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2015 J. Phys.: Conf. Ser. 617 012006

(http://iopscience.iop.org/1742-6596/617/1/012006)

4th International Conference on Safe Production and Use of Nanomaterials (Nanosafe2014) IOP Publishing
Journal of Physics: Conference Series **617** (2015) 012006 doi:10.1088/1742-6596/617/1/012006

Occupational exposure to nano-TiO_2 in the life cycle steps of new depollutant mortars used in construction

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Abstract. The present work is focused on the measurement of workers exposure to nano-TiO_2 in the life cycle steps of depollutant mortars. It has been done in the framework of the SCAFFOLD project, which aims at the management of potential risks arising from the use of manufactured nanomaterials in construction. Main findings can be summarized as follows: (1) The occupational exposure to nano- TiO_2 is below 0.3 mg/m^3 for all measured scenarios. The highest concentrations were measured during the cleaning task (in the nano- TiO_2 manufacturing process) and during the application (spraying) of depollutant coatings on a wall. (2) It was found a high release of particles above the background in several tasks as expected due to the nature of the activities performed. The maximum concentration was measured during drilling and during adding powder materials (mean total particle concentration up to 5.591E+04 $particles/cm^3$ and 5.69E+04 $particles/cm^3$). However, considering data on total particle concentration released, no striking differences have been observed when tasks have been performed using conventional materials in the sector (control) and when using materials doped with nano-objects.

1. Introduction

In the recent years MNMs are being considered for various applications in the construction sector and it is expected that its use will grow in the future years. However there are concerns about their potential health effects and how to properly manage them to protect the workers.

A survey developed by FIEC and EFBWW (2009) showed that the majority of construction workers and their employers (~75%) were not aware that they work with nano-products. Additionally, the state of the art shows that there are currently few data on worker exposure to NOAAs (Clark, 2012) and more specifically in this sector. In this sense, it can be mentioned the papers from Van Broekhuizen et al (2011) that monitored several processes in the sector as spraying a liquid window coating, applying a cement repair mortar and nano-concrete drilling.

The present work is focused on the measurement of workers exposure to nano- TiO_2 in the life cycle steps of depollutant mortars. It has been done in the framework of the SCAFFOLD project (Grant agreement Nº 280535, 2011-2015), which aims at the management of potential risks arising from the use of manufactured nanomaterials in construction. The measurements include the following processes: depollutant mortar fabrication, its application in walls, machining of materials during use and finally, demolition. Additionally, the manufacturing process of nano TiO_2 has been considered. Measurements have been performed at pilot and industrial scale in similar conditions to those of real practice.

2. Method

The strategy to measure occupational exposure followed the method proposed by NIOSH (Bulletin 63) (NIOSH, 2011). According to it two samples at the personal breathing zone were collected for off-line ICP-MS and SEM/EDX analysis (respirable fraction). Simultaneously, the aerosols released in the activities have been characterized using on-line devices following the tiered approach established by Asbach et al (2012). Measurement equipment included CPC3007 (TSI, 10 nm->1 µm), CPC3775 (TSI, 4 nm->3 µm) W-CPC (TSI, 25 nm->3 µm) ELPI+ (Dekati, 6 nm->10 µm), OPS (TSI, 0,3- 10 µm) and Aerotrak (TSI, 10 nm-1 µm). The background (BG) aerosol was characterized following three different approaches including time series analysis, the spatial approach and comparative study with/without nanomaterials (Kuhlbusch et al, 2011).

Occupational exposure limits considered for nano- TiO_2 are 0.3 mg/cm3 (NIOSH, 2011) and 0.1 mg/cm3 proposed in Scaffold project (Stockmann-Juvala, H. 2014). Additionally, total particle concentration (particles/cm^3) was compared with nano reference values, NRV, that for nano- TiO_2 is 40.000 particles/cm^3 (SER, 2012; IFA, 2014).

3. Results

The description of the scenarios and the main results of the measurements performed are summarized in the next paragraphs; the table 2 collects the main data measured.

Scenario1: nano- TiO_2 manufacturing process.

This scenario relates to the manufacturing process of commercial nano- TiO_2, Tecnapow- TiO_2 (TECNAN). The industrial production process proceeds by batches consisting on five tasks: (T1) reaction (flame process, closed system), (T2) beating, (T3) final product collection, (T4) product transferring to small containers, and (T5) facility cleaning. It was performed in an industrial site with natural and general ventilation. During T1 and T2 the system was closed; the other three activities were performed by an operator using PPEs including respiratory protection (mask FPP3), Tyvek suit, gloves and protection gasses.

The results showed that the TiO_2 concentration during the (T5) cleaning task was 0.388 mg/m^3 (62 min sampling). However this task is an infrequent process for the company so the occupational exposure calculated to 8 h-TWA was much lower; in this case, considering that the task is performed 5 h/day, 1 day per week the occupational exposure to nano-TiO_2 was 0.048 mg/m3. For this task, the SEM analysis showed the evidence of nano-TiO_2 agglomerates at the PBZ. On the other side, the measurements of particle concentration showed that mean total particle concentration was between 3.85 E+3-1.33E+4 particles/cm^3 during the hole process, although high peaks of concentration up to 1.20 E+5 particles/cm^3 were observed during the cleaning task (data from CPC3007, BG corrected).

Scenario 2: Mortar manufacturing.

In this scenario it was manufactured three different types of depollutant mortar: material A (control) and material B and C filled with nano-TiO_2 (see table 1).

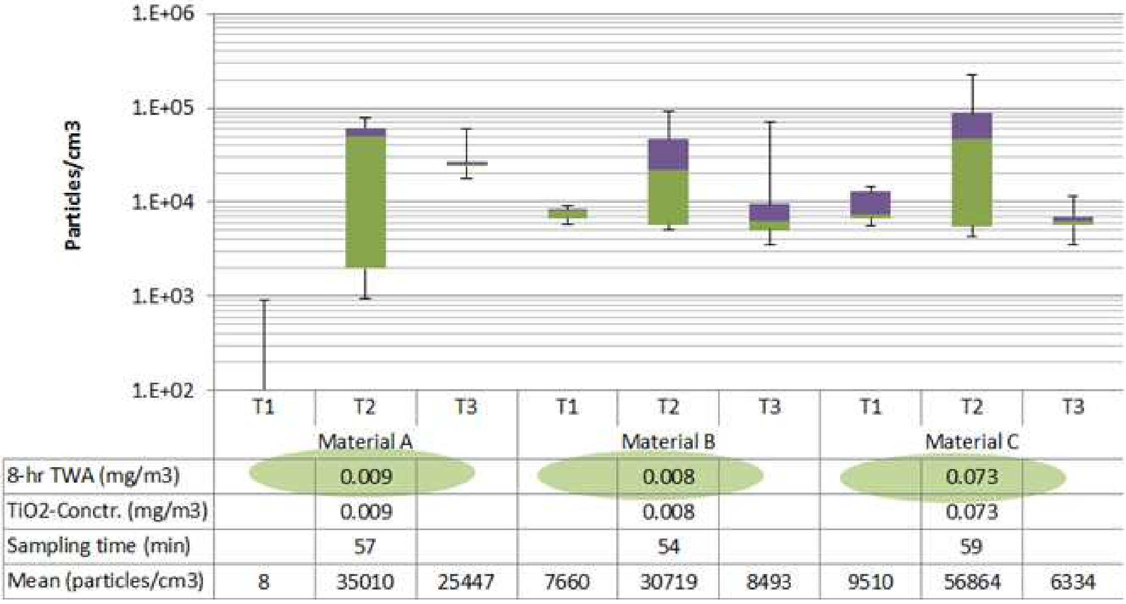
Table 1. List of materials manufactured in scenario 2

Product	Composition	Quantity
Material A	Conventional mortar: 20% cement, 80% sand (approx..) +3,7 kg standard additives	1 Ton
Material B	Depollutant mortar: conventional mortar + 8,2 kg nano-TiO$_2$ supported on sepiolite (1)	1 Ton
Material C	Depollutant mortar: conventional mortar + 4,1 kg nano- TiO$_2$ (Aeroxide P25, Evonik)	1 Ton

(1) The additive for Material B has been developed by TOLSA to achieve better TiO$_2$ dispersions and following the "safe by design" concept (nanoTiO$_2$ fixed on sepiolite).

Three batches of products were processed, 1 ton each one. The process includes three tasks: (T1) additive weighing, (T2) additive adding to the hopper and (T3) mortar bagging. It was performed in an industrial site with natural ventilation by an operator using respiratory protection and gloves.

The main data measured are showed in figure 1. As can be observed, the TiO$_2$ concentration during the manufacturing of each material was between 0.008-0.073 mg/m3 (the sampling time was nearly 60 min for each product). In this case the occupational exposure calculated to 8 h-TWA had the same value than the measured concentration because it was assumed the worst case, so the operator was performing that task during the 8-day, 40 h-week. From the data it should be also highlighted that the TiO$_2$ concentration for material C was higher than for material B (nano-TiO$_2$ supported on sepiolite).The analysis of the samples at the PBZ showed the evidence of nano-TiO$_2$ agglomerates during the manufacturing of product C (see figure 2). Finally, regarding the release of particles, the highest particle concentration observed was during adding additives to the hopper (T2) were mean particle concentration was 5.69E+4 particles/cm^3 for the material C (filled with nano-TiO$_2$).



	Material A T1	Material A T2	Material A T3	Material B T1	Material B T2	Material B T3	Material C T1	Material C T2	Material C T3
8-hr TWA (mg/m3)		0.009			0.008			0.073	
TiO2-Conctr. (mg/m3)		0.009			0.008			0.073	
Sampling time (min)		57			54			59	
Mean (particles/cm3)	8	35010	25447	7660	30719	8493	9510	56864	6334

Figure 1. Main data measured in scenario 2. Boxplot, background-corrected average number of particles/cm^3 during the tasks (data from CPC3007).

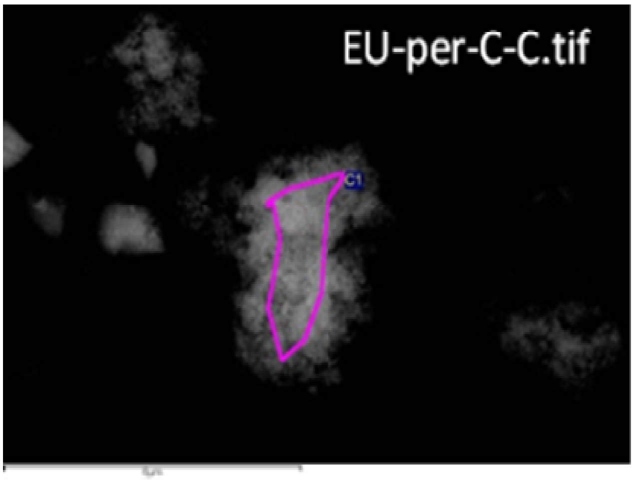


Figure 2. SEM image of collected PBZ samples during manufacturing material C, mortar filled with nano-TiO_2.

Scenario 3: Mortar application.
The three materials previously developed in Scenario 2 were applied in a wall. The process includes three tasks: (T1) adding mortar and mixing with water, (T2) mortar application and (T3) scrapping. The work was performed outdoors by two operators who wear respiratory masks, gloves and work ropes.

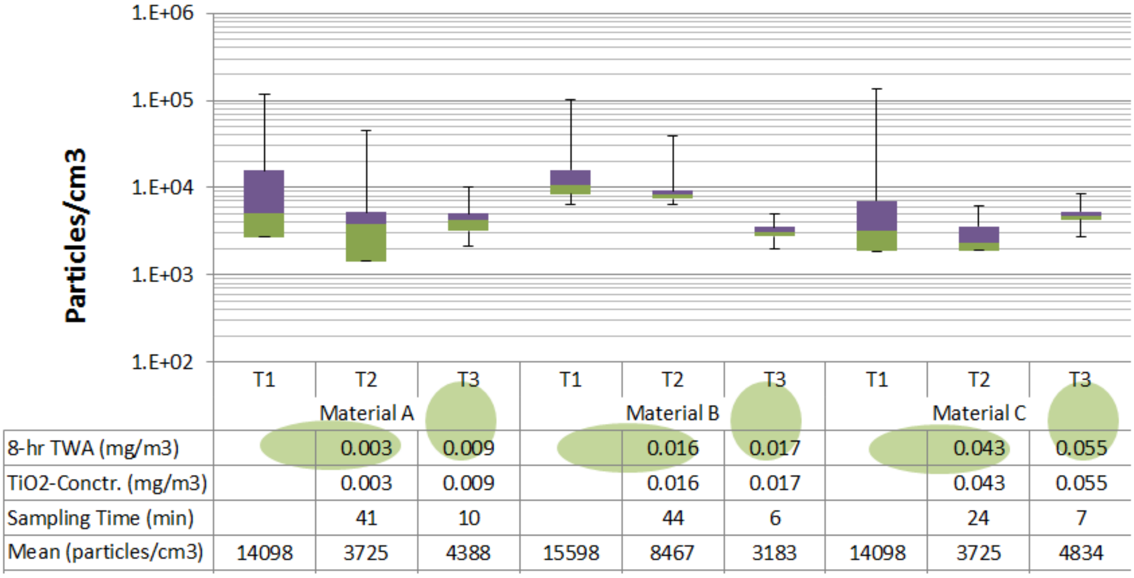
Figure 3 shows the main results for this scenario. As can be observed, the TiO_2 concentration was between 0.003-0.055 mg/m^3 during the time sampled (7-44 minutes), and the occupational exposure 8 h-TWA was calculated assuming the worst case. Similar to previous scenario, the TiO_2 concentration for material C was higher than for material B. Regarding the release of particles, the highest particle concentration observed was during adding mortar and mixing with water (T1); mean particle concentration between 1.41E4-1.56E4 particles/cm^3 with peaks of maximum values up to 1.34E+5 particles/cm^3 for Mat. C.

Scenario 4. Sol-Gel spraying.
Two sol-gels coatings were sprayed in a wall: material A was a sol-gel with 1.7% of nano-TiO_2 (Aeroxide P25 Evonix); material B was a sol-gel with 1.3% of nano-TiO_2 supported on sepiolite. The process was performed outdoor by an operator using a manual spray gun. The operator used PPEs including respiratory protection (mask FPP3), Tyvek suit, gloves and protection glasses.

The results showed that TiO_2 concentration at the PBZ during the task was 0.069-0.195 mg/m^3 for materials A and B respectively (sampling time 13-15 minutes). Samples taken at the PBZ showed the evidence of nano-TiO_2 agglomerates during the two tasks. Mean particle concentration measured was 2.18E+4-2.28E+4 particles/cm^3 for the two products and maximum peaks up to 2.57E+5 particles/cm^3.

Scenario 5. Machining tasks (drilling)
An operator drilled different samples of mortar: mortar A, conventional (control); mortar B filled with 1% nano-TiO_2 (Aeroxide); mortar C filled with 1% nano-TiO_2 supported on sepiolite; sol-gel A (mortar with a coating containing 1% of nano-TiO_2, Aeroxide) and sol-gel B (mortar with a coating containing 1% of nano-TiO_2 supported on sepiolite). The task was performed outdoor by an operator using conventional PPEs (mask, gloves and glasses).

In this scenario the TiO_2 concentration was not measured because it was expected to find very low concentration of TiO_2 due to the short duration of the tasks and low percentage of nano-objects on the materials. The process was monitored using on-line devices to characterize the release of particles.



	Material A T1	Material A T2	Material A T3	Material B T1	Material B T2	Material B T3	Material C T1	Material C T2	Material C T3
8-hr TWA (mg/m3)		0.003	0.009		0.016	0.017		0.043	0.055
TiO2-Conctr. (mg/m3)		0.003	0.009		0.016	0.017		0.043	0.055
Sampling Time (min)		41	10		44	6		24	7
Mean (particles/cm3)	14098	3725	4388	15598	8467	3183	14098	3725	4834

Figure 3. Main data measured in scenario 3. Boxplot, background-corrected average number of particles/cm^3 during the tasks (data from CPC3007).

Data showed that the mean particle concentration was between 1.68E+4 - 5.59E+4 particles/cm^3 for all the different materials with maximum values up to 2.38E+5 particles/cm^3. It is important to highlight that the SEM analysis of the samples taking during the machining of materials filled with nano-TiO_2 did not showed particles of nano-TiO_2 free at the PBZ.

Scenario 6: Demolition

Two cabins were demolished; cab A was covered with mortar containing 2% of nano-SiO2 (Meyco 685) and cab B was covered with same quantity of mortar (304 kg) containing 2% of additive of nano-TiO_2 supported on sepiolite. The process was performed outdoors and two operators were involved: the one in the excavator and a second worker situated near the demolition area (4.5 m from the cab), both wearing conventional PPEs (see figure 4).

The results showed that the TiO_2 concentration during the demolition of cabin B was 0.008 and 0.009 mg/m3 for both operators. The measurement of particle concentration showed values of mean particle concentration between 1.02E+4-2.32E+4 for both cabins with maximum value up to 3.70E+5 particles/cm^3.

Figure 4. Pictures taken during the demolition of the cabs in scenario 6.

Table 2. Summary of measurements by scenario/tasks.

	Particle concentration (particles/cm^3) Data from CPC3007 (BG corrected)			**Occupational Exposure**		
Scenario/Tasks	***Mean***	***Max***	***Min***	***Time (min)***	***TiO_2 conc. (mg/m^3)***	***8 h-TWA (mg/m^3)***
ES1. TiO_2 manufacturing						
T1. Reaction	1.06E+04	2.48E+04	3.37E+03	161	0.007	
T2. Beating	4.86E+03	8.27E+03	2.87E+03			
T3. Collection	3.85E+03	5.48E+03	1.55E+03			
T4. Transferring	1.33E+04	1.97E+04	6.54E+03			
T5 Facility cleaning	9.95E+03	1.20E+05*	5.67E+02	62	0.388	0.048
ES2. Mortar manufact. A, B & C (1)						
T1. Weighing	9.51E+03	1.86E+03	5.72E+03		0.286	0.593
T2. Adding to the hopper	5.69E+04	1.38E+05*	5.00E+03		0.067	0.796
T3. Mortar bagging	2.54E+04	6.11E+04	1.77E+04			
All tasks				57-59	0.008-0.073	0.008-0.073
ES3:Mortar application A, B & C (1)						
T1. Adding and mixing	1.56E+04	1.34E+05*	6.28E+03			
T2. Mortar application	8.47E+03	4.58E+04	6.44E+03			
T3. Scrapping	4.83E+03	9.99E+03	2.68E+03			
All tasks				7-44	0.003-0.055	0.003-0.055
ES4: Sol-Gel spraying						
Sol-gel A	2.28E+04	2.57E+05*	0.00E+00	13	0.069	0.069
Sol-gel B	2.18E+04	2.45E+05*	0.00E+00	15	0.195	0.195
ES5: Machining (drilling)						
Mortar A	3.01E+04	1.76E+05*	0.00E+00			
Mortar B	2.66E+04	2.17E+05*	0.00E+00			
Mortar C	1.68E+04	1.79E+05*	6.46E+03			
Sol-gel A	3.25E+04	1.79E+05*	3.72E+03			
Sol-gel B	5.59E+04	2.38E+05*	9.72E+03			
ES6: Demolition						
Cabin A	2.32E+04	3.70E+05*	1.08E+04			
Cabin B	1.02E+04	3.01E+05*	0.00E+00	37	0.009	0.009

(*) Data above the upper limit of CPC3007; (1) Maximum values measured for mat.A, B and C

4. Conclusions

The following main conclusions can be highlighted from this work:

- The occupational exposure to nano-TiO_2 is below the OELs for all scenario measured, considering both limits, 0.1 mg/m^3 (SCAFFOLD, Stockmann-Juvala, 2014) and 0.3 mg/m^3 (NIOSH, 2011).
- The highest mass concentrations of nano-TiO_2 (mg/m3) were found during the cleaning task in the nano-TiO_2 manufacturing (scenario 1), and during the sol-gel spraying of depollutant on a wall (scenario 4).
- Mean total particle concentration released (particles/cm^3) was above NRV during two tasks: machining of depollutant mortar (scenario 5) and when adding additives to the hopper (while manufacturing depollutant mortar, scenario 2). However, these tasks are quite short (in time)

and concentration should be normalized to 8 h day- 40 h week to be compared with exposure limits (e.g. NRV).

- Data on total particle concentration released (particles/cm^3) showed no sticking differences using conventional materials (control) and materials filled with nano-objects.
- Results on mass concentration and on number concentration are inconsistent. More research on this issue is needed to achieve a consensus.

These findings contribute to clarify the discussion about whether the incorporation of nano-objects to the construction industry may originate an increase on the risks for workers in this sector.

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