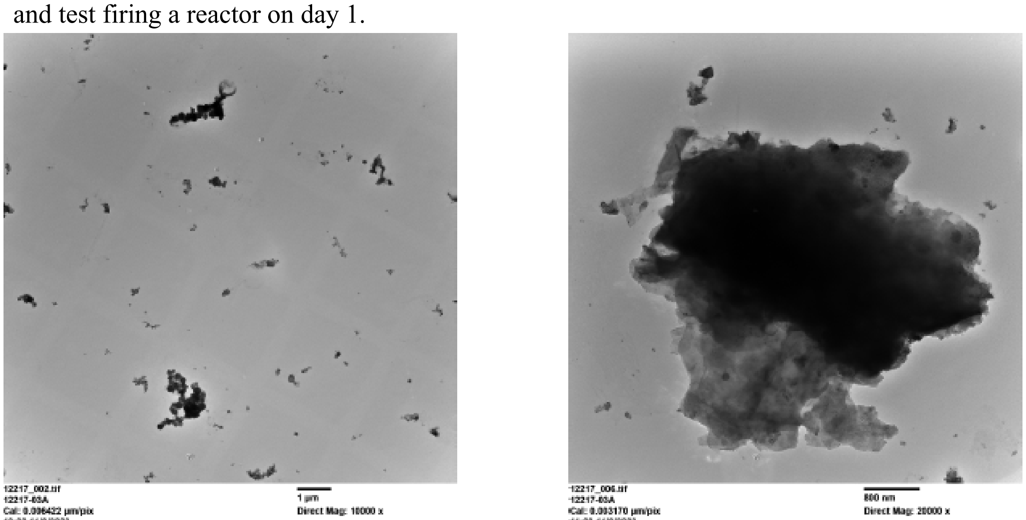

Figure 3. Graphene particles observed from MCE03 collected from a worker curing resins on day 1.

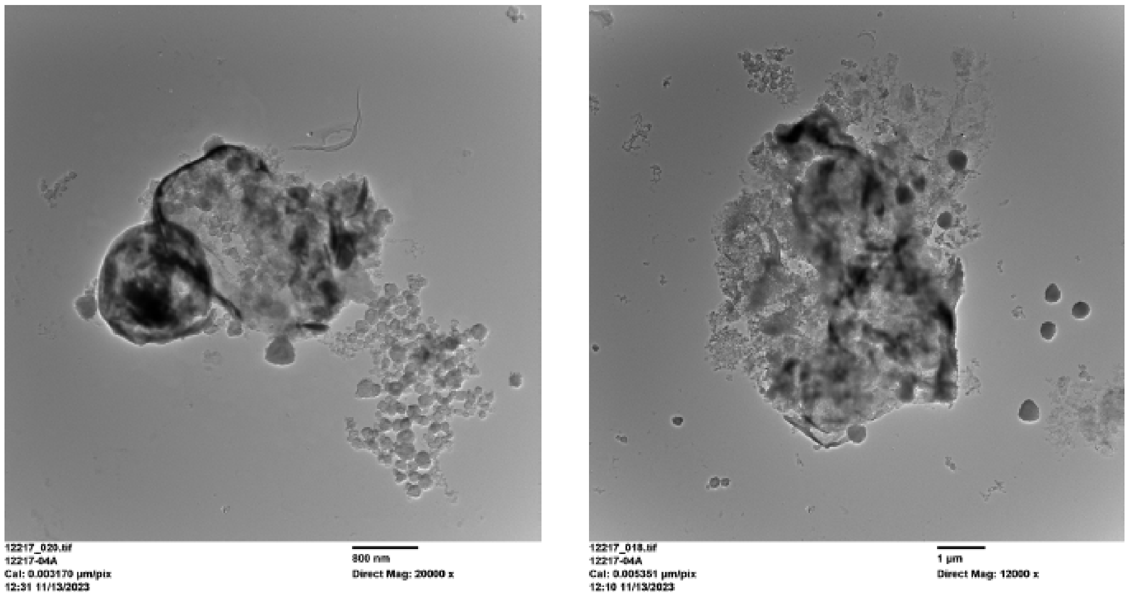

Figure 4. Graphene particles observed from MCE04 collected from a worker disassembling a reactor and performing maintenance on day 1.

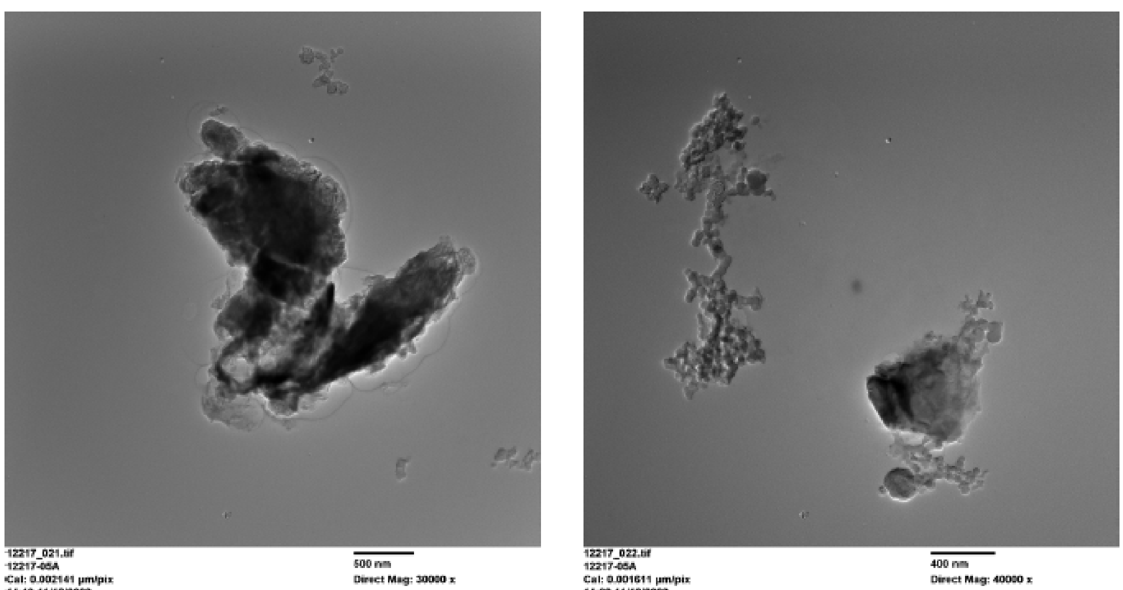

Figure 5. Graphene particles observed from MCE05 from the indoor background area sample on day 1.

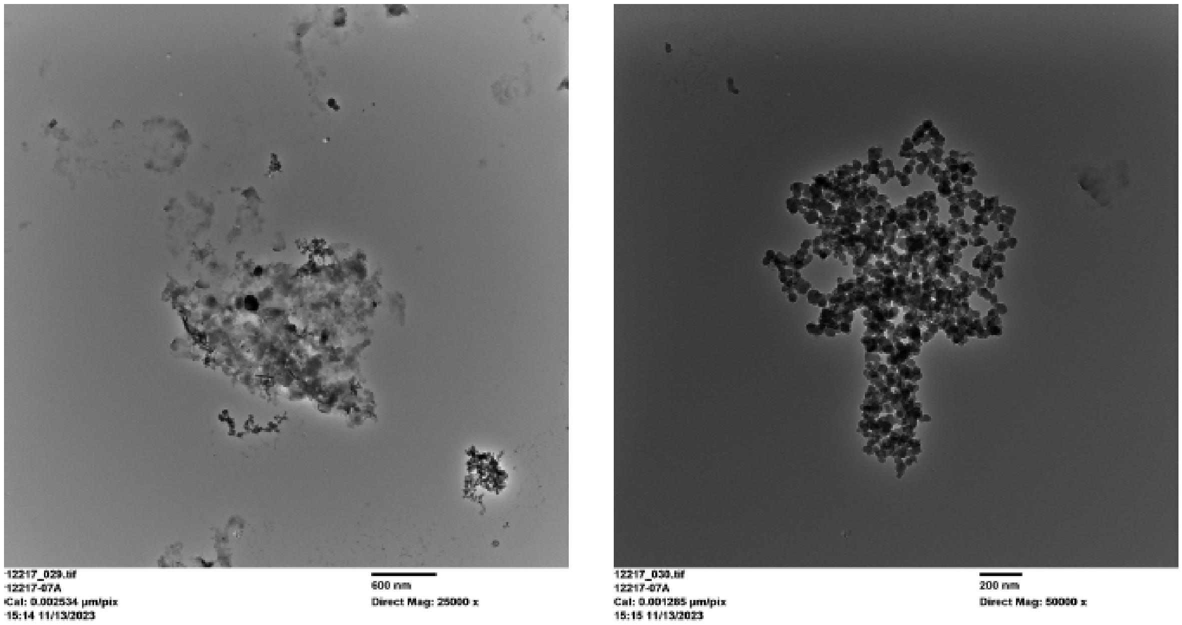

Figure 6. Graphene particles observed from MCE07 collected from a worker programming the reactor on day 2.

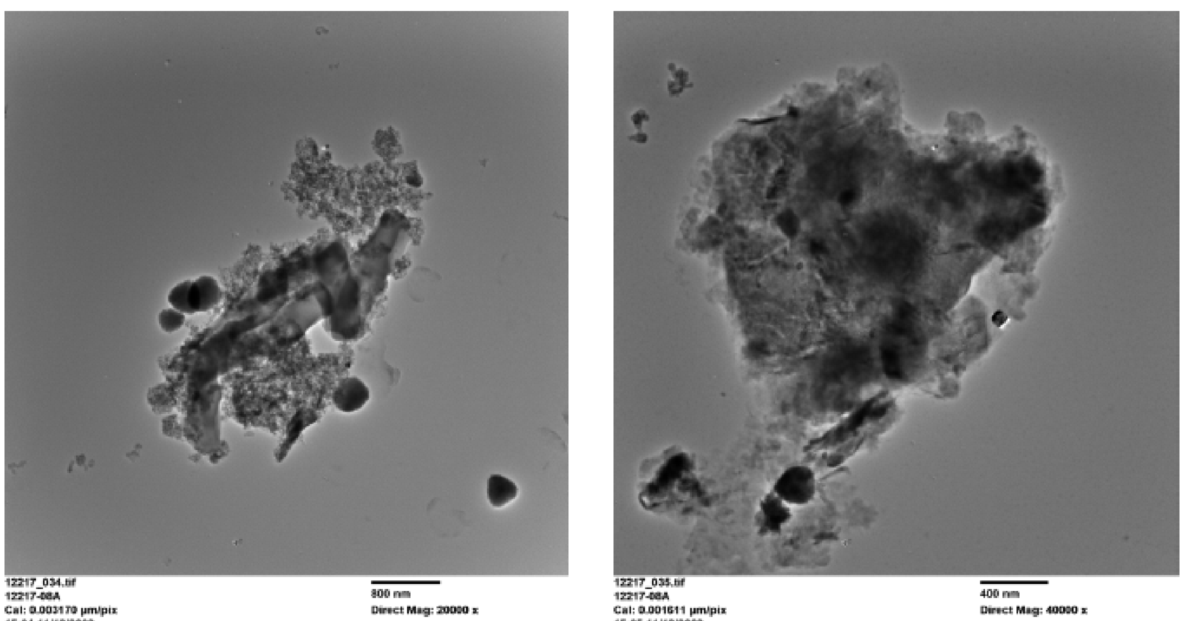

Figure 7. Graphene particles observed from MCE08 collected from a worker test firing a reactor on day 2.

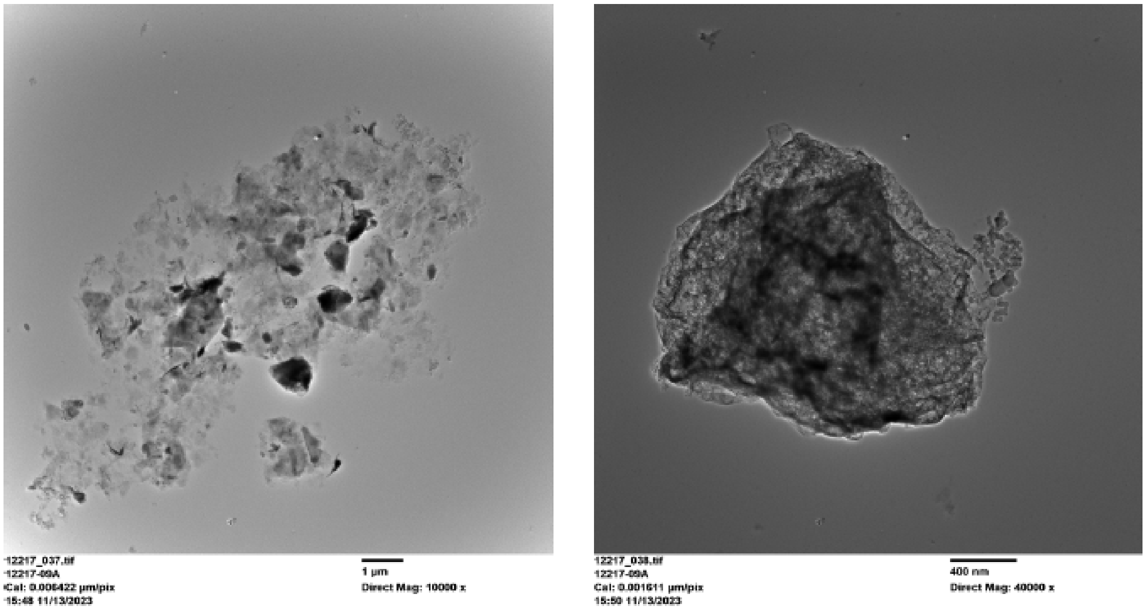

Figure 8. Graphene particles observed from MCE09 collected from a worker curing resins on day 2.

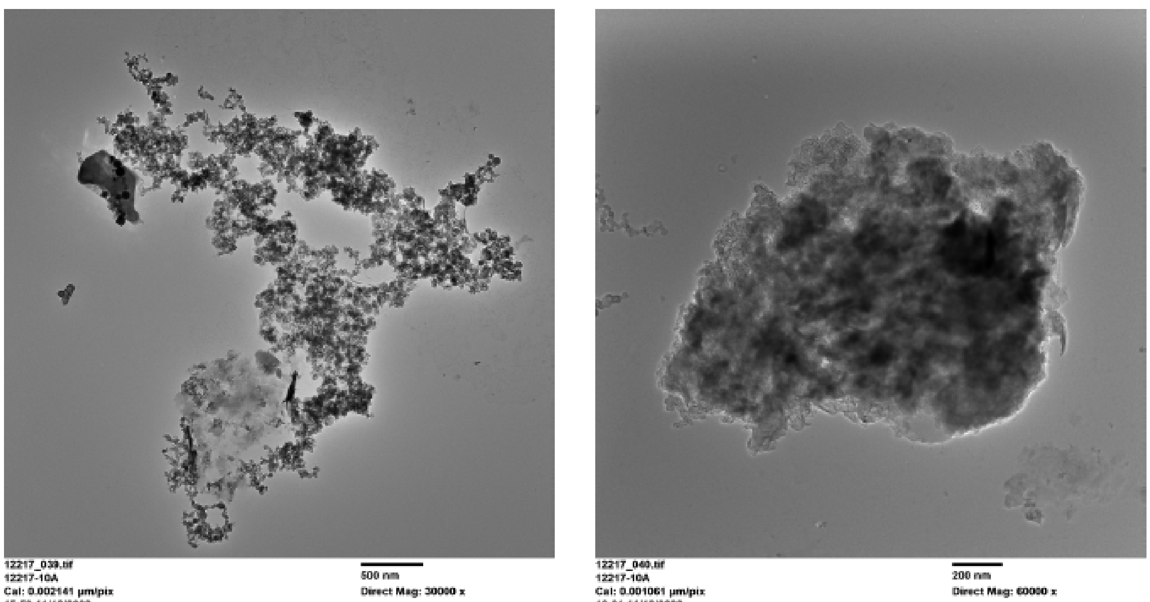

Figure 9. Graphene particles observed from MCE10 collected from a worker transferring material and operating a reactor on day 2.