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Exposure to graphene in a pilot production plant

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Abstract. Workers exposure to graphene was measured in a pilot production plant. Reduced graphene oxide was produced through graphite oxidation and posterior thermal reduction. The monitoring was performed using two handheld on-line devices covering the particle size range from 10 nm to 10 μm (CPC3007 and OPS3330). Simultaneously, personal and area filter samples were collected for off line analysis, including gravimetric, elemental carbon analysis and SEM/EDX. Significant releases of particles were identified in two tasks, during the graphene oxide washing, and during its milling. However, the analysis of the particles size distribution and of their morphology suggested that the released particles were not the target nanomaterial but engine generated nanoparticles. The mass of elemental carbon in the collected filters was below the quantification limit and the calculated graphene mass concentrations were quite below the selected reference exposure limit. Overall, this work showed that worker exposure to graphene was low in this pilot plant, contributing to guarantee a safe process, prior to its industrialization.

1. Introduction

Graphene is a two-dimensional engineered nanomaterial that is being investigated for its use in quite different technologies including electronics, batteries for energy storage, filtration or several biomedical applications, as for example, the development of scaffolds for tissue reparation like the ones developed within the project FAST (H2020, GA 685825) [1], where this work has been carried out. Despite the current use of graphene and the family of graphitic nanomaterials by research groups and the industry, few data are available on graphene exposures in occupational settings [2-4]. In this work we measure workers exposure in a production pilot plant synthesizing graphene oxide and reduced graphene oxide. The goal is to ensure operators safety in an early stage of the industrialization process.

2. Method

2.1. Process description

First, graphene oxide, GO, is produced from graphite through chemical reaction and posterior treatments. Thermally reduced graphene oxide (rGO) is obtained by flashing the GO powder in a tubular oven. The process includes the following tasks: (i) reaction (T1): in this task the graphite is oxidized in a mixture of sulfuric acid and potassium permanganate during several hours; (ii) washing



(T2): the produced GO is washed with dilute HCl in several steps for several days; the final GO is deposited as a laminar cake and is left to get dried during several days; (iii) milling & sieving (T3): the dried GO is milled in a closed mill inside a fume hood; subsequently, the powder is manually sieved; (iv) thermal reduction (T4): the GO powder is introduced into an oven at more than 350 °C; the produced rGO is collected at the oven output in a filter located inside a closed container.

The pilot plant has a production capacity in the order of kg/day and few hundred g/day for GO and rGO respectively, although at present it runs on demand. The facility is located inside an industrial warehouse with natural ventilation. Figure 1 shows the facility layout, the location of the stations for the performed tasks and the measurement points.

Measurements were performed in two consecutive days. During the first day, the monitoring was scheduled to measure the reaction process and the washing task (T1&T2). The next day, dried GO from previous batch cycles was milled and thermally reduced (T3&T4) to achieve the final product.

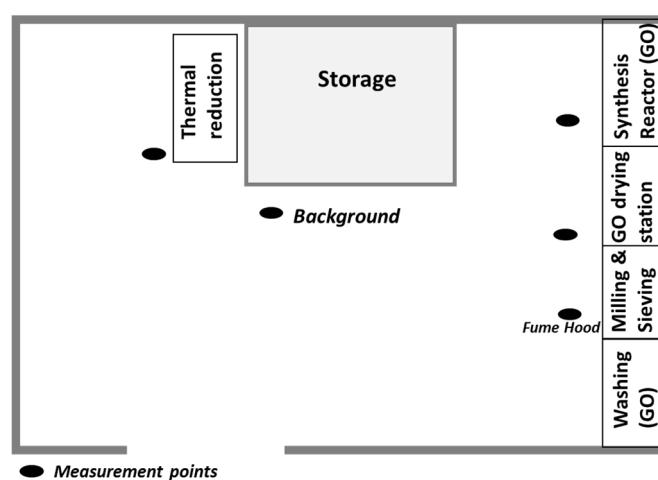


Figure 1. Workplace lay out.

2.2. Measurement strategy and instruments

Measurements were performed using simultaneously on-line devices and collecting filter samples for off-line analysis [5]. Two hand-held monitors were used to characterize the aerosols in the workplace from 10 nm to 10 μm , a TSI CPC3007 (10 nm- 1 μm) and a TSI-OPS330 (0.3-10) μm . The monitors were located in the work area, near the potential sources of particles. Filter based samples were collected for gravimetric, elemental carbon and for SEM/EDX analysis (MEB Quanta 200-FEI). Samples for gravimetric analysis were collected following NIOSH 0500 [6], on 37 mm PVC filters mounted in cassette holders; a 0.05 g precision balance was used. Elemental carbon analysis was performed following NIOSH 5040 [6]. Samples were collected in pre-treated quartz filter in 25 mm cassettes and evolved gas analysis (EGA) by thermal-optical analyzer was used to quantify the mass of elemental carbon in the filters (limit of quantification, LOQ, 1 μg); it was assumed that all the mass of elemental carbon was from the graphite materials. Finally, samples for SEM/EDX analysis were collected on 25 mm polycarbonate filters in open face cassettes. The samples were collected at source and at the operator personal breathing zone.

3. Results

3.1. Direct reading instruments

Figure 2 shows the time series of the total particle concentration during the two days measurement campaign. The lines represent: (i) the total concentration of ultrafine particles in the nano range (10 nm-1 μm) measured with the CPC3007 at source, (ii) the total particle concentration of micro particles

above 300 nm, measured with the OPS3330. Table 1 summaries the most relevant statistics regarding particle concentration: mean particle concentration, standard deviation (SD), minimum and maximum values. For the CPC3007 data, the table also includes the value of the ratio R defined as the difference of mean particle concentration during and before the task (considered as the temporal background) divided by three times the standard deviation of the background concentration. A release is considered significant if the value of R is higher than one (OECD, 2015).

For Day 1 (Figure 2(a), tasks T1&T2) the profile of ultrafine particle concentration (CPC3007) shows that concentration during the reaction (T1) is similar to the background concentration; however, during the washing (T2), the concentration increases and start to decrease slowly when this task finishes. Data showed that mean particle concentration in the background and during task T1 were 7715 particles/cm³, and 3151 particles/cm³ respectively. Mean concentration increased up to 48577 particles/cm³ during washing and it was 93304 particles/cm³ in the period of no-activity after the task. The Table 1 shows that the ratio R is higher than one for the washing task (T2), meaning that the release of particles is significant. The observed increase in the total particle concentration during T2 was coincident with the switch on of a compressor device that is used to pump the supernatant dispersions in the washing task. The concentration of the particles larger than 300 nm at source (OPS) showed a similar profile. However, in this case the data shows that the increase in mean particles concentration during T2 is quite low, from 17 particles/cm³ in the background to 22 particles/cm³ during T2.

For Day 2 (Figure 2(b), tasks T3&T4) the profile of ultrafine particle concentration (CPC3007) shows “peaks” of concentration during the GO milling & sieving (T3). Data showed that mean particle concentration increased slightly from 14185 particles/cm³ to 16598 particles/cm³ in this task; however, “peaks” of concentration up to 194642 particles/cm³ were observed which were coincident with the switch on of the electrical miller. Data showed no increase of particle concentration during the two cycles of thermal reduction (T4). However, a slight increase in concentration was observed after finishing T4, from 9974 particles/cm³ to 25830 particles/cm³. The data in Table 1 show no significant increase in total particle concentration in none of the tasks. The time series of particle concentration measured with the OPS show a similar profile. In this case the mean particle concentration was slightly lower during T3 than before starting the task, 23 and 39 particles/cm³ respectively, and maximum concentration peaks observed were 97 particles/cm³ also coincident with the start of the milling operation.

The Figure 3 shows the size distribution of the particles obtained from the OPS data. This figure shows that the highest measured concentration during all tasks was at 300 and that the size distribution did not change during none of the tasks, including the washing task (T2), where a significant release was identified, and the milling operation (T3), where peaks of concentration were observed. These data suggest that the particles released during these two tasks were smaller than 300 nm.

Table 1. Particle concentration at the workplace

	CPC3007 (particles/cm ³)					OPS (particles/cm ³)			
	Mean	SD	Max	Min	R	Mean	SD	Max	Min
<i>Day 1</i>									
no-activity	7715	3873	16501	4048		17	4	36	10
T1-Reaction	3151	266	5601	2643	< 0	10	2	22	5
T2-Washing	48577	44603	165831	1702	3.5	22	16	66	4
no-activity	93304	12078	122730	67913	7.4	42	3	53	32
<i>Day 2</i>									
no-activity	14185	3849	26230	6804		39	10	65	22
T3-Milling & Sieving	16598	22450	194642	5367	0.2	23	6	97	14
no-activity	8434	3464	54655	2582	< 0	16	3	35	9
T4-Thermal reduction (bach1)	13883	3177	21272	8268	< 0	13	1	18	10
no-activity	17571	3619	57904	8478	0.3	13	2	26	8
T4-Thermal reduction (bach2)	9974	915	18069	8045	< 0	10	1	15	7
no-activity	25830	7563	69638	11569	1	11	2	32	7

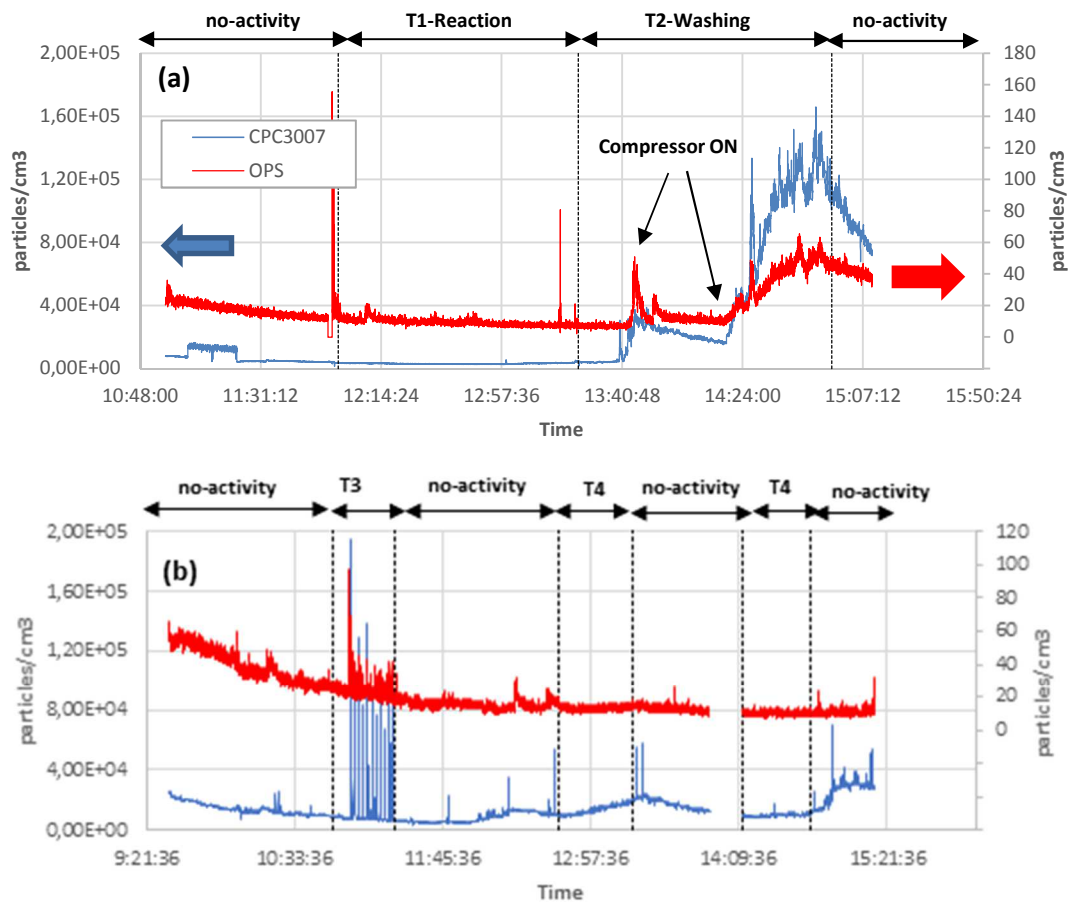


Figure 2. Temporal series of particle number concentration.

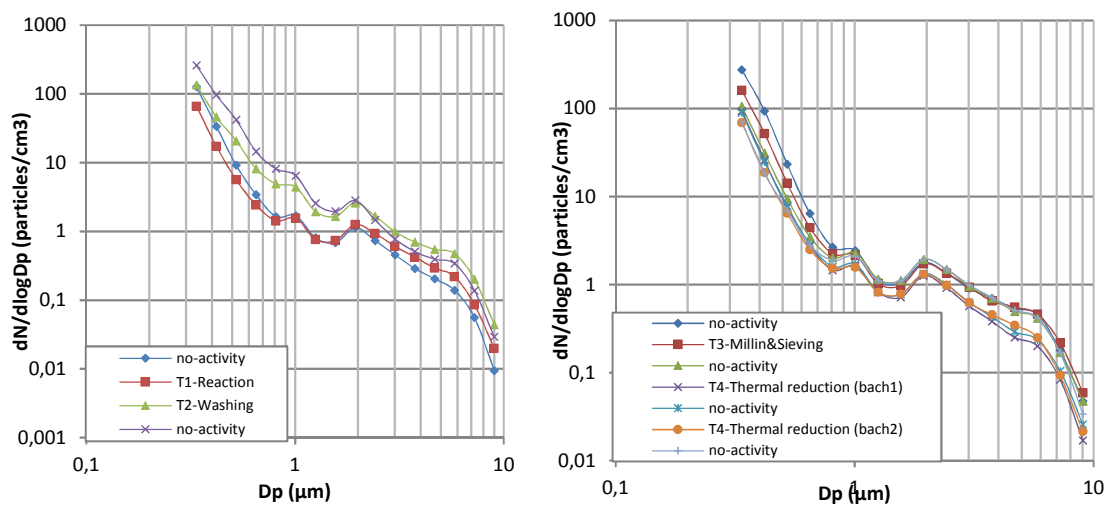


Figure 3. Particle size distribution

3.2. Filter analysis

The gravimetric analysis shows that the total mass of the particles collected in the filters is below the limit of detection, 0.05 mg (Table 2). Furthermore, the mass of elemental carbon in all the collected filters is also below the limit of quantification, 1 µg (Table 3).

The SEM analysis of the collected sample during the reaction and washing tasks (T1&T2) showed few particles, most of them common ambient particles not related to the production process. Carbon based particles were also identified. The Figure 4(a) shows a particle whose main element is carbon suggesting a graphite particle around 30 µm. The filter collected on the second day, during the GO milling and its thermal reduction (T3&T4) showed also few particles, most of them ambient particles. However, in this case more carbonaceous particles have been identified and several particles of layered rGO were observed. The Figures 4(b) and 4(c) show two agglomerates of thin rGO layers with micron-sized flakes. Figure 4(d) also shows a big agglomerate of layered rGO larger than 100 µm where the exfoliated sheets can be observed.

Table 2. Airborne total mass concentration

Tasks	Sampling time (min)	Sampling point	Q (lpm)	Volume (m3)	Total Mass (mg)	Total Concentration (mg/m3)
No activity	67	in the lab	2.2	0.1474	< 0.05	< 0.3
Oxidation & Washing	188	at source	2.2	0.4136	< 0.05	< 0.1
Milling & Sieving-Thermal reduction	148	at source	2.2	0.3256	< 0.05	< 0.1

Table 3. Elemental carbon concentration

Tasks	Sampling time (min)	Sampling point	Q (lpm)	Volume (m3)	EC Mass (mg)	EC Concentration (mg/m3)
Background	67	in the lab	2.5	0.1675	< 0.001	< 0.006
Oxidation & Washing	188	at source	2.5	0.47	< 0.001	< 0.002
Milling & Sieving-Thermal reduction	148	PBZ	2.5	0.37	< 0.001	< 0.003
	148	at source	2.5	0.37	< 0.001	< 0.003

3.3. Considerations about risk

No exposure limits for reduced graphene oxide (rGO) or graphene have been found in the literature; however, some general suggested reference values based on mass concentration and in particle number concentration could be adopted for considerations about the risk.

- Mass concentration. The British Standards Institution BSI-PD 6699-2:2007 [7] proposes for insoluble nanomaterials a benchmark exposure level (BEL) calculated as 0.066 x bulk WEL (workplace exposure limit). NIOSH recommends an 8 hr TWA exposure limit of 2.5 mg/m³ (respirable) for graphite. Following the BSI standard, a BEL can be derived for rGO from the graphite limit: BEL = 0.066 x 2.5 (mg/m³) = 0.165 mg/m³. The Table 3 shows that the elemental carbon concentration was quite below this exposure limit considered for graphene.
- Particle number concentration. A nano-reference value (NRV) of 40000 particles/cm³ has been proposed bio-persistent granular nanomaterial [8, 9], which can be also applicable to rGO. Time series showed that mean particle concentration was higher than 40000 particles/cm³ during the washing task (T2) where a significant release of particles smaller than 300 nm was identified. However, SEM images showed that graphite materials are agglomerates in the micron range, suggesting that the particles released in this task were not graphene particles. It is hypothesised that the measured particles in this task and also the sudden increases of concentration observed during the milling task were generated by the

compressor and the miller used in the tasks. It is well documented that electrical equipment like compressors, universal motors, drilling machines, etc. generates ultrafine particles that are called by some authors “engine generated nanoparticles, EGNP [9]. Measurements performed in industrial settings showed that workplace concentrations due to EGNP emissions may exceed several $100.000 \text{ nanoparticles/cm}^3$ up to several million $\text{nanoparticles/cm}^3$ [10].

In summary, these data showed that worker exposure to rGO was low, quite below the recommended exposure limits, suggesting that implemented work procedures and engineering controls are adequate to achieve safe conditions.

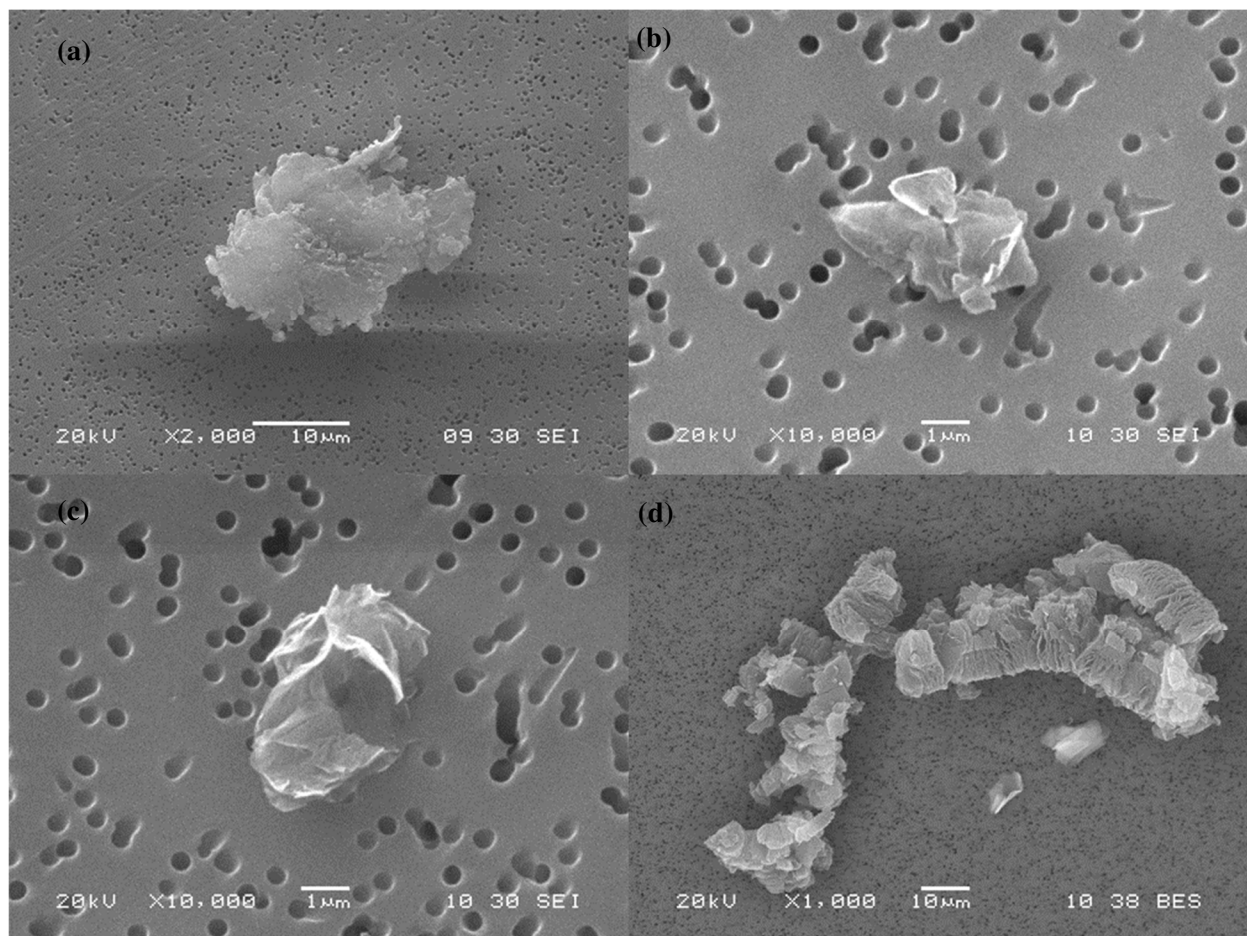


Figure 4. Graphene SEM images from collected samples

4. Conclusions

In this work we presented the measurements of particle release and workers exposure during the synthesis of reduced graphene oxide in a pilot plant. The data showed significantly increased particle concentrations during the washing of GO and during its milling. However, it is suggested that these particles are not the target nanoparticles, but engine generated nanoparticles produced by a compressor and a miller used during the tasks. The analysis of elemental carbon mass showed that worker exposure to rGO was below the quantification limits. These results suggested that the procedures and controls implemented in the workplace are successful to ensure workers safety.

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